

DS 31: Organic thin films II

Time: Thursday 14:45–17:00

Location: H8

DS 31.1 Thu 14:45 H8

Organic heteroepitaxy of PTCDA and SnPc on single crystalline metals — ●MARCO GRÜNEWALD, KRISTIN WACHTER, ROMAN FORKER, and TORSTEN FRITZ — University of Jena, Institute of Solid State Physics, Max-Wien-Platz 1, 07743 Jena, Germany

Here we report on the interaction mechanisms at metal-organic and organic-organic interfaces in heterostructures of highly-ordered ultrathin layers of the dye molecules 3,4,9,10-perylene-tetracarboxylicdianhydride (PTCDA) and tin(II)-phthalocyanine (SnPc) on Ag(111) and Au(111). The thin films were structurally characterized by Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM) as well as optically by in situ Differential Reflectance Spectroscopy (DRS). For the first monolayer PTCDA and the first monolayer SnPc we observe significant differences between the dielectric functions extracted from the DRS depending on the substrate used indicating a rather different nature of metal-organic interaction. From the structural point of view an one monolayer SnPc film on top of Au(111) arranges as a highly ordered layer with a quadratic unit cell in a point-on-line coincidence with the reconstructed Au(111) surface. PTCDA grown on top of the first SnPc layer, however, decouples from the substrate as well as from the interlayer and shows a spectral monomer-like behavior. Structural investigations indicate an ordered growth with a line-on-line coincidence between the PTCDA and the SnPc interlayer. Additional new spectral features in the optical spectra on both substrates have been observed which can be explained by a vertical compression of the organic layer in contact with the substrate.

DS 31.2 Thu 15:00 H8

In situ Spectroscopic Ellipsometry Monitoring of Alq₃ and α -NPD Alkali Metal Doping — ●FRANCISC HAIDU¹, OVIDIU D. GORDAN¹, CHRISTOPH WERNER², MACIEJ NEUMANN², NORBERT ESSER², and DIETRICH R. T. ZAHN¹ — ¹TU Chemnitz, 09126 Chemnitz, Germany — ²ISAS Berlin, 12489 Berlin, Germany

The electron- and hole-transport organic materials Tris-(8-hydroxyquinoline)-aluminium(III) (Alq₃) and N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-(1,1'-biphenyl)-4,4'-diamine (α -NPD), respectively, were investigated in their pristine and reduced form via alkali metal (AM) doping. The two organic molecules are seen as milestones in organic light emitting diode functionality, and moreover AM doped molecules show interesting magnetic, electric, and physical properties. Extensive photoemission, inverse photoemission, vibrational spectroscopy, and theoretical studies of n-doped Alq₃ and α -NPD were performed in the last decade. The optical properties of pristine materials were previously established via spectroscopic ellipsometry (SE). This work is the first SE analysis of the doping process. *In situ* SE studies in the (0.7-5.0) eV energy range were performed by a lab-based SE and extended up to 9.5 eV by a vacuum ultraviolet ellipsometer at the synchrotron facility BESSY II, Berlin. The determined optical band gaps show evolution in agreement with filling and splitting of the lowest unoccupied molecular orbital due to AM electron donation [1, 2]. [1] M. Knupfer, H. Peisert, and T. Schwieger, Phys. Rev. B **65** (2001) 033204; [2] T. Schwieger, M. Knupfer, W. Gao, and A. Kahn, Appl. Phys. Lett **83** (2003) 500.

DS 31.3 Thu 15:15 H8

Origin of pinning-levels at molecularly modified electrodes: Mixed monolayer — ●STEFANIE WINKLER^{1,2}, JOHANNES FRISCH², RAPHAEL SCHLESINGER², MARTIN OEHZELT^{1,2}, RALPH RIEGER³, JOACHIM RÄDER³, JÜRGEN P. RABE², KLAUS MÜLLEN³, and NORBERT KOCH^{1,2} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin — ²Humboldt-Universität zu Berlin, Institut für Physik, 12489 Berlin — ³Max Planck Institute für Polymerforschung, 55128 Mainz

Our photoemission study reveals strong work function (Φ) increases by up to 2.1 eV when strong electron acceptors comprising tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) or hexaazatriphenylene-hexacarbonitrile (HATCN) are deposited on indium tin oxide (ITO) surfaces (pristine ITO $\Phi=4.2$ eV). The evolution of the sample- Φ and the hole injection barrier upon subsequent deposition of the hole transport material N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α -NPD) on various submonolayer acceptor-coverages is reported for the modified ITO electrodes. We

find the highest occupied molecular level of multilayer α -NPD pinned 0.5 eV below the Fermi-level, when employing the acceptor interlayers. Surprisingly pinning is achieved at a 0.4 eV (5.2 eV) higher initial Φ than one would expect according to the ionization energy of α -NPD ($I_E=5.3$ eV). With a simple model including a uniform electrostatic field above the first organic layer (mixture of acceptor and α -NPD) we can assign the origin of the shifted pinning-level to be caused by the pushback effect of α -NPD completing the only partly covered monolayer.

