

DS 27: Organic Thin Films II

Time: Wednesday 15:00–18:30

Location: CHE 91

DS 27.1 Wed 15:00 CHE 91

All-UHV growth of organic/ZnO hybrid structures — ●MINO SPARENBERG, SYLKE BLUMSTENGEL, and FRITZ HENNEBERGER — HU zu Berlin, Institut für Physik, AG Photonik

Conjugated organic molecules have a great potential for opto-electronic devices when used in hybrid components together with inorganic semiconductors where the advantages of both materials are combined. Crucial for the fabrication of hybrid structures is the understanding of the interaction at the interface between the organics and the inorganics. To achieve this the growth is conducted and observed in an all-UHV MBE system where growth conditions of the conjugated molecules can be controlled and analysed in-situ with electron diffraction techniques as well as scanning probe microscopes. The inorganic semiconductor investigated here is epitaxially grown ZnO which has been proven for its suitability in hybrid structures with several conjugated molecules. As model systems of the present study, serve aromatic hydrocarbons like the linear sexiphenyl (6P) and its fluorinated derivatives to investigate how the electrostatic interaction at the interface of the ZnO substrate influences the growth of the molecules, as it is predicted in theory, as well as the planar molecule hexabenzocoronene (HBC), which is due to its hexagonal symmetry a promising candidate to create an epitaxial-like growth on top of the ZnO crystal. Our measurements have shown that the fluorination of 6P leads to an interaction with the substrate surface, changing the growth mode in comparison unfluorinated 6P species. Furthermore STM and LEED investigations of HBC samples indicate a predominant growth direction correlated with the substrate.

DS 27.2 Wed 15:15 CHE 91

The role of a molecular dipole in thin-film growth kinetics: *In situ* X-ray studies of 6P and 6P-3,5-F₂ — ●ANTON ZYKOV¹, SEBASTIAN BOMMEL^{1,2}, PETER SCHÄFER¹, FRANCESCO CARLÀ³, ROBERTO FELICI³, and STEFAN KOWARIK¹ — ¹Inst. f. Physik, Humboldt Universität Berlin — ²DESY, Deutsches Elektronen-Synchrotron, Hamburg — ³ESRF, Grenoble

An understanding and ideally a control of thin-film growth is needed to rationally fabricate organic-inorganic heterostructures for optimized devices like efficient OLEDs. However, growth control is up to now almost exclusively limited to substrate temperature and growth rate. The incorporation of tunable static dipoles into well-known organic molecules may thus establish a new degree of freedom to design the thin-film morphology. Here we want to present first results of a growth study of 6P and its dipolar derivative 6P-3,5-F₂ on SiO₂. The films were deposited in a vacuum chamber by OMDB under variation of the growth rate and the substrate temperature. Simultaneous *in situ* X-ray measurements of the growth oscillations and GISAXS were carried out at the ID03 beamline at the ESRF to access growth-mode, island-sizes and -densities, which in the end determine the film morphology. We find that films from the dipolar molecule 6P-3,5-F₂ form smaller islands while at the same time yielding smoother films than 6P. Interestingly the inter-layer crystallographic orientation is also lost in 6P-3,5-F₂. These results suggest a different growth mode due to the additional source of disorder through random orientation of dipoles.

DS 27.3 Wed 15:30 CHE 91

Investigation of Interfaces between Pentacene and C₆₀ - Diffusion-Controlled Growth of Two-, One-, and Zero-Dimensional C₆₀-Nanostructures — ●TOBIAS BREUER and GREGOR WITTE — Philipps-Universität Marburg, Deutschland

A variety of low dimensional C₆₀ structures has been grown on supporting pentacene multilayers. By choice of substrate temperature during growth the effective diffusion length of evaporated fullerenes and their nucleation at terraces or step edges can be precisely controlled. AFM and SEM measurements show that this enables the fabrication of either 2D adlayers or solely 1D chains decorating substrate steps, while at elevated growth temperature continuous wetting of step edges is prohibited and instead the formation of separated C₆₀ clusters pinned at the pentacene step edges occurs. Remarkably, all structures remain thermally stable at room temperature once they are formed. In addition, the various fullerene structures have been overgrown by an additional pentacene capping layer. Utilizing the different probe depth of XRD and NEXAFS we found that no contiguous pentacene

film is formed on the 2D C₆₀ structure, whereas an encapsulation of the 1D and 0D structures with uniformly upright oriented pentacene is achieved, hence allowing the fabrication of low dimensional buried organic hetero-structures.

