

O 76: Organic, Polymeric, Biomolecular Films - also with Adsorbates

Time: Thursday 15:15–17:30

Location: MA 043

O 76.1 Thu 15:15 MA 043

The Adsorption of Calcium on Regioregular Poly(3-Hexylthiophene) Studied by Microcalorimetry and X-Ray Photoemission Spectroscopy — •FABIAN BEBENSEE¹, WANDA LEW², JUNFA ZHU³, JACK HESS BARICUATRO², HANS-PETER STEINRÜCK¹, J. MICHAEL GOTTFRIED¹, and CHARLES T. CAMPBELL² — ¹Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany — ²Department of Chemistry, University of Washington, Seattle, WA 98195, USA — ³National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China

Regioregular poly(3-hexylthiophene) (rr-P3HT) is a semiconducting polymer used in organic electronics (OLED, OFET). In such applications, the interface structure and the interaction strength between the polymer and the electrode (e.g. Ca) play a crucial role in the performance of the device. The energetics of the interface, which directly reflects the interactions strength between the polymer and the metal film, is not accessible with conventional surface science techniques, but can be studied using adsorption microcalorimetry. We present a microcalorimetric study of the adsorption of Ca onto freshly prepared and, via electron irradiation, predamaged rr-P3HT films. Calorimetric measurements are supplemented by high-resolution XPS. The unusual combination of these complementary techniques leads to a new level of understanding of this technologically relevant interface. Financial support by the DAAD and the NSF is gratefully acknowledged.

O 76.2 Thu 15:30 MA 043

Mercaptopyridine and 4-aminothiophenol self-assembled layers in metal-molecule-metal contacts: a computational DFT study — •JAN KUCERA and AXEL GROSS — Institute für Theoretische Chemie, Universität Ulm, Germany

Recently it has become possible to deposit two-dimensional Pd layers on top of a 4-mercaptopypyridine (Mpy) or a 4-aminothiophenol (4-ATP) self-assembled monolayer (SAM) on Au(111) leading to metal-molecule-metal contacts [1]. We performed periodic density functional theory (DFT) calculations in order to contribute to the interpretation of the experimentally observed geometric and electronic structures.

The calculations show that the adsorption structures of Mpy and 4-ATP on Au(111) are very similar. Both molecules prefer to bind to bridge-hollow sites at low as well as at high coverages. At low coverages, the molecules are significantly tilted from the Au(111) surface normal, whereas a denser packing leads to more upright configurations. The Pd/SAM interfaces correspond to metastable configurations in spite of the relatively strong Pd-Au interaction. The Pd-SAM contact is made through one-fold coordinated Pd-N bonds. In agreement with the experiment, the density of states (DOS) of Pd layer shows a significant reduction close to the Fermi level with respect to bulk Pd due to the Pd-N interaction. Also in agreement with experiment, the calculations confirm that 4-ATP is able to form bilayer structures connected through hydrogen bonds between the sulfur head group and up to three hydrogen atoms of the amino group.

[1] H.-G. Boyen et al., *Nature Materials* 5, 394 (2006)

O 76.3 Thu 15:45 MA 043

Self-assembled monolayers of aromatic tellurides on gold and silver substrates — TOBIAS WEIDNER¹, ANDREY SHAPORENKO¹, JAN MÜLLER², MICHAEL HÖLTIG², ANDREAS TERFORT², and •MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — ²Faculty of Chemistry, University of Marburg, 35032 Marburg, Germany

Self-assembled monolayers (SAMs) formed from bis(4'-methylbiphenyl-4-yl) ditelluride (BBPDTe) precursors on Au(111) and Ag(111) substrates were characterized by high-resolution X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. BBPDTe was found to adsorb dissociative on both substrates, resulting in the formation of well-defined, densely packed, and ordered BPTe SAMs, with a larger molecular inclination, a lower packing density, and inferior crystallinity on Au than on Ag. However, both BPTe/Au and BPTe/Ag were not stable under ambient conditions, but underwent a rapid autoxidation, which affected exclusively the tellurolate headgroups. The BPTe molecules in the oxidized films remained, however, bound to the substrate by the terminal O atoms

coordinated to the Te moieties, and the quality of the films, given by parameters such as packing density, degree of the orientational order, and average tilt angle of the SAM constituents was not noticeably affected by the autoxidation. In addition, the BPTe SAMs were compared with the analogous thiol- and selenol-based systems, and common tendencies for the different chalcogen headgroups, ranging from Te to O, were derived.

