

O 30: Metal substrates: Adsorption of organic / bio molecules IV

Time: Wednesday 10:30–13:00

Location: SCH A118

O 30.1 Wed 10:30 SCH A118

Evidence of Charge Transfer in UHV-Deposited Coronene-hexaone and Hexamethoxycoronene Sandwich Layers — K. MEDJANIK¹, S. NAGHAVI², R. RIEGER³, D. KUTNYAKHOV¹, S.A. NEPLJKO¹, ●G. SCHÖNHENSE¹, V. ALIJANI², C. FELSER², M. BAUMGARTEN³, and K. MÜLLEN³ — ¹Institut für Physik, Universität Mainz — ²Institute for Analytic and Anorganic Chemistry Univ. Mainz — ³Max-Planck-Institute for Polymer Research, Mainz

The electronic structure of UHV-deposited sandwich layers of the donor hexamethoxycoronene and the acceptor coronene-hexaone on Au has been studied by UPS. In a donor-acceptor multilayer superstructure a new signal close to the Fermi energy arises that is absent in films of the pure species. The electron injection barrier of the acceptor is lowered such that charge transfer occurs into its LUMO. The charge depletion in the donor molecules leads to a shift of their HOMO position to higher binding energies by 0.26eV. A significant band bending occurs due to the polar interface between the metal and the organic film as discussed by Koch [1]. In turn, the UPS signal of the charge transfer complex rises significantly above that of the Au substrate (by 0.35eV in the as-deposited multilayer film and by 0.55eV upon annealing of the film at 80°C). In AFM and optical microscopy we observe triangular-shaped nanocrystals with dendritic growth mode.

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[1] N. Koch, J. Phys. Cond. Matt. 20 (2008) 184008

O 30.2 Wed 10:45 SCH A118

Reactions on surfaces for the creation of template structures — ●MEIKE STÖHR¹, MANFRED MATENA¹, MARKUS WAHL¹, THOMAS A. JUNG², JÖRG ZEGENHAGEN³, and LUTZ H. GADE⁴ — ¹University of Basel, Switzerland — ²Paul-Scherrer-Institute, Switzerland — ³ESRF Grenoble, France — ⁴University of Heidelberg, Germany

Molecular assemblies on surfaces can be used as templates that allow the study of host guest interactions and provide in a further step an ideal starting point for the generation of more complex hierarchic structures. An important prerequisite besides the regularity of such structures is their stability. We reported the formation of a molecular honeycomb network generated by thermal dehydrogenation of a perylene derivative (DPDI) on a Cu(111) surface [1]. By thermal activation, these molecules become H-bond donors/acceptors and form a highly regular honeycomb structure which is commensurate to the Cu substrate. This network can be used as a template for the incorporation of guest molecules in its hexagonal 'holes' [2]. In addition, XSW (x-ray standing wave) experiments were carried out to determine the height of the DPDI molecules above the Cu surface before and after annealing the sample. It turned out that for the not annealed sample the DPDI molecules mainly interact through their amine end groups with the substrate while the molecule is in a bridge-like configuration. After annealing, the height difference between the end groups and the perylene core is lowered what is required to enable H-bonding between the molecules. [1] M. Stöhr et al., Angew. Chem. Int. Ed. 44 (2005) 7394 [2] M. Stöhr et al., Small 3 (2007) 1336

O 30.3 Wed 11:00 SCH A118

Covalent interlinking on the surface by condensation polymerization of *p*-phenylenediamine and terephthaloyl chloride — ●CHRISTOPH H. SCHMITZ, JULIAN IKONOMOV, and MORITZ SOKOLOWSKI — Inst. f. Physikal. u. Theoret. Chemie, Universität Bonn

Long-range ordered structures of organic adsorbates on metal surfaces are mainly based on weak adsorbate-adsorbate interactions, such as van der Waals-forces, dipole interactions and hydrogen bonds. Technical applications require more robust and durable layers, that may be realized by covalent networks. Examples of the direct covalent interlinking of small organic molecules on the surface are scarce [1-3] and the reactions are mainly induced by heating, which limits the range of possible substances. We herein report on the formation of covalently interlinked structures of a polyamide via condensation polymerization directly on the surface. The vapour-deposition polymerization (VDP) technique was combined with ultra-high vacuum preparations methods to obtain polymer monolayers. We demonstrate this concept by the reaction of *p*-phenylenediamine (PPD) and terephthaloyl chloride (TPC) to form poly(*p*-phenylene terephthalamide) (PPTA) on the Ag(111)

surface at room-temperature. After removal of the excess monomer, the polyamide chains arrange in long-range ordered islands on the surface. The structures have been characterized by variable temperature scanning tunneling microscopy (VT-STM). (Funded by DFG through SFB 624) [1] L. Grill et al., *Nature Nanotech.* **2007**, 2, 687. [2] N. A. A. Zwaneveld et al., *J. Am. Chem. Soc.* **2008**, 130, 6678. [3] S. Weigelt et al., *Angew. Chem.* **2008**, 120, 4478.