[1] T. Breuer, G. Witte, ACS Applied Materials & Interfaces 5, 9740 - 9745 (2013)

DS 27.4 Wed 15:45 CHE 91

Dynamics at Pentacene/C₆₀ interfaces studied by time resolved photoluminescence — ●NILS ROSEMANN, ANDREA KARTHÄUSER, GREGOR WITTE, and SANGAM CHATTERJEE — Philipps-Universität Marburg, Marburg, Germany

The combination of Pentacene (PEN) and C₆₀ is a promising model system for next-generation solar cells based on organic semiconductors. Here, the C₆₀ acts as an electron acceptor while PEN, on the other hand, attracts the holes. One of the remaining challenges in this system is the underlying charge-transfer mechanism. In general the efficiency of this charge separation will depend on the structural and electronic states at the interface. To study these dynamics, we performed time-resolved photoluminescence measurements on a thin PEN layer of standing molecules covered by C₆₀. The data indicate the formation of correlated states across the interface.

DS 27.5 Wed 16:00 CHE 91

Order in functional self-assembled monolayers for transistor applications — ●THOMAS SCHMALTZ¹, HANS-GEORG STEINRÜCK², ARTOEM KHASSANOV¹, and MARCUS HALIK¹ — ¹Organic Materials & Devices (OMD), University Erlangen-Nürnberg, Germany — ²Crystallography and Structural Physics, University Erlangen-Nürnberg, Germany

Self-assembled monolayers (SAMs) of functionalized molecules containing semiconducting moieties can be utilized to fabricate monolayer transistor devices (SAMFETs) by a simple, solution based process. However, the order in such systems is not always inherently as desired. For example, C₆₀ functionalized alkylphosphonic acids (C₆₀C₁₈-PA) tend to arrange in a poor 2D order, but it can be increased by introducing alkyl-based monolayers in mixed SAMs as a supporting matrix [1]. In other systems, in which the size of the head group matches better to alkyl chain and anchor group, e.g. in (benzo[b]benzo[4,5]thieno[2,3-d]thiophene)-functionalized alkylphosphonic acids (BTBT-C₁₂-PA), self-assembly of the pure molecules already yields highly ordered layers [2]. To obtain a deeper insight into the order of those monolayers, X-ray reflectivity and X-ray grazing incidence diffraction measurements on those SAMs were performed. Information from those analytical investigations is crucial to understand the relation between the chemical structure, the molecular order and electrical properties of those systems.

[1] C.M. Jaeger, T. Schmaltz et al., JACS, 135, 4893-4900 (2013).

[2] T. Schmaltz, A. Y. Amin et al., Adv Mater, 25, 4511-4514 (2013).

DS 27.6 Wed 16:15 CHE 91

Study of the structure of solution processed bulk heterojunction organic solar cells — ●THAER KASSAR¹, TORBEN SCHINDLER¹, TILO SCHMUTZLER¹, CHRISTOPH BRABEC², and TOBIAS UNRUH¹ — ¹LKS FAU, Erlangen, Germany — ²i-MEET FAU, Erlangen, Germany

Solution processed bulk heterojunction polymer solar cells are becoming viable technology due to their potential as a low-cost, printable, and flexible renewable energy source. Little is known about their structure formation and how it can be controlled. It was thought that conjugated polymers and fullerene derivatives separate into pure domains. However, recent reports suggest that intercalation of fullerenes between the side chains of the polymers is possible. Our working group has built a dedicated cell with an integrated doctor blading coater to perform in situ measurements of the evolution of the blend structure during the drying process. To access the 3D structure of the studied thin films from the molecular to the mesoscale, we probe the inner structure through the methods of grazing incidence X-ray diffraction (GIXD) and grazing incidence small angles X-ray scattering (GISAXS). Grazing incidence geometry is used to enhance the scattered intensity and limit it to the films. We exploit SAXS to study the solutions before coating them. We also study ternary cells which overcome the absorption limitation of organic semiconductors and how solvent mixtures,

processing additives, thermal/solvent annealing and multilayer stack build-up of the device affect the final dried blend structure. In this talk, first results on the structure formation of active layers of solution processed solar cells will be presented.