DS 31.4 Thu 15:30 H8

Molecular Tilt Angle Determination of CuPc Deposited under Different Vacuum Conditions — ●FALKO SEIDEL, OVIDIU D. GORDAN, and DIETRICH R. T. ZAHN — Semiconductor Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

Thin films of organic molecules are used in applications such as organic photovoltaic cells and organic field effect transistors. Nevertheless, ring structured planar molecules have a high intrinsic anisotropy due to the delocalised highest occupied molecular orbital parallel to the molecular plane. Therefore, the electrical respectively optical properties of these devices depend on the orientation of molecules within the film, which is accessible via the complex dielectric function. Variable angle spectroscopic ellipsometry (VASE) measurements of copper phthalocyanine (CuPc) films enable to quantitatively evaluate the anisotropic complex dielectric function. Considering the ratio of the out of plane optical extinction coefficient to the in plane one (substrate plane) of a uniaxial film, one can determine the average molecular tilt angle with respect to the substrate. CuPc film growth parameters such as vacuum pressure and substrate type have a strong influence on the molecular orientation. Hence, in this work in total 26 differently prepared CuPc films deposited on hydrogen passivated silicon respectively natively oxidized silicon were investigated using VASE. A critical vacuum pressure could be estimated, below which a clear influence of the substrate on the molecular orientation was visible. Moreover, the mathematical limitations are determined taking into account the optical properties of amorphous CuPc film deposited on liquid nitrogen cooled substrates.

DS 31.5 Thu 15:45 H8

Growth of p-6P thin films on graphene studied by AFM — ●MARKUS KRATZER¹, STEFAN KLIMA¹, BORISLAV VASIĆ², RADOŠ GAJIĆ², ALEKSANDAR MATKOVIĆ², and UROŠ RALEVIĆ² — ¹Institute of Physics, Montanuniversität Leoben, Austria — ²Institute of Physics, University of Belgrade, Serbia

Graphene is a potential candidate as transparent and flexible electrode material in organic electronics. In this study we investigated the growth morphology of the rodlike para-hexaphenyl (6P) molecule on graphene as a model system. Exfoliated graphene transferred onto a silicon oxide support was used as substrate. Sub-monolayer amounts of 6P were deposited by means of hot wall epitaxy at substrate temperatures between 280 K and 420 K. The evolving film morphologies were investigated via atomic-force microscopy. While on the SiO₂ support just 6P islands consisting of upright standing molecules were found, the 6P film on the graphene evolves needle like structures which are known to be composed of flat lying molecules [1] and which also have been observed for 6P deposited onto epitaxial graphene on Ir(111) at 350 K [2]. The needle formation on graphene is favored at elevated temperatures, resulting in 6P films solely consisting of needles for deposition temperatures over 360 K.

[1] C. Teichert, G. Hlawacek, A. Andreev, H. Sitter, P. Frank, A. Winkler, N.S. Saricic, Appl. Phys. A **82** (2006) 665. [2] F.S.Khokhar, G. Hlawacek, R. v. Gastel, H. J. W. Zandvliet, C. Teichert, B. Poelsema, Surf. Sci. **606** (2012) 475.

DS 31.6 Thu 16:00 H8

Growth and stability: The impact of fluorination of pentacene on Cu(111) — ●HENDRIK GLOWATZKI^{1,2}, GEORG HEIMEL³, ANTJE VOLLMER¹, SWEE LIANG WONG², HAN HUANG², WEI CHEN², ANDREW T. S. WEE², JÜRGEN P. RABE³, and NORBERT KOCH³ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH Bessy II, Albert-Einstein-Str. 15, 12489 Berlin, Germany — ²National University of Singapore, Department of Physics, 2 Science Drive 3, 117542, Singapore — ³Humboldt -Universität zu Berlin, Institut für Physik, Newtonstr. 15, D-12489 Berlin, Germany

In this study, the organic semiconductor pentacene (PEN) and its fully fluorinated analogue perfluoropentacene (PFP) were investigated on Cu(111) by STM, LEED, UPS and XPS. While PEN molecules at room temperature could only be imaged by STM at full monolayer coverage, PFP was found to stabilize in disordered clusters already in the sub-monolayer regime. Moreover, PFP formed only a disordered first wetting layer, whereas for PEN long-range order was already observed for closed molecular monolayers. However, highly ordered domains of PFP molecules were found for the second layer. Supported by additional STM measurements on graphite and theoretical modelling, it was concluded that the molecular planes in this layer are inclined to the surface. Therefore, careful consideration of the structural details in the transitional growth regime from molecular mono- to multilayers emerges as a key factor to achieving a deeper understanding of metal/organic interfaces relevant for organic electronic devices.

