

O 6: Organic/bio Molecules on Metal Surfaces I

Time: Monday 10:30–13:00

Location: H38

O 6.1 Mon 10:30 H38

adsorption structure of PbPc on the surface Ag(111) — ●PENG JIANG and MICHAEL HIETSCHOLD — Chemnitz University of Technology, Institute of Physics, Solid Surface Analysis Group, D-09107 Chemnitz, Germany

We have investigated the adsorption of PbPc on Ag(111) surface. Using OMBE technology, ultrathin films of PbPc have been deposited on Ag(111) and annealed at 100°C for 20min. The ordered molecular arrangement is observed when the molecular film is close or more than one monolayer. We have found two different adsorption structures with molecular unit cells characterized by side lengths of 1.53nm*1.45nm and 1.61nm*1.37nm, and angles of 85° and 89° respectively. On Ag(111) surface we found the shuttle-cock shaped molecules are in both Pb -up and -down adsorption configurations forming the chess-board like pattern. The reversible flipping between molecular configurations on the surface recorded during the scanning process proposes a new mechanism to control the single-molecular adsorption configuration on Ag(111) surface. With a slightly thicker film the molecules on the second layer lie directly on top and have the same orientation of that from the first layer making a direct stack.

O 6.2 Mon 10:45 H38

LEEM investigation of the initial growth of hetero-organic layers — ●CAROLINE HENNEKE, BENJAMIN STADTMÜLLER, THOMAS DUDEN, and CHRISTIAN KUMPF — Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany, and Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology

One crucial issue for the success of organic materials in electronic devices is the ability to specifically design the interfaces between different active layers according to their functional purpose. The initial growth, i.e., the formation of the first molecular layer, is of particular interest in this context as this layer acts as a template for further growth.

We recently started to investigate hetero-organic layers consisting of Copper-II-phthalocyanine (CuPc) and 3,4,9,10-perylene-tetracarboxylic-acid dianhydride (PTCDA) on Ag(111). Using LEEM/PEEM, LEED and STM, we have identified three mixed phases with different stoichiometry. Kinetic processes like thin film growth, the formation of the organic mixed layer, and the transition between different phases were studied in real time with LEEM. The lateral structure of the different phases was investigated with SPA-LEED and STM.

O 6.3 Mon 11:00 H38

Electronic coupling in hetero-organic structures on Ag(111) — ●BENJAMIN STADTMÜLLER^{1,2}, MARTIN WILLENBOCKEL^{1,2}, DANIEL LÜFTNER³, EVA M. REINISCH³, CHRISTOPH SCHMITZ^{1,2}, SERGEY SOUBATCH^{1,2}, MICHAEL G. RAMSEY³, PETER PUSCHNIG³, F. STEFAN TAUTZ^{1,2}, and CHRISTIAN KUMPF^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — ²Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology — ³Institut für Physik, Karl Franzens-Universität Graz, 8010 Graz, Austria

The performance of organic materials in electronic devices depends on the ability to control the properties at the interfaces between different active layers. While almost all studies up to now focused on organic layers containing only one molecular species, some groups have recently started to investigate hetero-organic films with two different types of molecules. We have chosen mixed monolayer structures of CuPc and PTCDA adsorbed on Ag(111) as a model system. Our structural data revealed different long range ordered structures depending on the relative coverage of CuPc to PTCDA. The influence of intermolecular interactions on the electronic structure was studied by angle resolved photoelectron spectroscopy (ARPES). Analyzing the ARPES data in the orbital tomography approach [1] indicated a significant change in the occupation of the molecular orbitals in the mixed films. These modifications are correlated to the formation of an interface state expanding over both molecular species which leads to a coupling of the molecular valence states. [1] P. Puschnig et al, PRB 84, 235427 (2011)

O 6.4 Mon 11:15 H38

Identification of two different charge transfer mechanisms at

Phthalocyanines/Ag interfaces — ●ERIC SALOMON and THIERRY ANGOT — Aix-Marseille university, Marseille, France

As the performance of organic molecule based electronic devices depends critically on the electrode-organic interfaces it appears crucial to have thorough understanding of the fundamental processes governing the metal-molecule interactions.

The vibrational properties of several M-phthalocyanines (here with M=H2, Zn, Cu, Co, Fe) adsorbed on Ag surfaces have been carefully investigated using high resolution electron energy loss spectroscopy (HREELS). In the monolayer range, a wide loss feature ranging from 200 up to 800 meV is commonly observed that displays a positive quadratic dispersion. It is interpreted as a surface-plasmon resulting from a space-charge region arising from an electron-vibration coupling at the interface between the organic monolayer and the metallic substrate. Nevertheless, significant differences are observed depending on the metal atom M. In most cases, while Infra Red active modes dominate, some vibrational motions of the adsorbate are damped by energy transfer to the metal substrate leading to Raman active modes with Fano line shape. However, this is not the case for Co- and Fe-Pc, in which systems no Fano line shape mode is observed. This demonstrates that electron-phonon coupling strongly depends on the property of the central metal atom. This is further confirmed by photoemission spectroscopy measurements demonstrating that the alteration of the valence band upon adsorption depends of the central atom.

