O 22: Organic-Inorganic Hybrid Systems and Organic Films

Time: Monday 18:15–20:30 Location: Poster E

O 22.1 Mon 18:15 Poster E

Ordered films of the charge-transfer salt DTBDT-F4TCNQ on Au(111) — • Torge Mashoff and Hans-Joachim Elmers — Institut für Physik, Johannes Gutenberg-Universität, Mainz

The interplay of electronic correlation effects with low dimensionality and geometric frustration of charge-transfer compounds provides a large playground for variable many-body interactions. Novel systems of molecules with tailored donor and acceptor character provide a vast multitude of possible modifications. Understanding the electronic structure of this class of materials as well as their metalorganic interfaces is crucial for designing specific electronic properties. An important precondition for the implementation of organic charge-transfer salts in electronic devices is the fabrication of thin films with appropriate molecular orientation. Deposition of films under ultrahigh vacuum (UHV) conditions promises the formation of well-defined interfaces [1]. In this work, an in-situ prepared molecular monolayer of the novel charge-transfer salt dithienobenzodithiophenetetrafluorotetracyanoquino-dimethane (DTBDT-F4TCNQ) has been deposited on a gold substrate and investigated by low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS), allowing the characterization of occupied and unoccupied electronic states of the donor-acceptor compounds near the Fermi level. [1] D. Bayer et. al., Phys. Rev. B 89, 075435 (2014)

O 22.2 Mon 18:15 Poster E

Substrate-directed growth of aromatic molecules on a metal surface — $\bullet \text{Friedrich Maass}^1, \text{ Arnulf Stein}^1, \text{ Bernd Kohl}^2, \text{ Lena Hahn}^3, \text{ Lutz H. Gade}^3, \text{ Michael Mastalerz}^2, \text{ and Petra Tegeder}^1 — ^1\text{Physikalisch-Chemisches Institut} — ^2\text{Organisch-Chemisches Institut} — ^3\text{Anorganisch-Chemisches Institut}, \text{ Ruprecht-Karls-Universität Heidelberg, Germany}$

The influence of the substrate on the adsorption behaviour of π -conjugated molecules on metal surfaces is of immense interest for understanding the structural and electronic properties of small molecule organic semiconductors.

We investigated the adsorption geometry and the electronic properties of benzene, pentacene, 1,3,8,10-tetraazaperopyrene (TAPP) and quinoxalino[2',3':9,10]phenantro[4,5-abc]-phanzine (QPP) on the Au(111) surface with vibrational and electronic high-resolution electron energy-loss spectroscopy (HREELS), thermal-programmed desorption (TPD), and density functional theory calculations. In all cases we found a clear difference between the structure of thin-films and the bulk-structure obtained by X-ray structure analysis. [1] While in the bulk all molecules show a herringbone like orientation with π -stacked molecules and angles ranging from 35 to 90° between the molecular planes in neighbouring stacks, we observe planar adsorption on the surface for the monolayer (ML) as well as for higher coverages (up to 10 ML).

[1]L. Hahn, F. Maass et al., Chem. Eur. J. 2015, 21, 17691.

O 22.3 Mon 18:15 Poster E

Studying the F4TCNQ/Au(111) Interface with Two-Photon Photoemission — •Sascha Feldmann, David Gerbert, and Petra Tegeder — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Deutschland,

In our ongoing efforts pointing towards a deeper understanding of the electronic properties at metal/organic interfaces a convenient approach could be the characterization of well-studied organic molecules adsorbed on single crystal noble metal surfaces. Tetrafluorotetracyanoquinodimethane (F4TCNQ) adsorbed on Au(111) was chosen as a prototypical system to investigate a negatively charged organic acceptor molecule on a noble metal surface by means of two-photon photoemission (2PPE). 2PPE enables the observation of occupied and unoccupied electronic states as well as the study of photo-induced processes via photo-induced changes in the electronic structure. Varying photon energies, angle of incidence or time delay between two laser pulses further information about dispersion and lifetime of electronic states can be obtained, resulting in a detailed picture of the electronic properties of the F4TCNQ/Au(111) interface.