DS 31.7 Thu 16:15 H8

In-situ x-ray scattering studies of co-evaporated organic thin films: Dependence on mixing ratio — ●RUPAK BANERJEE, JIŘÍ NOVÁK, CHRISTIAN FRANK, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik - Universität Tübingen, Tübingen, Germany

Organic molecular semiconductors have attracted substantial research interests due to their attractive optical, structural and electronic properties [1]. The efficiency of an organic photovoltaic (OPV) composed of organic semiconductors mainly depends on the diffusion length of the generated exciton and the charge carrier collection at the electrodes [1]. For applications in the OPV, further enhancement of efficiency can be achieved by mixing donor and acceptor organic semiconducting molecules. One of the ways of tailoring this is by changing the mixing ratio of the constituents during co-evaporation. We present in-situ and real-time depth resolved grazing incidence x-ray diffraction, grazing incidence small angle scattering and x-ray reflectivity studies on the structure of mixed C60 and Diindinoperylene (DIP) films as a function of mixing ratio. We observe enhancement in the out-of-plane ordering (very smooth films up to 20 nm) upon co-evaporation of C60:DIP thin films (in different mixing ratio) which are otherwise well known to phase separate. We also observe differences in the size of the grains of the co-evaporated thin film on changing the mixing ratio.

[1] A. Hinderhofer and F. Schreiber, Chem. Phys. Chem. 13, 628 (2012).

DS 31.8 Thu 16:30 H8

Triangular dewetting of a PCDTBT-PS blend — ●PAUL FREYBERG¹, IOAN BOTIZ^{1,2}, and GÜNTER REITER^{1,2} — ¹Institute

of Physics, University of Freiburg, Freiburg, Germany — ²Freiburg Institute for Advanced Studies, Freiburg, Germany

Normally the dewetting of thin polymer films results in the growth of circular holes. The symmetry of this process is well understood by current theories. Interestingly, a breaking of this symmetry is found in a particular case: We observe highly anisotropic growth of holes leading to a triangular dewetting shape for the dewetting of thin polymer blend films consisting of rigid, conjugated PCDTBT* and polystyrene (PS).

By varying physical parameters like the volume fraction or by changing the substrate we can control the transition from circular to triangular dewetting. The presence of PCDTBT in thin polystyrene films leads to symmetry breaking for all dewetting temperatures in the experiments. We tentatively explain our experimental observations by an ordering of PCDTBT molecules at the contact line, leading to a breaking of the symmetry. The triangular shape is very stable, allowing triangular growth up to large scales.

*Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzo-thiadiazole-4,7-diyl-2,5-thiophenediyl]

DS 31.9 Thu 16:45 H8

Temperature dependent growth and dewetting behavior of tetraseleno-tetracene on Au(111) and Ag(111) studied by photoelectron spectroscopy — ●JENS NIEDERHAUSEN¹, STEFFEN DUHM^{2,5}, CHRISTOPH BÜRKER³, QIAN XIN^{2,6}, ANDREAS WILKE¹, ANTJE VOLLMER⁴, FRANK SCHREIBER³, SATOSHI KERA², NOBUO UENO², and NORBERT KOCH^{1,4} — ¹Humboldt-Universität zu Berlin, Institut für Physik, 12489 Berlin, Germany — ²Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan — ³Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ⁴Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, BESSY II, 12489 Berlin, Germany — ⁵Present address: FUNSOM, Soochow University, Suzhou, P. R. China — ⁶Present address: School of Physics and Microelectronics, Shandong University, 5 Hongjialou, Jinan, P. R. China

The organic donor tetraseleno-tetracene (TSeT) was vacuum deposited on Au(111) and Ag(111) with the substrates (i) at room temperature and (ii) at 77 K. For these two cases we find:

(i) High resolution X-ray photoelectron spectroscopy indicates strong chemisorption of the molecules on the metal surfaces, mitigated by the diselenide groups.

(ii) Fast dewetting of TSeT multilayers is observed for samples grown at 77 K as the temperature is gradually increased. Ultraviolet photoelectron spectroscopy measurements during sample annealing reveal that the concomitant morphological changes in the TSeT film have a significant effect on its electronic structure.