

Surface Science

Room 2004 - Session SS2+EM-ThM

Self-Assembled Monolayers

Moderator: C. Wöll, Ruhr-Universität Bochum, Germany

8:00am **SS2+EM-ThM1 Odd-Even Effects in Self-Assembled Monolayers of Biphenyl-Substituted Alkaneselenolates on Noble Metal Substrates**, *M. Zharnikov*, A. Shaporenko, Universität Heidelberg, Germany; *J. Müller*, A. Terfort, Universität Hamburg, Germany

Self-assembled monolayers (SAMs) of selenolates can be considered as an alternative to thiolates for the functionalization of noble metal surfaces. In view of this option, we studied SAMs formed from biphenyl-substituted dialkanediselenides ($\text{CH}_3(\text{C}_6\text{H}_4)_n\text{Se}_2$) (BPNSe, $n = 1 - 6, 10, 11$) on polycrystalline (111) gold and silver substrates. The SAMs were characterized by several complementary experimental techniques. Similar to the analogous systems with the thiolate headgroup, the packing density of the SAM constituents and the orientation of the biphenyl moieties in the BPNSe films exhibited a pronounced odd-even variation with the number of methylene groups in the aliphatic linker, which was opposite on silver as compared to gold. A higher packing density and a corresponding smaller inclination of the biphenyl moieties was observed for odd numbers of the methylene units in BPNSe on Au, and for even numbers of these units in BPNSe on Ag. The observed odd-even effects are explained by the strong dependence of the bending potentials in the metal-Se-C bond on the deviation of the respective angle from an optimal value of about 104° for Au and about 180° for Ag. The optimal metal-Se-C angles are presumably determined by the hybridization of the selenium in the metal-selenolate bond, which seems to have sp^3 hybridization on Au and an sp hybridization on Ag, respectively.

8:20am **SS2+EM-ThM2 Structure and Stability of Acene-SAMs**, *D. Kaefer*, G. Witte, A. Bashir, Ruhr-Universität Bochum, Germany; *P. Cyganik*, Institute of Physics Krakow, Poland; *J. Mueller*, A. Terfort, University Hamburg, Germany; *Ch. Woell*, Ruhr-Universität Bochum, Germany

In addition to tailoring mechanical and chemical surface properties self-assembled monolayers (SAMs) have also attracted significant interest in connection with studies on molecular electronics or as contact primers for organic electronic devices. The high electrical conductivity required for the latter applications has favoured the use of aromatic SAMs which generally reveal a more complex ordering mechanism as compared to aliphatic SAMs. While an improved ordering has been achieved by using additional alkyl-units within the backbone this in turn reduces the conductivity and increases the band gap of the molecular film. Recently, we have demonstrated for the case of anthracene-2-thiol that also well ordered SAMs with a completely conjugated backbone can be prepared on Au(111). In the present study we have further varied the anchoring group and prepared also an anthracene-2-selenol SAM. Here we present a comprehensive multi-technique study (based on XPS, NEXAFS, TDS, STM and LEED measurements) on the formation, molecular structure and thermal stability of both acene-based SAMs on gold. Interestingly, a remarkably improved long-range ordering and a somewhat reduced thermal stability is obtained for the anthracene-2-selenol SAM. The different films were also analyzed theoretically in the frame of DFT calculations and the microscopic interactions and energetics of both films are compared and discussed.

8:40am **SS2+EM-ThM3 A Survey on the Structural Properties of Alkanethiols Self Assembling on Au(111)**, *E. Barrera*, C. Munuera, C. Ocal, Instituto de Ciencia de Materiales de Madrid, Spain

INVITED

The potential application of Self-Assembled Monolayers (SAMs) in different fields of both science and technology has motivated a large number of studies in recent years. It has become clear that the design of films with specific controlled properties requires a better understanding of the parameters governing the self-assembling process. Without doubt Alkanethiols ($\text{SH}(\text{CH}_2)_n$) on Au(111) are the archetypal systems among SAMs. They possess important characteristics as stability, structural simplicity and well-defined order, which make them ideal for understanding the role that the fundamental interactions play in determining the self-assembled structure. In spite of their simplicity, a rich spectrum of structures has been reported. In this talk I will present a survey on the structural properties of Alkanethiols on Au(111) mainly focused on

the submonolayer regime. I will show that molecular configurations consisting of molecules presenting different tilt angles and periodicities are formed for submonolayer coverage with an extraordinary degree of order. Experimental studies carried out by combining Atomic Force Microscopy and X-ray diffraction measurements will be presented showing different aspects on their growth, structure, stability including chain length dependent investigations.

