

CPP 34: Organic Electronics and Photovoltaics (joint session with DS/HL/O) IV

Spectroscopy, OFETs, OLEDs, Photo switches

Time: Wednesday 15:00–18:15

Location: ZEU 260

CPP 34.1 Wed 15:00 ZEU 260

Comprehensive efficiency analysis of organic light-emitting diodes featuring horizontal emitter orientation and triplet-to-singlet up-conversion — ●TOBIAS SCHMIDT¹, BERT SCHOLZ¹, CHRISTIAN MAYR¹, ANDREAS RAUSCH², THOMAS WEHLUS², DIRK MICHAELIS³, NORBERT DANZ³, THILO REUSCH², and WOLFGANG BRÜTTING¹ — ¹Institute of Physics, University of Augsburg, 86135 Augsburg, Germany — ²OSRAM Opto Semiconductors GmbH, Leibnizstrasse 4, 93055 Regensburg, Germany — ³Fraunhofer Institute for Applied Optics and Precision Engineering, 07745 Jena, Germany

The external quantum efficiency (EQE) of an organic light-emitting diode can strongly be affected by orientation of the emissive dipole moments, and for fluorescent dyes, by triplet-to-singlet up-conversion leading to an enhanced radiative exciton fraction (η_r), exceeding the spin-statistical limit of 25%. By a combination of EQE investigations with time resolved photo- and electroluminescence measurements we are able to quantify the lower limit of the additionally created singlet excitons, e.g. by thermally activated delayed fluorescence, as well as the factors being responsible for light-outcoupling. For the investigated fluorescent system the EQE is boosted by two effects. First, due to horizontal alignment of the transition dipole moments, the outcoupling factor is enhanced by a factor of 1.3. Second, the enhanced η_r value of 36%, results in an additional efficiency increase by a factor of 1.44. As a consequence of the combination of both effects the EQE almost doubles and values up to 5% are achieved for direct emission in spite of a comparatively low emitter efficiency of 40% only.

CPP 34.2 Wed 15:15 ZEU 260

Multi-analytical investigation of SAM formation in printing relevant timescales III: OFET devices — ●MILAN ALT^{1,2,6}, JANUSZ SCHINKE^{2,3}, SABINA HILLEBRANDT^{2,5}, MARC HÄNSEL^{2,4}, KAJA DEING^{2,6}, ULI LEMMER^{1,2}, and NORMAN MECHAU^{1,2} — ¹Karlsruher Institute of Technology — ²InnovationLab, Heidelberg — ³TU Braunschweig — ⁴TU Darmstadt — ⁵Uni Heidelberg — ⁶Merck KGaA

Self-assembled monolayers (SAMs) can be used to effectively reduce contact resistances originating from energetic misalignments at metal-semiconductor interfaces. Solution processing of SAMs has been intensively studied and is in principle compatible with high throughput printing techniques. However, most studies on SAMs feature immersion in very dilute solutions for many hours, in some cases up to several days. The objective of this work is to understand SAM accumulation with a focus on short time scales in order to estimate whether the deposition of well performing SAMs can be speeded up sufficiently to be compatible with typical film drying times in printing. We combined analytical characterization of SAM treated metal surfaces via photoelectron- and IR-spectroscopy, as well as Kelvin Probe with measurements of the actual injection barriers in OFET devices. We chose the widely used 1H,1H,2H,2H-Perfluorodecanethiol SAM and investigated its quality and charge injection performance in dependency of the process parameters immersion time and molecular concentration. Additionally, we studied the impact of ambient condition on SAM deposition and the resulting SAM performance, in order to account for a realistic fabrication environment.

CPP 34.3 Wed 15:30 ZEU 260

Multi-analytical investigation of SAM formation on printing-relevant time scales I: Kelvin probe and photoelectron spectroscopy — ●JANUSZ SCHINKE^{1,5}, MARC HÄNSEL^{2,5}, MILAN ALT^{3,4,5}, SABINA HILLEBRANDT^{2,5}, ERIC MANKEL^{6,5}, WOLFRAM JAEGERMANN^{6,5}, WOLFGANG KOWALSKY^{1,5}, and ROBERT LOVRINCIC^{1,5} — ¹TUBS, Inst. f. Hochfrequenztechnik — ²Uni HD, Kirchhoff-Inst. für Physik — ³Karlsruher Inst. f. Technologie — ⁴Merck KGaA — ⁵InnovationLab GmbH, Heidelberg — ⁶TUD, Materials Science Inst.

