

O 25 Organic films II

Time: Tuesday 15:45–18:30

Room: PHY C213

O 25.1 Tue 15:45 PHY C213

Electronic Effects in the Adsorption Structure of Organic Molecules: STM and STS of Phthalocyanines and Naphthalocyanines on Graphite — ●THIRUVANCHERIL G. GOPAKUMAR and MICHAEL HIETSCHOLD — Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany.

The adsorption structure and electronic properties of various metal phthalocyanines and naphthalocyanines organized on graphite surface have been investigated using STM and STS. PdPc and PtPc show similar type of adsorption structure (quadratic lattice) although the central metal atoms are different, however PtPc (300°) adlayer shows almost three times thermal stability compared to PdPc (80-90°). Naphthalocyanine shows a distorted quadratic superstructure, the difference is expected in this case due to the long arms of the molecule (additional benzene ring) compared to phthalocyanine. The metal (Sn) naphthalocyanine shows quite interesting superstructure (hexagonal) compared to all other molecules studied may be due to the geometry (non-planar) arises due to the large Sn²⁺ ionic radius. These differences in the adsorption structures give insight in to how internal electrical properties of molecules affect the adsorption structure. Moreover we demonstrate the tip-sample distance dependant tunneling spectroscopy of these molecules which gives quantitative information about the electronic properties especially the transport at the molecule-substrate interface in the adlayer.

O 25.2 Tue 16:00 PHY C213

Combined investigation of the disordered phases of PTCDA on Ag(111) with STM and STS — ●RUSLAN TEMIROV, SERGUEY SOUBATCH, and STEFAN TAUTZ — International University Bremen, Bremen, Germany

Adsorption of large organic molecules is a topic of increasing importance. Among other materials PTCDA has got a lot of attention as a model system for studying complex absorption phenomena. Due to the unique properties of its chemisorptive bond PTCDA demonstrates a commensurate monolayer growth on Ag(111). Such ordered PTCDA/Ag(111) interface has been characterized recently on atomic scale using STM, STS and NXSW techniques [1],[2]. In our contribution we present a study of the disordered PTCDA overlayers grown on Ag(111) at 100K. We studied the structure and the thermal stability of the layer employing Low Temperature STM. Electronic properties of the interface have been characterized by STS on a single molecular scale. STM induced single molecular manipulation combined with the STS measurements have been used for the tracking of the changes of interface electronic structure during the transition of the disordered film into the ordered one. These data are further used for the identification of the nature of the disordered PTCDA phases on Ag(111).

[1] A. Hauschild et al. Phys. Rev. Lett. 94, 0360106 (2005)

[2] A. Kraft et al. submitted

O 25.3 Tue 16:15 PHY C213

Self-assembled monolayers of molecular switches - azobenzene carrying alkanethiols on gold — ●R. SCHMIDT¹, W. FREYER¹, T. GIESSEL¹, K. HERRMANN¹, H. PRIMA GARCIA¹, R. WEBER¹, and M. WEINELT^{1,2} — ¹Max Born-Institute, Berlin, Germany — ²Freie Universität Berlin, Germany

Alkanethiols form self-assembled monolayers (SAMs), e.g., bound to gold films via the sulphur headgroup and are thus promising candidates for molecular devices. For this purpose the thiols need to be functionalized by an appropriate endgroup. We chose azobenzene a cis-trans-conformation switch. Adsorption measurements prove that in solution azobenzene attached to decanethiols switches reversible upon irradiation at 360 nm and 450 nm.

By NEXAFS-spectroscopy (U41 at BESSY II) we investigated both the azobenzene-decanethiol adsorption geometry and its subsequent change upon irradiation. The layers are well ordered at 90 K, but less ordered at 300 K. Switching seems to be seldom reproducible. However, the temperature dependence of both the adsorption geometry and the switching process makes conceivable a fundamental change of the isomerization energetics at the surface. Autoionization after resonant excitation (N1s, C1s to pi*) reveals strong Resonant-Raman-Auger contributions. Thus charge transfer between azobenzene switch and Au substrate is substantially slowed down by the thiol spacer.

O 25.4 Tue 16:30 PHY C213

Intermolecular, interface, and dipole-dipole interactions in organic thin films — ●ACHIM SCHÖLL¹, SELAMI YILMAZ¹, CHRISTOPH STADLER¹, SATOSHI KERA², and EBERHARD UMBACH¹ — ¹Exp. Phys. II, Univ. Würzburg, Germany — ²Faculty of Engineering, Chiba Univ., Japan

The interactions at metal-organic interfaces are of crucial importance for electronic devices, since they influence the layer morphology and the charge carrier transport through the interface due to the formation of interface dipoles and band offsets. We present a high-resolution PES and NEXAFS study on the adsorption behaviour and interface interaction of ordered thin films of the molecules titanyl- (TiO-Pc) and vanadyl-phthalocyanine (VO-Pc), which offer the possibility to tune the work function change of metal surfaces due to their high static dipole moments. Strong changes in the XPS and NEXAFS data of TiO-Pc consistently show the chemisorptive bonding of the first layer. In addition, UPS and work function measurements clearly indicate a parallel orientation of the molecular dipoles which increases the work function by ~0.1 eV in comparison to non-polar adsorbates. A further increase of the coverage leads to the formation of a second layer with anti-parallel dipoles and reduced work function. The careful analysis of the high-resolution XPS and NEXAFS data shows no significant covalent contribution to the intermolecular interaction. However, the desorption temperature of the second layer is increased by more than 150 K in respect to the multilayer, which is attributed to dipole-dipole interaction. This project is financed by the BMBF under contract 05KS4WWC/2.

