

CPP 39: Focus: Controlling Phase Formation Dynamics in Solution Processed Semiconductors - organized by Christoph Brabec, Jens Harting and Hans-Joachim Egelhaaf

Time: Wednesday 15:00–18:45

Location: H14

Invited Talk CPP 39.1 Wed 15:00 H14

Film formation, microstructure and ferroelectricity of MAPbI₃ light-harvesting layers — HOLGER RÖHM^{1,2}, TOBIAS LEONHARD^{1,2}, ALEXANDER SCHULZ^{1,2}, SUSANNE WAGNER^{1,3}, MICHAEL HOFFMANN^{1,3}, and ●ALEXANDER COLSMANN^{1,2} — ¹Karlsruhe Institute of Technology (KIT), Material Research Center for Energy Systems, Strasse am Forum 7, 76131 Karlsruhe, Germany — ²Karlsruhe Institute of Technology (KIT), Light Technology Institute (LTI), Engesserstrasse 13, 76131 Karlsruhe, Germany — ³Karlsruhe Institute of Technology (KIT), Institute for Applied Materials - Ceramic Materials and Technologies (IAM), Haid-und-Neu-Strasse 7, 76131 Karlsruhe, Germany

Among the remarkable properties of MAPbI₃ is its ferroelectricity. Since the ferroelectric polarization influences the charge carrier recombination and transport, the orientation and shape of polarized domains within grains directly influences the device performance. This renders engineering of the grain orientation and size pivotal for the optimization of perovskite solar cells. In a combined EBSD, PFM and KPFM study, we spatially resolve and correlate the crystal orientation and the ferroelectric polarization of MAPbI₃ with sub-grain resolution. These tools are indispensable for the relation of the microscopic thin-film structure to the optoelectronic device properties as they allow to monitor film formation, device optimization and to understand fundamental processes in perovskite solar cells. Understanding the microstructure and the film formation will not least be the key to future ab-initio engineering of new non-toxic and efficient solar cells.

Invited Talk CPP 39.2 Wed 15:30 H14

How do evaporating thin films evolve? Unravelling phase-separation mechanisms during solvent-based fabrication of polymer blends — ●OLGA WODO — University at Buffalo, Materials Design and Innovation Department

Solvent-based fabrication is a flexible and affordable approach to manufacture organic thin films made from any combination of polymer, copolymers and/or small molecules. It is of paramount importance to understand morphology evolution during fabrication. However, it is challenging to experimentally visualize morphology evolution during processing.

In this talk, I will present our computational model to predict the evolving three-dimensional morphology during the fabrication of organic thin films. I will focus on multiscale challenges that when addressed allowed to resolve nano-morphological features while being able to simulate device scale domains. More importantly, I will discuss four modes of phase formation and subsequent propagation within the thinning film during solvent-based fabrication. I will address fundamental questions such as when and where phases are formed, and how they evolve to form the final structure. Finally, I will demonstrate how this analysis can be leveraged to ask questions on manufacturing designs with the ultimate goal of precise, yet affordable, morphology manipulation for a large spectrum of applications.

CPP 39.3 Wed 16:00 H14

Supramolecular structures of amphiphilic dyes for photochemical and photophysical applications — ●MARTIN PRESSELT^{1,2,3}, MAXIMILIAN HUPFER^{1,2}, MARTIN KAUFMANN¹, FELIX HERRMANN-WESTENDORF^{1,2}, SAUNAK DAS^{1,2}, and BENJAMIN DIETZEK^{1,2} — ¹Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany — ²Leibniz Institute of Photonic Technology (IPHT), Jena, Germany — ³scielus GmbH & Co. KG, Moritz-von-Rohr-Str. 1a, 07745 Jena, Germany

Beyond molecular properties the supramolecular structures essentially determine photonic [1] and electric [2] material properties. One of the approaches to control the supramolecular structure is by means of interface assembly of dyes that have been made amphiphilic. This assembly is utilized in the Langmuir-Blodgett (LB) technique [3, 4] as well as in the Liquid-Liquid Interface Precipitate (LLIP) [2] technique. In our work we utilize both methods for the fabrication of model layers with tunable supramolecular structure for optoelectronic devices and self-healing membranes. This supramolecular structural tuning enables variation of the LUMO energy of fullerene films by 120 meV, that translate to 70 mV variation in open circuit voltage of correspond-

ing pi-Si-hybrid solar cells [2].

- [1] S. Das et al., ACS Appl Mater Interfaces, 2016, 8, 21512-21521.
- [2] S. K. Das et al. Advanced Energy Materials, 2018, accepted.
- [3] M. L. Hupfer et al., ACS Appl Mater Interfaces, 2017, 9, 44181-44191.
- [4] M. Kaufmann et al., J. Colloid Interface Sci., 2018, 526, 410-418.