O 30.4 Wed 11:15 SCH A118

Controlling the organization and heat induced coupling of biphenyl derivatives on metal surfaces — ●SERPIL BOZ¹, MEIKE STÖHR¹, UMUT SOYDANER², and MARCEL MAYOR² — ¹University of Basel, Department of Physics, Klingelbergstrasse, CH-4056 Basel, Switzerland. — ²University of Basel, Department of Chemistry, St. Johansring 19, CH-4056 Basel, Switzerland.

The development of scanning probe methods enabled the investigation of molecules on surfaces with impressive resolutions. A delicate balance between molecule - substrate and intermolecular interactions such as van der Waals interactions, H-bonding or dipolar coupling guides the arrangement of the molecules in well ordered patterns.

A very appealing concept is to profit from the order of these pre-organized structures and to interlink the molecular building blocks to macromolecules.

Previously, we presented our new concept to control both, the molecular self-assembly and the subsequent intermolecular coupling reactivity by protection group chemistry and described the heat induced formation of individual polymeric structures from a biphenyl derivative on single crystal Cu (111) and Ag(111) substrates. Here we would like to present how to control the arrangement and the size of the resulting polymeric structures by modification of the end groups of the previously presented biphenyl unit.

O 30.5 Wed 11:30 SCH A118

Molecules with "wheels" on a metal surface — ●CARLOS VILLAGOMEZ¹, TAKASHI SASAKI², JAMES M. TOUR², and LEONHARD GRILL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin — ²Chemistry Department, Rice University, Houston Texas, USA

The design and creation of molecular nanostructures with specific mechanical functions is one of the fundamental issues in nanotechnology. In this context, wheels are an interesting component for the molecular motion, because they are expected to alter the diffusion properties on surfaces, for instance by allowing only directed motion. In the presented work, we show the adsorption of functional molecules studied by scanning tunneling microscopy under ultrahigh vacuum at low temperatures of about 7 K. The molecules consist of a phenyl chain, equipped with carborane side groups that represent the molecular "wheels". Additionally, bromine atoms are attached to the terminal groups of the molecules, which should allow the covalent connection of individual molecules, according to our recently presented "on-surface-synthesis" method. The high mobility of the molecules during deposition, at room temperature, enables them to form molecular nanostructures. Characteristic appearances of the molecules, due to different molecular configurations, are found. Furthermore, lateral manipulation was used to displace molecules and to probe their intermolecular interactions.

O 30.6 Wed 11:45 SCH A118

Tuning surface reactivity by alloying - Acrolein adsorption on well ordered Pt_xCe/Pt(111) alloys — ●JAN MARKUS ESSEN, CONRAD BECKER, and KLAUS WANDEL — Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

The reactivity of Pt(111) surfaces towards acrolein is mainly determined by the d-band molecule interaction at the Fermi edge. Depending on the initial coverage a η_4 -trans, a η_3 -cis and a η_2 -cis and -trans conformation of adsorbed acrolein is stable. A Pt-O interaction is not favored. Acrolein decomposition proceeds via C₁-C₂ bond cleavage by a Pt addition into the C-C bond which leads mainly to CO and ethene. In contrast to that, the reactivity of acrolein on pure polycrystalline cerium films is mainly caused by the stability of simultaneously generated cerium oxides. A Ce-O interaction is favored which leads to a

strongly distorted adsorption geometry. The decomposition proceeds via C₁-O bond cleavage by a reductive coupling forming benzene and 1,3,5-hexatriene. Alloying of cerium with Pt results in the formation of several well ordered alloy phases. In general these phases have the same adsorption properties in common. Acrolein adsorbs on the top-most Pt-layer in the same conformation as on Pt(111). Only the η_4 conformation is not stable caused by ensemble effects. In contrast to pure Pt(111) however no decomposition takes place. Acrolein desorbs completely intact from these alloy phases at about 230 K.

O 30.7 Wed 12:00 SCH A118

A quantitative model for the monolayer growth of hydrocarbons on noble metals: HBC on Ag(111) and Au(111) — ●CHRISTIAN WAGNER, DANIEL KASEMANN, MORITZ ESSLINGER, ROMAN FORKER, CHRISTIAN GOLNIK, and TORSTEN FRITZ — Institut für Angewandte Photophysik, TU-Dresden, George-Bähr-Str. 1, 01069 Dresden

In our contribution we compare the growth of hexa-perihexabenzocoronene (HBC) on Ag(111) and Au(111) for monolayer (ML) and sub-ML coverage[1,2]. Despite the always present *attractive* van der Waals force we observe a net *repulsive* interaction between individual HBC molecules on the Au(111) surface, resulting in a complex growth behavior: Unlike the situation on Ag(111) no lattice epitaxy is observed for HBC MLs on Au(111) in the predominant phase. Instead, we find a coverage dependent lattice constant (between 13.6 Å and 14.7 Å). Including coulomb and van der Waals forces as well as Pauli repulsion (by the respective OPLS force fields) between the molecules on one hand, and the influence of the metal substrates, namely attractive binding, mirror charges and even a screening of the van der Waals attraction on the other hand, we propose a quantitative model of the interaction potential of HBC on both metals that can be fitted to the experimental results and is indeed able to explain all findings with reasonable values for the parameters used. Furthermore, we can assign the orientation of HBC domains on Au(111) to the interaction with the surface reconstruction pattern.