O 22.4 Mon 18:15 Poster E

A combined photoemission and LEED study of SnPc/Ag

(111) — •STEPHAN JAUERNIK, MAX GURGEL, PETRA HEIN, and MICHAEL BAUER — Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel

Recently, the adsorption of tin-phthalocyanine (SnPc) on Ag(111) has attracted considerable interest due to peculiarities in the adsorbate-substrate interaction [1] and switching capabilities reported for the adsorbed SnPc [2]. In a combined Low Energy Electron Diffraction (LEED) and Photoemission/Two-Photon Photoemission (PES/2PPE) study of SnPc/Ag(111) we address in this work the correlation of the structural and the electronic properties of this model system in the sub-monolayer coverage regime. The study focuses on the transition regime from a gas - like phase at coverages <0.90 monolayers (ML) to an incommensurate phase observed for coverages between 0.90 ML and 1.0 ML. The photoemission data reveal distinct changes in the occupied as well as unoccupied electronic structure of this model-type organic adsorption system as the coverage increases. The experimental results are discussed under consideration of past LEED, STM and STS studies [1,2].

[1] C. Stadler et al., Nature Physics 5, 153-158 (2009)

[2] Y. Wang et al., J. Am. Chem. Soc., 2009, 131 (10), 3639-3643

O 22.5 Mon 18:15 Poster E

Naphthalocyanine on metal surfaces studied with a variable temperature STM — •MALTE SCHULTE, ISMAIL BALTACI, PATRICK MEHRING, and CARSTEN WESTPHAL — Experimentelle Physik 1, TU Dortmund, Otto-Hahn-Straße 4, 44221 Dortmund, Germany

The class of naphtalocyanine molecules received large attention within the recent years. In particular, the dependence of their geometric and electronic properties on the central metal ion causes high interest. Therefore, their adsorption and structural formation were determined in several studies. Especially their self-assembly on different surfaces was studied at room temperature.

In this study metal free naphtalocyanine (H2Nc) is investigated on metal surfaces at various low temperatures by scanning tunneling microscopy. STM imaging at low temperature allows to increase the resolving of single molecules. The coverage of the studied surface is less than a monolayer H2Nc while analyzing their self-assembly formation.

O 22.6 Mon 18:15 Poster E

A molecular ruler for measuring the mesoscopic relaxations in Co/Au(111) interfaces — •Zheng Wei^{1,2}, Jobynson Kollamana¹, Benjamin Stadtmüller¹, Mirko Cinchetti¹, and Martin Aeschlimann¹ — ¹Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, Erwin-Schrödinger-Strasse 46, 67663 Kaiserslautern, Germany — ²College of Material Science and Engineering, Chongqing University, 400044 Chongqing, P. R. China

The contact between a molecular and ferromagnetic electrode contributes or even determines the performance of molecular spintronic devices. Here we report on scanning tunneling microscopy experiments on the $\rm C_{60}/\rm Co/Au(111)$ system. We observed a disorder-order molecular transition at evaluated temperature of 620K, independent of the cobalt thickness. However, the ordered molecular superstructures depend on the thickness of cobalt, reflecting the lattice dilatation in cobalt and inter-diffusion of Au. This means that $\rm C_{60}$ is a sensitive molecular ruler to measure the mesoscopic relaxation of cobalt films on Au(111) substrate. Furthermore, our results suggest an alternative way to tailor the perpendicular magnetic anisotropy of $\rm Co/Au(111)$ interfaces besides the coverage of $\rm C_{60}$ [1].

[1] K. Bairagi et al., Phys. Rev. Lett. 114, 247203 (2015).

