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In-situ real-time x-ray scattering for probing the processing-structure-performance relation

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ABSTRACT

In-situ x-ray scattering methodology is discussed, in order to analyze the microstructure development of soft functional materials during coating, annealing, and drying processes in real-time. The relevance of a fundamental understanding of coating processes for future industrial production is pointed out.

INTRODUCTION

The field of organic electronics has made great progress over the last decade. An ever-growing variety of excellent materials is available. Their performance in lab tests is highly promising. However, there is still something missing in this picture. For a future mass production of organic electronics we will have to learn how to process materials with coating and printing techniques, while maintaining their favorable properties. At this point most of the work in the lab is still done with drop casting and spin coating which cannot be reasonably scaled up to industrial production.

Fortunately we do not have to re-invent the wheel: Industrial coating techniques, such as dip coating, knife coating, slot-die coating, etc. and their many variants have been around for over 100 years. And it would be highly desirable to modify existing coating machines for the purpose rather than needing large investments for new machines.

For functional materials, however, the focus of research and development has to shift from achieving homogeneity and precise thickness – think magnetic tape or photographic film – to precise control of the microstructure. The latter encompasses crystal structure and polymorphism, preferential orientation, grain size and mosaicity as well as in-plane texture and grain boundaries – all features that can be conveniently probed by synchrotron x-ray scattering methods in-situ and in real time.

EXPERIMENT and DISCUSSION

Solution shearing

Let me illustrate the above point with a recent example. In a collaboration between CHESS, King Abdullah University of Science and Technology (KAUST, Saudi Arabia), and Stanford University, we developed the instrumentation to study solution shearing *in-situ*, a technique recently developed in Zhenan Bao's group at Stanford [1]. In solution shearing a small quantity of solution, typically around 10 µL per 1 cm of substrate, is spread with a coating blade onto a substrate at controlled temperature and coating speed. Performing this experiment required an x-ray microbeam of 20 µm, to achieve the necessary spatial resolution, a fastframing x-ray area detector with a time resolution of as low as 10 ms, as well as a temperature-controlled sample stage and position, angle, and speed control of the coating blade [2].

Focusing on the shearing speed v, coating can be divided into two regimes [3]: At slow coating speeds up to about 0.1 mm/s the coating process is dominated by evaporation and the solute crystallizes at the end of the meniscus. In this regime the coating thickness decreases inversely proportional to the shearing speed. At coating speeds higher than 10 mm/s the coating layer thickness is determined by hydrodynamics in the Landau-Levich regime [4]. At these speeds a hydrodynamic boundary layer forms at the interface, the thickness of which scales as $v^{2/3}$ and coating becomes essentially a two-step process, deposition of a liquid film and drying of this film thereafter. In the transition regime around v=1 mm/s the thinnest coatings are achieved, in the range of 10-100 nm which is the sweet spot for reliable device function and minimum use of material (cost!) and solvent (environment!).

Such a test coating system for the lab does not have to be a huge investment in money and space. In fact for use at the beamline we developed a microcoater that easily fits in the palm of my hand [2]. The important characteristic of such a test coater is that coating conditions can be achieved that are scalable to industry-size coating frames. In our case the microcoater reliably reproduced results obtained at Stanford with a much larger laboratory-scale coater [1]. For x-ray scattering resolution reasons the coated substrates were 6 mm wide; using a drop of typically 10 µL, we obtained homogeneous coatings of about 10 mm length. The x-ray beam probed the time development of the film close to the center of the coated region, where steady-state coating conditions were obtained.

For illustration, Figure 1 presents some typical results obtained in a successful coating experiment. We were coating TIPS-pentacene dissolved in toluene (16 mg/mL) at a speed of 0.8 mm/s and a 0.1 mm gap using a coating angle of 20°. The substrate was held at 50°C. The unpolarized optical microscope showed beautiful interference colors indicating that the films had thicknesses around 50-100 nm. The x-ray detector first showed a liquid scattering ring, as the meniscus swept through the microbeam. Then the liquid ring faded due to solvent evaporation, and immediately the diffraction pattern of the TIPS-pentacene thin film phase appeared.