DS 27.7 Wed 16:30 CHE 91

Correlation between exciton diffusion and morphology in thin films of Diindenoperylene — ●ALEXANDER STEEGER¹, ANNA KATHARINA TOPCZAK¹, and JENS PFLAUM^{1,2} — ¹Experimental Physics VI, University of Würzburg, 97074 Würzburg — ²ZAE Bayern, 97074 Würzburg

The exciton diffusion length (EDL) of organic thin films is known to strongly depend on the respective organic compound and can be attributed to a combination of intrinsic material properties and morphological impacts. In order to investigate the latter, we controlled the morphology of thin films of diindenoperylene (DIP) during evaporation by means of the substrate temperature T_S . The EDL was extracted from film thickness dependent photoluminescence measurements in consideration of quenching quality, interference effects and interface roughness. In good agreement with atomic force microscopy and X-ray diffraction measurements showing an enhanced dewetting and significantly larger crystallite sizes at higher T_S , polycrystalline DIP layers grown at $T_S = 300$ K and 400 K exhibit high EDLs of 59 nm and 115 nm, respectively. In contrast, X-ray amorphous DIP deposited at $T_S = 100$ K shows minor transport properties of excitons. This result emphasizes that exciton diffusion is substantially promoted by the long range order in molecular thin films. Financial support by the DFG focus program SPP 1355 is gratefully acknowledged.

Coffee break (15 min)

DS 27.8 Wed 17:00 CHE 91

In-situ GIWAXS on slot die coated highly conductive PEDOT:PSS as electrode for ITO-free organic electronics: Crystallinity and molecular orientation — ●CLAUDIA M. PALUMBINY¹, FENG LIU², CHENG WANG³, ALEXANDER HEXEMER³, ERIC SCHAIBLE³, THOMAS P. RUSSEL², and PETER MÜLLER-BUSCHABUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching — ²UMass Amherst, Department of Polymer Science and Engineering, Amherst, MA 01003, USA — ³Advanced Light Source, LBNL, Berkeley, CA 94720, USA

The potential to manufacture organic photovoltaic devices on flexible substrates enables roll-to-roll mass production. Thereby, techniques such as slot die coating are used. In this study, we use a mini slot die coater, specially designed and made at ALS Berkeley in collaboration with UMass Amherst and Jema Technology, Berkeley, for the implementation at a synchrotron facility. This enables in-situ Grazing Incident Wide Angle X-ray Scattering measurements during the slot die coating process. It allows us to follow the changes in molecular orientation and crystallinity. Further, there are still challenges for roll-to-roll processed flexible devices such as the brittleness of ITO. In this study we therefore investigate PEDOT:PSS modified with the co-solvent ethylene glycol (EG) during the slot die process with in-situ GIWAXS. The results are correlated to the conductivity of the thin films. Doping with EG increases the conductivity of PEDOT:PSS films up to the value of ITO conductivity[1] and can thereby replace ITO as a stand-alone electrode. [1] Palumbiny, C.M. et al., 2014 (submitted)

DS 27.9 Wed 17:15 CHE 91

Island size evolution and molecular diffusion during growth of organic thin films followed by time-resolved specular and off-specular scattering — CHRISTIAN FRANK¹, JIŘÍ NOVÁK¹, RUPAK BANERJEE¹, ●ALEXANDER GERLACH¹, FRANK SCHREIBER¹, ALEXEI VOROBIEV², and STEFAN KOWARIK³ — ¹Institut für Angewandte Physik, Universität Tübingen, Germany — ²European Synchrotron Radiation Facility, Grenoble, France — ³Institut für Physik, Humboldt Universität Berlin, Germany

We report on a combined off-specular and specular X-ray scattering growth study of ultra-thin films of the prototypical organic semiconductor diindenoperylene (DIP, $C_{32}H_{16}$) [1,2]. We investigate the evolution of the in-plane correlation length and the growth kinetics of the films including their dependence on the substrate temperature and the growth rate. We observe a temperature dependent collective rearrangement of DIP molecules from the thin-film to the bulk phase, which can be rationalized by incorporating a thickness-dependent out-of-plane lattice parameter. We further observe that the nucleation

behavior of DIP changes from the 1st to the 2nd monolayer, which we relate to a difference in the diffusion of the molecules.

[1] S. Kowarik et al., Phys. Rev. Lett. **96** (2006) 125504

[2] A. Aufderheide et al., Phys. Rev. Lett. **109** (2012) 156102

DS 27.10 Wed 17:30 CHE 91

Telechelic polymers and magnetic nanoparticles nanocomposites: thin dry films and hydrogels — ●ANTONELLA CAMPANELLA — JCNS Institute of Forschungszentrum Jülich GmbH, Lichtenbergstraße 1 85747 Garching, Germany

The incorporation of inorganic nanoparticles into polymer matrix has extended the particle application because of the several advantages of the polymer thin films like homogeneity and tunable physicochemical properties by increasing mechanical, magnetic and conductive properties. Such kind of nanocomposites are suitable for several modern applications, e.g. as electromagnetic wave absorbers, photovoltaic cells, OLED, data storage. In this context, the object of our study are nanocomposite systems composed of a polymer matrix which consists of hydrophobically modified ethoxylated urethane polymers (a relatively new class of industrially important macromolecules, which are gaining increasing industrial use due to their ability to impart improved rheological behavior to particulate dispersions) with core-shell magnetite nanoparticles embedded. The shell of the magnetite nanoparticles is composed by oleic acid and oleylamine, in order to provide more stability in organic solvent. We are now focusing on the structural characterization of such nanocomposites in two different morphologies: as thin dry films and as hydrogels, in order to understand the influence of the water on the structural organization of the system. The presence of magnetic nanoparticles in the dry polymer matrix shows also an interesting magnetic aspect of the system, which could be interesting for specific applications mentioned above.

