Interrupted Growth to Manipulate Phase Separation in DIP:C60 Organic Semiconductor Blends

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ABSTRACT: We studied the influence of periodic growth interruptions during codeposition of diindenoperylene (DIP) and buckminsterfullerene (C60) in an equimolar mixing ratio. DIP and C60 are known to phase-separate when codeposited, but the details and, in particular, the length scales depend on kinetic factors. Using X-ray scattering and atomic force microscopy, we demonstrate that the phase separation mechanism is in fact influenced by growth interruptions, with more pronounced effects if the deposition rates are low. For high deposition rates, growth interruptions have no appreciable effect. We discuss our proof-of-concept investigation in the context of the relevant processes and their time scales.

INTRODUCTION

Organic semiconductors have shown great potential for electronic and optoelectronic device applications, with potential advantages being ease of preparation, better tunability, and higher oscillator strength for certain transitions.1,2 In addition to single-component systems studied mostly for transistor applications, multicomponent systems and, in particular, donor–acceptor combinations are in focus for photovoltaics and light-emitting devices.3 One strategy is to employ donor–acceptor blends, such as obtained by codeposition of the two materials. The structural complexities and the rich phase behavior in such blends4–9 make detailed quantitative investigations imperative, but also rather complicated.10 This includes both the molecular structure as well as the mesoscopic morphology, since, e.g., the length scale of potential phase separation, compared to length scales of electronic processes such as charge carrier diffusion lengths, can be crucial for device performance.11–13 Optimizing structure and morphology for device performance is a nontrivial multicomponent problem, so it is not easy to pin it down to any one particular structural or morphological feature because often the device properties show complex relationship to their inherent structure. Nevertheless, it seems to be accepted in the community that a certain level of roughness of the interface between the donor and the acceptor is favorable to enhance chances for exciton dissociation and thus organic photovoltaic device efficiency.16,17 Our present results provide one additional handle as to how to tailor these structural and morphological features.

Growth phenomena are nontrivial to comprehend and sometimes very difficult to account for quantitatively since these are essentially nonequilibrium processes where new material continually impinges on the substrate and causes hindrance to equilibration of growth.10,18–21 Concepts based on the minimization of energy alone are insufficient to account for thin organic crystalline structures grown on inert substrates using vapor sublimation since the structure formation involves many kinetic processes, e.g., diffusion, nucleation, adsorption, desorption, and dissociation.22–24 These concepts are neglected in purely energetic considerations of growth. However, understanding of growth mechanisms involves essentially all of these processes which are inherently connected to the dynamic aspects of thin film growth. The diversity of the growth phenomena for thin films is huge, and often a smart model has to be invoked for a quantitative explanation of the parameters involved.18,25 Changes in the preparation conditions of thin film growth, for instance, substrate temperature and deposition rate, often lead to significantly different structural and morphological features. These complexities are already found for pure materials. The case when materials are codeposited (almost invariably leading to intermixing at different levels) becomes even more difficult to understand. Previous studies have categorized three case scenarios4 essentially determined by the adsorbate–adsorbate interaction and the temperature: (a) a solid solution constituting of a stochastic mixture of the mixing materials, (b) a new periodically ordered complex which is different from the...
mixing materials, and (c) phase segregation of the mixing materials into separate domains of individual material. In a thin film, the occurrence of these mixing scenarios might also depend on the layer height above the substrate. An appreciable effect of steric compatibility is also observed in such mixed blends giving rise to an even broader range of scenarios than parts a–c above. Using complementary X-ray scattering and atomic force microscopy measurements, several studies have revealed how the length scale of phase separation proceeds and how different growth parameters may be tuned to alter the growth and consequently the structural properties.

The combination of diindenoperylene (DIP) and buckminsterfullerene (C60) (see Figure 1, parts a and b, for molecular structures of DIP and C60, respectively) as a donor–acceptor combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have demonstrated good solar cell performance, most notably a combination in the active area of the OPV cells have 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always same. Grazing incidence X-ray diffraction (GIXD), which gives information on the in-plane crystallinity of the thin film by measuring the intensity as a function of the in-plane component \((q_{xy})\) of \(q\), was performed by fixing the incident angle to 0.12° such that the signal originates predominantly from the top organic layer. The experiment was performed with a Cyberstar scintillation counter with a beam size of 0.1 mm from the top organic layer. The experiment was performed with a typical GID took around 60 min. The Bragg peaks in radiation damage. Typical XRR measurements took around 20 min and typical GID took around 60 min. The Bragg peaks in the GIXD data were fitted with Gaussians (refer to Figure S2 in Supporting Information) to obtain the full width at half-maximum (fwhm) of the peaks. Scherrer’s equation \((d_{coh} = 2\pi / K/fwhm\) with \(K = 0.94\) for spherical crystallites and fwhm being the full width at half-maximum of the particular peak) was used to calculate \(d_{coh}\). Possible effects of the instrumental broadening were not included, hence the estimated values are lower limits only. Atomic force microscopy (AFM) was performed using the JPK Nanowizard II instrument (JPK Instruments AG, Berlin, Germany), in the intermittent tapping mode under ambient conditions. The resonant frequency of the cantilever used was 300 kHz. The pyramidal-shaped tip was made of silicon and had a tip radius of less than 10 nm. The images were collected at a scan rate of 0.5 lines per second. The Gwyddion image processing software was used to refine and analyze the AFM images.

