

O 14: Organic-inorganic hybrid systems and organic films II

Time: Monday 15:00–18:15

Location: MA 042

Invited Talk

O 14.1 Mon 15:00 MA 042

Non-commensurate epitaxy with and without coincidences — ●ROMAN FORKER — Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Helmholtzweg 5, 07743 Jena, Germany

The self assembly of atoms or molecules at surfaces is governed by the balance between adsorbate–adsorbate and adsorbate–substrate interactions. Energetic minimization may be achieved through different types of epitaxy. Besides the well-known commensurate registries there are also the less familiar “on-line coincidences”, where the surface unit cells of the adsorbate and of the substrate have a common periodicity in one direction only [1]. Recently, highly ordered molecular monolayers were found to be room-temperature-stable even in the absence of any coincidence with the substrate. Hence, the concept of lattice epitaxy fails to explain the evident energy minimum in such a case. Instead, we found that stabilization occurs through so-called static distortion waves that manifest in measurable sub-Ångström lateral shifts away from the positions of a translationally symmetric lattice (which itself is incommensurate) [2]. In the talk I will classify epitaxy using an easy-to-grasp scheme applicable both in reciprocal space and in real space. Several instructive literature examples of experimental structural characterization using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) will be elaborated. The ultimate goal is to emphasize the importance of non-commensurate overlayer structures for the systematic understanding of epitaxy.

[1] R. Forker *et al.*, *Soft Matter* **13**, 1748 (2017).

[2] M. Meissner *et al.*, *ACS Nano* **10**, 6474 (2016).

O 14.2 Mon 15:30 MA 042

Electrospray deposition of P3HT on Au(110): An STM study — ●THERESA SIMON¹, ERIK SCHRECK¹, STEFAN FÖRSTER¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max Planck Institut für Mikrostrukturphysik, Halle, Germany

In the course of characterizing the structure of polymers in contact with solid surfaces, the adsorption of Poly(3-hexylthiophene) (P3HT) on Au(001) [1] leads to a 2D random coil like chain configuration but also molecules in straight *all-trans* geometry are found.

Here we present the investigation of P3HT on the (2 × 1)-missing-row reconstructed Au(110) surface, which provides a stronger 1D template for polymere adsorption. *In situ* scanning tunneling microscopy reveals molecular P3HT chains which are constraint into a fully stretched configuration along the $\bar{1}10$ and 001 high symmetry directions indicating a strong molecule-substrate interaction. Chains parallel to the $\bar{1}10$ direction are embedded into the surface by the removal of one or two Au reconstruction rows. Beside these straight polymer sections also polymers aligned in the 001 direction or under discrete angles with respect to the surface reconstruction are present together with a minority in random coil configuration.

[1] Förster *et al.*, *JCP* **141**(2014)054713

O 14.3 Mon 15:45 MA 042

Oligomers on nanostructured surfaces: Adsorption-induced alteration of the surface reconstruction — ●LAURA KATHARINA SCARBATH-EVERS¹, MILICA TODOROVIĆ², RENÉ HAMMER¹, WOLF WIDDRA¹, DANIEL SEBASTIANI¹, and PATRICK RINKE² — ¹Faculty of Natural Sciences II, Martin-Luther University, Halle-Wittenberg — ²Department of Applied Physics, Aalto University, Finland

Theoretical studies of organic adsorbates on metal surfaces have mainly focused on the adsorption of small molecules on ideal surfaces. However, many surfaces, e.g. low index surfaces of Au, Ir, and Pt, have complex reconstructions that are challenging for surface science studies. In this work, we approach such complex (or nano-structured) surfaces with a combination of density-functional theory (DFT) calculations and scanning tunnelling microscopy (STM) measurements for the example of the α -sexithiophene (α -6T) oligomer adsorbed on the reconstructed Au(100) surface. We find that due to its corrugation pattern the reconstructed Au(100) surface offers a wide range of adsorption sites than can be broadly classified into *on-ridge* and *in-valley* types with energetic adsorption preferences for the latter. Surprisingly, adsorption in energetically ill-favored *on-ridge* positions leads to strong alterations of the surface reconstruction, facilitated by the “soft” nature of gold. As a result of electrostatic effects and charge transfer

between the surface and the molecule, α -sexithiophene displaces the ridge instead of migrating into the valley.

