

DS 4: Organic Thin Films I

Time: Monday 9:30–12:45

Location: H11

Invited Talk

DS 4.1 Mon 9:30 H11

Controlling and tailoring molecular thin film growth — ●STEFAN KOWARIK — Institut für Physik, Humboldt Universität Berlin, Newtonstr. 15, 12489 Berlin

Organic thin films are widely used in applications ranging from (opto-) electronic devices such as OLEDs to functional coatings e.g. in biosensors. Tailoring the thin film properties, such as molecular orientation, crystal structure and phase purity, surface roughness and grain size for a given application is therefore an important challenge. Here we demonstrate different strategies to tailor film growth and showcase important analytical tools to control film growth with in situ X-ray scattering and X-ray spectroscopy (XRR, GISAXS, NEXAFS) as well as UV-vis spectroscopy. We will discuss how micro-kinetic models of growth are starting to become available to predict the influence of the important parameters temperature and growth rate in determining (non-equilibrium) thin film structures. We will discuss how lattice matching with the substrate can be used to change the molecular orientation and how slight chemical modification of molecules can be used to alter the growth mode. Finally we will highlight novel ways to control molecular film growth e.g. by fast temperature cycles to separately control nucleation and coalescence in each monolayer or using laser light to increase phase purity in thin films.

DS 4.2 Mon 10:00 H11

Ultra-robust thin film devices from self-assembled metal-terpyridine wires — ●FLORIAN VON WROCHEM¹, FRANK SCHOLZ¹, WILLIAM FORD¹, ZOI KARIPIDOU¹, MARIA RAMPI², BARBARA BRANCHI², WOLFGANG WENZEL³, and VELIMIR MEDED³ — ¹Sony Deutschland GmbH, Stuttgart, Germany — ²Department of Chemistry, Ferrara University, Italy — ³Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany

Considerable efforts have been undertaken within the past decades to shift organic-based thin-film devices from basic research to the application level. A major hurdle towards the practical realization of large area, thin film circuits is however given by the thermal deposition of the metal electrodes, which remained elusive due to the damage and the electrical shorts experienced by the fragile molecular layers.

Here, we show that large area molecular junctions of outstanding electronic properties and robustness can be realized using densely packed molecular wires consisting of FeII-terpyridine complex oligomers, despite a conventional fabrication process involving top electrode evaporation directly on the molecular layer. Surprisingly, these oligomer-based devices are stable for over 2 years under regular current-voltage cycling, withstanding a wide range of temperatures (150-360 K) and applied voltages (3 V). Electrical studies in conjunction with ab-initio calculations reveal that charge transport occurs via electron (hopping) conduction and is limited by the charge injection through a Shottky barrier of 0.72 eV, following Richardson-Schottky injection.

DS 4.3 Mon 10:15 H11

Patterning functional organic molecules based on the liquid behavior — ●HONG WANG, WENCHONG WANG, and LIFENG CHI — Physikalisches Institut und Center for Nanotechnology (CeNTech), Universität Münster, 48149 Münster, Germany

Small organic molecules were reported to have the probability to perform like liquid on a surface under vacuum condition, which enable us to fabricate functional organic patterns through focusing on the liquid behavior of it. Here we demonstrate the versatility of the technique in vacuum chamber to create organic hetero-patterns on hierarchically pre-pattern surface through temple-directed growth to locate N,N'-Di[(N-(3, 6-di-tbutyl-carbazyl)ndecyl)] quinaclidone (DtCDQA) at pre-defined area firstly, and then anneal at optimized temperature to tune the pattern in situ. Meanwhile, the controlling of organic liquid can also be taken in ambient condition. By using N-ethyl- d -glucamine (NEDG) as the liquid source, we succeeded to pattern organic films on Au stripes directly through self-driven microfluidics. Furthermore, the fluid can be used to transport other functional molecules, e.g., dye molecules, creating multicolored patterns in one step.

DS 4.4 Mon 10:30 H11

Domain size distribution of PTCDA on KCl(100) deter-

mined by SPA-LEED and optical spectroscopy — ●CHRISTIAN MARQUARDT¹, ALEXANDER PAULHEIM¹, ALEXANDER EISFELD², and MORITZ SOKOLOWSKI¹ — ¹Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstr. 12, 53115 Bonn, Germany — ²Max-Planck-Institut für Physik komplexer Systeme, Noethnitzer Str. 38, 01187 Dresden, Germany

The organic dye molecule 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA) forms a monolayer with a commensurate ($2\sqrt{2} \times 2\sqrt{2} R45^\circ$) brickwall structure on the KCl(100) surface. Within this structure, the molecules arrange in a head-to-tail configuration forming two-dimensional J-aggregates with optical properties correlated to the size of the exciton delocalization [1]. Under real growth conditions and at cryogenic temperatures, the exciton delocalization is mainly limited by the size of the PTCDA domains. Here, we present a combined SPA-LEED and optical spectroscopy study, to demonstrate the huge impact of the present domain size distribution on the obtained spectral features in optical fluorescence (FL) and FL excitation spectra. Supported by DFG.

