

O 17: Metal substrates: Adsorption of organic / bio molecules III

Time: Monday 17:15–19:15

Location: TRE Phy

O 17.1 Mon 17:15 TRE Phy

Opto-electronically active block copolymers on metallic surfaces — ●CORMAC TOHER, JÖRG MEYER, LOKA MANI, ANJA WADEWITZ, FRANCESCA MORESCO, and GIANAURELIO CUNIBERTI — Institute for Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, 01062 Dresden, Germany.

Opto-electronically active organic polymer materials offer several advantages over traditional solid-state semiconductors in the fabrication of devices such as solar cells and light emitting diodes, including their low cost, low weight, and flexibility. Here, we present the results of ongoing combined theoretical and experimental analytical studies of a block copolymer consisting of a covalently bound polythiophene donor and fullerene acceptor, with the goal of developing a fundamental, systematic, atomistic-scale understanding of the origin of specific optoelectronic properties in order to facilitate the enhancement of the efficiency and functionality of these materials. The electronic structure and transport properties of both the full polymer chains and the individual components were investigated using *ab initio* density functional theory (DFT) and non-equilibrium Green's function calculations. The molecular components were then deposited on metallic surfaces for study using scanning tunnelling microscopy, in conjunction with DFT simulations of the density of states and investigations of the interaction with the substrate.

O 17.2 Mon 17:30 TRE Phy

Direct formation of a polyamide on Ag(111): Joint XPS and STM studies — ●MARTIN SCHMID¹, CHRISTOPH H. SCHMITZ², JULIAN IKONOMOV², HANS-PETER STEINRÜCK¹, J. MICHAEL GOTTFRIED¹, and MORITZ SOKOLOWSKI² — ¹Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg — ²Institut für Physikalische und Theoretische Chemie, Universität Bonn

The polymer poly(*p*-phenylene terephthalamide) (PPTA) was synthesized on Ag(111) by co-adsorption of the reactive monomer compounds terephthaloyl chloride (TPC) and *p*-phenylenediamine (PPD) at 300 K. The resulting adsorbate phases were characterised by photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). A detailed study of the chemical composition and morphology revealed a complex reaction mechanism, by which the formation of amide bonds leads to folded PPTA polymer chains. According to XPS, the chloride of the TPC precursor is not released as HCl as in the bulk reaction, but remains on the surface as chemisorbed Cl or AgCl. Further temperature-programmed XPS studies of pure TPC on Ag(111) reveal that the molecule decomposes already above 130 K, forming chemisorbed Cl (or AgCl) and a phenylene-dicarbonyl species, which is presumably stabilized by the substrate. The adsorbed chlorine partially desorbs above 800 K as molecular AgCl. Financial support by the Deutsche Forschungsgemeinschaft through SFB 624 and SFB 583 is gratefully acknowledged.

O 17.3 Mon 17:45 TRE Phy

Modeling of the adsorption of bis(terpyridine) molecules at the solid/liquid interface — ●DANIELA KÜNZEL and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Force field and DFT calculations have been quite successful in addressing properties of adsorbed organic molecules [1,2]. However, the calculations are typically performed at the solid/vacuum interface whereas the experiments are often done at the solid/liquid interface. This might be the reason for remaining discrepancies between experimental and theoretical results. Therefore, we attempt to implicitly include the effect of solvents into our force field calculations in order to obtain a better model of the experimental systems.

As a first step, we have determined average energies of solvated systems using molecular dynamics simulations. Calculations of solvent densities and solvation energies of small test molecules serve to validate the applicability of different force fields to the problem. Based on the knowledge gained from these validation steps, the solvation of BTP molecules and the adsorption of dissolved molecules on graphite is analyzed.

[1] C. Meier et al., *Angew. Chem. Int. Ed.*, 2008, 47, 3821.

[2] D. Künzel, Th. Markert, A. Groß, and D. M. Benoit, *Phys. Chem. Chem. Phys.*, 2009, 11, 8867.

O 17.4 Mon 18:00 TRE Phy

Scanning Tunneling Microscopy of Proteins in Ultrahigh Vacuum — ●STEPHAN RAUSCHENBACH¹, NICHA THONTASEN¹, DENG ZHITAO¹, RINKE GORDON¹, and KERN KLAUS^{1,2} — ¹Max-Planck-Institute for Solid State Research, Stuttgart, Germany — ²Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Proteins are biosynthesized, self-assembled, functional polymers of unprecedented complexity and specificity in their function. Since the shape which determines their behavior depends strongly on the environment they typically are investigated under physiological conditions. The functionalization of well defined surfaces with such molecules would be an important step towards using high performance vacuum based techniques, like scanning probe microscopes. Here we show the controlled deposition and *in situ* characterization of intact proteins on clean metal surfaces in ultrahigh vacuum by electrospray ion beam deposition (ES-IBD). We demonstrate that depending on the charge state, the protein can be deposited in a folded or unfolded state. For unfolded proteins, scanning tunneling microscopy reaches single amino acid level resolution.

O 17.5 Mon 18:15 TRE Phy

Dynamic Force Spectroscopy at a Single Molecule Junction — ●CHRISTIAN LOTZE, MARTINA CORSO, GUNNAR SCHULZE, KATHARINA J. FRANKE, and JOSE IGNACIO PASCUAL — Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin

Recent Developments in Atomic Force Microscopy made it possible to probe not only electronic properties of single molecules and atoms on (conducting) surfaces but also acquiring information about forces in the pN regime simultaneously. Determination of the charged state of single metal atoms [1] or resolving the chemical structure of a molecule [2] are just some of the possibilities, opening a new field of scanning probe spectroscopy.