Further analysis of the scattering pattern revealed that this film had a well-defined growth plane with small mosaicity and moreover, was laterally aligned: The shearing had broken the isotropy of the amorphous silicon oxide layer of the substrate [2]. The full story turned out to be even more complex: we observed a new diffraction spot that had previously been assigned to a shear-induced metastable polymorph [1]. By varying the incident angle of the x-ray beam and thus the penetration of the sample we could determine that the equilibrium polymorph first formed at the surface of the film. Then the remaining entrained liquid formed the metastable polymorph [5].

The processing parameters of a solution shearing experiment are the shear rate (speed/gap), the substrate temperature and the initial solute concentration. In addition, there can be a modification of the surface energy to promote better sticking of the film to the substrate, there can be additives to act as nucleation agents, a low vapor pressure co-solvent to slow down the final drying stage, and other adjustments that influence nucleation and growth. In the above example the substrate was modified with a self-assembled monolayer exposing phenyl rings to improve the wetting of the solution; no additives were used. Finally the choice of solvent is of paramount importance and ultimately determines where the transition region exactly occurs.

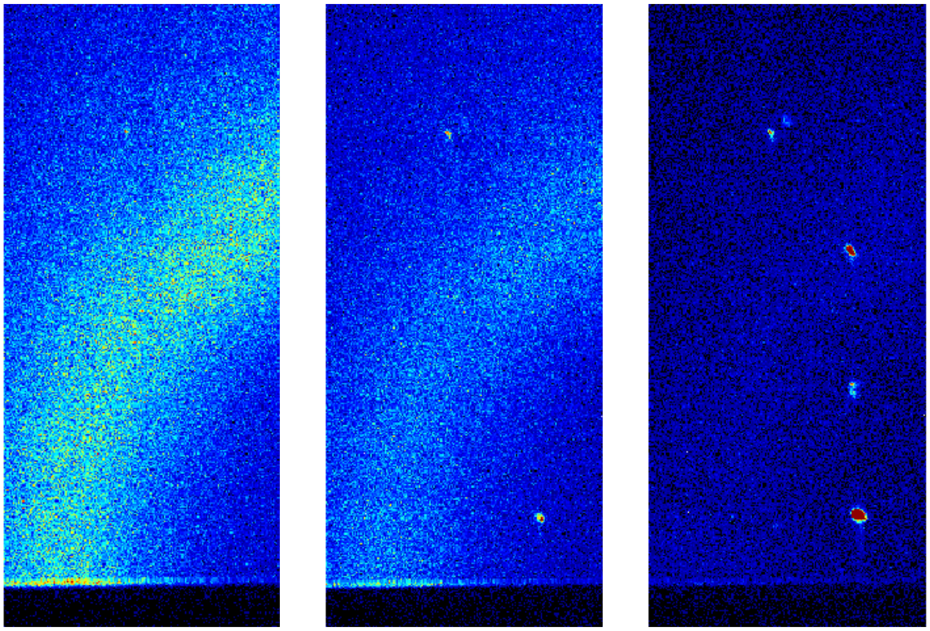

Figure 1. Microbeam grazing-incidence wide-angle x-ray scattering from a TIPS-pentacene film during solution shearing at a speed of 0.8 mm/s. The left panel shows the solution scattering ring from the toluene solvent. As the solvent evaporates, material is already starting to crystallize (middle panel). Shortly afterwards a biaxially aligned film is fully crystallized as evidenced by the appearance of x-ray diffraction spots. Elapsed time between images is 100 ms, exposure per image was 20 ms. For details see text and Reference [2].

Post-processing

If the coating parameter space still does not suffice to obtain high-performance films, post-processing can be applied. In fact many industrial coaters already feature a thermal drying stage. In the case of functional materials, thermal treatment as well as solvent vapor annealing has been used to further improve performance. The general principle is sketched in Fig. 2: the functional film is attacked with solvent vapor or heat, the vapor pressure or temperature is sustained at a certain level and for a certain duration, and finally the film is released to ambient conditions again. Thus post-processing provides another four process parameters. Often the available range of the control parameter has some principal limit, such as the equilibrium vapor pressure, solvent induced phase separation or dewetting, or thermal decomposition, that needs to be taken into consideration as well. Finally, the choice of solvent or solvent mixtures for vapor processing opens another rich opportunity space.

