

CPP 32: Organic Thin Films I (joint session CPP/DS/HL, organized by DS)

Time: Wednesday 9:30–13:15

Location: CHE 91

CPP 32.1 Wed 9:30 CHE 91

Photochromic self-assembled monolayers of phosphonate diarylethene switches on polar ZnO surfaces — ●QIANKUN WANG¹, GIOVANNI LIGORIO², BJÖRN KOBIN³, STEFAN HECHT³, EMIL J. W. LIST-KRATOCHVIL², and NORBERT KOCH¹ — ¹Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin — ²Institut für Physik, Institut für Chemie & IRIS Adlershof, Humboldt-Universität zu Berlin — ³Department of Chemistry, Humboldt-Universität zu Berlin

Photochromic molecular switches are attractive components in multifunctional devices, such as phototransistors and optical memories. By inserting a molecular switch interlayer into these devices, they can be used to modulate the charge injection properties by forming photoswitchable charge traps or charge barriers under the stimulation by external light. Here, we investigate the interfacial chemical and switchable properties of the phosphonic-acid diarylethene (PA-DAE) switch in form of a self-assembled monolayer (SAM) on ZnO(0001) and ZnO(000-1) surfaces by photoelectron spectroscopy. The observed work function increase is attributed to the introduced surface dipole moment; the binding modes of the phosphonate linker were retrieved from the deconvolution of core level (O 1s) spectra. Upon appropriate illumination with ultraviolet and visible light, we observe a 0.7 eV energy level shift at the onset of the highest occupied molecular orbitals (HOMO) level of the switches, which might be used to reversibly switch the energy level alignment at the ZnO/PA-DAE interface in device structures.

CPP 32.2 Wed 9:45 CHE 91

Donor-acceptor mixtures of diindenoperylene (DIP) and hexafluoro-tetracyanonaphthoquinodimethane (F6TCNNQ) studied by Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PMIRRAS). New insights into the signatures of charge-transfer interactions. — ●GIULIANO DUVA, ALEXANDER HINDERHOFER, ALEXANDER GERLACH, and FRANK SCHREIBER — Universität Tübingen, Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Probing intermolecular interactions in donor:acceptor (D:A) binary mixtures of organic semiconductors (OSC) [1] requires high sensitivity techniques to overcome the intrinsic limitation of having a limited amount of material and typically a weak signal. A widely used technique for studying the effects of charge-transfer (CT) interactions on molecular vibrations is Fourier-transform IR spectroscopy (FTIR) [2]. However, interference from atmospheric water and the possibly low oscillator strength of some modes may severely limit the amount of reliable information that can be extracted from the final spectrum. We present a new approach for the study of mixtures of OSCs employing PMIRRAS as high-sensitivity technique to overcome the above limitations. Supported by the structural characterization of the films via X-ray scattering, we identify and discuss the spectral signatures of CT in correlation with the formation of D:A co-crystals. [1] A. Hinderhofer et al. Chem. Phys. Chem. 13 (2012). [2] D. Nanova et al. Org. Electr. 13 (2012).

CPP 32.3 Wed 10:00 CHE 91

Coherent absorption in organic thin-film layered structures — ●TONY HENSELEIT, TIM WAGNER, MARKAS SUDZIUS, HARTMUT FRÖB, and KARL LEO — IAPP, Dresden, Deutschland

Development of strongly absorbing materials and devices has been a long-standing research field. Many of these efforts are based on an intriguing concept of perfect coherent absorption, which (assuming, that all required conditions are set up correctly) leads to a perfect conversion of optical energy to some form of an internal energy within the optically active material.

In this study, we focus on coherent absorption in layered thin-film structures with an organic absorbing material. The structures consist of a high optical quality dielectric distributed Bragg reflector and thermally evaporated layer of small organic molecules on it. We demonstrate both experimentally and numerically, that careful control of the resonator design and optical properties of an absorbing layer, allows to reduce amount of reflected light to the minimum and, therefore, to enhance absorption efficiency of thin organic layer up to almost 100 percent.

CPP 32.4 Wed 10:15 CHE 91

Determination of the molecular orientation in thick organic emission layers — ●CHRISTIAN HÄNISCH — IAPP, TU Dresden

The orientation of the transition dipole moment of light emitting molecules in organic thin films of up to 150nm is determined via angular resolved photoluminescence spectroscopy.

