

Tuesday Morning, November 1, 2011

Surface Science Division

Room: 110 - Session SS2-TuM

Self Assembled Monolayers and Networks

Moderator: J.E. Reutt-Robey, University of Maryland

8:20am **SS2-TuM2 In Situ UHV Growth and XPS/NEXAFS Characterization of Aromatic Self-Assembled Monolayers on Gold Substrates**, A. Nefedov, Karlsruhe Institute of Technology, Germany, H. Muzik, University of Bielefeld, Germany, M. Naboka, Karlsruhe Institute of Technology, Germany, A. Turchanin, A. Götzhäuser, University of Bielefeld, Germany, C. Wöll, Karlsruhe Institute of Technology, Germany
Aromatic self-assembled monolayers (SAMs) on gold show high potential for applications in nanobiotechnology [1]. Although the SAMs are typically prepared by immersing gold substrates in a solvent, their growth by vapor deposition in vacuum has various advantages both for the technological applications and fundamental studies [2, 3]. Thus, it is possible to characterize in detail the monolayer growth by various UHV compatible surface science techniques such as, e.g., electron spectroscopy. Here, we employ a new endstation of the HESGM beamline at BESSY II to study the *in situ* growth of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) SAMs on gold/mica substrates by X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS). XPS C1s, N1s, O1s and S2p spectra as well as NEXAFS CK-, NK- and OK-absorption edge spectra were analyzed. These results demonstrate the formation of NBPT SAMs by vapor deposition in UHV with a similar packing density and molecular orientation as usually obtained in solvents. Moreover, we analyze the electron-radiation-induced modification of NBPT SAMs, that is widely employed in chemical nanolithography [4]. By varying the dose of electron irradiation we study two effects: (i) mechanisms of the electron-induced cross-linking [5] and (ii) conversion of the nitro groups into amino groups [6]. We analyze these transformations and compare the experimental NEXAFS data with calculations made by the StoBe software package.

[1] A. Turchanin, A. Tinazli, M. Ei-Desawy, H. Großmann, M. Schnietz, H. H. Solak, R. Tampé and A. Götzhäuser, *Adv. Mater.* **20**, 2008, 471.

[2] L. Kankate, H. Großmann, U. Werner, R. Tampé, A. Turchanin, A. Götzhäuser, *Biointerphases* **5**, 2010, 30.

[3] L. Kankate, A. Turchanin, and A. Götzhäuser, *Langmuir* **25**, 2009, 10435-10438.

[4] A. Götzhäuser, W. Eck, W. Geyer, V. Stadler, T. Weimann, P. Hinze, M. Grunze, *Adv. Mater.* **13**, 2001, 806.

[5] A. Turchanin, D. Käfer, M. Ei-Desawy, Ch. Wöll, G. Witte and A. Götzhäuser, *Langmuir*, **25**, 2009, 7342.

[6] W. Eck, V. Stadler, W. Geyer, M. Zharnikov, A. Götzhäuser, M. Grunze, *Adv. Mater.* **12**, 2000, 805.

8:40am **SS2-TuM3 Structure, Bonding and Electronic Properties of Self-assembled 2D Organic Nanostructures at Surfaces: Negatively Charged TCNQ Networks and Other Systems**, S.L. Tait, Indiana University

INVITED

Interfaces between organic materials and inorganic supports are critical for the design and function of new organic-based technologies (e.g., OLEDs, organic photovoltaics, and molecular electronics) as well as novel routes to chemical sensors and catalysts. There are vast opportunities for designing structure-function relationships in these systems due to the immense library of organic compounds and metal-organic chemistries available. Molecular self-assembly at surfaces by covalent, metal-organic, ionic, and weaker interactions are active fields of research, but much remains to be determined with regard to the complex interplay of intermolecular and adsorbate-substrate interactions and how these impact structure and function. TCNQ undergoes a charge transfer from a Cu surface to adopt a bond conformation to the surface that enables stable adsorption and the self-assembly of highly ordered 2D structures via surface-mediated attractive interactions. These structures are stable at room temperature. Addition of Mn triggers a structural transformation to a highly-ordered porous network with Mn centers in a high spin state. These studies have allowed new insight into organic / metal interfaces by collaborative work involving high-resolution scanning tunneling microscopy, photoelectron spectroscopy methods, synchrotron measurements, other UHV surface experiments, and density functional theory calculations. Recent progress on other 2D and multilayer organic systems in our group lends further evidence to the significance of direct organic-surface interactions in such systems, the problems those interactions may pose, and solutions for balancing them at a desired level. We are making progress towards tailored chemical function by rational

design of molecular architectures at surfaces and tuning such function through supramolecular design strategies.

