In Situ Printing

In the field of organic a solar cells, great success has been achieved by the synthesis of new materials and hence, the obtained power conversion efficiencies (PCEs) increased significantly and are already above the threshold for marketability. However, most research was carried out on spin-coated, small-area organic solar cells with an active layer of some square centimeters only. Towards real-world application, an up-scaling of thin film deposition methods is indispensable. As organic solar cell materials are solution processible, printing of active layers is assumed to be a technique to overcome the up-scaling challenge. Unfortunately, knowledge gained from spin-coating cannot simply be transferred to other deposition techniques. Therefore, the process of printing and drying needs to be studied to enable an optimization of the bulk-heterojunction (BHJ) morphology and the photovoltaic device performance of printed organic solar cells.

We developed a meniscus-guided slot-die coating technique which is compatible with roll-to-roll production and allows printing of active layers for application in organic solar cells. We perform *in situ* experiments to follow the structure formation and evolution of optical properties during the drying of printed thin films. Various methods such as grazing incidence small-angle X-ray scattering (GISAXS), grazing incidence wide-angle X-ray scattering (GIWAXS), optical microscopy (OM) and ultraviolet/visible light (UV/Vis) spectroscopy can be applied to follow the formation of amorphous or crystalline structures and the evolution of optical properties during the thin film drying. An illustration of an *in situ* GISAXS experiment is presented in Figure 1. The X-ray beam (yellow) impinges the printed thin film and the 2D scattering pattern is detected. The process of drying of the printed active layer based on a conjugated polymer (blue) and a small molecule acceptor (red) is followed from the initial wet film to the final dry film. During drying, evaporation of solvent (green spheres) and growth of amorphous polymer domains (blue cylinders) is observed.

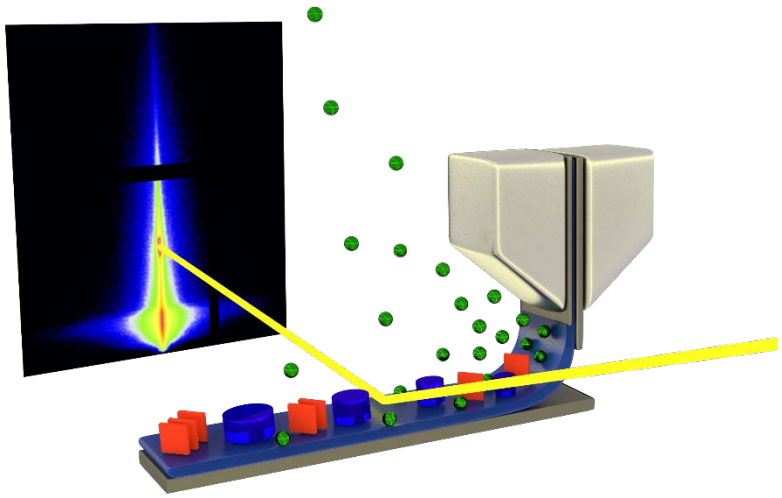

Figure 1: Illustration of an *in situ* GISAXS experiment. The drying of the slot-die coated active layer is followed form the initial liquid film state to the final dry film state.

So far, most studies focused on the model system P3HT:PCBM[1]. Therefore, a fundamental understanding of the structure formation is very limited today and *in situ* studies on printing of new high-efficiency materials are not sufficiently provided. We focus on printing of high-efficiency BHJ films based on conjugated low band gap polymers combined with fullerene and nonfullerene small molecule acceptors. Furthermore, we print blocking layers for organic solar cells such as PEDOT:PSS[3] or TiO_2. We aim on understanding the process of slot-die coating

and the drying kinetics of printed active layers or blocking layers for application in organic solar cells. In our previous work[2], we performed an *in situ* study on printing of the conjugated polymer PBDB-T-SF and non-fullerene small molecule acceptor IT-4F out of chlorobenzene which can achieve a PCE of about 13 %. The drying process is followed from the initial liquid state to the final dry film state. In this study, five phases of drying were determined with *in situ* GISAXS, UV/vis spectroscopy and optical microscopy. The morphological evolution is illustrated in Figure 2. In the initial wet film, the compounds are dissolved and surrounded by chlorobenzene molecules (green spheres) but some agglomerates (blue cylinders) of polymer chains (blue chains) are already observed. In the second phase, polymer domains start to grow by integration of polymer chains. In the third phase, a fast structure growth occurs. In the fourth phase, average distances are reduced. In the fifth phase, the solvent is completely evaporated and the final, stable morphology is formed. The results share similarity with a previous study performed on P3HT:PCBM which determined five phases of drying [1]. However, the observed stages of structure formation differ significantly in particular concerning the temporal evolution. Therefore, the knowledge gained from one material cannot simply be transferred to other materials and new compositions need to be studied individually in order to optimize the thin film deposition process.