9:20am **SS2+EM-ThM5 The Electronic Structure and Polymerization of a Self-Assembled Monolayer**, *D. Feng*, D. Wisbey, University of Nebraska-Lincoln; *Y. Tai*, Universität Heidelberg, Germany; *Y. Losovyj*, Louisiana State University; *M. Zharnikov*, Universität Heidelberg, Germany; *P. Dowben*, University of Nebraska-Lincoln, U.S.A

Although organic adsorbates and thin films are generally regarded as "soft" materials, the effective Debye temperature, indicative of the dynamic motion of the lattice normal to the surface, can be very high, e.g., in the multilayer film formed from [1,1'-biphenyl]-4,4'-dimethanethiol (BPDMT). The effective Debye temperature, determined from core level photoemission from the all carbon arene rings, is comparable to that of graphite, and follows the expected Debye-Waller behavior for the core level photoemission intensities with temperature, but this is not always the case. (We associate this rigidity to the stiffness of the benzene rings, and the ordering in the ultrathin multilayer molecular thin film.) We find that a monomolecular film formed from [1,1'-terphenyl]-4,4'-dimethanethiol deviates from Debye-Waller temperature behavior and is likely caused by temperature dependent changes in molecular orientation. Intermolecular lateral interactions for [1,1'-terphenyl]-4,4'-dimethanethiol (TPDPT), were evident from the considerable dispersion of the TPDPT molecular orbitals with changing the wave vector k . The highest occupied molecular orbitals hybridize to electronic bands, with a band dispersion of about 300 to 400 meV. The wave vector dependence is consistent with a lateral spacing of about 5.1 Å, found in STM. We also find evidence for the increase in dielectric character with cross-linking in spite of the decrease in the HOMO-LUMO gap upon irradiation of TPDPT. The cross-linking processes are also accompanied by changes in molecular orientation.

9:40am **SS2+EM-ThM6 Kinetics and Mechanism of Displacement in 1-Adamantanethiolate Self-Assembled Monolayers**, *H.M. Saavedra*, C.M. Barbu, T.J. Mullen, V.H. Crespi, P.S. Weiss, The Pennsylvania State University

We have investigated the kinetics of solution-phase displacement of 1-adamantanethiolate self-assembled monolayers on Au(111) by *n*-dodecanethiol molecules using Fourier transform infrared-external reflectance spectroscopy (FTIR-ERS) and scanning tunneling microscopy (STM). The displacement reaction can be divided into three regions: a fast insertion and nucleation of small *n*-dodecanethiolate islands around defects in the 1-adamantanethiolate monolayer; an island growth regime in which the rate of growth is dependent on the perimeter of the island; and a final slow ordering of the *n*-dodecanethiolate domains leading to denser and more crystalline *n*-dodecanethiolate domains. A study of displacement as a function of concentration revealed that the full displacement of 1-adamantanethiolate monolayers has a $[n\text{-dodecanethiol}]^x$ dependence. An analytical model has been derived to describe the displacement process, and using this model a rate constant has been determined.

10:00am **SS2+EM-ThM7 High Thermal Stability of Cross-Linked Aromatic Self-Assembled Monolayers: New Pathways for Nanopatterning by Selective Desorption**, *A. Turchanin*, M. El-Desawy, A. Götzhäuser, University of Bielefeld, Germany

Molecular structures with high thermal stability are very desirable for applications in nanoscience and nanotechnology. We report on the thermal stability of cross-linked aromatic self-assembled monolayers (SAMs) on gold surfaces. Cross-linked monolayers were formed by low-energy electron irradiation of biphenylthiol SAMs. The pristine and the cross-linked monolayers were heated in ultra high vacuum to temperatures from 300 up to 1000K and then analyzed by X-ray photoelectron spectroscopy (XPS). We found that the pristine SAM desorbs at 400K, which is accompanied by a breaking of C-S bonds. Despite of a similar C-S bond cleavage of cross-linked SAMs in the same temperature range, their carbon matrix shows a high thermal stability and remains on the surface up to 1000K. We present