O 25.5 Tue 16:45 PHY C213

Metal Electrodes to the Molecular World: Evidence for Size-dependent Interactions — ●H.-G. BOYEN¹, P. ZIEMANN¹, U. WIEDWALD¹, V. IVANOVA², M. MANOLOVA², D.M. KOLB², S. SAKONG³, A. GROSS³, A. ROMANYUK⁴, M. BÜTTNER⁴, and P. OELHAFEN⁴ — ¹Abteilung Festkörperphysik, Universität Ulm, D-89069 Ulm — ²Abteilung Elektrochemie, Universität Ulm, D-89069 Ulm — ³Abteilung Theoretische Chemie, Universität Ulm, D-89069 Ulm — ⁴Institut für Physik, Universität Basel, Klingelbergstr. 82, CH-4056 Basel

Organic molecules generally need to be attached to metal electrodes via chemical bonds in order to take advantage of their electrical properties for molecular electronics applications. These chemical bonds, on the other hand, might have strong impact on the electronic properties of the metal leads themselves at the metal/molecule interface.

Here we report experiments aiming to unravel the electronic structure of the metal at the metal/molecule interface representing the early stage of electrode formation. For this purpose, strictly 2-dimensional Pd islands of different size are prepared on top of 4-mercaptopyridine (4MP) Self-Assembled Monolayers (SAMs) by means of a novel electro-chemical approach. Electron spectroscopy together with density functional theory reveal strong interactions between the organic molecules and the metal atoms forming the electrical contact resulting in a drastically reduced density of states at the Fermi level for a nearly closed Pd monolayer and even non-metallic properties in case of nanometer-sized islands.

O 25.6 Tue 17:00 PHY C213

Optimizing the charge carrier injection from Au electrodes in organic electronic devices — ●STEPHAN RENTENBERGER¹, ANTJE VOLLMER², EGBERT ZOJER¹, and NORBERT KOCH³ — ¹Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria — ²Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH, Albert-Einstein-Str. 15, D-12489 Berlin, Germany — ³Humboldt-Universität zu Berlin, Institut f. Physik, Newtonstrasse 15, D-12489 Berlin, Germany

The performance of organic-based devices (e.g. light emitting diodes, transistors) is governed by two key factors: charge carrier transport within the active organic material and injection of charge carriers from the electrodes into the organic layer. We demonstrate that the work function of Au electrodes can be increased by exposure to UV/ozone. Consequently, the hole injection barriers (HIBs) between such Au electrodes and organic materials were lowered by as much as 1.4 eV compared to untreated Au electrodes. HIBs were measured using photoelectron spectroscopy. The lowering of HIBs was observed for a wide variety

of organic materials [N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine, sexiphenyl, sexithiophene, poly-(3-hexylthiophene), and poly-fluorene], which indicates the universal applicability of our Au electrode modification method.

O 25.7 Tue 17:15 PHY C213

Molecular Lifetime Contrast in Thin Pentacene Layers — ●F.-J. MEYER ZU HERINGDORF, D. THIEN, P. KURY, L.I. CHELARU, and M. HORN-VON HOEGEN — Institut für Experimentelle Physik, Universität Duisburg-Essen, Lotharstrasse 1, 47057 Duisburg

Whenever excited electrons are required to tailor specific properties of a thin film, the decay of the initial excitation over time defines an intrinsic limit for the performance. To determine the lifetime of such an electronic excitation in a heterogeneous layer requires a combination of microscopic and spectroscopic methodologies. We used an ultrahigh vacuum spectroscopic photoemission microscope (SPE-PEEM) together with a fs Ti:Sapphire laser to study the decay of electronic excitations in thin films of the aromatic molecule pentacene. This molecule, deposited on a Si surface, initially forms a wetting layer of flat-lying molecules, while subsequent layers stand upright and develop a typical dendritic shape. The change in morphology is reflected in the decay channels for the electronic excitation: while we determine a time constant of less than 200fs for the wetting layer, the lifetime in the dendritic islands is more than twice as high as the wetting layer. Mapping of the lifetime reveals that the morphology of the layer is in fact different for islands of different heights.