[1] H. Proehl et al. *Phys. Rev. B* **63**, 205409 (2001)

[2] P. Ruffieux et al. *J. Am. Chem. Soc.* **129**, 5007 (2007)

O 30.8 Wed 12:15 SCH A118

Covalently bound molecular chains on an ultrathin insulating film — ●CHRISTIAN BOMBIS¹, LEIF LAFFERENTZ¹, HAO YU², STEFAN HECHT², FRANCISCO AMPLE³, CHRISTIAN JOACHIM³, and LEONHARD GRILL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Institut für Chemie, Humboldt Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany — ³CEMES-CNRS, 29 rue J. Marvig, PO Box 4347, 31055 Toulouse Cedex, France

The adsorption of single covalently bound molecular chains on an ultrathin insulating film of NaCl on a metallic substrate is presented for the first time. In the emerging field of molecular electronics, ultrathin films of NaCl are attracting increasing attention since it was successfully demonstrated that they provide mandatory electronic decoupling of single organic molecules from an underlying metallic substrate while still allowing a sufficient flow of current for the investigation by scanning tunneling microscopy (STM). Conjugated polymers are promising candidates as organic nano-wires. The studied covalently bound molecular chains are formed by organic on-surface-synthesis of dibromoter-

fluorene (DBTF) molecules on a Au(111)-surface. The adsorption of these polymeric chains, which form molecular interconnects from the metallic substrate on top of an insulating NaCl film, is investigated at the single-molecule level with an STM working at low temperatures (13 K). To further illuminate the adsorption properties of DBTF on top of the ultrathin film of NaCl, electron scattering quantum chemistry (ESQC) calculations are performed.

O 30.9 Wed 12:30 SCH A118

Nanostructuring of an ultrathin insulating film of NaCl on Cu(111) — ●CHRISTIAN BOMBIS¹, JOHANNES MIELKE¹, MICHAEL MANNSBERGER¹, FRANCISCO AMPLE², CHRISTIAN JOACHIM², and LEONHARD GRILL¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²CEMES-CNRS, 29 rue J. Marvig, PO Box 4347, 31055 Toulouse Cedex, France

By using the atomic scale scanning tunnelling microscope (STM) manipulation ability, the nano-mechanical properties and the nanostructuring of NaCl crystalline nanoplates adsorbed on Cu(111) were investigated. Thin films of NaCl as spacer layers are attracting increasing attention, because they retain many of the insulator characteristics while still allowing sufficient current flow to enable STM probing. The thus enabled electronic decoupling of organic molecules from an underlying metal substrate was recently demonstrated and is of particular interest in the emerging field of molecular electronics. Here, we present the nanostructuring of an insulating film of NaCl, which covers cutting of different atomic layers, breaking of nano-islands as well as island manipulation on the metallic substrate. The achieved manipulation abilities are highly relevant with respect to the controlled formation of desired planar molecular interconnects. To further illuminate our current understanding of the nano-mechanical behaviour of the ultrathin film of crystalline NaCl on Cu(111), molecular mechanics calculations will be presented.

O 30.10 Wed 12:45 SCH A118

Vibrational Kondo effect in a metal-free organic self-assembled molecular layer — ●ISABEL FERNANDEZ-TORRENTE, KATHARINA JENNIFER FRANKE, and JOSE IGNACIO PASCUAL — Institut für Experimentalphysik, Freie Universität Berlin, Germany

Molecular magnetism is achieved by localising unpaired electrons within molecules. The traditional approach entails the synthesis of metal-organic coordination compounds, where the unpaired spin is provided by paramagnetic transition metal atoms. Here we show that localization of a spin also occurs in a molecular layer of a pure organic charge transfer compound, TTF-TCNQ, self-assembled on a metal surface. The structure adopted by this salt on Au(111) leads to localization of an unpaired electron in a pi-molecular orbital (LUMO) of the acceptor molecule. This free radical state can be demonstrated by the observation of the Kondo effect, obtained in transport experiments carried out in a low temperature scanning tunneling microscope. The unpaired electron is also coupled with molecular vibrations. This phonon-assisted spin flip induces splitting of the Kondo resonance in vibrational sidebands that exhibit different intensities across the TCNQ molecule. These variations arise from intramolecular alterations of the electron-phonon coupling. The analysis of STS curves taken along individual TCNQ molecules allows us to identify the atomic motion involved in the vibrations.