O 14.4 Mon 16:00 MA 042

Adsorption and Monolayer Formation of Sexiphenyl on In₂O₃(111) investigated with STM/AFM — ●MARGARETA WAGNER¹, JAKOB HOFINGER¹, MARTIN SETVÍN¹, LYNN A. BOATNER², MICHAEL SCHMID¹, and ULRIKE DIEBOLD¹ — ¹TU Wien, Austria — ²Oak Ridge National Laboratory, USA

The performance of an organic-semiconductor device is critically determined by the geometric alignment, orientation, and order of the organic molecules. While an organic multilayer eventually adopts the crystal structure of the organic material, the interface with the substrate/electrode material is often less well-defined. This work focuses on the prototypical organic molecule para-sexiphenyl (6P) and the thermodynamically most stable surface of the most-common transparent conducting oxide, indium (tin) oxide, In₂O₃(111). The onset of nucleation and the formation of the first monolayer are followed with scanning tunneling microscopy (STM) and constant-height non-contact atomic force microscopy (nc-AFM). At room temperature, 6P adsorbs lying on the surface and randomly oriented, i.e., without an ordered structure. Annealing to 200 °C provides sufficient thermal energy for the molecules to orient themselves along the high-symmetry directions of the surface, leading to a single adsorption site. With increasing coverage, the 6P molecules first form a loose network with poor long-range order but eventually the molecules re-orient and the first monolayer is established. It is a densely-packed, well-ordered (1 × 2) structure with one 6P per In₂O₃(111) substrate unit cell.

O 14.5 Mon 16:15 MA 042

Investigation of Caffeine Monolayer Formation on Au(111) — ●MALTE SCHULTE, ADAM BUDDÉ, ISMAIL BALTACI, PETER ROESE, and CARSTEN WESTPHAL — Experimentelle Physik 1, TU Dortmund, Otto-Hahn-Straße 4a, 44227 Dortmund, Germany

Research on self-assembled molecules on metal surfaces has attracted strong interest in the last few years. Additionally, different phases and polymorph behavior of molecules is in the focus especially for pharmaceutical studies. Caffeine is a psychoactive drug and solid caffeine molecules show polymorph behavior with a stable β and a metastable high-temperature α phase. In order to study these aspects from a bottom-up approach we deposited caffeine molecules on an Au(111) surface under ultra-high vacuum conditions. We investigated monolayer self-assembly of caffeine molecules on the surface with scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) and observed different orientations of the caffeine molecules on the substrate.

15 min. break

O 14.6 Mon 16:45 MA 042

Contact formation at organic-inorganic interfaces — ●STEFFEN DUHM — Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, China

Conductivities in organic semiconductor thin films are notoriously low and engineering injection barriers at active layer-electrode interfaces is a successful approach to increase charge carrier concentrations. Strongly coupled organic-metal interfaces involve charge transfer and hybridization and vertical bonding distances and adsorption induced molecular distortions are crucial for the energy-level alignment and thus for the charge injection properties at these interfaces. Element-specific bonding distances of organic (sub)monolayers on the (111)-surfaces of coinage metals have been measured by the X-ray standing wave (XSW) technique. Interface energetics and chemical reactions have been accessed by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). By increasing the complexity of the systems from pure hydrocarbon systems like pentacene or perylene to oxygen and/or nitrogen substituted derivatives we could identify the pivotal role of these side-groups in the process of surface-induced aromatic stabilization, which results in metallic organic monolayers.

O 14.7 Mon 17:00 MA 042

Monitoring ligand induced assembly of PbS nanocrystals on the liquid surface by in-situ grazing incidence X-ray scattering — ●SANTANU MAITI¹, SONAM MAITI^{1,2}, JAN HAGENLOCHER¹, ANDRE MAIER², ANDREI CHUMAKOV³, MARCUS SCHEELE², and FRANK SCHREIBER¹ — ¹Institute of Applied Physics, University of Tuebingen, Auf der Morgenstelle 10, 72076 Tuebingen, Germany — ²Institute of Physical and Theoretical Chemistry, University of Tuebingen, Auf der Morgenstelle 18, 72076 Tuebingen, Germany — ³ID10, European Synchrotron Radiation Facility (ESRF), 38000 Grenoble, France

Hybrid nanostructures, composed of inorganic nanocrystals (NCs) and organic semiconductor (OSC) molecules exhibit efficient charge transport and optoelectronic properties[1,2]. The OSC ligand (CuTAPc) induced structural evolution and growth kinetics of PbS NC superlattices at the acetonitrile/air interface has been monitored by in-situ grazing incidence small angle X-ray scattering and grazing incidence X-ray diffraction in real time[3-4]. A continuous in-plane contraction of the superlattice monolayer with time and an overall shrinkage of 5% in lattice constant after complete exchange has been observed. In addition, the atomic orientation of the NCs has been figured out during the exchange process. The combined results provide a complete understanding of atomic and nano-scale assembly of NCs during ligand exchange. 1. M. P. Boneschanscher et al., Science 344, 1377 (2014); 2. M. Scheele et al., PCCP 17, 97 (2015); 3. S. Maiti et al., JPCM, 29, 095101 (2017); 4. A. Andre et al., Chem. Mater. 27, 8105 (2015).