O 22.7 Mon 18:15 Poster E

Temperature Dependent Structure Formation of Phthalic Acid on Cu (111) — ◆FEIFEI XIANG, TOBIAS SCHMITT, ANASTASIA SOKOLOVA, and M. ALEXANDER SCHNEIDER — Solid State Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

Carboxylic acids are popular building blocks in molecular self-assembly and many examples show that deprotonation at surfaces changes the obtained structures. Here we investigate an example where surface-induced anhydride and poly-anhydride formation were found previously on a Ag(100) surface [1]. We studied the self-assembly of ph-

thalic acid (1,2-Benzenedicaboxylic Acid) by low-temperature scanning tunneling microscopy on Cu(111) surface as function of the substrate temperature. At room temperature and above phthalic acid forms phthalic anhydride on Cu(111). However, contrary to the situation on Ag(100) [1], we find that monomers of phthalic anhydride are present on Cu(111) and form linear ribbon structures at room temperature. Our experiments also indicate that multilayer molecular packing is still stable at 423K. The extraordinarily ordered structures found finally decompose above 473K.

[1] M. Franke, et al. J. Phys. Chem. C, 2015, 119, 23580*23585

O 22.8 Mon 18:15 Poster E

In-situ Kelvin Probe Study of the Work Function Evolution of Molybdenum Oxide Upon Gas Exposure — Sebastian Hietzschold^{1,2,3}, Sebastian Beck^{1,3}, •Stefan Brackmann^{1,2}, Robert Lovrincic^{1,2}, and Wolfgang Kowalsky^{1,2,3} — ¹InnovationLab GmbH, Heidelberg, Germany — ²Institute for High Frequency Technology, TU Braunschweig, Braunschweig, Germany — ³Kirchhoff Institute for Physics, Heidelberg University, Heidelberg, Germany

The electronic properties of transition metal oxides are very sensitive to many processing parameters. It is still not completely understood if just oxidative adsorption at the surface or also diffusion into bulk vacancies is the reason for the observed changes in the effective surface potential. To clearly separate surface from bulk effects, we measure simultaneously the bulk conductivity (via current-voltage measurements) and work function (via Kelvin probe) of MoOx layers of varying thicknesses in-situ during gas exposure.

We find that shortly after evaporation of thin MoOx onto a silicon substrate with native oxide the work function starts at a maximum of 6.9 eV and then decreases monotonously down to 5.7 eV for exposure with pure oxygen and well below 5 eV for air exposure. We observe the saturation of the work function change even for low exposure. We also show that the gradient of this decrease as well as the saturation value of the decreased work function does not only depend on the total exposure but also on the time of the exposure, the base pressure and gas species supplied during the exposure.

O 22.9 Mon 18:15 Poster E

Adjusting the Work Function of Solution Processed Nickel Oxide by Self-Assembled Monolayers — •FLORIAN FRIEDRICH^{1,2}, SEBASTIAN HIETZSCHOLD^{1,2,3}, PATRICK REISER^{1,4}, ERIC MANKEL^{1,4}, SABINA HILLEBRANDT^{1,2}, ROBERT LOVRINCIC^{1,3}, and Wolfgang Kowalsky^{1,2,3} — ¹InnovationLab, Heidelberg, Germany — ²KIP, Heidelberg University, Germany — ³IHF, TU Braunschweig, Germany — ⁴MAWI, TU Darmstadt, Germany

Solution processed nickel(II) oxide (NiO) is a promising hole selective anode material in organic devices. However, the work function of NiO is too low for many currently used organic materials [1]. The purpose of this work is to adjust the work function of solution processed NiO thin films via self-assembled monolayers (SAMs). A few nanometer thin NiO layers, formed by monoethanolamine with nickel acetate tetrahydrate in ethanol, were spin-coated on an indium tin oxide (ITO) surface and were thermally annealed in ambient atmosphere. The effective surface work function of this NiO layers were adjusted by chemisorption of phosphonates in terms of dipolar SAMs such as perfluorohexyloctyl phosphonic acid. Work function changes were examined by Kelvin probe measurements and photoelectron spectroscopy. The surface has been further characterized with atomic force microscopy, ellipsometry and goniometry. The results can be used to improve energy level alignment at interfaces in organic opto-electronic devices and increase their overall efficiency. References: [1] Schulz et al., NiOX/MoO3 Bi-Layers as Efficient Hole Extraction Contacts in Organic Solar Cells. Adv. Funct. Mater., 24: 701-706 (2014)