CPP 39.4 Wed 16:15 H14

In-situ study of printed films of PBDB-T-SF:IT-4F for application in organic solar cells — ●KERSTIN WIENHOLD¹, VOLKER KÖRSTGENS¹, SEBASTIAN GROTT¹, XINYU JIANG¹, MATTHIAS SCHWARTZKOPF², STEPHAN ROTH^{2,3}, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²DESY, 22607 Hamburg — ³KTH, Department of Fibre and Polymer Technology, SE-100 44 Stockholm, Sweden

Recent research in organic photovoltaics focuses on identifying new high-efficiency polymers and acceptor molecules to reach high power conversion efficiencies (PCEs). To date, a PCE of 13% could be obtained with a PBDB-T-SF:IT-4F based organic solar cell device. However, towards commercialization, the solar cell performance must be optimized and an up-scale of the thin layer deposition is necessary. Printing of the active layer of organic solar cells can overcome the up-scale challenge. In-situ grazing incidence small angle X-ray scattering (GISAXS) during printing provides fundamental knowledge to better understand the drying kinetics and structure formation mechanism during printing. Characterization techniques such as UV/Vis spectroscopy, photoluminescence, optical microscopy and scanning electron microscopy (SEM) are applied after printing to get to a deeper insight into the composition and morphology of the active layer of the printed films with the aim to further improve the solar cell efficiencies.

CPP 39.5 Wed 16:30 H14

Simulation of active layer formation in solution-processed organic solar cells — ●OLIVIER RONSIN and JENS HARTING — Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg (IEK-11), Dynamics of Complex Fluids and Interfaces, Fürther Straße 248, 90429 Nürnberg, Germany

Solution-processed organic bulk-heterojunction active layers form sophisticated structures during the drying of the wet-deposited solution, because of complex physical processes such as crystallization and/or phase separation. This structure highly impacts the photovoltaic performance. In order to reach significant improvements, a better understanding of the physics driving the active layer formation is strongly needed.

We propose a phase-field simulation framework to determine the dry film structure. To this end, evaporation, crystal nucleation and growth, phase separation are taken into account as well as concentration-dependent diffusion coefficients. The model's behaviour for these basic physical processes will be shown, as well as simulation results for evaporation-induced phase separation and crystallization. First quantitative simulations for real photovoltaic systems and the comparison with in-situ experimental characterization on the drying structure will be presented.

CPP 39.6 Wed 16:45 H14

Inner structure analysis of quantum dot solids for photo-devices — ●WEI CHEN and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany

Quantum dots (QDs) with near infrared emission are promising in both photodetectors (PDs) for sensing and photovoltaics (PVs) for solar energy conversion. High quality QDs are normally synthesized in solution and capped with organic ligands. To efficiently functionalize the QDs' array for PD or PV devices, the ligand exchange treatments, in solution or on solids, to colloidal QDs are necessary by exchanging or removing the long chain organic ligands. These treatments will not only decrease the inter-dot spacing between neighboring QDs to improve their electro-coupling behavior, which is beneficial for the energy transfer, but also change the stacking behavior of QD particles in solid from colloidal state to close packed state. This structure transition is

now investigated by grazing incidence X-ray scattering and it is found that QDs prefer to stack in a face-centered cubic when they are in superlattice structure (colloidal state) by spin-coating. The stacking structure will change to a body-centered cubic style in a close packed solid after ligand exchange. Thus, the inner morphologies of QDs' close packed solids by different treatments are well studied. The optimized devices demonstrate a better device performances.

15 min. break

Invited Talk

CPP 39.7 Wed 17:15 H14

Thin film structuring upon liquid-vapor mass exchange — ●JASPER MICHELS — Max Planck Institute for Polymer Research, Mainz, Germany

Organic and hybrid thin film electronic devices, such as memory diodes, solar cells and transistors, typically contain a functional layer comprising a blend of polymeric or small-molecular species whose properties cooperatively give rise to a specific function. Depending on the desired device functionality, phase transitions during solution processing of these blends is either encouraged or suppressed. In many cases a microstructure evolves during solidification on account of, for instance, demixing or crystallization from solution. These processes may lead to drop-like or spherulitic structures, with associated feature sizes and domains shapes that depend on the processing conditions.

This presentation focuses on how phase separation couples with mass exchange across the liquid-vapor boundary, i.e. solvent evaporation and vapor condensation. I give an overview of the work we have done to understand the influence of liquid-vapor exchange rates on the dynamics of structure evolution. Modeling multi-component mixtures in the thermodynamic limit elucidates how microstructures evolve. Numerically simulated morphologies are consistent with experimentally observed ones and demonstrate in what way domain size and phase composition are affected by internal and environmental factors.

CPP 39.8 Wed 17:45 H14

Controlling Aggregate Formation in Conjugated Polymers by Spin-Coating Below the Critical Temperature of the Disorder Order Transition — ●ANNA KÖHLER — Soft Matter Optoelectronics and Bayreuth Institute of Macromolecular Research, University of Bayreuth, Germany

Aggregates, that is short-ranged ordered moieties in the solid-state of p-conjugated polymers, play an important role in the photophysics and performance of various optoelectronic devices. We have previously shown that many polymers change from a disordered to a more ordered conformation when cooling a solution below a characteristic critical temperature T_c . Using in situ time-resolved absorption spectroscopy on a range of semiconducting polymers including P3HT, PFO, PCPDTBT, and PCE11 (PffBT4T-2OD), we show that spincoating at a temperature below T_c can enhance the formation of aggregates with strong intra-chain coupling. An analysis of their time-resolved spectra indicates that the formation of nuclei in the initial stages of film formation for substrates held below T_c seems responsible for this. We observe that the growth rate of the aggregates is thermally activated with an energy of 310 meV, which is much more than that of the solvent viscosity (100 meV). From this we conclude that the rate controlling step is the planarization of a chain that is associated with its attachment to a nucleation center. The success of our approach for the rather dynamic deposition method of spin-coating holds promise for other solution-based deposition methods.