9:20am **SS2-TuM5 Ultrafast Self-Assembly of 1-Adamantanethiol and p-Terphenylthiol on Au(111)-surface**, V.V. Korolkov, S.A. Allen, C.J. Roberts, S.J.B. Tendler, The University of Nottingham, UK

Study of organic thiols adsorption on noble metals continues to be a subject of many research papers within the last three decades. Such steady interest arises mainly from the possibility to design metal surfaces with predefined chemical and physical properties that makes them suitable for a whole range of theoretical and applied studies.

Here we propose and investigate an idea that thiols with rigid or spherical hydrocarbon moieties should self-assemble on Au-surface much quicker than those with long-chain moieties. To support this idea we have investigated adsorption dynamics and monolayer structure for 1-adamantanethiol¹ (AdSH) and [1,1':4',1''-terphenyl]-4-thiol (TPT) molecules self-assembled on Au(111)-surface at 393K. We have demonstrated that both thiols form defect free and uniform SAMs almost instantly at elevated temperature. It takes ~1sec for AdSH to self-assemble on gold. In case of TPT ~90% of the monolayer forms within the first ~10 seconds of adsorption, and then it takes ~60 seconds to develop into a well-ordered structure. Both SAMs on Au were characterized with ambient STM up to a single-molecule level, X-ray photoelectron spectroscopy and spectroscopic ellipsometry. We were able to obtain near atomic resolved STM images for AdSH SAM on Au. They clearly showed that all AdSH molecules adsorbed in the same conformation with the molecular tilt and the twist angles being 114° and 0° correspondingly. We have also demonstrated that most AdSH molecules are arranged in a head-to-tail orientation, with some molecules having a head-to-head orientation without forming a disulfide bond.

Molecular resolved STM images of TPT SAM/Au clearly demonstrated that within first seconds of adsorption the Au-surface is equally covered with two different phases (α - and β -). β -phase dominates on the Au-surface from ~10 sec of exposure and onwards. A closer inspection of the β -phase on a single molecule level allowed us to propose an upright conformation for TPT molecule on Au with the tilt angle of $0\pm 5^\circ$. We also estimated the tilt angle for the α -phase to be within 10-20°. For both systems STM and XPS analysis suggest a high chemical and structural quality of the monolayers.

Overall we have proposed a simple and straightforward protocol for ultrafast fabrication of AdSH and TPT SAMs on Au-surface, which we believe can be readily extended for other similar molecular systems.

¹Korolkov et al. *J. Phys. Chem. C*, Vol. 114, No. 45, 2010

9:40am **SS2-TuM6 Role of van der Waals Interaction in the Binding of 1,4 diaminebenzene to the Au(111) Surface**, D. Le, M. Aminpour, University of Central Florida, A. Kiejna, University of Wrocław, Poland, T.S. Rahman, University of Central Florida

The physisorption of 1,4 diaminebenzene (BDA) molecule on Au(111) surface is studied within the generalized gradient approximation of the density functional theory with the PBE [1], vdW-DF [2], and vdW-DF2 [3] exchange correlation functionals. The binding energy of an isolated BDA adsorbed on Au(111) surface calculated from vdW-DF (vdW-DF2) is 0.78 eV (0.84 eV) in better agreement with the experimental value (1.0 eV) [4] than that from PBE (0.37 eV), while the alignment of the molecule along the surface obtained from PBE (20°) is closer to the experimental value of 24° [4] than that of about 5° derived from vdW-DF (or vdW-DF2). On the other hand, when interactions between the BDA molecules is included in the calculations, as would be the case if the molecules were to self-assemble, say in the form of a linear line structure on Au(111), inclusion of vdW interactions gives excellent agreement with experimental observations. In particular vdW-DF and vdW-DF2 predict the BDA tilt angles to be 23° and 21°, respectively. The binding energy of a BDA on Au(111) in this case is 0.70 eV and 0.71 eV, respectively. As is to be expected, PBE does not account for intermolecular interactions and does not give good agreement with the data. We suggest the presence of such alignment of molecules along the surface in the experiments, and that they are governed by hydrogen bonding between N and H atoms of neighboring BDA molecules. We compare our results also with unpublished STM data for the system.