We utilize our tuning fork based LT STM/AFM in the well known qPlus design operated at 5K to do single molecule force spectroscopy combined with tunneling differential conductance measurements. With our STM tip we contact a functionalized polyarene molecule in one side and lift it up from the surface, while the other side remains attached to the substrate [3]. During lift up we observe sawtooth like features in the df spectra that allow us to determine potential barrier heights during the molecule pulling process.

[1] Leo Gross, *et al.*, *Science* **324**, 1428 (2009) [2] Leo Gross, *et al.*, *Science* **325**, 1110 (2009) [3] F. Pump, R. Temirov, O. Neucheva, S. Soubatch, S. Tautz, M. Rohlfing, G. Cuniberti, *Appl. Phys. A* **93**, 335 (2008)

O 17.6 Mon 18:30 TRE Phy

Modification of the electronic properties of Au/molecule/Pd junctions by adsorbed hydrogen: a DFT study — ●JAN KUČERA and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

Metal-molecule-metal contacts assembled from a Pd monolayer deposited on a Au-supported self-assembled monolayer (SAM) of 4-mercaptopyridine or 4-aminothiophenol were recently achieved by means of an electrochemical approach [1]. Subsequent photoelectron spectroscopy showed a strongly reduced Pd density of states (DOS) at the Fermi energy [2]. This phenomenon is still not fully comprehended, however, its understanding is crucial for the use of the sandwich design as a platform for future nanoelectronics.

Periodic density functional theory (DFT) calculation revealed that the dehydrogenation of the amino group and the subsequent strong bonding of the remaining nitrogen atom to the Pd layer could explain the observed modification of the DOS [3]. We have now extended this study in order to clarify the role of hydrogen atoms for the electronic properties of the Pd layers. In equilibrium, these layers should always show a considerable hydrogen coverage in an aqueous environment. Our calculations demonstrate that indeed the adsorbed hydrogen atoms significantly modify the electronic structure of the Pd layers.

[1] F. Eberle et al., *Angew. Chem. Int. Ed.* 49, 341-345 (2010)

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

[3] J. Kučera and A. Groß, *Phys. Chem. Chem. Phys.* 12, 4423

(2010)

O 17.7 Mon 18:45 TRE Phy

Interface properties of a biphenyl-based metal-molecule-metal junction — ●MARC SAITNER¹, FELIX EBERLE², DIETER M. KOLB², JOHNNY BACCUS¹, PATRICK WAGNER^{1,3}, MARC D'OLIESLAEGER^{1,3}, and HANS-GERD BOYEN¹ — ¹Institute for Materials Research (IMO), Hasselt University, B-3590 Diepenbeek, Belgium — ²Institute for Electrochemistry, Ulm University, D-89069 Ulm — ³IMEC, Division IMOMECE, B-3590 Diepenbeek, Belgium

Here we report on the successful preparation of a metal/molecule/metal junction, in which a biphenyl (BP) self-assembled monolayer (SAM) on Au(111) is metalized by Pd using a recently developed electrochemical approach.[1] The junction is studied by cyclic voltametry (CV), in-situ scanning tunneling microscopy (STM) and ex-situ X-ray as well as ultraviolet photoelectron spectroscopy (XPS, UPS). A quantitative chemical analysis of the BP SAM points towards the formation of a densely packed molecular layer attached to the base electrode (Au single crystal) via Au-S bounds. The successful metallization of such SAMs with a Pd monolayer is demonstrated by means of angle-resolved XPS. Both metal-molecule interfaces in the junction can be studied in more detail using angle-resolved UPS thereby allowing to identify local-density of states effects [2,3] in the electronic structure of the involved metals.

- [1] T. Baunach et al., Adv. Mater. 16, 2024 (2004)
- [2] H.-G. Boyen et al., Nat. Mater. 5, 394 (2006)
- [3] M. Manolova et al., Adv. Mater. 21, 320 (2009)

O 17.8 Mon 19:00 TRE Phy

STM investigation of the morphology of biphenylthiol self-assembled monolayers on Au(111) — ●HEIKO MUZIK, DAN G. MATEI, LAXMAN KANKATE, ARMIN GÖLZHÄUSER und ANDREY TURCHANIN — Physik supramolekularer Systeme und Oberflächen, Universität Bielefeld

Self-assembled monolayers (SAMs) with an aromatic moiety directly attached to the sulfur head group are known to build highly corrugated surface morphologies on Au(111). A commonly observed pattern is the formation of islands with a gold step-edge height. The nature of this phenomenon has been rarely investigated, although it stands in contrast to the observation of so-called 'etch pits' in alkanethiol SAMs. In this contribution we present a scanning tunneling microscopy study of SAMs of 4'-nitro-1,1'-biphenyl-4-thiols and 1,1'-biphenyl-4-thiols on Au(111). We relate the different SAM morphologies to the molecular coverage, which was complementary determined by X-ray photoelectron spectroscopy. Based on these data we discuss why the classical picture of the molecule/substrate interface with the Au(111) binding sites has to be reviewed.