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Dewetting of an Organic Semiconductor Thin Film Observed in Real-time**

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The breakup of thin films into droplets with a lower surface energy is a commonly observed phenomenon in liquids, but dewetting also occurs for thin solid films.^[1] In technological applications of thin solid films, dewetting is often considered a problem affecting growth of smooth films as well as a limitation for device stability. However, it can also be used as a nanopatterning technique to produce arrays of nanostructures with controlled lateral distances and size. It has recently been shown that dewetting and thermal stability are of particular importance for organic semiconductors,^[2–5] because crystalline thin film of these materials are bound by weak van der Waals forces and therefore molecular diffusion sets in already at moderate temperatures. Dewetting studies therefore are important for applications of organic semiconductors in devices such as thin film transistors,^[6] organic photovoltaics and organic light emitting diodes. In this paper we study the planar aromatic molecule diindenoperylene (DIP) as a model system, which has been shown to exhibit high structural order,^[7] good charge carrier mobility,^[8] and interesting opto-electronic properties such as a long exciton diffusion length.^[9] Further, a recent study shows that under appropriate growth conditions DIP forms nano-dots on top of a wetting layer indicating its potential for self-assembled nanostructures.^[10]

Besides its relevance for the long-time stability of devices, dewetting also offers a challenge for the fundamental understanding of these molecular materials. Dewetting is a complex process that can be started by an external stimulus such as a thermal or mechanical perturbation and is closely related to the growth of the potentially metastable thin film. Adding to the complexity molecular semiconductor films often exhibit polymorphism and therefore one or more

metastable structures are common during growth. Also, organics show strong surface anisotropy because of the generally anisotropic molecular building blocks, which has to be taken into account for dewetting theories, as simple models for isotropic liquids do not apply. In particular for very thin films such as a molecular monolayer (ML) the discreteness of the underlying crystal lattice becomes important and therefore continuum models have to be altered as shown in reference [11]. Experimental data for dewetting of such ultra-thin crystalline organic layers is scarce though and in particular the kinetics and mechanisms of dewetting require further elucidation.

In this paper, we report clear evidence of DIP ML dewetting via the formation of bilayer islands. We use real time X-ray scattering to determine the time constant of interlayer molecular diffusion during dewetting and use AFM to determine the dewetted morphology and in-plane length scales.

Experimental

DIP was purchased from Institut für PAH-Forschung (Greifenberg, Germany) and purified by gradient sublimation before use. As substrate, Si(100) wafers covered by their native oxide were cleaned ultrasonically with acetone, isopropanol, and ultrapure water, followed by heating to 700 K in the UHV growth chamber. The heating prior to DIP deposition removes water from the silicon oxide surface, but is not high enough to remove all impurities. Indeed XPS measurements show that there is some carbon contamination present on the surface after this sample treatment. From X-ray reflectivity measurements the roughness of the cleaned substrate surface is determined to be 3 Å.

Thin DIP films were prepared by organic molecular beam deposition (OMBD) at a growth rate of $\sim 1 \text{ \AA min}^{-1}$ under UHV conditions (pressure during growth 5×10^{-9} mbar). The *in situ* X-ray measurements were carried out at beamline ID10B at the ESRF in Grenoble, France, with a wavelength of 1.08 Å, using a vacuum chamber dedicated to OMBD equipped with a beryllium window, evaporation cells, and a quartz crystal microbalance.^[12] Real-time scans of the specular reflectivity up to the second order Bragg reflection can be performed comparatively fast at 3.5 min per scan so that kinetic data can be obtained during growth and dewetting of a DIP ML. For details of the morphology and the in-plane length scales AFM images were acquired. The dewetted DIP sample was cooled down to room temperature to freeze

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dewetting after the X-ray measurement and studied by AFM after intermediate exposure to air.

Results and Discussion

Real Time X-ray Reflectivity

Figure 1 shows the evolution of the X-ray reflectivity both during DIP growth and subsequent dewetting at 130 °C substrate temperature. The reflectivity changes from that of the bare silicon oxide substrate in the back to the reflectivity of the (dewetted) DIP thin film in the front. During growth the appearance of a first and second order "Bragg-reflection" corresponding to the ML height of ~17 Å can be seen (arrows). The "Bragg reflections" are obviously still very broad in reciprocal space, as the ML film is very thin in real space and there is no constructive interference between multiple lattice planes of a crystal yet. After the effusion cell shutter is closed (that is no more molecules are deposited), the reflectivity still changes and clearly an additional interference fringe (Kiessig oscillation) appears next to the Bragg reflection indicating that dewetting occurs after growth has stopped.