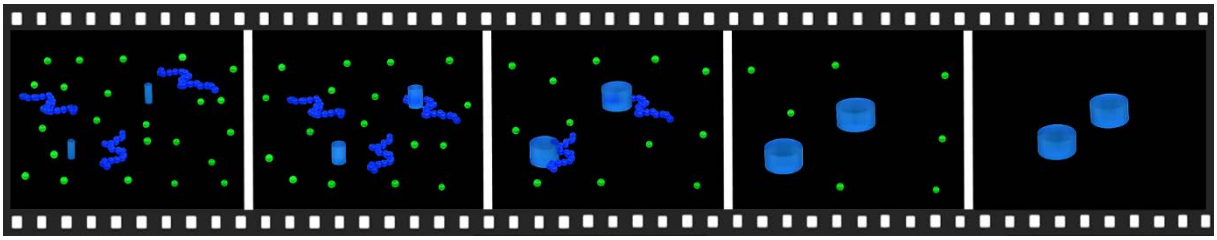

Figure 2: Schematic of the drying process**.** The structure growth observed during drying of active layers based on PBDB-T-SF:IT-4F is illustrated for one selected domain size. In the beginning, the thin film is completely wet. The polymer chains (blue) are dissolved and surrounded by solvent molecules (green spheres) but some agglomerates can already be observed (blue cylinders). In the second phase, polymer domains grow by integration of polymer chains. In the third phase, a fast structure growth occurs. In the fourth phase, the average distance between polymer domains is reduced significantly. In the fifth phase, the film is completely dry and no further changes occur.

In situ printing gives insight into the morphology formation and evolution of optical properties during thin film drying and provides fundamental information needed to optimize the thin film deposition process, the BHJ morphology and the solar cell performance. In the slot-die coated active layer, it is observed that the nanoscale structures are similar to that reported for spin-coated thin films, which demonstrates that well-suited BHJ structures can be prepared via printing as well after optimization of the printing parameters.

Therefore, slot-die coating of active layers is highly promising for application in organic solar cells as it allows overcoming the up-scaling challenge by realization of a roll-to-roll fabrication process and enables a real-world use of large-area, low-cost, organic solar cells with outstanding power conversion efficiencies. However, the evolution of morphology and optical properties is system specific and knowledge gained from one material cannot simply be transferred to other systems. Therefore, our current research is focused on studying new materials or material combinations *in situ*. In addition, scanning of parameters such as varying

the solvent, temperature or other processing conditions will play an important role. Moreover, new solvent additives and multi-component systems such as ternary solar cells will probably be developed and need to be studied. Therefore, more *in situ* printing studies have to be performed to gain fundamental knowledge about printed photovoltaics and enable a real-world application of organic solar cells in various areas such as solar windows, solar trees, art, architecture and clothes.

Selected publications

[1] Pröller, S.; Liu, F.; Zhu, C.; Wang, C.; Russell, T. P.; Hexemer, A.; Müller-Buschbaum, P.; Herzig, E. M. Following the Morphology Formation *In Situ* in Printed Active Layers for Organic Solar Cells. *Adv. Energy Mater.* **2016**, *6*, 1501580, (DOI: 10.1002/aenm.201501580).

[2] Wienhold, K. S.; Körstgens, V.; Grott, S.; Jiang, X.; Schwartzkopf, M.; Roth, S. V.; Müller-Buschbaum, P. *In situ* Printing: Insights into the Morphology Formation and Optical Property Evolution of Slot-Die Coated Active Layers Containing Low Band Gap Polymer Donor and Non-Fullerene Small Molecule Acceptor. *Sol. RRL.* **2020***, (*DOI: 10.1002/solr.202000086).

[3] Palumbiny, C. M.; Liu, F.; Russell, T. P.; Hexemer, A.; Wang, C.; Müller-Buschbaum, P. The Crystallization of PEDOT:PSS Polymeric Electrodes Probed *In Situ* during Printing. *Adv. Mater.* **2015**, *27*, 3391–3397, (DOI: 10.1002/adma.201500315).