CPP 39.9 Wed 18:00 H14

Phase Formation Dynamics of Mixed-halide Perovskites by Real-time In-Situ Optical and X-ray Spectroscopy — ●JUSTUS JUST¹, KLARA SUCHAN², PASCAL BECKER³, EVA UNGER^{2,3}, and THOMAS UNOLD³ — ¹MAX IV Synchrotron Laboratory, Fotongatan 2, 22484 Lund, Sweden — ²Lund University, Paradisgatan 2, 22350 Lund, Sweden — ³Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

We present a detailed investigation of the phase formation dynam-

ics of the chlorine derived one-step synthesis of MAPbI₃ perovskite. In a specially designed atmosphere controlled in-situ reactor, synchrotron based in-situ quick scanning X-ray absorption spectroscopy (QEXAFS), X-ray diffraction (XRD) as well as X-ray fluorescence (XRF) are applied in combination with in-situ optical reflection and photoluminescence spectroscopy. This enables us to correlate the evolution of the chemical reaction from XAS, the formation of crystalline phases from XRD and the chemical composition from XRF with the evolution of the optoelectronic properties of the film on one single timeline. We observe a delayed formation of crystalline MAPbI₃ and attribute it to a concentration threshold in the decreasing chlorine content of the sample. Our results give detailed insight into the formation process and can help to provide a mechanistic understanding of the reactions and intermediates involved. This knowledge can be utilized to optimize synthesis strategies and to tune the optoelectronic properties of organic-metal-halide perovskite semiconductors.

CPP 39.10 Wed 18:15 H14

On the colloidal behaviour of hybrid perovskite precursor dispersion and tracking structural heterogeneities arising from mixed perovskites: insights into the nano and macroscale — ●SHAMBHAVI PRATAP^{1,2}, JOHANNES SCHLIPF¹, KIRAN JOHN¹, VOLKER KÖRSTGENS¹, FELIX FISCHER¹, SUNDEEP VEMA³, ALEXANDER HOLLEITNER⁴, ANTON DAVYDOK⁵, CHRISTINA KRYWKA⁵, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²Lawrence Berkeley National Laboratory, Advanced Light Source — ³Cambridge University, Department of Chemical Engineering — ⁴TU München, Walter Schottky Institut — ⁵DESY, Helmholtz Zentrum Geesthacht, Hamburg

A colloidal nature of perovskite precursors used for film fabrication is suggested, and phenomena such as glass-transitions, crystal twinning, and growth instabilities are explored in order to explain diffusion-limited self-organization of thin films. Morphological and structural heterogeneities within thin films are identified to be a consequence of deposition through dynamic precursors, far from thermodynamic equilibrium. The significance of such a finding suggests that perovskite films possess soft properties, implying there exists a delicate balance between entropic and enthalpic contributions towards the free energy of the dynamically changing system, which needs to be regulated for controlling film morphology; which has been established as a crucial prerequisite for improving solar cell performances.

CPP 39.11 Wed 18:30 H14

Following the perovskite crystallization in printed mesoscopic organometal halide perovskite solar cells — ●OLIVER FILONIK¹, MARGRET EVA THORDARDOTTIR^{1,2}, JENNY LEBERT¹, STEPHAN PRÖLLER¹, SEBASTIAN WEISS¹, LEW JIA HAUR³, ANISH PRIYADARSHI³, NRIPAN MATHEWS³, PETER MÜLLER-BUSCHBAUM², and EVA M. HERZIG^{1,4} — ¹TU München, Munich School of Engineering, Herzig Group, 85748 Garching, Germany — ²TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ³Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, 637553 Singapore, Singapore — ⁴Universität Bayreuth, Physikalisches Institut, Herzig Group - Dynamik und Strukturbildung, 95440 Bayreuth, Germany

Printable perovskite solar cells based on carbon electrodes have shown outstanding device stability and upscalability in recent years. In this work, we follow the perovskite crystallization within the all-porous device architecture during fabrication and investigate the influence of the processing additive aminovaleric acid iodide (5-AVAI) on the perovskite formation. Using time-resolved grazing incidence wide angle X-ray scattering (GIWAXS), we are able to identify the suppression of large polycrystalline grains early in the fabrication process due to the processing additive. With the optimized processing conditions, an improved material backfilling and a significant device performance increase from (1.22 ± 0.03)% up to (10.69 ± 0.44)% is achieved. Our results grant us a better understanding of the initial perovskite crystallization phases and are of key importance for further developments.