

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+SS+AS-FrM

Self Assembled Ultrathin Organic Interfaces

Moderator: S.L. McArthur, Swinburne University of Technology, Australia

8:40am **BO+SS+AS-FrM2 Photo-Patterned SAMs on Au(111) and SiO_x: An XPS Investigation**, *A.M. Track*, University of Graz, Austria, *A. Lex*, *T. Höfler*, *T. Griesser*, *P. Pacher*, *H.-G. Flesch*, Graz University of Technology, Austria, *G. Hlawacek*, University of Leoben, Austria, *R. Schenach*, *G. Trimmel*, Graz University of Technology, Austria, *W. Kern*, University of Leoben, Austria, *G. Koller*, *M.G. Ramsey*, University of Graz, Austria

Self-assembled monolayers (SAMs) can provide a simple, flexible, highly ordered and convenient system to tailor and functionalize surface and interface properties of metals, metal oxides and semiconductors. For instance a simple way to change the chemical reactivity of the substrates is to use organic photosensitive SAMs which will also allow patterning with UV illumination. We focus on the characterization of the reactions occurring in SAMs and thin interfacial layers using X-ray photoemission spectroscopy (XPS). To increase the contrast between the non-illuminated and illuminated SAMs (or thin films) we perform a selective post modification of the patterned films with organic reagents containing heteroatoms. The chemical differences of the structured film have been followed with spatially resolved XPS. Further chemical and structural information has been obtained with reflection absorption infrared spectroscopy (RAIRS), friction force microscopy (FFM), contact angle measurements and X-ray reflectivity (XRR). Two different types of photo-reactive functional groups have been investigated: a benzyl thiocyanate and a phenylester. First we present thin films of silanes on SiO_x, which bear the photoreactive benzyl thiocyanate (-SCN) unit. This photoisomerizes to the corresponding isothiocyanate (-NCS). The photoisomerization can be detected by a significant shift of the S2s core level. Additionally, we can prove the change of chemical reactivity due to the illumination via a post modification with fluorinated amines introduced in gas phase. Here more fluorine could be detected with the spatially resolved XPS on the illuminated areas of the sample.¹ In the second example the SiO_x substrates are modified with photosensitive silanes of different chain length containing the phenylester group. The phenylester can undergo the Photo-Fries rearrangement upon UV illumination forming a hydroxyphenyl keton. The different chemical reactivity of these two groups is again shown with a selective post modification with, e.g., fluorinated acid chlorides. The corresponding reaction has again been followed by the appearance of the F1s signal only on the illuminated areas of the samples. Finally, results of investigations extended to patterned photo-reactive thiol-SAMs on Au(111) will be discussed.

¹ A. Lex et al., Chem. Mater. 2008, 20, 2009-2015.

9:00am **BO+SS+AS-FrM3 Odd-Even Effect in Molecular Packing and Stability of ω-Biphenyl-Alkane-Selenol SAMs on Au(111)**, *P. Cyganik*, *K. Szelagowska-Kunstman*, Jagiellonian University, Poland, *M. Zharnikov*, Universität Heidelberg, Germany, *A. Terfort*, Marburg University, Germany
To fabricate aromatic self-assembled monolayers (SAMs) of practical importance for molecular electronics and other applications, high level of control over the SAMs properties should be achieved. In particular, besides monitoring the electronic properties, control of structure, i.e., crystallinity and defects, is an issue of equal importance. Our experimental approach to gain a general concept for the rational design of high-quality SAMs includes a systematic modification of the chemical composition of the SAM constituents and detailed investigation of the structure of the resulting films. Following this general idea, we studied the influence of the substitution of the headgroup atom (S versus Se, which binds SAMs constituent to the substrate) on the microscopic structure of hybrid aromatic-aliphatic SAMs formed on Au(111). The talk focuses on STM experiments¹ performed for the homologue series of BPhSe (CH₃-(C₆H₄)₂-(CH₂)_n-Se, n =2-6) molecules. Obtained data are discussed and analysed in view of the spectroscopic results reported by us recently for these systems^{2,3}, as well as compared to the previously reported STM data^{4,5} for the corresponding thiol-based analogues, i.e. BPhS/Au(111). The main conclusions are: (1) higher structural quality of the Se based SAMs, (2) drastic changes in the BPhSe film structure depending on either odd or even value of the parameter n, accompanied by (3) the respective odd-even changes in their thermal stability.

¹ P. Cyganik et al. J. Phys. Chem. C, submitted.

² A. Shaporenko et al. 2007 J. Am. Chem. Soc. 129, 2232.

³ T. Weidner et al., J. Phys. Chem. C, submitted.

⁴ P. Cyganik et al. 2006 J. Am. Chem. Soc. 128, 13868.

⁵ P. Cyganik et al. 2007 J. Phys. Chem. C. 111, 16909.