In organic electronic devices, charge injection at the contacts is crucial for electrical performance. The devices require electrodes with a sufficiently low contact resistance at the metal-semiconductor interface to inject into or collect charge carriers from the transporting layer. A smart way to align the energetics at the interface is the use of self-assembled monolayers (SAMs). We have studied the properties of 1H,1H,2H,2H-Perfluorodecanethiol using photoelectron spectroscopy

(XPS/UPS), infrared spectroscopy (IR), ambient Kelvin probe (KP), and contact angle (CA) measurements and the injection barriers were also measured in actual devices - organic field effect transistors. Using these methods we were able to obtain a very deep understanding of the whole SAM adsorption process, as well as the impact of immersion time, concentration and the influence of ambient conditions on the resulting monolayer and its performance. With this knowledge we estimate optimized parameters to speed up the treatment process, in contrast to most studies where long immersion times are used, to be compatible with typical times used in standard printing methods.

CPP 34.4 Wed 15:45 ZEU 260

Multi-analytical investigation of SAM formation on printing-relevant time scales II: infrared-reflection-absorption-spectroscopy — ●SABINA HILLEBRANDT^{1,5}, JANUSZ SCHINKE^{2,5}, MILAN ALT^{3,4,5}, ROBERT LOVRINCIC^{2,5}, TOBIAS GLASER^{1,5}, and ANNEMARIE PUCCI^{1,5} — ¹Universität Heidelberg, Kirchhoff-Institut für Physik — ²Technische Universität Braunschweig, Institut für Hochfrequenztechnik — ³Karlsruher Institut für Technologie — ⁴Merck KGaA, Darmstadt — ⁵Innovationlab GmbH, Heidelberg

In organic semiconductor devices the improvement of charge carrier injection between metal contact and organic semiconductor is a major concern. Self-assembled monolayers (SAMs) built up interface dipoles on metal surfaces that can increase or lower the work function of the material. Therefore SAMs can be used as injection layers. The properties of solution-processed SAMs such as orientation and interface dipole are influenced by various factors like concentration of the molecule in solution, immersion time and purity of the solution or substrate.

Infrared-reflection-absorption-spectroscopy (IRRAS) is very sensitive to changes in the orientation of SAMs on metal surfaces, thus we performed IRRAS measurements on SAMs consisting of 1H,1H,2H,2H-perfluorinated decanethiol on evaporated gold substrates. Orientation, ordering and quality of the SAM were investigated under systematic variation of immersion time and concentration of the molecule in solution. Taking into account realistic printing conditions we also investigated very short immersion times and high concentrations as well as the impact of oxygen in solvent and substrate on the layer formation.

CPP 34.5 Wed 16:00 ZEU 260

Towards fully printed organic light-emitting diodes: investigation of solution processed electron injection layers — ●SEBASTIAN STOLZ^{1,4}, GERARDO HERNANDEZ-SOSA^{1,4}, MICHAEL SCHERER^{2,4}, ERIC MANKEL^{3,4}, ROBERT LOVRINCIC^{2,4}, JANUSZ SCHINKE^{2,4}, ULI LEMMER^{1,4}, and NORMAN MECHAU^{1,4} — ¹Karlsruhe Institute of Technology, Light Technology Institute — ²Technische Universität Braunschweig, Institut für Hochfrequenztechnik — ³Technische Universität Darmstadt, Materials Science Institute, Surface Science Division — ⁴InnovationLab GmbH, Heidelberg

The fabrication of organic light-emitting diodes (OLEDs) by high throughput printing techniques requires the development of solution processable electron injection layers. Today, either alkali salts or low work-function alkaline earth metals are used as cathode layers in OLEDs. As these materials are highly reactive, they cannot be easily solution processed. In this work, we present blue fluorescent light-emitting diodes which use silver in combination with Polyethylenimine (PEI) and Polyethylenimine-ethoxylated (PEIE) as cathode layer. We demonstrate that both materials can be effectively used as electron injection layers in OLEDs and correlate the performance of the devices to the characteristics of the PEI(E) layers. Photoelectron spectroscopy is used to estimate the polymer thickness and the corresponding change in cathode work-function while the homogeneity of the layers is evaluated by AFM measurements. We show that OLEDs using PEI/PEIE and silver as cathode layer yield an improved performance and shelf lifetime compared to reference devices that use calcium, instead.

15 min. break

CPP 34.6 Wed 16:30 ZEU 260

Micro-structured organic field effect transistor on commercial poly(urethane) resin as substrate and gate dielectric — JAN

HARTEL, DERCK SCHLETTWEIN, and CHRISTOPHER KEIL — Institute of Applied Physics, Laboratory of Materials Research, Justus-Liebig-University Giessen, Germany.