**RESULTS AND DISCUSSION**

It is expected that if the routine growth processes are altered systematically, it will have an influence on the resulting structure and morphology of the samples. Here, we focus on the attempt to manipulate the phase separation via interruption in the growth process. In an earlier report, we demonstrated how the other experimental control parameters affect the structure and morphology of equimolar films of DIP:C60. Since the growth of such thin films has kinetic limitations, we investigated this behavior by changing the deposition rates \((r_{dep})\) and the interruption time \((t_{int})\) during the growth process. We define the average rate \((r_{avg})\) as the time averaged deposition rates for the growth of the entire thin film (see Figure 2 for different \(r_{dep}\) and inset for a comparison between continuous and interrupted growth together with the assignment of the time-averaged rate of growth). In order to gain a total film thickness of 200 Å at different deposition rates while keeping the number of interruptions constant, the duration of deposition and interruption periods were adjusted accordingly.

XRR data are plotted in Figure 3. It is observed that the films grown at a higher \(r_{dep}\) have more pronounced oscillations than the ones with much lower \(r_{dep}\). However, we see a signature of a broad Bragg reflection in the films with lower \(r_{dep}\) compared to the ones at higher \(r_{dep}\). The broad reflection is a signature of crystalline domains of the pure materials, meaning that the phase separation is more pronounced in films with a stronger Bragg reflection. This is in accordance with the general behavior of organic thin film growth for most pristine molecules that slower growth rates actually enhance the crystallinity of the sample but at the same time make it rougher. Usually, higher \(r_{dep}\) leads to smoother films with decreased crystallinity. The same trend is visible even for codeposited films although the degree of crystallinity is much less in a mixed system of DIP:C60 when compared to growth behavior of pure DIP or pentacene (PEN) molecules.

In addition, upon a comparison of the films deposited either continuously or by systematic interruptions we observe that the crystallinity is enhanced for all the different \(r_{dep}\) in the case of interrupted growth. The effect is more pronounced for the low \(r_{dep}\) films than the ones for the high \(r_{dep}\) films. This is a clear signature that the interruptions actually enhance the out-of-plane structure of the mixed films. The low \(r_{dep}\) rate films already show some crystallinity during continuous growth and the enhancement is more prominent for the synchronized interrupted growth at the same \(r_{dep}\). Importantly, we observe that if the film is already crystalline during continuous growth (Figure 3a), there is further enhancement in the crystallinity during interrupted growth (Figure 3b). As is expected, the roughness decreases in accordance with the increase in the fraction of crystallinity of the films. It is noted that the out-of-plane crystallinity does not vary monotonously with the decreasing flux rate from C-5 to C-2.5 (continuously growing films) and we also see this in the in-plane crystallite size in Figure 5 estimated from the GIXD. However, in all the other films grown continuously at higher rates or grown with...
interruption at all different rates we observe the trend of decreasing crystallinity and increasing roughness. We speculate that since the flux is not very different between the samples C-5 and C-2.5, they form similar structure with similar crystallinity when grown continuously.

GIXD was also measured for the same films with different deposition procedures (Figure 4). The peak width and corresponding crystalline size estimated from GIXD measurements of thin films of similar thickness of the pure phases of DIP and C60 at the same growth temperature are roughly 200 Å, and 80 Å, respectively. In comparison to the pure phases, the mixed films have lower crystallite size of the constituent domains. Upon comparison of the films with the same rate, we observe that the films which were grown by interrupted growth clearly have more pronounced DIP reflections, at least for low \( r_{dep} \) which indicates that the interruption in growth indeed enhances the in-plane crystallinity of the film, too. The C60 thin film is known to grow in a polycrystalline form (with a broad distribution of orientations)\(^2\) as opposed to DIP thin films which grow as strongly textured domains.\(^2\) We do not observe any change in the width of the C60 peak (which is already broad due to codeposition of molecules) to infer about the C60 phase. We think that while the increase in crystallinity of the DIP domains increases the peak intensities and decreases the fwhm of the DIP diffraction peaks (as observed in the GIXD profiles) there is no obvious change perceived in the diffraction peaks for the polycrystalline C60 domains.