O 22.10 Mon 18:15 Poster E

Energy-Level-Engineering of Indium-Tin-Oxide (ITO) - Linking Simulation and Experiment for Small Molecule Self-Assembled-Monolayers (SAMs) — •JOHANNES BREUER, JULIA RITTICH, SEBASTIAN MÄDER, CAROLIN C. JACOBI, and MATTHIAS WUTTIG — I. Institute of Physics (IA), RWTH Aachen University

Organic electronics promise cost-effective and easy fabrication of highly energy-efficient and versatile devices. Over the last decade these prospects have motivated a vast variety of research activities. One of the major issues that still has to be addressed is the energy-level-mismatch at the critical electrode-organic interface.

Indium tin oxide (ITO) is a transparent conductive electrode-

material that is crucial for the development of organic electronic applications like organic thin-film transistors (OTFTs) or organic light emitting diodes (OLEDs). Understanding and controlling the surface properties of ITO allows molecular engineering of the ITO organic interface which enables precise control of the interfacial chemistry and electronics. One way to optimize the energy-level alignment at the ITO interface is the use of monolayers based on organic molecules with tailored functional groups.

In this work the modified surfaces of ITO coated with self-assembled-monolayers (SAMs) are characterized by means of photoelectron spectroscopy, contact angle and kelvin probe measurements. Via gas-phase simulations of these organic molecules it is possible to link calculated properties and experimental results.

O 22.11 Mon 18:15 Poster E

Functionalization of Gallium nitride surfaces — \bullet Stefan Brackmann^{1,2,3}, Sebastian Hietzschold^{1,2,3}, Robert Lovrincic^{1,2}, and Wolfgang Kowalsky^{1,2,3} — ¹InnovationLab, Heidelberg, Germany — ²IHF, TU Braunschweig, Germany — ³KIP, Heidelberg University, Heidelberg, Germany

Gallium nitride (GaN) is an often used III-V semiconductor due to its favorable optoelectronic properties. GaN nanowires with different doping domains are a promising candidate for blue LEDs. However the material suffers from surface states that are detrimental to its electronic properties 1. One approach to mend the problematic surface states is passivation with different self-assembled monolayers (SAMs) such as amines, tiols and phosphonates. Here, we study GaN surfaces with atomic force microscopy (AFM), ambient Kelvin probe (KP), Surface photo voltage (SPV), UV-Vis spectroscopy and goniometry. Clean (0001) n-type GaN surfaces are compared with functionalized surfaces. Modification of the surface changed the work function as well as the SPV by several 100mV. We will discuss the impact of our surface functionalizations on the band diagram and charge carrier recombination.

1. Reshchikov, M. a., Visconti, P. & Morkoc*, H. Appl. Phys. Lett. 78, 177 (2001).

O 22.12 Mon 18:15 Poster E

Development of a New Update Mechanism for High Charge Carrier Densities in Kinetic Monte Carlo Simulations — •Markus Krammer¹, Chris Groves², and Karin Zojer¹ — ¹Institute of Solid State Physics and NAWI Graz, TU Graz, Austria — ²School of Engineering and Computing Science, Durham University, United Kingdom

Kinetic Monte Carlo simulations (KMC) have become a widely used tool to get a better understanding of the behaviour of charge transport in organic semiconductors and devices [1]. With the help of such simulations, the transport-related properties of a system are derived from the trajectories of all particles hopping through a three-dimensional grid of sites as a function of individually chosen site properties.