O 6.5 Mon 11:30 H38

Site and orbital-dependent charge donation and spin manipulation in electron doped metal-phthalocyanines — ●CORNELIUS KRULL¹, ROBERTO ROBLES², AITOR MUGARZA¹, and PIETRO GAMBARDELLA^{1,3} — ¹Catalan Institute of Nanotechnology (ICN), Barcelona, Spain — ²Centre d'Investigacions en Nanociència i Nanotecnologia (CIN2), Barcelona, Spain — ³Institució Catalana de Recerca i Estudis Avançats (ICREA) Universitat Autònoma de Barcelona, Barcelona, Spain

Similar to silicon-based electronics, chemical doping offers a tool for tailoring the electrical characteristics of organic molecular compounds. Contrary to inorganic semiconductors, however, controlling the position of dopants and charge donation in molecular complexes is a complicated task due to the existence of multiple doping sites, electron acceptor levels, and intramolecular correlation effects. Here we use scanning tunneling microscopy to observe the position of single Li dopants within Cu-phthalocyanine and Ni-phthalocyanine molecules in contact with a metal substrate and probe the charge transfer process with unprecedented spatial resolution. We show that individual phthalocyanines can accommodate at least three stable nonequivalent doping sites and up to six dopant atoms. Ligand and metal orbitals can be selectively charged by modifying the configuration of the Li complexes. Because of strong charge-spin correlation in confined molecular orbitals, alkali atoms provide an effective way to tune the molecular spin without introducing magnetic dopants.

O 6.6 Mon 11:45 H38

Investigation of the adsorption of vanadiumoxide-phthalocyanine on Cu(111) — ●CHRISTOPH BÜRGER¹, ALEXANDER GERLACH¹, JENS NIEDERHAUSEN², STEFFEN DUHM³, TAKUYA HOSOKAI⁴, BLANKA DETLEFS⁵, NORBERT KOCH², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, DE — ²Institut für Physik, Humboldt-Universität zu Berlin, DE — ³Institute of Functional Nano & Soft Materials, Soochow University, CN — ⁴Department of Materials Science and Technology, Iwate University, JP — ⁵European Synchrotron Radiation Facility, FR

We study the adsorption geometry of the non-planar vanadiumoxide-phthalocyanine (VOPc) molecule on Cu(111) using X-ray standing wave (XSW) measurements and complementary techniques. The XSW analysis of the C 1s, N 1s, V 2p and O 1s core-levels, accompanied by simulations and scanning tunneling microscopy measurements, indicates that the molecules adsorb predominantly with their oxygen atom pointing towards the Cu(111) surface. Upon adsorption, the geometry of the VOPc molecule suffers a significant distortion compared to the molecular geometry in the crystal. Finally, we compare these results with published data of GaClPc on Cu(111) [1] and VOPc on Au(111) [2].

- [1] A. Gerlach et al., *Phys. Rev. Lett.* **106**, 156102 (2011)
 [2] D. A. Duncan et al., *Surf. Sci.* **604**, 47 (2010)

O 6.7 Mon 12:00 H38

Systematic X-ray standing wave study of pentacene and pentacenederivatives on coinage metals — ●ALEXANDER GERLACH¹, CHRISTOPH BÜRKER¹, JENS NIEDERHAUSEN², STEFFEN DUHM³, TAKUYA HOSOKAI¹, BLANKA DETLEFS⁴, NORBERT KOCH², GEORG HEIMEL², and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, DE — ²Institut für Physik, Humboldt-Universität zu Berlin, DE — ³FUNSOM, Soochow University, CN — ⁴European Synchrotron Radiation Facility, FR

We present X-ray standing wave data for pentacene (PEN), pentacenequinone (P2O) and pentacenetetrone (P4O) on Cu(111), Ag(111), and Au(111). The bonding distances d and the distortions of the adsorbed molecules measured with this technique are characteristic for the interaction mechanism with the different substrates [1,2]. Depending on the number of C=O groups attached to the molecule we find surprisingly different bonding distances and adsorption geometries on the three coinage metal surfaces. On Au(111) [Cu(111)], there is a relatively weak [strong] interaction, i.e. $d_C \approx 3.3 \text{ \AA}$ [2.3 \AA], with negligible [significant] distortion of the molecules. On Ag(111), as the intermediate case, both scenarios are observed: While for PEN and P2O we find a weak substrate interaction with $d_C \approx 3.0 \text{ \AA}$ and 3.3 \AA , P4O shows a chemisorptive bonding with $d_C \approx 2.7 \text{ \AA}$. Finally, we discuss consequences of the different bonding behavior with regard to the electronic structure and the energy-level alignment at the organic-metal interface. [1] N. Koch et al., *J. Am. Chem. Soc.* **130** (2008) 7300 [2] A. Gerlach et al., *Phys. Rev. B* **75** (2007) 045401