9:20am **BO+SS+AS-FrM4 The Molecular Structure and Orientation of Phenylboronic Acid Derivatives and the Interaction with Dopamine: A NEXAFS, XPS and SPR Study**, *C. Vahlberg*, *L. Johansson*, *K. Uvdal*, Linköping University, Sweden

Our aim is to design well organized self-assembled monolayers as model systems for biological recognition such as the selective ligand - receptor interaction. These systems are important for future applications within nanoscience and the development of specific biosensors. A phenylboronic ester and a phenylboronic acid are used for surface functionalisation. Both are linked to an alkanethiol through the formation of an amide bond. Formation of a self-assembled monolayer on gold surfaces is done by common thiol chemistry. The molecular orientation and chemical composition of the two molecular systems were investigated using X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection Absorption Spectroscopy (IRAS) and Near Edge X-ray Absorption Fine Structures (NEXAFS). IRAS and NEXAFS measurements showed that the two molecular systems form a well organized monolayer. The average tilt of the aromatic ring and the main molecular axis has been estimated based on NEXAFS measurements. The thicknesses of the self-assembled monolayer of the two molecules were investigated with ellipsometry and supported with XPS based measurements. The properties of the functionalized surfaces were also investigated using contact angle goniometry. Boronic acid based SAM is a simple mimicry of an adrenergic receptor. Investigation of the neurotransmitter dopamine recognition in real-time, using Surface Plasmon Resonance (SPR), is in progress.

9:40am **BO+SS+AS-FrM5 Unravelling Molecular Mechanism of Electron-Induced Cross-Linking in Aromatic SAMs**, *A. Turchanin*, University of Bielefeld, Germany, *D. Käfer*, Ruhr-University Bochum, Germany, *M. El-Desawy*, University of Bielefeld, Germany, *Ch. Wöll*, *G. Witte*, Ruhr-University Bochum, Germany, *A. Götzhäuser*, University of Bielefeld, Germany

Irradiation of aromatic self-assembled monolayers (SAMs) with low energy electrons¹ or UV-light² results in a lateral cross-linking and the formation of aromatic carbon nanosheets with a thickness of only one molecule. These films possess a high mechanical stability that allows their separation from the substrate and fabrication of free standing membranes with a thickness of ~1nm³ and exhibit further a remarkable thermal stability⁴ sustaining temperatures above 1000 K. Because of the promising potential of these ultrathin membranes for various applications in nano-devices, the knowledge of their molecular microstructure and the mechanisms of cross-linking are of great interest. We have employed a variety of in situ spectroscopic techniques including X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure spectroscopy (NEXAFS), thermal desorption spectroscopy (TDS), and UV photoelectron spectroscopy (UPS) to characterize the electron irradiation of 1,1'-biphenyl-4-thiol (BPT) SAMs on Au. Experimental data are further compared with quantum chemical calculations of the electronic structure of cross-linked species, which allowed the identification of distinct molecular species leading to the formation of carbon nanosheets upon electron irradiation of BPT SAMs. Molecular mechanisms of the electron induced changes in aromatic SAMs will be discussed.

¹Geyer, W.; Stadler, V.; Eck, W.; Zharnikov, M.; Götzhäuser, A.; Grunze, M.; Appl. Phys. Lett. 75 (1999) 2401;

²Turchanin, A.; Schmietz, M.; El-Desawy, M.; Solak, H. H.; David, C.; Götzhäuser, A.; Small 3 (2007) 2114;

³Eck, W.; Küller, A.; Grunze, M.; Völkel, B.; Götzhäuser, A.; Adv. Mater. 17 (2005) 2583;

⁴Turchanin, A.; El-Desawy, M.; Götzhäuser, A.; Appl. Phys. Lett. 90 (2007) 053102.

10:00am **BO+SS+AS-FrM6 Surface-Active Catechol Derivatives on Metal Oxide Surfaces: Influence of Molecular Architecture and Conditions on Polymer Adlayer Formations and Stability**, *B. Malisova*, ETH Zurich, Switzerland, *K. Gademann*, EPFL Lausanne, Switzerland, *S. Zuercher*, *S. Tosatti*, *M. Textor*, ETH Zurich, Switzerland

In recent works, L-3,4-dihydroxyphenylalanine (DOPA), a catechol which is found in mussel adhesive proteins (MAPs), served as basis for poly(ethylene glycol) (PEG) ultra thin coatings capable of rendering surfaces non-fouling,¹ i.e. resistant to non-specific protein adsorption and capable of withstand formation of biofilm by microorganisms.² However, it was found that the negative charge of DOPA at physiological pH where most metal oxide surfaces are negatively charged reduces adsorption due to electrostatic repulsion effects unless at least three residues per PEG chain are used.³ We have been able to overcome this problem by synthesizing a

new positively charged catechol derivative (anacat)⁴ based on the iron chelator anachelin which was evolutionarily developed by cyanobacteria to bind Fe(III). Incorporation of an additional positive charge resulted in a stable, protein-resistant, non-fouling coating of TiO₂.⁵ In order to further study the effect of the charge of binding groups on the adlayer formation process as well as the effect of acidity of catecholic -OH groups, 5 different catechol binding feet were synthesized and coupled to PEG chains. Adsorption and stability properties together with the abilities to resist protein adsorption are analyzed as function of different adsorption parameters (pH, substrate type, salt concentration and temperature) by Ellipsometry (ELM) and X-Ray Photoelectron Spectroscopy (XPS). Current results suggest that the charge of the binding group, which should be opposite to the one of the substrate, as well as the difference between adsorption pH and the isoelectric point of the substrate are important parameters for all investigated molecules. Final goal of the present work is the development of a general model that explains the binding mechanism of catechols onto metal oxide substrates as function of the binding group acidity.