CPP 32.5 Wed 10:30 CHE 91

Influence of bulk heterojunction morphology on performances of organic solar cells — ●VLADISLAV JOVANOV, HIRWA HIPPOLYTE, ARNE MÜLLER, NIVEDITA YUMNAM, and VEIT WAGNER — Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

The bulk heterojunction morphology of solution processed organic solar cells can be determined by using atomic force microscopy phase imaging as we have demonstrated in our previous studies. The energy dissipated in the cantilever tip interaction with the film surface depends on the material that is present at the surface. Consequently, phase contrast is observed if different materials are forming the film surface. In this study, we have investigated the influence of a bulk heterojunction morphology on the electrical properties of organic solar cells. We have chosen a blend mixture of polymer PTB7 (donor) and fullerene PC[60]BM (acceptor) deposited from DCB/DIO solution as a materials system. In the first step, we have measured the morphologies of bulk heterojunction for different concentrations of the polymer and fullerene material. The determined structure is correlated to the electrical properties of solar cells such as short circuit current, fill factor and series resistance. The results show that bulk heterojunction morphology is crucial not only for the dissociation of generated excitons, but also for the transport of the free charge carries. Finally, we discuss the optimal organization of polymer and acceptor material.

CPP 32.6 Wed 10:45 CHE 91

The growth of α -6T on different silver surfaces — ●THORSTEN WAGNER, EBRAHIM GHANBARI, ANDREA NAVARRO-QUEZADA, and PETER ZEPPENFELD — Johannes Kepler University, Linz, Austria

The combination of photoelectron emission microscopy (PEEM) and differential (optical) reflectance spectroscopy (DRS) is used to compare the growth of the prototype organic semiconductor α -sexithiophene (α -6T) on different silver surfaces, namely the Ag(111), the Ag(110), and the vicinal Ag(441) surface.

An unpolarized Hg lamp was used as excitation source for the photoelectrons. For all three substrates, the transient of the mean intensity obtained with PEEM follows the same trend: The first layer decreases the emission barrier for the photoelectrons and, hence, increases the electron yield. The deposition of additional molecules just decreases the electron yield, because the electron exclusively excited from the silver substrate have to pass through the molecular layers which do not further alter the emission barrier. In all three cases, at least an equivalent of two monolayers has to be deposited before nucleation of 3D crystallites is observed in PEEM.

After being reflected at the sample surface, the light of a white LED was split by a prism into its two linearly polarized components (pol-DRS). For the isotropic Ag(111) surface, the spectra obtained for s and p polarized light do not differ qualitatively. For the Ag(110) surface, the optical spectra indicate an orientation of the α -6T molecules along the [001] direction. On the Ag(441) surface, the molecules align parallel to the steps, i.e., along the [110] direction.

CPP 32.7 Wed 11:00 CHE 91

How molecular quadrupole moments affect the energetics in organic thin films — ●MARTIN SCHWARZE¹, CHRISTOPHER GAUL², KATRIN ORTSTEIN¹, FRANK ORTMANN², and KARL LEO¹ — ¹Dresden Integrated Center for Applied Physics and Photonic Materials, TU Dresden, 01069 Dresden, Germany — ²Institute for Materials Science and Dresden Center for Computational Materials Science, TU Dresden, 01069 Dresden, Germany

The efficiency of organic semiconductor devices crucially depends on the precise energy level alignment of different organic layers. In most organic semiconductors, the ionization energy (IE) and the electron affinity (EA) of single molecules determine the electronic levels in organic devices and, therefore, their optimization is usually based on the

IE and the EA of neat materials. However, these values can change substantially with the film morphology, at interfaces or in blends of different molecules.

By photoelectron spectroscopy, we obtain the IE of neat films at different molecular orientations and of blends with varying mixing ratios for a variety of small molecule materials. The changes of the IE, as a function of molecular orientation and mixing ratio, scale directly with the magnitude of the molecular quadrupole moments, as obtained by density functional theory simulations. By adjusting the mixing ratio of two different donor molecules, namely ZnPc and F4ZnPc, such electrostatic effects can be exploited in organic solar cells to tune the open-circuit voltage [1].

[1] Schwarze et al., *Science* 352, 1446 (2016)

15 min. break.