O 76.4 Thu 16:00 MA 043

Fabrication of multifunctional surface structures via laser patterning of silicon bound organic monolayers — •BENJAMIN KLINGEBIEL¹, LUC SCHERES², STEFFEN FRANZKA¹, NILS HARTMANN¹, and HAN ZUILHOF² — ¹Fachbereich Chemie und Center for Nanointegration Duisburg-Essen (CeNIDE), Universität Duisburg-Essen (UDE), 45141 Essen, Germany — ²Laboratory of Organic Chemistry, Wageningen University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

Silicon substrates are widely used as platforms in many micro- and nanofabrication schemes, e. g. in order to build up functional organic templates. For this purpose suitable patterning and functionalization techniques are needed [1-2]. Here we present a facile routine which allows to fabricate multifunctional organic surface structures. H-terminated Si(111) samples were functionalized with 1-hexadecene and 1-hexadecyne, respectively. Laser patterning of the primary monolayer then was carried out following a photothermal routine creating structures down to 100 nm and below [2]. For secondary functionalization of the depleted lines the samples were etched in ammonium fluoride solution and coated with hexadecynoic acid. Using N-hydroxysuccinimide (NHS) coupling chemistry this provides a means to bind biochemical compounds with primary amine groups. In order to test this functionality the samples were treated with NHS and dodecylamine.

1. L. Scheres, A. Arafat, H. Zuilhof, *Langmuir* 23 (2007) 8343.

2. D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, *Nano Letters* 6 (2006) 2358.

O 76.5 Thu 16:15 MA 043

Selective polymerization on laser patterned organic templates: Towards switchable surface structures — MAREIKE MATHIEU, ALEXANDER FRIESE, STEFFEN FRANZKA, MATHIAS ULBRICTH, and •NILS HARTMANN — Fachbereich Chemie and Center for Nanointegration Duisburg-Essen (CeNIDE), Universität Duisburg-Essen (UDE), 45141 Essen, Germany

Stimuli responsive polymeric hydrogels provide a means to build up membranes with switchable pore structures [1]. Here we present results from experiments which aim at the fabrication of hydrogel nanostructures on planar surfaces. Native silicon wafers were coated with octadecylsiloxane monolayers and patterned following a photothermal procedure. In conjunction with postfunctionalization routines hydroxyl-terminated organic surface structures with a lateral dimension down to 100 nm and below have been prepared [2], and those were used to introduce initiator sites for heterogeneous graft copolymerization. Temperature-responsive poly(N-isopropylacrylamide) (PNIPAAm) was then grafted onto these structures via surface-initiated atom transfer radical polymerization (ATRP). The thickness and structure of the polymer coating were characterized using atomic force microscopy (AFM). Work in progress also addresses the temperature responsive properties of these polymer structures.

1. A. Friese, M. Ulbricht, *Langmuir* 23 (2007) 10316.

2. D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, *Nano Letters* 6 (2006) 2358.

O 76.6 Thu 16:30 MA 043

Discrete laser patterning of phospholipid multilayers — •MAREIKE MATHIEU, DANIEL SCHUNK, STEFFEN FRANZKA, CHRISTIAN MAYER, ECKART HASSELBRINK, and NILS HARTMANN — Fachbereich Chemie and Center for Nanointegration Duisburg-Essen (CeNIDE), Universität Duisburg-Essen (UDE), 45141 Essen, Germany

Phospholipid bilayers are widely recognized as model systems for biological membranes. Phospholipid multilayers also have been used as a matrix to arrange metallic nanoparticles into 2D structures [1]. Here we report on a photothermal procedure to pattern such phospholipid bilayer stacks. For patterning dioleyl-phosphatidic acid (DOPA) films

were deposited on native silicon samples using the spin coating technique. Irradiation with a focused beam from an argon ion laser operated at a wavelength of 514 nm allows to locally remove the coating [2]. At a spot diameter of about 2.5 microns structures with lateral dimensions down to 400 nm were prepared. Most remarkably, however, partial removal can be carried out at incremental steps leaving a distinct number of bilayers behind. This offers an opportunity to build up discrete topographies, which could be used as 3D templates for the fabrication of multilevel architectures of nanoscopic components.

