

IN-SITU MONITORING THE FILM FORMATION OF SOLUTION CAST POLYMER-FULLERENE BLENDS FOR ORGANIC SOLAR CELLS

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Control of polymer-fullerene-blend morphology is crucial for optimizing power conversion efficiencies of polymer solar cells. A widely used material combination is the conjugated polymer P3HT and fullerene derivative PCBM. It is known that the drying process affects the final film morphology which determines the solar cell efficiency [1-3]. For a better understanding of the solidification process of the solution cast blend and the control of the fabrication process both the drying kinetics and the phase behavior are investigated.

For determining phase diagrams of the binary systems P3HT-Solvent and PCBM-Solvent (e.g. 1,2-dichlorobenzene (DCB)), a method dealing with low amounts of solid materials was established. Different temperature dependent models for the interaction parameter χ were applied to the measured data and binodal curves plotted.

With the knowledge of the phase diagrams the solution composition can be designed to purposely generate a gel state. The increased viscosity from about $2\text{ mPa}\cdot\text{s}$ to $500\text{ mPa}\cdot\text{s}$ affords coating techniques such as gravure coating in addition to low viscosity compatible coating techniques. Furthermore it could be shown that solar cells efficiencies increase if coated in gel state by knife coating. This could be due to a preaggregation in the dissolved state which is beneficial for the molecular assembly and crystallization during drying.

The drying kinetics of knife coated films of 100-200 nm dry film thickness is measured by in-situ reflectometry [4] and real time spectroscopic ellipsometry. The measured evolution of film thickness during film drying is calculated into the evolution of film composition for single solvents and mixtures neglecting excess volume [5]. This affords for the first time a reconstruction of the pathway through the phase diagram of the drying film from micrometer to nanometer scale as shown in figure 1.

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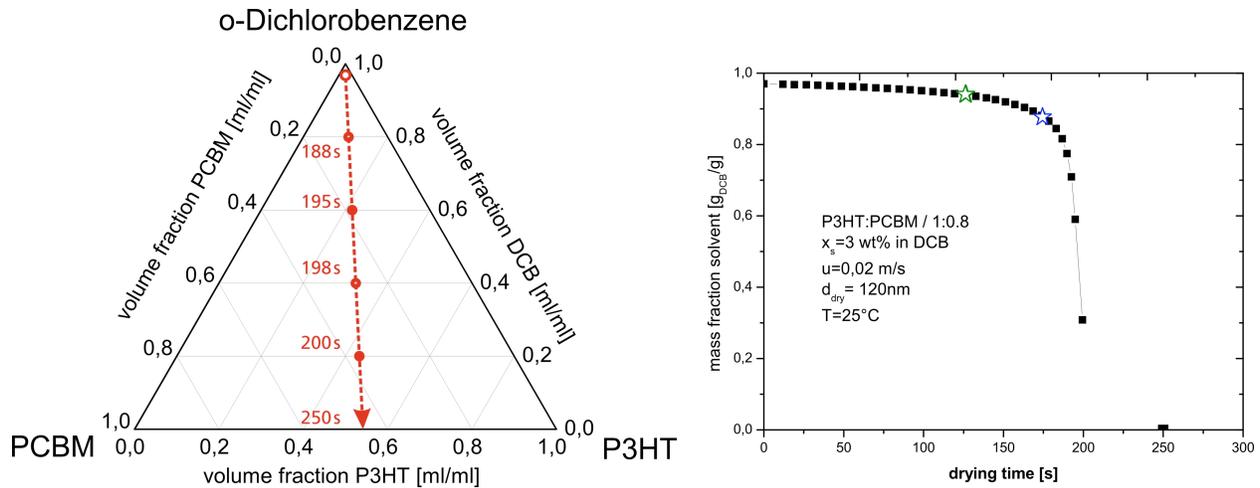


Fig. 01: Schematic ternary phase diagram with the pathway of the drying process (left). Measured drying kinetics with indicated expected phase transitions of the polymer (right).

This is crucial for the understanding of the interplay in-between an aspired thermodynamic equilibrium state and the applied kinetics which determine how far the equilibrium state is reached.

In order to correlate the applied drying conditions with the resulting film morphology comparative studies of atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM) are carried out. The morphologies are further correlated with optoelectronic properties such as light absorption, current-voltage-characteristics and external quantum efficiencies.