The X-ray reflectivity measurements in Figure 1 probe the out-of-plane structure normal to the sample surface, that is the film thickness and the out-of-plane lattice constant. For a quantitative analysis the reflectivity curves were fitted with the Parratt algorithm,^[13,14] which gives film thickness and lattice spacing, but importantly also gives information about the electron density. Assuming that the first ML closes essentially completely before the second one nucleates, which is a reasonable assumption as confirmed by the growth studies in references,^[15,16] it is possible to determine the molecular surface coverage in the first and second ML from the respective electron density as compared to the electron density of the completed first ML.

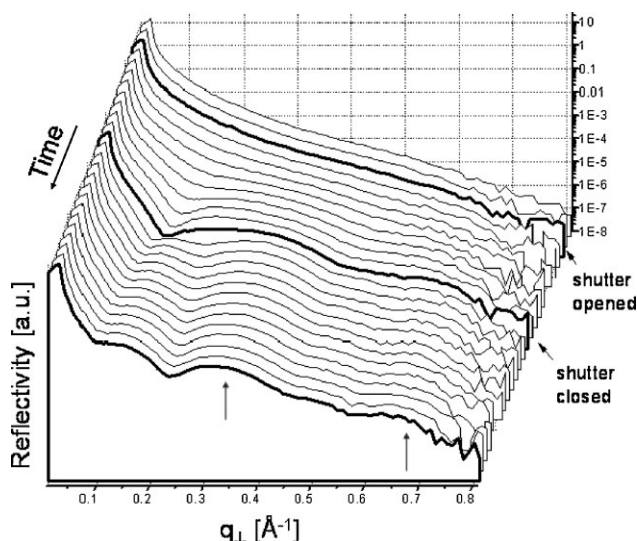


Fig. 1. Time evolution of the specular X-ray reflectivity during and after growth of a DIP thin film on silicon oxide at 130 °C substrate temperature.

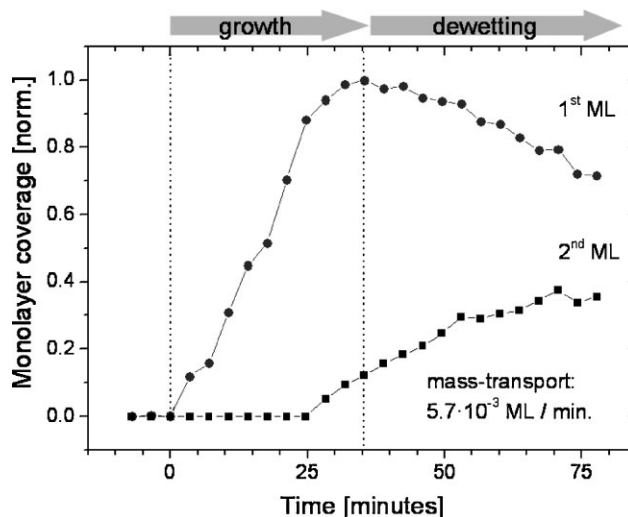


Fig. 2. Fractional layer coverages as a function of time. During evaporation of DIP the coverage of the first ML increases until growth is stopped upon nucleation of the second ML. As can be seen significant interlayer diffusion from the first into the second ML takes place at a rate of $5.7 \times 10^{-3} \text{ ML min}^{-1}$ directly after stopping the growth.

Figure 2 shows the surface coverages (layer filling factors) of the first and second ML as a function of time as obtained from a fit to the X-ray reflectivity data in Figure 1. As expected for layer-by-layer growth of DIP the first layer nearly completes before nucleation of the second layer starts. The growth is interrupted shortly after one ML has been deposited, but because of the dewetting process the surface coverage still changes. The filling of the first ML is decreasing at a rate of $\sim(5.8 \pm 1.0) \times 10^{-3} \text{ ML min}^{-1}$, while the second ML coverage is increasing at a rate of $\sim(5.7 \pm 1.0) \times 10^{-3} \text{ ML min}^{-1}$. These rates are identical within experimental uncertainty, showing that no significant desorption of molecules from the surface occurs at 130 °C. Instead, the structure dewets as molecules diffuse from the first into the second ML. Assuming that detachment of molecules from step edges is the rate-limiting step for interlayer diffusion, the order of magnitude for the diffusion rates can be reproduced using typical binding energies of 1 eV per molecule and attempt frequencies of 10^{13} s^{-1} in an Arrhenius law.

We note that the coverage decrease in the first ML in Figure 2 is approximately linear as a function of time, whereas from theoretical considerations in reference^[11] a power-law behavior is expected. This discrepancy may be partly explained by experimental uncertainties, but also the Ehrlich-Schwoebel barrier, which has not been included in the theoretical models yet, may be significant for organic molecules when compared to their weak van der Waals interactions with the substrate.