1. A. Terheiden, C. Mayer, K. Moh, B. Stahlmecke, S. Stappert, M. Acet, B. Rellinghaus, *Appl. Phys. Lett.* 84 (2004) 3891.
2. T. Balgar, S. Franzka, N. Hartmann, *Appl. Phys. A* 82 (2006) 689.

O 76.7 Thu 16:45 MA 043

Growth of phospholipid membrane systems on self-organized semiconductor templates — GERALD TRUMMER, GREGOR HLAWACEK, DANIEL PRESSL, and •CHRISTIAN TEICHERT — Montanuniversität Leoben, Austria

Here, we use atomic force microscopy (AFM) to study the formation of solid-supported lipid bilayers on a variety of nanofaceted self-organized SiGe films on Si(001)[1] and ion eroded semiconductor surfaces [2] in comparison to smooth Si(001) wafers. 1-Palmitoyl-2-Oleoyl-sn-Glycero-3-Phosphoethanolamine (POPE) and 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC) were used as model systems. The resulting film morphology and the change of surface roughness have been investigated as a function of initial roughness and morphology of the substrate. Phase imaging is used to distinguish between the soft lipid layers and the hard semiconductor substrate. On SiGe templates showing a dislocation network it was found that the ridge trench structures appearing at the surface guide the terrace edges of DPPC layers. When the lipid coverage is very low, 100 nm x 100 nm pits of {105} faceted SiGe film act as preferential deposition sites for lipid bilayers resulting in ordered arrays of small POPE islands.

- [1] C. Teichert, *Phys. Rep.* 365 (2002) 335. [2] S. Facsko, et. al., *Science* 285 (1999) 1551; T. Bobek, et al., *Phys. Rev. B* 68 (2003) 085324.

O 76.8 Thu 17:00 MA 043

High Frequency QCM Flow Cell with Enhanced Accuracy for Liquid and Biochemical Sensing — •BRIGITTE PAULA SAGMEISTER¹, HERMANN GRUBER², and REINHARD SCHWÖDIAUER¹ — ¹Soft Matter Physics, Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria — ²Institute for Biophysics, Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria

Throughout the last twenty years, acoustic wave sensors have been proven to be an extremely sensitive and accurate device for a wide variety of physical, chemical and biochemical sensing applications. Systems based on thickness shear mode (TSM) quartz resonators, working in a liquid environment with resonance frequencies between 5 and 15 MHz, are already established for real-time measurements of biochemical interactions and commercially available on the market. The utilisation of high frequency fundamental (HFF) quartz resonators, with resonance frequencies up to 150 MHz (and beyond), could further improve the sensitivity of such systems by orders of magnitude. We present a fully biocompatible flow cell, designed for HFF quartz resonators which, in spite of their small size, can be removed and exchanged quickly and with ease. The system performance is evaluated and quantified by a number of experiments including various viscosity measurement of sugar based solutions, the detection of a BSA protein monolayer and other biochemical reactions. We further address some specific problems especially related to reusability and cleaning procedures.

O 76.9 Thu 17:15 MA 043

Preparation and Surface Characterisation of Thermally Deposited Ultrathin Ionic Liquid Films — •TILL CREMER¹, MANUELA KILLIANI¹, CLAUDIA KOLBECK¹, J. MICHAEL GOTTFRIED¹, PETER WASSERSCHEID², FLORIAN MAIER¹, and HANS-PETER STEINRÜCK¹ — ¹Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen — ²Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen

Due to their unique physico-chemical properties, ionic liquids (ILs) are promising candidates for many applications in electrochemistry, analysis, synthesis, separation and lubrication technology, and in catalysis.

In surface science, ILs open up interesting new possibilities: Since most ILs exhibit negligible vapour pressures at room temperature, various surface science techniques that employ ultra-high vacuum can be applied, enabling detailed investigations of their surface chemical composition and electronic structure. Furthermore, at elevated temperatures, thermal evaporation of ILs takes place, providing a new way for the in-situ preparation of ultrathin IL films on planar substrates.

In an angular dependent photoelectron spectroscopy (XPS) study we investigated imidazolium-based IL films of nanometer thickness, deposited on glass. For 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{EMIM}]^+ [\text{Tf}_2\text{N}]^-$), we were able to demonstrate that the initial film growth occurs via a bilayer structure, with the $[\text{Tf}_2\text{N}]^-$ anions pointing away from the surface while the $[\text{EMIM}]^+$ cations are oriented towards the surface.

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