DS 27.11 Wed 17:45 CHE 91

Synthesis of Two-Dimensional Polymer/Copolymers Sheets — ●ZHUKUN ZHENG¹, LOTHAR OPILIK², FLORIAN SCHIFFMANN¹, WEI LIU³, RENATO ZENOBI², JOOST VANDEVONDELE¹, and A. DIETER SCHLÜTER¹ — ¹Department of Materials, ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland — ²Department of Chemistry and Applied Biosciences, ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland — ³Physical Chemistry and Electrochemistry, Technical University Dresden, 01062, Dresden, Germany

The current interest in graphene, a naturally occurring two-dimensional polymer (2DP), highlights the necessity to produce other chemically different analogues. Until very recently there was no organic synthetic method available that would allow accessing a laterally infinite, one-monomer-unit thick, freestanding, unimolecular network with a defined internal periodicity. This talk will overview current efforts towards 2DPs with detailed discussion of our concepts, which rest upon carefully designed monomers, interfacial ordering, and both metal-complexation and light-induced polymerizations. In addition, we will report the synthesis of 2D random copolymers and a 2D block copolymer, which provide unprecedented structural diversity of 2DPs.

DS 27.12 Wed 18:00 CHE 91

Film Growth, Adsorption and Desorption Kinetics of Indigo on SiO₂ — ●BORIS SCHERWITZL, ROLAND RESEL, and ADOLF WINKLER — Institute of Solid State Physics, Petersgasse 16, A-8010 Graz, Austria

Understanding the initial stages of organic film growth is the first step of manufacturing organic microelectronic devices. Due to hydrogen bonding and π -stacking, unlike most organic materials, the natural dyes indigo and tyrian purple form highly crystalline films with interesting semiconducting characteristics. In this contribution we report our recent efforts and studies on the initial growth behavior of thin indigo films (C₁₆H₁₀N₂O₂) on a silicon dioxide substrate under UHV conditions with respect to sample treatments. Films from sub-monolayer up to multilayer range were created using physical vapor deposition and subsequently analyzed with Auger Electron Spectroscopy, Thermal Desorption Spectroscopy, Atomic Force Microscopy and X-Ray Diffraction. It could be shown that indigo films tend to dewet at sub-monolayer coverages and form bulk-like structures bound by hydrogen bonds once a certain film thickness is reached. Repeating the measurements on a sputter-cleaned surface and considering heat of evaporation calculations, yields interesting results regarding growth kinetics and surface diffusion.

DS 27.13 Wed 18:15 CHE 91

Organic surface nano-patterns prepared by using nanoporous templates — •YAN ZHENG, WENXIN WANG, AHMED AL-HADDAD, HUAPING ZHAO, CHENGLIANG WANG, and YONG LEI — Ilmenau University of Technology, Institute of Physics & IMN MacroNano* (ZIK) Prof. Schmidt-Str. 26, 98693 Ilmenau (Germany)

Tris(8-hydroxyquinoline) aluminum (Alq3) is an organic semiconductor which attracted considerable attention for the applications in optical and electrical devices. Nanostructured metallic surface associated with organic semiconductor molecule can result unique electronic and optical properties. In this work, large area of Alq3 nanoparticle pattern with high uniformity and periodicity was successfully prepared using ultra-thin alumina membranes (UTAMs) through organic

molecular sublimation under ultrahigh vacuum conditions. The various photoluminescence properties of Alq3 nanoparticle pattern can be realized from the particle diameters by adjusting the pore size of the alumina template. Enhanced photoluminescence was observed when Alq3 deposited onto metallic nanoparticle arrays. The PL enhancement of Alq3 material covered on metallic nanoparticle arrays could be attributed to the increased absorption and quantum yield of surface plasmon resonance. All the results indicate that the controllable highly ordered Alq3 nanoparticle pattern, which is based on the low cost and convenient method of UTAMs template-directed by organic molecular sublimation with PL enhancement performance, has potential applications in nano-optoelectronic devices.