[1] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

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[4] M. Dell'Angela, G. Kladnik, A. Cossaro, A. Verdini, M. Kamenetska, I. Tamblin, S. Y. Quek, J. B. Neaton, D. Cvetko, A. Morgante, and L. Venkataraman, *Nano Lett.* 10, 2470–2474 (2010)

*Work supported by DOE Grant DE-FG02-07ER15842.

10:40am **SS2-TuM9 Conformational Chirality, Chiral Switching and Chiral Induction in Self-Assembled Molecular Structures**, *T.R. Linderoth*, University of Aarhus, Denmark **INVITED**

Chiral self-assembled structures formed from organic molecules have been subject to intense investigation, motivated both by applications such as enantiospecific heterogeneous catalysis as well as by fundamental interest e.g. in relation to the origin of biomolecular homochirality. Chirality on surfaces may arise both for intrinsically chiral molecules and for prochiral molecules that become chiral due to reduced symmetry upon adsorption. However, chiral effects originating from conformational degrees of freedom have received relatively little attention.

Here we use a combination of organic synthesis and UHV-STM experiments to address how rational design of molecular building blocks allows transfer of chirality from the molecular to the supra-molecular level. We investigate a class of custom-designed molecules based on a linear oligo-phenylene-ethynylene backbone and characterize their adsorption structures on the Au(111) surface. Most of these compounds are prochiral and display conformational chirality in the sense that they can adsorb in different chiral conformations distinguished by the positions of two tert-butyl side-groups. A novel chiral switching mechanism, involving a conformational change where the terminal groups rotate around the molecular axis, is directly revealed from time-resolved STM. We demonstrate that it is possible through control of the terminal group functionalization to steer the molecular backbones into surface assemblies that are either mirror symmetric or display pronounced organizational chirality in the form of a characteristic windmill motif. We furthermore achieve control over the absolute chirality of windmill assemblies by synthesizing an intrinsically chiral variant where the tert-butyl side pendant is replaced by a chiral (*S*)-*sec*-butyl group. This intrinsically chiral compound is finally used in co-deposition experiments as an induction seed to control the chirality of assemblies formed from the original prochiral compound.

Chiral switching by spontaneous conformational change in adsorbed organic molecules

S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K.V. Gothelf, F. Besenbacher, and T.R. Linderoth, *Nature Materials*, 5 11 (2006)

Steering organizational and conformational surface chirality by controlling molecular

chemical functionality

C. Bombis, S. Weigelt, M. M. Knudsen, M. Nørsgaard, C. Busse, E. Lægsgaard, F. Besenbacher,

K. V. Gothelf, and T. R. Linderoth, *ACS NANO* 4, 297 (2010).

Controlling chiral organization of molecular rods on Au(111) by molecular design

M. Knudsen, N. Kalashnyk, F. Masini, J. Cramer, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, K. Gothelf, *Journ. Am. Chem. Soc.* 133 4896 (2011).