Interestingly, the dewetting occurs despite very slow deposition at a growth rate of 1 Å min^{-1} (>30 min per ML), which may indicate that even at these slow growth rates the structure does not directly adopt a thermodynamically favored structure but is kinetically limited. Another possibility is that dewetting by diffusion into the second layer

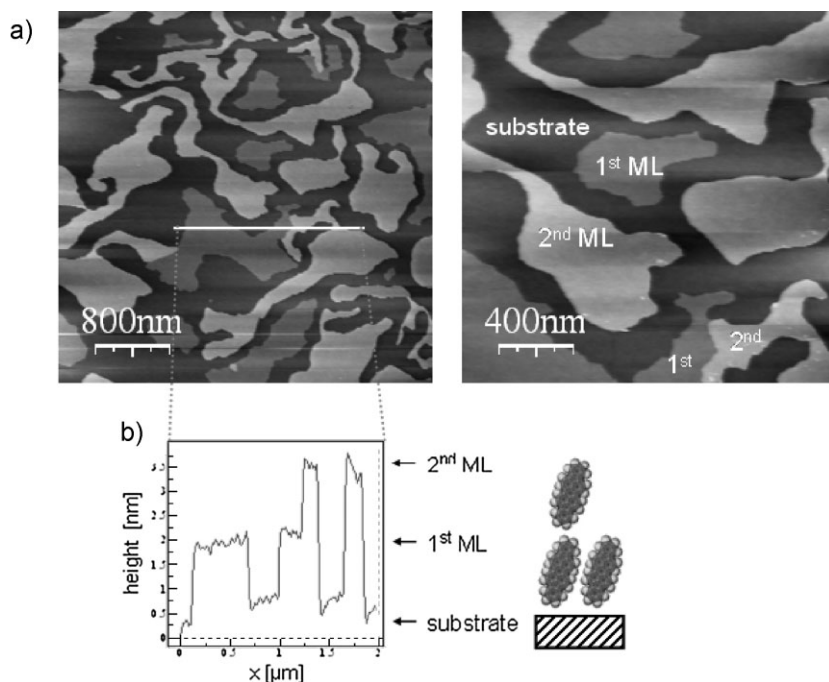


Fig. 3. a) AFM images showing the dewetted structure after DIP molecules from the first ML have diffused into the second ML. b) A linescan shows that the island height corresponds to the height of one and two standing upright DIP molecules, respectively.

can only start once nucleation in the second ML has occurred, which seems plausible as no dewetting is observed during deposition of the first ML.

AFM Measurements

To confirm the results from the real-time X-ray reflectivity measurements and get information about the in-plane structure we performed AFM measurements as shown in Figure 3(a). The surface morphology of the dewetted DIP ML exhibits uncovered patches of the silicon oxide substrate and partially filled first and second MLs. The AFM line scan in Figure 3(b) exhibits step heights of ~ 15 and ~ 30 Å, which have to be compared to the lattice spacing of ~ 17 Å determined from X-ray reflectivity. These step heights confirm that the islands consist of one and two layers of standing upright DIP molecules, respectively. The lateral length scales of around $1 \mu\text{m}$ found in the AFM images may be intrinsic to the DIP dewetting process, but the carbon contamination of the substrate surface may induce heterogeneous nucleation of the dewetting process. Further studies on substrates cleaned with different recipes would be necessary to find the intrinsic dewetting length scales.

The in-plane patterns of the dewetted DIP films in Figure 3(a) with "finger-like" elongated islands are typical for dewetting structures as they have lower line tension than round islands. At the same time it is important to realize that not only surface energy considerations apply, but the dewetting process is also influenced by the crystal structure of the DIP thin film. In reference^[16] it was found that the first DIP ML has an in-plane crystal structure that is strained by

more than 2% compared to the structure in films of three and more ML thickness. Therefore, it is plausible to assume that the dewetted islands with a height of two ML are more stable than islands of one ML height, providing a thermodynamic driving force for dewetting. We do not observe any dewetting for relaxed DIP films of three or more ML thickness, giving a further indication that strain in the first ML might be connected to the dewetting process.

Conclusions

We have shown that a ML of DIP molecules dewets on a timescale of tens of minutes via formation of bilayer islands. Real-time X-ray measurements allow us to determine the rate constants for interlayer diffusion to be $\sim 5.7 \pm 1.0 \times 10^{-3} \text{ ML min}^{-1}$ at 130°C , and AFM measurements confirm the conclusions from X-ray scattering. Previously observed strain in the first ML suggests that a structural transition to a more relaxed bilayer structure may be one driving force for the dewetting.

The present work will allow for a better control for growth of ultrathin DIP films and organic heterostructures containing DIP layers as knowledge of the dewetting timescales makes it possible to freeze in a desired structure by changing the substrate temperature.

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