O 25.8 Tue 17:30 PHY C213

Determination of the transport gap by UPS and IPES — ●STEFAN KRAUSE, DETLEF EICH, BENEDETTA CASU, and EBERHARD UMBACH — Experimentelle Physik II, Universität Würzburg

The transport gap in semiconductors is defined as the minimum energy needed to produce a separated electron and hole. In a conventional semiconductor such as Si or GaAs this gap can be determined by means of optical absorption taking into account that the optical gap is only slightly smaller than the transport gap because of the small exciton binding energy (few meV). Organic materials are in general believed to have very weak intermolecular interaction leading to a localized charge and hence to a large exciton energy. Thus transport and optical gap may differ by several 100 meV. Then, other methods like UPS and IPES are needed to measure the position of the highest occupied and lowest unoccupied molecular orbital directly. We did such measurements for the organic molecules PTCDA, Alq₃ and Cu-Pc and compared the results to those obtained from GaAs, Si, HgTe, and CdTe. In both groups of materials, the peak-to-peak distances of the leading peaks in UPS and IPES are much larger (1-3 eV) than the optical gap, i.e. also much larger than the known or expected exciton energies. The agreement is much better if one uses the peak onsets in all cases. However, then the exciton energies in organic materials are surprisingly small. The origin of the failure of the peak-to-peak approach and the implications of the findings will be discussed.

O 25.9 Tue 17:45 PHY C213

A Metal Surface as a Complex Ligand: Adsorption of Co(II)-Porphyrins on Ag(111) — ●T. LUKASCZYK, K. FLECHTNER, K. COMANICI, H. MARBACH, F. MAIER, J. M. GOTTFRIED, and H.-P. STEINRÜCK — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, D-91058 Erlangen, Germany

Metalloporphyrins control the decisive steps in various natural and technological processes that often involve the reversible attachment of a molecular ligand on the central metal ion. In order to study this key step on a model compound in a solvent-free environment, we investigated ordered monolayers of Tetraphenylporphyrin-Co(II) and Tetrakis-(3,5-di-tert-butylphenyl)porphyrin-Co(II) on Ag(111). First, we focused on the interaction of the Co-d_{z²} orbital with the Ag surface, because the coordination of an additional ligand is most likely mediated by this orbital. We made use of the different "heights" of the molecules to vary the distance between the Co atom and the Ag substrate. The monolayers were studied with XPS, UPS, and LEED. In the Co 2p_{3/2} photoemission signal, a peak appears at 778.3 eV that is absent at multilayer coverages and that probably reflects the interaction of the Co ion with the Ag substrate. Complementary evidence for this interaction is provided by a new signal close to E_F in the monolayer UP spectrum. The UP signal position varies with the Co-Ag distance, as expected from MO theory. This work was supported by the DFG through SFB 583.

O 25.10 Tue 18:00 PHY C213

Electronic structure of thin organic films on metal surfaces studied by UV- and resonant photoemission — ●AZZEDINE BENDOUNAN, FRANK FORSTER, ACHIM SCHÖLL, JOHANNES ZIROFF, EBERHARD UMBACH, and FRIEDRICH REINERT — Experimentelle Physik II, Universität Würzburg, am Hubland, 97074 Würzburg, Germany

We present high-resolution photoemission data on the valence band structure of organic thin films on noble metal surfaces, in particular on the epitaxial systems PTCDA/Ag(111) and NTCDA/Ag(111). The valence band of one monolayer PTCDA on Ag(111) is characterized by two spectral features located close to the Fermi energy. Both features are associated to the formation of a strong chemical bond between the substrate and the molecule. The binding energy of these features show an immediate dependence on the PTCDA film thickness. The NTCDA molecule is less strongly bonded to the Ag(111) substrate, but also for this system the formation of hybrid orbitals can be observed in the photoemission spectra. The observed HOMO structure shifts slightly as the NTCDA coverage increases. Moreover, by combination of NEXAFS and resonant photoemission data, we identify the NTCDA and Ag contributions to the various peaks in the photoemission spectrum. In addition, an information is obtained about the coherent and incoherent processes occurring after excitation by analysis of the evolution of the Auger and photoemission features in the resonant photoemission spectra.

O 25.11 Tue 18:15 PHY C213

In-situ electrical investigations of the growth of dihexyl-oligothiophenes in organic field effect transistors — ●TORSTEN BALSTER, TOBIAS MUCK, ARNE HOPPE, JÖRG SEEKAMP, and VEIT WAGNER — International University Bremen, Bremen, Germany

Optimized contact properties are essential for applications of thin film organic field effect transistors (OFET) enabling higher current level and switching frequencies. We have grown thin films of dihexyl-oligothiophene with 4 to 7 thiophene rings (DHnT) on Ti/Au bottom contact transistor templates in ultrahigh vacuum, because the energetic difference between the HOMO and the Fermi energy of the Au contact is varied by the number of chromophores in oligothiophenes. The channel width of the transistors ranges from 100 down to 5 μm. The in-situ electrically characterized samples of these thiophene derivatives demonstrates oscillatory behaviour of the charge carrier mobilities during growth indicating layer-by-layer mode. The onset of the current could be found in excess of 2/3 of a monolayer, whereas saturation after more than 2 monolayers is observed. Furthermore, higher mobilities (up to 10⁻¹Vs/cm² for DH7T) could be found for increasing number of thiophene rings at optimized growth temperatures (190°C) of the sample. The voltage drops at the source and drain electrode are independently determined by means of 4-point measurements using additional, screened electrodes within the organic channel showing a major drop up to 1 V for DH6T at the source electrode.