Dielectric layers of a commercial cross-linked poly (urethane) (PU) were prepared on a conductively coated film and served as gate dielectric and as substrate for the growth of an organic semiconductor film in an alternative approach to all-organic field effect transistors (OFET). A method was developed to process micro-structured electrodes on top of the PU dielectric layer which proved superior to the traditional lift-off-procedure. The influence of the aspect ratio of the electrodes within the organic transistor on a given dielectric layer will be discussed with respect to the calculation of the relative permittivity and the gate capacitance. A method is proposed to compensate short electrode effects which would otherwise lead to an underestimation of the gate capacitance and hence to a miscalculation of the OFET properties.

CPP 34.7 Wed 16:45 ZEU 260

Time-resolved potentiometry of organic thin film transistors — JAN MURAWSKI, TOBIAS MÖNCH, MORITZ PHILIPP HEIN, PETER MILDE, and LUKAS M. ENG — Technische Universität Dresden, Institut für Angewandte Photophysik

High speed application still poses a challenge for organic thin film transistors (OTFTs) due to their low charge carrier mobilities, high driving voltages, and low on/off-current ratios. Few investigations have been reported on the switching dynamics of OTFTs on the nanoscale, even fewer in the relevant temporal operation regime as required for high speed applications. Yet, such investigations are crucial for understanding the bottle-necks in OTFTs dynamic performance.

Here, we introduce time-resolved Kelvin probe force microscopy (tr-KPFM) to track the time evolution of surface potential wave fronts inside the channel of a pentacene-based bottom-gate coplanar OTFT. The relevant dynamical evolution proceeds in the microsecond regime and is easily resolved by our quantitative tr-KPFM method. Comparing our experiment with simulations reveals the presence of Schottky barriers in the real device to be responsible not only for a reduced effective electric field across the transistor channel (and thus a reduced field mobility) but also for inducing a delayed re-injection of charge carriers at the electrode-semiconductor interface. Although the charge-carrier mobility would allow for faster switching, charging the Schottky barrier constitutes the bottle-neck to be overcome for higher working frequencies in OTFTs.

CPP 34.8 Wed 17:00 ZEU 260

High-Mobility, Low-Voltage Organic TFTs based on Air-Stable DNNT Derivatives: Time-Dependent Improvement in Contact Resistance and Dynamic Performance — ULRIKE KRAFT^{1,3}, UTE ZSCHIESCHANG¹, KAZUO TAKIMIYA², EDWIN WEBER³, and HAGEN KLAUK¹ — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²RIKEN Advanced Science Institute, Wako, Japan — ³Technical University Bergakademie Freiberg, Germany

The organic semiconductor dinaphthothienothiophene and its derivatives C10-DNNT and diphenyl-DNNT provide larger carrier mobilities and better air stability than, e.g., pentacene. We present a detailed comparison of the thin-film morphology, static and dynamic performance and stability of low-voltage (3 V) thin film transistors based on vacuum-deposited films. Freshly fabricated TFTs (channel length: 100 μm) have hole mobilities ranging from 3 cm^2/Vs (DNNT) to 5 cm^2/Vs (diphenyl-DNNT), with on/off ratios of 10^7 .

During the first few hours after fabrication, the effective mobility of short-channel TFTs ($L=1 \mu\text{m}$) increases by about 20-30%, due to an improvement in the contact resistance (measured with TLM). The dependence of this effect on the exposure to different gas atmospheres, humidity and to light was investigated. To study the impact on the dynamic performance of the TFTs, we fabricated unipolar ring oscillators on flexible PEN substrates. The stage delay of DNNT TFTs ($L=1 \mu\text{m}$) measured at 3 V drops from 920 to 410 ns during the first 4 days of exposure to ambient air, which is the shortest delay reported for flexible organic TFTs at supply voltages $<10 \text{ V}$.

CPP 34.9 Wed 17:15 ZEU 260

Continuously tunable organic semiconductor distributed Feedback (DFB) lasers as an example for optical components built from shape-memory polymers — SENTA SCHAUER¹, XIN LIU², TOBIAS MEIER¹, MARC SCHNEIDER¹, MATTHIAS WORGULL¹, ULI LEMMER^{1,2}, and HENDRIK HÖLSCHER¹ — ¹Karlsruhe Institute of Technology, Institute of Microstructure Technology, Hermann-

von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — ²Karlsruhe Institute of Technology, Light Technology Institute, Engesserstraße 13, 76131 Karlsruhe, Germany

Phase gratings are important tools for many applications in optics and photonics, e.g., they serve as resonators in DFB-lasers. We manufactured Bragg gratings from a shape-memory polymer (SMP) to tune their period over a wide range without any mechanical components. SMPs can remember a predefined shape and recover to it even after strong deformations, if they are triggered by a stimulus. We used the polyurethane Tecoflex(R), which is a thermally triggered SMP, to fabricate nanostructured gratings via hot embossing. After stretching, these gratings feature an increased period which shrinks back to its original length after the activation of the recovery process. In order to demonstrate the practical applicability of these gratings as useful components for photonics, we successfully fabricated continuously tunable DFB-lasers based on SMP grating substrates with Alq3:DCM serving as active material. By changing the grating period via the shape-memory effect, the emitted wavelength of the laser changes likewise. So far we demonstrated shifts of the emission spectrum by 30nm.