O 6.8 Mon 12:15 H38

Coadsorption of Metal-phthalocyanines and PTCDA on Ag(111) — ●CHRISTOPH SAUER^{1,2}, MARCO GRÜNEWALD³, BENJAMIN STADTMÜLLER^{4,5}, ACHIM SCHÖLL^{1,2}, and FRIEDRICH REINERT^{1,2} — ¹Physikalisches Institut, Experimentelle Physik VII, Universität Würzburg, D-97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie (KIT), D-76021 Karlsruhe — ³Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, D-07743 Jena — ⁴Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, D-52425 Jülich — ⁵Jülich Aachen Research Alliance (JARA) - Fundamentals of Future Information Technology, D-52425 Jülich

By means of high-resolution photoelectron spectroscopy (PES) we demonstrate that annealing a heteromolecular film of sub-monolayers of metal-phthalocyanine (MePc) deposited on top of one monolayer (ML) of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on Ag(111) results in a mixed MePc:PTCDA-monolayer. The replacement of PTCDA by the MePc is explained within a model based on intramolecular Coulomb repulsion. The PES investigation of the mixed MLs exhibits variations of the spectral signatures of the individual components with respect to the pure ML spectra on Ag(111), thus indicating significant differences in the bonding of the respective molecules. Remarkably these spectral variations are more pronounced

for mixed CuPc:PTCDA-MLs than for the respective SnPc:PTCDA-ML films.

O 6.9 Mon 12:30 H38

Substrate-mediated band-dispersion of adsorbate molecular states — ●MICHAEL WIESSNER¹, PETER PUSCHNIG², MASASHI ARITA³, KENYA SHIMADA³, ACHIM SCHÖLL¹, and FRIEDRICH REINERT¹ — ¹Universität Würzburg, Experimentelle Physik VII, 97074 Würzburg, Germany — ²Institut für Physik, Karl-Franzens Universität Graz, Austria — ³Hiroshima Synchrotron Radiation Center, Hiroshima University, Hiroshima 739-0046, Japan

Charge carrier mobilities in molecular condensates are usually small, since the coherent transport, which is highly effective in conventional semiconductors, is impeded by disorder and the small intermolecular coupling. A significant band dispersion can usually only be observed in exceptional cases such as for π -stacking of aromatic molecules in organic single crystals. Based on angular resolved photoemission, we demonstrate on the example of planar π -conjugated molecules, that the hybridisation with a metal substrate can substantially increase the delocalization of the molecular states in selective directions along the surface. Supported by *ab initio* calculations we show how this mechanism couples individual 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) molecules via the Ag(110) substrate within the organic layer resulting in a four times larger in-plane charge carrier mobility.

O 6.10 Mon 12:45 H38

Temperature influence on the self-assembly of phthalocyaninato complexes on gold studied by second harmonic generation (SHG). — ●NADEZHDA LILICHENKO¹, ULRICH GLEBE², FRANK HUBENTHAL¹, ULRICH SIEMELING², and FRANK TRÄGER¹ — ¹Institut für Physik, Universität Kassel and CINSaT, Germany — ²Institut für Chemie, Universität Kassel and CINSaT, Germany

Self assembled monolayers (SAMs) attracted great attention in different fields of science. Due to their designable physical and chemical properties SAMs are used in a variety of applications, e.g. as biosensors, switchable interfaces or in molecular electronics. Phthalocyanines (Pcs) are ideal candidates for SAMs due to their outstanding optical and electronic properties. These molecules bind to the surface by multiple anchor groups and they have large footprints, which are preconditions for the formation of stable monolayers. In our experiments we have used thioether substituted (sub-)phthalocyanines for SAM formation. To extract the adsorption kinetics the film formation was monitored by optical second harmonic generation and subsequently the SHG data was fitted by the standard Langmuir kinetic models. Depending on the molecular structure, the adsorption can be described either by 1^{st} or 2^{nd} order Langmuir kinetic models. Additionally, the temperature and the molecular concentration of the Pc-solution has been systematically varied to optimise SAM formation. The most important result, among other, is, a strong dependence on the temperature. While for $T = 2^\circ\text{C}$ the SAMs were only loosely packed, at $T = 25^\circ\text{C}$ dense films are generated.