¹ Gunawan, R. et al. Langmuir 2007, 23, (21), 10635-10643.

² Hall-Stoodley, L. et al. Nature Reviews Microbiology 2004, 2, (2), 95-108.

³ Dalsin, J. et al. Langmuir 2005, 21, (2), 640-646.

⁴ Gademann, K. et al. Angew. Chem. Int. Ed. 2004, 43, (25), 3327-3329.

⁵ Zurcher, S. et al. JACS 2006, 128, (4), 1064-1065.

10:20am **BO+SS+AS-FrM7 Self-Assembly of Methanethiol on the Reconstructed Au(111) Surface, G. Nenchev, B. Diaconescu**, University of New Hampshire, *F. Hagelberg*, East Tennessee State University, *K. Pohl*, University of New Hampshire

The molecular self-assembly of alkanethiols (CH₃(CH₂)_{n-1}SH) on Au(111) surface has been studied extensively in the last 20 years. Despite the abundance of experimental and theoretical data, the true nature of the processes involved in the monolayer formation is still not fully established. We will present a combined UHV VT-STM and DFT study of the adsorption of the simplest alkanethiol, methanethiol (CH₃SH), on the reconstructed Au(111) surface. Our findings challenge the established notion that methanethiol is too short to form ordered structures even at low temperature. At sub-monolayer coverage, dimer chains are resolved on the FCC areas of the reconstruction pattern. At higher coverage the monolayer evolves into two continuous self-assembled phases: a rectangular c(4√3 x 2) phase, which coexists with the substrate reconstruction network, and a close-packed p(√3 x √3)R30° hexagonal phase. Our DFT calculation, which takes the reconstruction of the surface into account, confirms the non-dissociative character of the methanethiol adsorption and derives the bonding geometry of the molecular dimers - a sequence of shifted hollow-top and hollow-bridge bonding positions. The numerical calculation reveals that, in stark contrast to longer alkanethiols, at low temperature the self-assembly process of methanethiol is not driven by Van der Waals forces, but by a surface-mediated interaction. These novel results clearly demonstrate the unique nature of the methanethiol adsorption and self-assembly.

This work is supported by the National Science Foundation under Award #0425826 for the Center for High-Rate Nanomanufacturing and under Grant No. DMR-0134933. The computations are performed on the CRAY XT3 machine Sapphire at US Army/Engineer Research and Development Center (ERDC, Vicksburg, MS) in collaboration with Jackson State University, and supported by the DoD through Contract #W912HZ-06-C-005.

10:40am **BO+SS+AS-FrM8 Thermo Scientific Theta Probe : Measuring the Quality of Self-Assembled Monlayers on Gold, P. Mack**, Thermo Fisher Scientific, UK, *D.J. Graham*, Asemblon Inc, *J. Wolstenholme*, *R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMs) are becoming increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The attributes of angle resolved X-ray photoelectron spectroscopy (ARXPS), such as surface specificity, chemical selectivity and non-destructive depth profiling, make it the ideal technique for characterising these layers. The Thermo Scientific Theta Probe was used to characterise the quality of self assembled monolayers on gold surfaces. For alkanethiol layers with high coverage, bonding was almost entirely via the thiol group (forming Au-S bonds). Mixed bonding modes were observed, however, with lower coverage, in agreement with a proposed mechanism for the formation of these films. The influence of the head group of the self-assembly precursor was investigated by analysing hydroxyalkanethiol and ethylene glycol monolayers.

11:00am **BO+SS+AS-FrM9 Morphology and Bonding in Alkene and Alkyne Based Monolayers Chemomechanically Formed on Si Surfaces, T.M. Willey**, Lawrence Livermore National Laboratory, *M.V. Lee*, Materials Nanoarchitectonics, Japan, *J.R.I. Lee*, Lawrence Livermore National Laboratory, *M.R. Linford*, Brigham Young University

One of the most simple and economical methods for attaching and patterning alkenes or alkynes on silicon surfaces is through

chemomechanical modification. Scribing the Si removes the oxide passivation layer, allowing the alkene or alkyne to chemisorb to the exposed and highly reactive Si surface. Near-edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy reveals chemically homogeneous films with nearly monolayer coverage. Both alkene and alkyne precursors show no orientational order; however, more rigid perfluorinated molecules do have some incident angle dependence in NEXAFS resonances. Both alkenes and alkynes retain significant sp²/sp³ content. Hypothesized mechanisms of chemisorption are presented based on comparing the intensity of the sp² features in the NEXAFS acquired from monolayers to measurements of precursor alkenes and alkynes in the gas-phase.

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