CPP 32.8 Wed 11:30 CHE 91

Correlation of Structure, Morphology, and Spectroscopic Properties of Polymorphic, Textured Squaraine Thin Films —

•FRANK BALZER¹, HEIKO KOLLMANN², MARTIN SILIES², MATTHIAS SCHULZ³, ARNE LÜTZEN³, CHRISTOPH LIENAU², and MANUELA SCHIEK² — ¹University of Southern Denmark, Sønderborg, Denmark — ²University of Oldenburg, Germany — ³University of Bonn, Germany

The dihydroxy anilino squaraine 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl]squaraine (SQIB) crystallizes into at least two polymorphic structures: a monoclinic and an orthorhombic phase. Spin-coated thin films are, depending on the annealing temperature, highly textured with two distinct morphological features, which are assigned to the two polymorphic forms. These features exhibit different absorption spectra with characteristic spectral signatures of molecular excitons with oblique transition dipole alignment and large Davydov splitting. The monoclinic form shows a blue-shifted absorption compared to the monomer band, while the absorption profile of the orthorhombic form is red-shifted. The transitions of the excitonic states for each polymorph are polarized mutually perpendicular, probed by polarization-resolved confocal spectro-microscopy. X-ray diffraction reveals a strong out-of-plane orientation. Crystalline domains are distributed with random in-plane orientation on the samples. Their local in-plane orientation is deduced from spectro-microscopy recordings as well as from polarized light microscopy.

CPP 32.9 Wed 11:45 CHE 91

Combined structural and optical real-time study on growth of a charge transfer complex —

•VALENTINA BELOVA, ALEXANDER HINDERHFER, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

Molecular arrangement and structure formation in binary mixed thin film organic semiconductors being in a close correlation with intermolecular interaction [1] directly influence device functionality [2]. We present a real-time investigation of structure evolution during growth (by organic molecular beam deposition OMBD) of a small-molecule donor:acceptor pair (diindenoperylene DIP : N,N'-1H,1H-perfluorobutyl-cyanoperylenediimide PDIF-CN2 [Polyera ActivInk N1100]) combining X-ray scattering methods with differential reflectance spectroscopy (DRS) in the visible range. We found strong changes in the structural and optical properties upon mixing of donor and acceptor molecules that evidence the complex formation. A strong influence of substrate temperature was observed. DRS was performed during film growth in order to establish the correlation between changes in optical spectra due to the intermolecular coupling and structural/mixing behavior. The analysis is complemented with atomic force microscopy (AFM), ellipsometry, photoluminescence and UV-Vis absorption. [1] J. Dieterle et al. *J. Phys. Chem. C*, 2015, 119 (47) 26339; [2] A. Opitz et al. *Phys. Status Solidi A* 2009, 206 (12) 2683

CPP 32.10 Wed 12:00 CHE 91

Evaluation of in-operando potential distributions in OLEDs combining experimental and drift-diffusion studies —

•MAYBRIT KÜHN^{1,2}, CHRISTOF PFLUMM³, WOLFRAM JAEGERMANN^{1,2}, and ERIC MANKEL^{1,2} — ¹Technische Universität Darmstadt, Institute of Materials Science — ²InnovationLab GmbH, Heidelberg — ³Merck KGaA, department OLED-Physics, Darmstadt
Nowadays organic light-emitting diodes are widely used as displays in

smart phones. As these devices consist of several functional layers it is not only important to know the driving voltage of the whole device but also the potential distributions within the single layers. Therefore we present a combined experimental and drift-diffusion study to determine in operando transport properties of the single layers. Two types of OLEDs that only differ in the emission layer but obviously exhibit different potential distributions are investigated. If the emission layer consists of TH-A a shift of the onset voltage in case of layer thickness variation can be observed while using TH-B, an isomer to TH-A, the onset voltage remains unchanged. The voltage development per layer is determined from IV curves of a set of devices with varying layer thickness. Empirically the voltage development can be described with a power law. Using the drift-diffusion model the current density dependent development of the coefficient and the exponent of the power law can be well described. With the model the mobility, the carrier injection mechanism into the respective layer and the barrier height are determined. Furthermore we are able to show that an electric field at or close to the contact is necessary to describe the TH-A behaviour.

CPP 32.11 Wed 12:15 CHE 91

Direct Micropatterning of Organic Thin Films by Electron Beam Processing —

•MARIE HOFFMANN, ELISABETH BODENSTEIN, BJÖRN MEYER, FALK WINCKLER, MATTHIAS SCHÖBER, and CHRISTOPH METZNER — Fraunhofer FEP, Winterbergstr. 28, 01277 Dresden

The patterning of organic layers becomes more and more important especially for applications in solar cells and organic electronics. Organic light-emitting diodes (OLEDs) offer numerous advantages compared to commercially used LCD technology for displays and lighting, e.g. no backlight is needed and the feasibility of very thin, flexible displays is given. The improvement of OLED displays regarding efficiency, lifetime and resolution is an ongoing effort. One of the major challenges is the realization of very small structure sizes. Current patterning methods like thermal evaporation through fine metal masks, printing or lift-off techniques have been demonstrated, however, deficiencies regarding the flexibility of new applications are still existing and desired structure sizes could not be achieved yet. Therefore a method for direct patterning by using electron beam technology has been investigated. Penetrating electrons heating a multilayer system locally lead to a structured evaporation of the organic material. In the current work several experiments and investigations of electron beam processing of organic layers were performed. The process window for a careful adjustment of defined material properties could be narrowed through additional simulation calculations. First results will be shown and the technology assessed to its prospective usability.