As indicated in figure 01 the first phase transition is expected after almost 50% of the drying time. Real time ellipsometry confirmed that no phase transitions occur over a wide initial drying phase. Hence, this phase can be skipped by exchanging the slow evaporating solvent DCB with fast evaporating solvents in order to shorten the drying process and increase the fabrication speed. In addition an initially fast drying, which leads to a fast gel formation, prevents dewetting effects after the gel state is reached once.

To systematically develop a suited solvent mixture and transfer the drying process-morphology-relationship to large area coating facilities a simulation of the drying process is required. Therefore experimentally determined drying kinetics are compared with simulations of thin film drying for single solvents and also for solvent mixtures as shown in figure 2. The experimental results show an acceleration of the drying rate due to an approaching drying front which leads to a moving concentration boundary layer [5]. A model after Brauer et al. [6] is able to describe this phenomenon and is included to the numerical simulation.

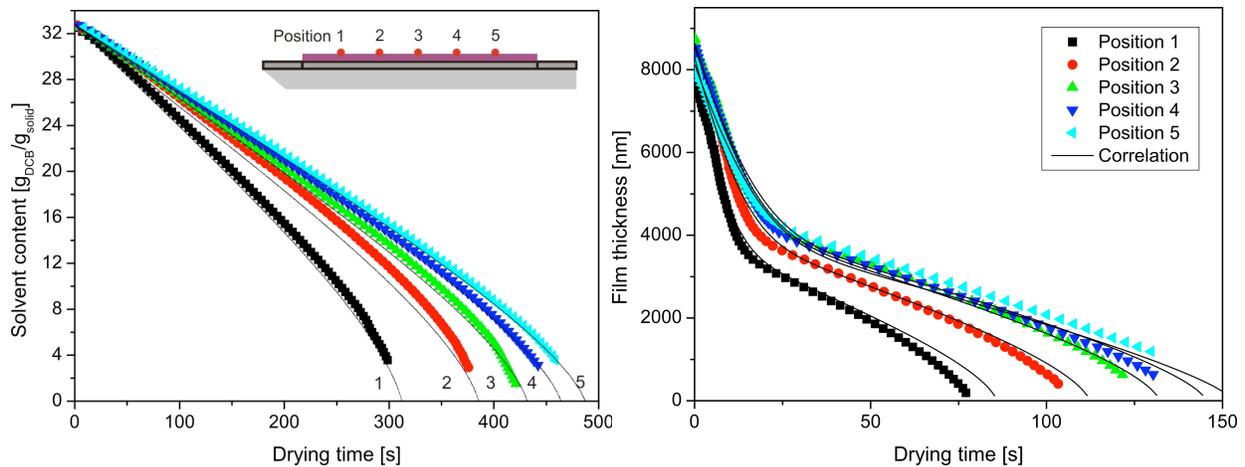


Fig. 02: Measurement (symbols) and simulation (lines) of thin film drying kinetics of a P3HT:PCBM solution in o-dichlorobenzene (left) and a solvent mixture of toluene and indane (1:1) (right) [5].

To investigate the dynamics of phase transitions and molecular assembly of polymers and fullerenes, time resolved grazing incidence x-ray diffraction (GIXD) and reflectometry measurements were accomplished simultaneously during the drying process. This enables an in-situ monitoring of the film composition and crystallization process in finally approximately 100-200 nm thin films.

These novel insights give a fundamental understanding of the film formation kinetics and prerequisites for the systematic optimization of the film morphology in solution processed organic photovoltaic devices. The obtained results are not only of paramount importance for material science but also for a transfer of the drying process-structure-relationship from lab scale to large area fabrication.

References:

- [1] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nature Mater.* 4, 864 (2005)
- [2] V.D. Mihailetschi, H. Xie, B. Boer, L. M. Popescu, J. C. Hummelen, P. W. M. Blom, *Appl. Phys. Lett.* 89, 012107 (2006)
- [3] B. Schmidt-Hansberg, H. Do, A. Colmann, U. Lemmer, W. Schabel, *Eur. Phys. J. – Spec. Top.* 166, 49 (2009)
- [4] B. Schmidt-Hansberg, M.F.G. Klein, K. Peters, F. Buss, J. Pfeifer, S. Walheim, A. Colmann, U. Lemmer, P. Scharfer, W. Schabel, *J. Appl. Phys.* 106, 124501 (2009)
- [5] B. Schmidt-Hansberg, M. Baunach, J. Krenn, S. Walheim, U. Lemmer, P. Scharfer, W. Schabel (submitted)
- [6] H. Brauer, *Stoffaustausch einschließlich chemischer Reaktion*, Verlag Sauerländer, Anrau und Frankfurt am Main (1971)