On the other hand, it was observed that for the high \( r_{dep} \), the difference between interrupted and continuous growth was negligible. This is corroborated with the XRR measurements.
where we observed an appreciable enhancement of the out-of-plane crystallinity only for the low $r_{dep}$ films. From the peak width of the known DIP and C60 Bragg reflections, we estimate the degree of phase separation by the crystallite sizes for the prominent peaks at different values of $r_{dep}$ (Figure 5).

AFM data of the DIP:C60 equimolar mixture grown both continuously and by systematic interruption at all different growth rates ($r_{dep}$) of 2.5, 5, 7.5, 10, and 20 Å/min are shown in Figure 6. In comparison to continuous growth, for interrupted growth there is a larger number of presumably crystalline domains, which grow in a 3D like fashion. On comparing the domain size of C-2.5 and I-2.5 (refer to Figure S3 in the Supporting Information) we see that the domain size is approximately 110 ± 10 nm for the continuous growth and 135 ± 22 nm for the interrupted growth, which is significantly larger than the average coherent in-plane island sizes determined from GIXD both for DIP and C60. Since GIXD is very sensitive to defect densities (like point defects and dislocations) in the scattering volume, we conclude that the defect density within one domain visible in AFM is still considerable and limits the determined coherent scattering island size. We assume, that the flat regions in between the domains are nearly amorphous which is also in agreement with our XRR and GIXD data. In continuous growth, the reduced surface coverage of these larger presumably crystalline domains of DIP results also in smoother films with less or no crystallinity in comparison to interrupted growth.

Since DIP is more crystalline than C60 in the mixtures and scales with deposition rate (Figure 5), we assume that the 3D domains in Figure 6 are mostly phase-separated crystalline DIP domains. The surface coverage of the crystalline DIP domains dependent on growth rate is shown in Figure 7. Data for the surface coverage was extracted from different AFM images for all the different growth rates both for the continuous and the interrupted growth scenarios. Images were considered with sizes of both 10 and 5 μm² for at least two to three different spots, and the average value of the coverage was plotted. Figure 6 clearly demonstrates the trend of the decreasing surface coverage as the growth rate increases for both continuous and interrupted growth modes. In general, the covered surface area of crystalline domains is significantly larger for interrupted growth compared to continuous growth. However, the differences in surface coverage for both growth modes decrease for larger $r_{dep}$. This observation is again in agreement with the crystalline coherent island size determined from GIXD.

We speculate that the large crystalline islands are pure domains which have been separated out from the nearly amorphous mixture by diffusion during the film growth. Interruptions in the growth process are expected to influence the morphology of the film if the interruption time scales are comparable to time scales which determine the processes shaping the film: surface diffusion, step diffusion, island formation and phase separation. Estimating the time scales of these processes for the studied mixture of DIP and C60 is a nontrivial problem. For films of pure materials, some information is available. Surface diffusion of free molecules appears to be a fast process. For C60 on C60 itself, all-atom simulations estimate order-of-magnitude diffusion constants.
Equimolar mixtures of DIP and C60 were grown using different experimental conditions with a focus on the variation of the time averaged growth rate in the context of interrupted growth. The effect of systematic interruption of growth was studied and compared to the continuous growth scenario. X-ray scattering measurements XRR and GIXD were used to probe the out-of-plane and in-plane crystallinity of the thin films. AFM measurements were performed on the same set of samples corroborating the finding that the crystallinity of the samples was higher for the lower rate of deposition as is usually observed for pristine organic thin films. On the basis of our measurements and analysis, we observe that phase separation mechanisms can be influenced by growth interruptions, in particular, if the deposition rates are already low. For high deposition rates, growth interruptions have little effect because based on the time scale considerations, the effect of the interruptions will be smeared out and gradually disappear for higher rates. It has also been mentioned that, due to the complex structure–property relationship, it is not always possible to single out any particular structural feature that might be useful in certain applications, but generally it is accepted in the community that a certain amount of roughness of the interface between the donor and the acceptor is favorable to enhance chances for exciton dissociation and thus organic photovoltaic device efficiency. Such information provides us a handle on the type of preparation conditions to tailor the length scale of phase separation in organic semiconductor thin film blends that lead to a specific type of growth and morphology preferred for a device or other applications in the field of organic electronics. Our results and comparison with time scales from simulation suggest the possibility of height-dependent time scales that may be further exploited to tailor the growth. Many other growth conditions can be investigated, for instance, the stoichiometry, functionalization of the substrate and thickness and time dependence of phase separation, but this would be beyond the scope of the present proof-of-concept study.

The Journal of Physical Chemistry C