Regarding the update mechanism, the Full Dynamic Monte Carlo Method (DMC) and the so-called First Reaction Method (FRM) [2] are currently established. Where DMC recalculates all rates after each step, FRM performs only a very local update. This leads to highly accurate results but high computational costs for DMC and fast simulations but imprecise results for FRM. Especially for high charge carrier densities, both methods are inappropriate. In this connection our new update method combines low computational cost and high accuracy. We present the performance of this improved update mechanism for bulk simulations as well as simulations of injection from a metal contact to an organic semiconductor.

[1] R. Kimber et al., Phys. Rev. B, 86, 235206 (2012)

[2] C. Groves et al., J. Chem. Phys., 133, 144110 (2010)

O 22.13 Mon 18:15 Poster E

DFT calculations on the etching of crystalline ZnO surfaces upon formation of phosphonic acid self-assembled monolayers — •Tobias Klöffel¹, Alexandra Ostapenko², Gregor Witte², and Bernd Meyer¹ — ¹Interdisziplinäres Zentrum für Molekulare Materialien und Computer-Chemie-Centrum, Universität Erlangen-Nürnberg — ²Fachbereich Physik, Philipps-Universität Marburg

Among the inorganic oxides, ZnO is of special interest for hybrid organic-inorganic interfaces in molecular electronics due to its high charge carrier mobility. However, in recent experiments it was observed that self-assembled monolayers of phenylphosphonic acids (PPAs), a typical representative for commonly used linker groups and functional organic units, are not stable but etch the ZnO substrate. Using density-

functional theory (DFT) calculations we show that the origin of this instability is the unusual strength of the PPA–ZnO interaction together with a geometric misfit between the pi-stacking of the phenyl rings and the ZnO lattice constant. As a result, the transformation of PPA layers on ZnO to ZnPPA crystals becomes a thermodynamically favorable reaction. Our DFT calculations provide a first simplified reaction pathway for this transformation process.

O 22.14 Mon 18:15 Poster E

On the Adsorption Behavior of Ionic Liquid (Sub)monolayers on Model Electrode Surfaces and their Interaction with Coadsorbed Lithium — •FLORIAN BUCHNER¹, KATRIN FORSTER-TONIGOLD¹, MARAL BOZORGCHENANI², BENDIKT UHL², AXEL GROSS^{1,3}, and R. JÜRGEN BEHM^{1,2} — ¹Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ³Ulm University, Institute of Theoretical Chemistry, D-89069 Ulm, Germany

Ionic Liquids (ILs) as 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [BMP][TFSA] have become attractive candidates for battery electrolytes. In this model study we investigated the adsorption behavior of (sub-)monolayers of [BMP][TFSA] on metallic substrates and now also on graphite(0001) as frequently used anode material under ultrahigh vacuum (UHV) conditions, applying scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and dispersion corrected density functional theory (DFT-D) calculations. After vapor deposition at 300 K, XPS reveals a 1:1 ratio of cations : anions on Ag(111) and graphite(0001). Upon subsequent cool-down to 100 K, STM demonstrates ordered molecular arrangements, which clearly differ on both surfaces: a detailed comparison is given in terms of adsorption geometry, intermolecular and substrateadsorbate interactions. In addition, we investigated the interaction with coadsorbed Li, which resulted in a decomposition of the ions. This will be discussed based on ongoing DFT-D calculations.

O 22.15 Mon 18:15 Poster E

Triplet emitters for OLEDs investigated by STM and STS — ◆Anne Bakker^{1,2}, Wu Xu³, Sebastian Wilde^{1,2}, Shiyu Zhu³, Haiming Guo³, Shixuan Du³, Hong Ying Gao^{1,2}, Hongjun Gao³, Cristian Strassert^{1,2}, and Harald Fuchs^{1,2} — ¹Physikalisches Institut, Westfälische Wilhelms-Universität, Münster, Germany — ²CeNTech, Westfälische Wilhelms-Universität, Münster, Germany — ³Institute of Physics, Chinese Academy of Sciences, Beijing, China

Pt(II)-triplet emitters are promising candidates for application in OLEDs. The heavy-metal atom with its large spin-orbit coupling enables emission via triplet states with high phosphorescence quantum yield. In previous work it has been shown that the HOMO-LUMO gap of such emitters can be tuned by adjusting the substituents in the periphery of the luminophoric pincer ligand coordinated to the metal centre [1,2].