For use in the laboratory, we again do not need to get into major investments. The thermal or solvent vapor processing can be done in a small vapor chamber [6]. As an illustration I would like to present another example from my beamline. The KAUST group lead by Aram Amassian investigated solvent vapor processing of TIPS-pentacene thin films using toluene at ambient conditions. They found that the mobility first dramatically increased, but then dropped similarly dramatically [7]. AFM on quenched samples revealed the reason: first solvent vapor processing lead to the growth of larger grains and the mobility improved due to fewer grain boundaries. However, at some point the grain size exceeded the percolation limit and grains became so large that holes formed and the mobility gain was lost again. Using in-situ x-ray scattering the time-evolution of the microstructure could be probed in detail. The experiment nicely demonstrates the necessity of well-defined and reproducible control of solvent vapor annealing conditions for a future production process. In general, solvent choice as well as solvent vapor or temperature ramps have to be carefully adjusted for each material. Within these boundaries the process profile (attack, sustain, release – see Figure 2) needs to be optimized for efficient production and minimum energy cost or solvent use.

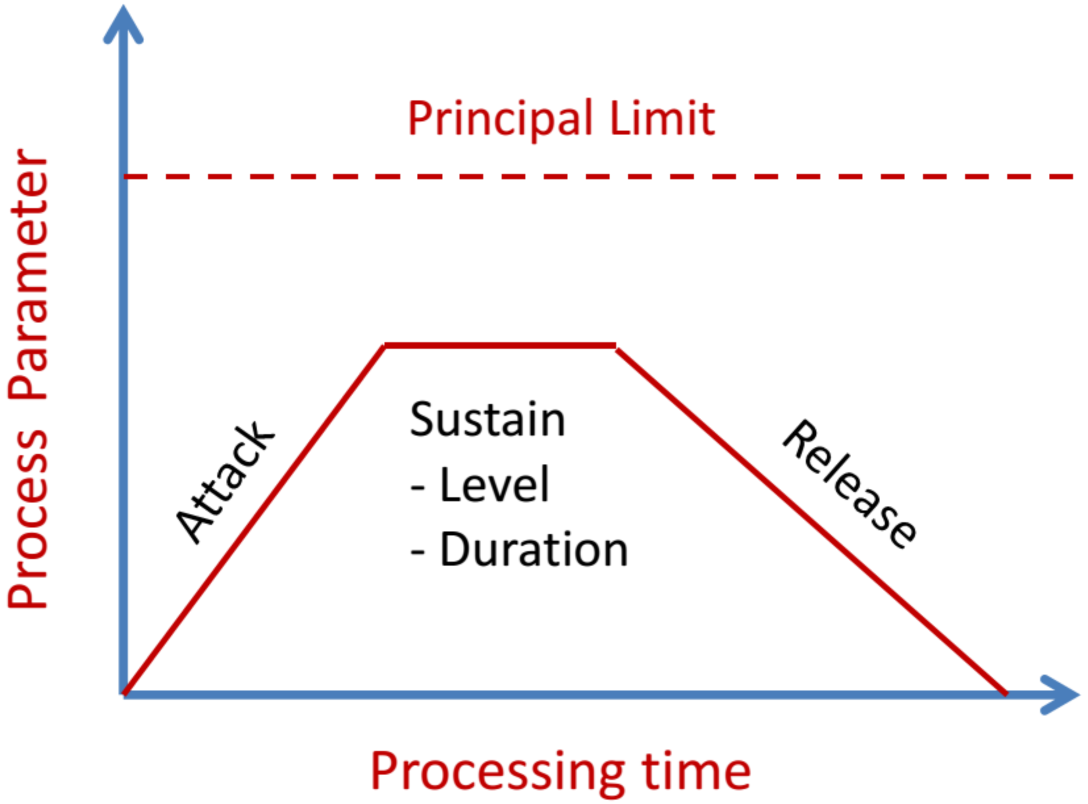

Figure 2. General principles of post-processing. Process parameters can be solvent vapor pressure or temperature. Principal limits can be set by the equilibrium vapor pressure, phase separation, or dewetting as well as thermal decomposition of the film.

CONCLUSIONS

Soft materials show the promise of low-cost production of flexible electronics as well as functional nanostructures for a large variety of other applications. In order to transfer lab results to the production line, it will be necessary to quantify all processing parameters precisely. A fundamental understanding of solution-phase processing and the ensuing microstructure of the material will be essential for a future industrial production of devices based on soft materials and offers a rich science opportunity. Synchrotron-based x-ray scattering studies can efficiently reveal important structural and kinetic properties on the molecular and mesoscopic length scales in real-time and *in-situ*.

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