CPP 34.10 Wed 17:30 ZEU 260

Optical studies of excitonic precursor spin species under magnetic resonance in organic light emitting diodes. — HERMANN KRAUS, SEBASTIAN BANGE, and JOHN M. LUPTON — Universität Regensburg, 93040 Regensburg, Deutschland

Large magnetoresistance effects e.g. due to spin-dependent recombination rates are well-known for OLEDs [C. Boehme et al., Nat. Nano 8, 612 (2013)], although models are still under debate given that they remain hard to verify from a measurement of integrated current and luminance values [J. M. Lupton et al., Nature Mat. 7, 598 (2008)]. Spin resonance of paramagnetic species enables direct manipulation of carrier and excitonic precursor spins, providing a wealth of new insight into dynamic spin properties. Previous work on electrical or optical detection of spin manipulation [W. J. Baker et al., Nature Comm. 3, 898 (2012); W. J. Baker et al., Phys. Rev. B 84, 165205 (2011)] misses out on the opportunity to directly observe the presence of triplet exciton species that are at the heart of spin-dependent recombination models. A few polymeric and small-molecular compounds are now known to exhibit reasonable triplet emission without modification of the polaron pair and exciton dynamics by strong spin-orbit interaction [D. Chaudhuri et al., Angew. Chem. Int. Ed. DOI 10.1002/anie.201307601(2013); J. M. Lupton et al., Phys. Rev. Lett. 89 167401(2002)]. Those materials are ideal candidates to directly track spin singlet and triplet excitonic species in organic light-emitting diodes under conditions of magnetic resonance, by comparing the fluorescence (singlet) to phosphorescence (triplet) intensity.

CPP 34.11 Wed 17:45 ZEU 260

Ab-initio quantum dynamics simulation of photo-induced molecular switching: Azobenzene on coinage metals — REINHARD J. MAURER and KARSTEN REUTER — Department Chemie, Technische Universität München, Germany

The constant pursuit towards further miniaturization of electronic devices slowly reaches the point where individual molecules may serve as the main functional units. Unfortunately, more often than not, an inherent molecular function is quenched by overly strong coupling to the environment; a permanent danger, specifically in the case of metal surface adsorption. Nevertheless, metal surface adsorption may also introduce new functionality, such as in the case of photo-induced molecular switching of tetra-*tert*-butyl-functionalized Azobenzene (TBA) on Au(111). In this work we attempt a full *ab-initio* description of the explicit nuclear and electronic dynamics to analyze a novel substrate-mediated process that was suggested for this system [1]. The immense system size and a continuum of electronic states demand an effective modelling approach explicitly accounting only for the most important degrees of freedom. Employing an efficient density-functional theory based ΔSCF approach [2] we construct and analyze the involved excited-state potential energy surfaces (PESs), and establish a mixed-quantum classical dynamics simulation. A particular focus is the effect of the image-charge induced changes on the excited-state PESs and the excited-state lifetime- and temperature-dependence of the quantum yield. [1] Wolf, Tegeder, Surf. Sci. **603**, 1506-1517 (2009); [2] Maurer, Reuter, J. Chem. Phys. **139**, 014708 (2013)

CPP 34.12 Wed 18:00 ZEU 260

Reversible switching and light-induced structural changes in spin-coated thin films of Azobenzene-polymers —

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Functionalized surfaces with molecules whose conformation can be reversibly switched between two isomeric forms by light are relevant for future devices -e.g. for switching adaptive materials, storing two states in memory applications, and switching current in molecular electronics. Here we use grazing incidence x-ray diffraction (GIXD), atomic force microscopy (AFM) and differential reflectance spectroscopy (DRS) to study light-induced structural changes in spin-coated thin films

of Azobenzene-polymers with Alkyl side-chains. In solution, the individual Azobenzene-polymer shrinks upon UV-irradiation. Sub-monolayers of Azobenzene-polymers on Silicon oxide are still switchable with high efficiency, but do not show the same shrinking behavior, as suggested by AFM measurements before and after UV-illumination. Increasing the thickness to multilayers drastically changes the switching behavior, because of strong sterical hindrance. Interestingly, GIXD shows that the in-plane Bragg peaks corresponding to the coherent ordering of the Alkyl side-chains disappear when the sample is illuminated with UV-light and partially reappear after a few minutes in the dark, showing that switching is still possible in the crystalline state albeit with slower kinetics.