[1] M. Müller et al., J. Chem. Phys. 139 044302 (2013).

DS 4.5 Mon 10:45 H11

Origin of F1s NEXAFS Dichroism in oriented perfluorinated acenes — ●MICHAEL KLUES¹, PAUL JERABEK¹, TOBIAS BREUER¹, MARTIN OEHZELT², ROBERT BERGER¹, and GREGOR WITTE¹ — ¹Uni. Marburg, Marburg, Germany — ²Helmholtz Zentrum Berlin, Berlin, Germany

NEXAFS is a widely used technique to determine molecular orientations on surfaces. Especially for planar molecules with extended π -systems the analysis of angle-dependent intensity variations (dichroism) is straightforward. Surprisingly the analysis of NEXAFS data of fluorinated aromatic molecules measured at the F1s-edge has led to misleading results in the past. In a recent theoretical study [1] this has been attributed to an unexpected overlap of π and σ resonances in the energy region of interest. To further investigate this phenomenon highly ordered multilayers of Perfluoropentacene (PFP) were grown on HOPG and SiO₂. PFP crystallizes flat lying respectively nearly upright standing on these substrates. This structural difference results in diverging dichroisms, enabling a detailed assignment of underlying excitations. To gain detailed insights into the nature of these excitations the NEXAFS-signature was calculated using the StoBe-code. Thereby, relaxation effects turned out to be of central importance. To cover this effects the computational approach was improved to determine excitation energies as well as oscillator strength within a Δ SCF-method. Finally these results were able to reproduce not only the signature but also the angle dependants of the experimental spectra.

[1] Oteya et al. Phys. Rev. B 2012, 86, 075469.

DS 4.6 Mon 11:00 H11

Monolayer phases of a dipolar perylene derivative on Au(111) and surface potential built-up in multilayers — ●JENS NIEDERHAUSEN^{1,2}, HEATH R. KERSELL³, CHRISTOS CHRISTODOULOU^{1,2}, GEORG HEIMEL¹, HENRIKE WONNEBERGER⁴, KLAUS MÜLLEN⁵, JÜRGEN P. RABE¹, SAW-WAI HLA³, and NORBERT KOCH^{1,2} — ¹Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — ²Humboldt-Universität zu Berlin, Institut für Physik & IRIS Adlershof, Berlin, Germany — ³Ohio University, Physics & Astronomy Department, Ohio, USA — ⁴BASF SE, Ludwigshafen, Germany — ⁵Max Planck Institut für Polymerforschung, Mainz, Germany

The molecular self-assembly and the electronic structure of a strongly polar perylene derivative on Au(111) was elucidated with room temperature scanning tunneling microscopy and spectroscopy in combination with ultraviolet and X-ray photoelectron spectroscopies. The molecular arrangements and the increase of the average number of molecules per unit cell via ripening indicate a significant influence of the dipole moment on the molecular assembly. Applying an electric field with the STM tip is found to induce a phase change that can alter the anisotropy of the molecular film. Multilayer molecules arrange with a slightly preferred out-of-plane orientation, inducing a surface potential of up to 1.2 eV. This resembles the giant surface potential effect that was reported before for other polar molecules and deemed applicable

for data storage. Notably, the surface potential in the present case can in part be *reversibly* removed by visible light irradiation.

15 min. break.

DS 4.7 Mon 11:30 H11

Evolution of Crystalline C₆₀ Films: Influence of the Subjacent Pentacene Layer — ●ANDREA KARTHÄUSER, TOBIAS BREUER, and GREGOR WITTE — Molekulare Festkörperphysik, Philipps-Universität Marburg, Renthof 7, D-35032 Marburg, Germany

A key process in organic photovoltaic devices is the charge transfer that takes place at the heterojunction between molecular donors and acceptors. In many cases, however, an intermixture of both materials hampers detailed studies of the elementary optoelectronic excitations and their structure interrelation. Here we report on the hetero-growth of Buckminster-Fullerene (C₆₀) films on Pentacene (PEN, C₂₂H₁₄) bottom layers. While C₆₀ deposition on SiO₂ yields amorphous films only, crystalline islands are formed when the substrate is precoated with a PEN buffer layer [1]. Using atomic force microscopy in combination with x-ray diffraction we show that the thickness of the PEN buffer layer is decisive for the crystallinity of the resulting C₆₀ films, which can be explained by an interplay of diffusion and nucleation of the impinging C₆₀ molecules.