CPP 32.12 Wed 12:30 CHE 91

Structural Properties of Thin Films of Phenacenes —

•JAN HAGENLOCHER¹, ALEXANDER HINDERHOFER¹, KERA SATOSHI², and FRANK SCHREIBER¹ — ¹Eberhard Karls Universität, Tübingen — ²Institute for Molecular Science, Okazaki, Japan

We studied the structural properties of the high band gap organic semiconductors Picene, [6]Phenacene and [7]Phenacene which exhibit high conductivity. X-ray reflectivity, grazing incidence X-ray diffraction and atomic force microscopy were applied to study the influence of a small length difference between the molecules on the crystallographic structure and morphology of the resulting mixed thin film. The compounds employed are well suited since they consist of different numbers of benzene rings fused together in a zig-zag pattern and differ only in length. It was found that the crystallographic structure remains unchanged upon mixing but the wetting behaviour, the morphology and especially the films roughness changes significantly. Different explanations are discussed and further explored using real-time X-ray reflectivity and analysis of terrace coverage of individual islands. Additionally, the optical properties of the thin films were investigated with UV-Vis spectroscopy.

CPP 32.13 Wed 12:45 CHE 91

Cyano-phenyl porphyrin on Cu(111): A STM, XPS and DFT study —

•JUAN CARLOS MORENO-LÓPEZ¹, ALISSON CECATTO DOS SANTOS², MICHAEL LEPPER³, HUBERTUS MARBACH³, HENRY P. PINTO¹, and ABNER DE SIERVO² — ¹Yachay Tech University, School of Physical Sciences and Nanotechnology, 100119-Urcuquí, Ecuador — ²Universidade Estadual de Campinas, Instituto de Física "Gleb Wataghin" CP 6165, CEP 13081-970, Campinas, SP, Brazil. — ³Lehrstuhl für Physikalische Chemie 2, Universität Erlangen-Nürnberg, Germany

The study of organic molecules on surface gained increasing interest during the last years in the research community. Studies of individual organic molecules and studies of self-assembled networks with complex interactions have shown the plausible technological applications of organic molecules on diverse fields, such as: molecular machines, molecular electronics, gas storage in molecular porous networks, etc. With this background we studied cyano-functionalized porphyrins, namely 2H-tetrakis-(p-cyano)-phenylporphyrin (2HTCNPP) on Cu(111). In this work, we performed a thorough study, by means of Scanning tunneling microscopy (STM), X-ray photoelectron Spectroscopy (XPS) and Density-functional theory (DFT) calculations, in order to gain insight into the adsorption behavior of 2HTCNPP on Cu(111) and its evolution after the deposition of Pd atoms as well as its behaviour after thermal treatment.

CPP 32.14 Wed 13:00 CHE 91

Influence of radiative efficiency and dipole orientation on optimal layer thicknesses of monochrome OLEDs for maximum EQE — •PAUL-ANTON WILL, CORNELIUS FUCHS, REINHARD SCHOLZ, SIMONE LENK, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and

Institute for Applied Physics, Technische Universität Dresden, Germany

For realizing highly efficient organic light-emitting diodes (OLEDs), the light-emitting molecule has to meet several requirements. Among chemical, energetic, and optical characteristics two crucial properties are the radiative efficiency η_{rad} and the emissive dipole orientation described by the anisotropy factor a . While the first is already close to its maximum for commonly used emitter molecules, a lot of research is currently ongoing to understand and control the dipole orientations of organic molecules. However, the external quantum efficiency (EQE) of OLEDs depends on the optical environment of the emitting molecules. As known, the Purcell effect leads to an effective radiative efficiency η_{rad}^* for emitters in a cavity. In this work, we show how the radiative efficiency η_{rad} and the anisotropy factor a influence the optimal layer thickness of monochrome OLEDs to reach maximum EQE. We find that for emitters with $\eta_{\text{rad}} < 100\%$ the product of η_{rad}^* and the outcoupling efficiency η_{out} needs to be optimized, instead of solely optimizing η_{out} . When doing so, the EQE of planar OLEDs with highly oriented molecules but imperfect radiative efficiency can be pushed further. In this way, the full potential of planar OLEDs can be exploited.