Invited Talk

O 14.8 Mon 17:15 MA 042

Spotlight on Excitonic Coupling in Textured and Polymorphic Anilino Squaraine Thin Films — ●MANUELA SCHIEK — Institute of Physics, University of Oldenburg, Germany

Squaraines are small molecular quadrupolar donor-acceptor-donor (D-A-D) chromophores absorbing in the red spectral range considered for application as photovoltaic materials [1, 2]. A prototypical anilino squaraine with branched alkyl side chains (SQIB) crystallizes into two polymorphic bulk structures with different intermolecular interaction schemes. However, both crystal phases support Davydov splitting and thus show pleochroic absorbance spectra. In spin-casted [3] and vapor deposited [4] thin films X-ray diffraction probes these two phases with a strongly preferred out-of-plane orientation directed by the annealing temperature or by the choice of growth substrate, respectively. Linear polarized spectro-microscopy recordings locate the spatial orientation of the transition dipole moments and allow assignment of the Davydov components. Combined with cross-polarized and atomic force microscopy we obtain a complete picture of molecular orientation and excitonic coupling within the distinct morphological features and relative to the substrate [3].

[1] D. Scheunemann et al., Appl. Phys. Lett. 111 (2017) 183502.

[2] O.S. Abdullaeva, A. Lützen, K. Dedek et al., Langmuir 32 (2016) 8533. [3] F. Balzer, M. Silies, C. Lienau et al., Cryst. Growth Des. (2017) DOI: 10.1021/acs.cgd.7b01131. [4] T. Breuer, G. Witte et al., unpublished results.

O 14.9 Mon 17:45 MA 042

Adsorption of squaraine molecules to Au(111) and Ag(001): Role of the substrate symmetry — ●MAIKE LUFT, BORIS GROSS, MANUELA SCHIEK, and NIKLAS NILIUS — Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

The adsorption of squaraines, an important chromophore for the use in organic solar cells, to Ag(001) and Au(111) is studied with STM. Self-assembly into square building blocks is revealed on Ag(001), while no long-range order is observed on Au(111). Squaraine binding to Ag is mediated by carbonyl-oxygen and hydroxyl groups located in the molecular center, while hydrogen bonding between the terminal isobutyl groups and the oxygen species governs the intermolecular coupling. The latter is maximized by rotating the molecules by a few degrees against a perfect square orientation. On Au(111), no squared molecular network forms due to symmetry reasons. Moreover, the high electronegativity of gold reduces the directing effect of oxygen-metal bonds that control the ordering process on Ag. As a result, only frustrated three-fold symmetric molecular units but no extended network develops on Au(111).

O 14.10 Mon 18:00 MA 042

Azulene and naphthalene: two isomers with different adsorption on metal surfaces — ●JULIANA MORBEC and PETER KRATZER — Faculty of Physics, University of Duisburg-Essen, 47057 Duisburg, Germany

Azulene and naphthalene have the same molecular formula ($C_{10}H_8$) but different motifs and different electronic properties. Naphthalene has a regular 6-6 motif, with two hexagons, while azulene has a pentagon and a heptagon (5-7 motif). The non-alternant topology of azulene and the absence of mirror-related molecular orbitals lead to significant differences in its electronic structure when compared to naphthalene; in particular, azulene exhibits non-uniform charge distribution, more localized frontier orbitals, large in-plane dipole moment and blue color. Here, we present a first-principles study of the adsorption of these isomers on the Ag(111) and Cu(111) surfaces. We show that azulene interacts more strongly with the metal surfaces than naphthalene. On Cu(111), in particular, azulene presents a significantly larger adsorption energy (by a factor of 2) and larger deformation than naphthalene; analyses of the density of states show that the molecular features of azulene completely disappear upon adsorption on Cu(111), indicating a chemisorption process. We will compare our results with data obtained from NIXSW and TPD measurements.