[1] Itaka K. et. al. Adv. Mater. (2006), 18, 1713

DS 4.8 Mon 11:45 H11

Structure and thermal stability of dithiol SAM on Au(111) — ●JOHANNES VÖLKNER and GREGOR WITTE — AG Molekulare Festkörperphysik, Philipps-Universität Marburg

Self-assembling monolayers (SAMs) are commonly used for molecular modification of metal surfaces. It results in a variation of surface properties such as wetting behavior, friction, reactivity and biocompatibility. In this study an Au(111) surface is functionalized with aromatic trans-stilbene dithiol by means of wet-chemical preparation. While one thiol moiety binds to the surface under thiolate formation the opposite one stays intact. Latter terminates the self-assembling monolayer and thus enables binding events on top of the film. This was for instance recently exploited in a biosensor application based on photoexcitation of quantum dots [1].

Efficient coupling of additional layers however requires high stability and packing density of the film. We prepared stilbene dithiol SAMs under different conditions and verified intactness of the terminating group by means of XPS. Complementary, structural order was investigated in NEXAFS measurements. A clear alteration of the films upon annealing was identified and related to thermal desorption spectra.

[1] N. Sabir et al., Small 11, 5844 (2015)

DS 4.9 Mon 12:00 H11

1,4-phenylene diisocyanide adsorption on metals : from single crystals to supported nanoparticles — ●AHMED GHALGAOUI, NAS-SAR DOUDIN, and MARTIN STERRER — Institute of Physics, University of Graz, Universitätsplatz 5, A-8010 Graz, Austria

We have investigated the adsorption of PDI on single crystal metal

surfaces and metal nanoparticles supported by an insulating layer (Au/FeO/Pt(111)). Both, gas-phase and liquid-phase deposition methods were applied. The role of PDI concentration and Au nanoparticle size on the surface structure/adsorption mode of PDI has been investigated by STM and Sum Frequency Generation (SFG) Spectroscopy. The PDI molecule adsorbs either with both - NC groups interacting with the surface, leading to flat adsorption geometry, or by only one - NC group, assuming a vertical adsorption structure. SFG measurements in the -NC stretching region show that PDI deposited from the gas-phase always binds with both - NC groups to Au(111), independent of surface coverage. In the case of liquid-phase deposition, PDI molecules adsorb in the flat adsorption geometry at low concentration, but change to the vertical geometry upon increasing the concentration. This concentration dependence is absent on Pt(111), where PDI exclusively adsorbs in the vertical geometry. Finally, the influence of Au particle size on the adsorption structure of PDI will be discussed.

DS 4.10 Mon 12:15 H11

A novel strategy for enhancing layer-by-layer growth of organic thin films: Temperature variation during individual monolayer growth — ●LAURA BOGULA, LINUS PITHAN, ANTON ZYKOV, and STEFAN KOWARIK — Inst. für Physik, Humboldt-Universität zu Berlin, Germany

We investigate the influence of a time dependent substrate temperature on the thin film growth of the organic semiconductor PTCDI-C₈. We show that varying the substrate temperature during the growth of each monolayer allows one to control the nucleation and coalescence regimes and to enhance layer-by-layer growth. We analysed the PTCDI-C₈ films with *in situ* X-ray reflectivity at the Anti-Bragg point and post-growth atomic force microscopy and consistently found smoother films when the dynamic heating method was applied as compared with static substrate temperatures. We thus demonstrate a novel method to induce enhanced layer-by-layer growth of organic molecules, which is highly relevant for applications in organic electronics.

DS 4.11 Mon 12:30 H11

3-D hybrid inorganic-organic structures: metallic nanoparticles self-assembled in organic molecular crystal — ●OLGA MOLODTSOVA^{1,2}, SERGEY BABENKOV¹, IRINA ARISTOVA³, DENIS VYALIKH⁴, OLEG VILKOV⁴, MAXIM TCHAPLYGUINE⁵, RALF NYHOLM⁵, KARINA SCHULTE⁵, ANDREI HLOSKOVSKY¹, and VICTOR ARISTOV^{1,3,6} — ¹DESY, Hamburg, Germany — ²ITMO, Saint Petersburg, Russia — ³ISSP RAS, Chernogolovka, Russia — ⁴BESSY, Berlin, Germany — ⁵Max-lab, Lund, Sweden — ⁶TU Bergakademie, Freiberg, Germany

The evolution of the morphology and the electronic properties of the hybrid organic-inorganic systems composed of metallic nanoparticles distributed in semiconductor organic matrix (FxCuPc, x=0,4,16), as a function of nominal metal content was studied by transmission electron microscopy and by surface- and bulk sensitive photoelectron spectroscopy. This work supported by the RFBR Grant No. 13-02-00818 and the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211