11:20am **SS2-TuM11 Electronic Structure and Charge Injection Barriers of Self Assembled Peptide Nucleic Acid Monolayers on Au**, *M.A. Wolak*, University of South Florida, *A. Balaeff*, Duke University, *S. Gutmann*, *M.M. Beerbom*, University of South Florida, *E. Wierzbinski*, *D.H. Waldeck*, University of Pittsburgh, *S. Bezer*, *C. Achim*, Carnegie Mellon University, *D.N. Beratan*, Duke University, *R. Schlaf*, University of South Florida

Peptide nucleic acids (PNA) are a promising alternative to DNA for bio-sensing applications as well as for strategies for self assembly based on nucleic acid hybridization. This potential is a result of the PNA's neutral pseudopeptide backbone, which eliminates inter-strand electrostatic repulsion. In recent years charge transfer through PNA molecules has been a focus of research due to potential applications in self-assembled molecular circuits. This makes it interesting to investigate the electronic structure of PNA interfaces to electrode materials. A widely used strategy to 'connect' PNA molecules to metallic electrodes is through thiol-Au bonds using a terminal cysteine appended to PNA oligomers. This motivated the here presented research where the electronic structure of self-assembled PNA monolayers on Au substrates was investigated. Cys-appended PNA 7-mers of thymine (Cys-T7) were incubated on Au substrates in a nitrogen glove box attached to a photoemission spectrometer. Ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) measurements on the resulting SAMs revealed the hole injection barrier at the interface and the interface dipole. Electronic structure calculations based on molecular dynamics

sampling of the PNA structure yielded the band gap and the electronic density of states for PNA. Combined with the UPS data, the theoretical calculation enabled the estimate of the electron injection barrier at the interface, as well as the assignment of individual UP spectral features to specific molecular orbitals. Control measurements on Cys-appended, abasic PNA backbone 7-mers allowed the identification of the emissions related to the PNA backbone in the UP spectra. The orbital line-up at the interface between the Au substrate and the Cys-PNA indicates a significant interface dipole resulting in the alignment of the Au Fermi level near the center of the PNA HOMO-LUMO gap. This alignment causes large charge injection barriers for both holes and electrons, and thus impedes charge transfer from Au into the Cys-PNA SAM.

11:40am **SS2-TuM12 Immobilization of Single-Stranded DNA Probe on InAs Surfaces for Biosensor Application**, *E.K. Cho*, University of Wisconsin, *A. Brown*, Duke University, *T.F. Kuech*, University of Wisconsin

We study the immobilization of single-stranded DNA (ssDNA) probe on indium arsenide (InAs) surface and its characterization for diagnostic application. In contrast to other semiconductors, the Fermi level in InAs is typically pinned above the conduction band minimum, resulting two-dimensional electron gas (2DEG) located immediately below the surface. The InAs based system forms the basis of a DNA sensing platform because hybridization of complimentary DNA sequence with the immobilized DNA probes on InAs surface causes the conductivity changes due to negativity charges on the phosphorus backbone of DNA sequences. The DNA immobilization was done using weakly basic solution and characterized by X-ray photoelectron spectroscopy (XPS) and hall measurement. The DNA probe is modified with thiol for 5' end to anchor the DNA probes on InAs surface and fluoro adenosine for 3' end to reveal the existence of DNA on the InAs surface. The XPS spectrum of F 1s and N 1s peaks verify that the DNA is successfully attached on InAs surfaces. The As 3d peak shows that there are considerable amount of As-S observed with no As-Ox after exposing the basic DNA solution. In contrast, In-S is not found in the In 3d core-level. The XPS data suggest that the DNA probes are attached to the InAs surface exclusively via thiolate bonds to As atoms and the DNA functionalization effectively removes InAs oxide as well. This result is not consistent with what has been observed on InAs (100) surfaces, where the thiolate bond is predominantly anchored to Indium atoms. For example, it has been shown a predominance of In-S bonds of alkanethiols and thioacetamide self-assembled monolayer (SAM) on InAs [1, 2]. However, the bonding chemistry of thiolate to III-V surface has been of great debate in literature [3]. The predominance of As-S bonds has been shown with octadecanethiol SAM on GaAs (100) surfaces driven by kinetic competitions [3] even though Ga-S bonds are energetically more favorable than As-S bonds [4]. In addition, the sheet resistivity of initial InAs surface and DNA immobilized surface is measured, and the response of a DNA functionalized InAs surface with complimentary DNA sequence is monitored.

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[3] C. L. McGuinness et al., *J. Phys. Chem. C* 2007, 111, 4226-4234.

[4] T. Scimeca et al., *Phys. Rev. B* 1991, 44, 12927-12932.

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