Here we study the self-assembled nanostructures and electronic properties of a series of new triplet emitters by low-temperature scanning tunnelling microscopy and spectroscopy. In our case the metalorganic complex contains a platinum d8 cation and a tetradentate ligand. To systematically investigate the influence of different electron-

with drawing side groups on the alignment of the energy levels, ligands with $0,\ 2,\ 4$, and 6 Fluor atoms are used. Our experiments can provide in sight in the behaviour of Pt(II)-complexes on surfaces and the possibilities to specifically design new triplet emitters.

- [1] P.R. Ewen et al., Physical Review Letters 111, 267401, (2013)
- [2] J. Sanning et al., Angewandte Chemie 54, 786-791, (2015)

O 22.16 Mon 18:15 Poster E

Impact of a MoO₃ front contact buffer layer on the electric and interface properties in organic bilayer solar cells — •Patrick Reiser^{1,4}, Michael Scherer^{2,4}, Sabina Hillebrandt^{3,4}, Robert Lovrincic^{2,4}, Wolfgang Kowalsky^{2,4}, Sebastian Beck^{3,4}, Annemarie Pucci^{3,4}, Eric Mankel^{1,4}, and Wolfram Jaegermann^{1,4} — ¹Institute of Materials Science, Technische Universität Darmstadt — ²Institut für Hochfrequenztechnik, Technische Universität Braunschweig — ³Kirchhoff-Institut für Physik, Universität Heidelberg — ⁴InnovationLab GmbH, Heidelberg In this study we correlate the chemical and electronic interface properties at different front contacts of conventional $F_4ZnPc:C_{60}$ bilayer solar cells with their electric characteristics. Starting from device and Scanning Kelvin Probe Microscopy data, we examine the interface of $ITO/MoO_3/F_4ZnPc$ and ITO/F_4ZnPc using Photoelectron Spectroscopy on subsequently deposited layers of F₄ZnPc. As oxide substrates we used O₂-plasma cleaned ITO on glass and the same ITO coated with a 10nm thick intermediate MoO₃ buffer layer which shows a significant higher work function than bare ITO. There is a moderate impact of the buffer layer on the electronic band alignment difference of about 100meV. However, we observe chemical interactions of the F₄ZnPc with the ITO substrate. In-situ IR spectroscopy measurements were performed to study the F_4ZnPc adsorption mechanisms on differently treated oxide surfaces. Finally, the analytical measurements could successfully be correlated with the electric characteristics of the solar cell device.

O 22.17 Mon 18:15 Poster E

The OTFT Awakens - Live in-situ organic thin film transistor (OTFT) measurements during growth — •NILS NORRMAN, SEBASTIAN MÄDER, JULIA RITTICH, and MATTHIAS WUTTIG — I. Physikalisches Institut (IA), RWTH Aachen University

Organic semiconductors are of great interest for optoelectronic applications due to their high flexibility and efficiency. Indeed, first commercial products are already available like OLED displays and organic solar cells. The investigation of organic thin film transistors (OTFTs) provides a peerless opportunity for understanding the crucial properties influencing the electrical performance.

Here, we present live in situ measurements obtained during the growth of the very first layer of the organic-channel-material. The OTFTs were prepared using a bottom gate bottom contact geometry to enable electrical contacting during thermal evaporation of the organic material. Precisely controlling deposition rate and substrate temperature in a special vacuum setup allows to electrically characterize all critical properties right from the moment the first molecules arrive at the substrate.

These properties provide an excellent insight into the underlying effects governing efficiency in organic materials.