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a detailed analysis of the temperature transformations in pristine and cross-linked SAMs on the basis of XPS data. Using a stencil mask to locally cross-link the SAMs, it is then shown by scanning electron and atomic force microscopy that after the temperature treatment monomolecular sheets of aromatic molecules, corresponding to irradiated areas in the SAM, persist at the surface. This opens a new pathway for nanopatterning by the selective desorption of non-cross-linked regions on a e-beam patterned monolayers and for technological applications of SAM coatings.

10:20am **SS2+EM-ThM8 In-situ Studies of Protein Resistance of Oligo(Ethylene Glycol) Self-Assembled Monolayers**, *M. Skoda*, Oxford University, UK; *F. Schreiber*, Universit@um a@t T@um u@bingen, Germany; *J. Willis*, *R. Jacobs*, Oxford University, UK; *R. Dahint*, *M. Grunze*, University of Heidelberg, Germany; *M. Wolff*, ESRF, France

The structure of the interface between organic matter, such as self-assembled monolayers (SAMs), and water is currently subject of intensive studies due to its importance for the understanding of surface-solvent and surface-surface interactions.^{1,2} Our focus here are OEG-terminated SAMs which are used to make surfaces resistant to protein adsorption. We report our recent results from a combined Neutron Reflectivity (NR) and Polarisation Modulated (PM) Fourier Transform Infrared Spectroscopy (FTIR) study. The PM technique enables us to address the local interaction of water with OEG groups, and is ideally complementary to NR. Our data suggest a rather strong interaction of water molecules with the EG section of the SAM, potentially the penetration of water into the SAM. Also, the measurements reveal changes in the structure of water and the protein solution in the vicinity of the SAM upon changes in temperature. Our combined NR and IR investigation helps to shed light on the problem of the subtle interactions at the organic solid-liquid interface. The benefit of using IR along with NR is also that we are more sensitive to the defect structure of the organic interface, which has an impact on the interaction with water. ¹F. Schreiber, *J. Phys.: Cond. Matter* 16 (2004) R881 ²D. Schwendel et al., *Langmuir* 19 (2003) 2284

10:40am **SS2+EM-ThM9 Thiol-Modified Diamondoid Monolayers on Gold Studied with Near-Edge X-ray Absorption Fine Structure Spectroscopy**, *T.M. Willey*, Lawrence Livermore National Laboratory; *J.D. Fabbri*, Stanford University; *J.R.I. Lee*, Lawrence Livermore National Laboratory; *P.R. Schreiner*, *A.A. Fokin*, *B.A. Tkachenko*, *N.A. Fokina*, Justus-Liebig University Giessen, Germany; *J.E. Dahl*, *R.M.K. Carlson*, *S.G. Liu*, MolecularDiamond Technologies; *T. van Buuren*, Lawrence Livermore National Laboratory; *N.A. Melosh*, Stanford University

Higher diamondoids, hydrocarbon cages with a diamond-like structure, have evaded laboratory synthesis and have only recently been purified from petroleum sources. Initial calculations on these unique diamond-like molecules show they may have highly desirable properties similar to hydrogen-terminated diamond surfaces. Readily available adamantane, the smallest diamondoid, can be thiolated and has shown to adsorb on gold with high coverage. The availability of diamantane, triamantane, and tetramantanes opens new possibilities for surface-modification as multiple sites are available for thiol or other chemical functionalization. Surface-attached diamondoids have technological possibilities as high-efficiency field emitters in molecular electronics, as seed crystals for diamond growth, or in other nanotechnological applications, and fundamental studies of the properties of these molecules are a necessary precursor. We have investigated the effects of thiol substitution position and polymantane order on diamondoid film morphology. Using Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) we show that the orientation of the diamondoids within each type of monolayer depends highly upon both the location of the thiol and the diamondoid used. We thus demonstrate control over the assembly, and hence the surface properties, of this exciting new class of diamond-like carbon molecules.

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