

Evidence for a Layer-Dependent Ehrlich-Schwöbel Barrier in Organic Thin Film Growth

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We report direct experimental evidence for a layer-dependent step-edge barrier in organic thin film growth, investigating di-indenoperylene on SiO₂ as an archetypical system. In particular, we show that a noticeable Ehrlich-Schwöbel effect emerges only beyond the 3rd molecular layer, accompanied by mass step-upward diffusion. We further disclose that this thickness dependence of the interlayer transport is directly related to molecular reorientations during the first stages of the growth. This is ultimately responsible for a morphological transition from layer-by-layer growth to surface rapid roughening. These experimental findings should compel further development of molecular-scale models for organic thin film growth.

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For metals and inorganic semiconductors, the synergism between experiment and theory has tremendously improved our understanding of the kinetic growth mechanisms. This knowledge has led to discoveries of various routes for manipulating atomic processes to obtain controlled morphologies, for instance, by the use of surfactants or templates. In atomistic models for kinetic growth, the amount of mass transport between layers is primarily determined by the energy barrier for crossing steps, the so-called Ehrlich-Schwöbel barrier [1,2]. While this has turned out to be a very efficient concept to describe inorganic thin film growth, interlayer transport in organic systems is a much more complex phenomenon. The intrinsic anisotropy and internal degrees of freedom of the molecules evoke a series of activation barriers for crossing the steps that depend on molecular conformation and on the orientation of the diffusing molecule [3,4]. Unfortunately, we still lack a molecular-scale understanding of the kinetic growth phenomena for organic materials, in part because there are scarce experimental data as a basis for the development of a theoretical framework of organic growth. Attention has only recently focused on investigating various aspects of organic multilayer growth on chemically inert substrates commonly used for organic field effect transistors (OFETs), like glass or SiO₂/Si [5–7]. Although the weak molecule-substrate interaction favors multilayer growth of more or less upright standing molecules, a strong tendency to roughening is commonly observed disrupting the initial layer-by-layer growth after a few layers [8–11]. Most interestingly, for some organic systems, the evolution of the roughness (σ) versus time occurs even faster than the limit of stochastic roughening in the absence of interlayer transport [12–15]. This so-called rapid roughening leads to an anomalous power law of the roughness versus thickness (Θ), $\sigma \sim \Theta^\beta$ with $\beta > 0.5$ (stochastic limit). Such rapid roughening has been observed on the growth of di-indenoperylene (DIP) which exhibits a scaling behavior at moderately high substrate

temperatures (120–140 °C) associated with a growth exponent of $\beta \sim 0.8$ [13,14]. It was conjectured that in-plane disorder arising from the boundaries of the tilt domains in the organic thin film could be responsible for this observation. However, because the employed substrate temperatures were close to the DIP desorption temperature, thermodynamic driving forces may be dominantly responsible for the overall evolution of the morphology (rather than kinetic processes).

In this work, we have reexamined this intriguing system for lower growth temperatures (90 °C and room temperature), that is, closer to kinetic growth conditions, and found a similar rapid roughening behavior. We disclose that the microscopic processes which give rise to the rapid roughening is a pronounced layer dependence of the step-crossing barriers for descending and ascending mass transport. In particular, we find that the growth of the first layers occurs without an appreciable Ehrlich-Schwöbel barrier for downward molecular transport. A noticeable barrier for step-crossing only emerges beyond the 3rd layer, accompanied by mass step-upward diffusion. It is shown that this layer dependence of the interlayer transport is directly related with molecular reorientations during the first stages of the growth, as caused by the interaction with the substrate. This scenario is quantitatively similar for the studied growth temperatures, 35, 90, and 120 °C, indicating that the underlying mechanism is essentially the same.

Thin DIP films were prepared by organic molecular beam deposition (OMBD) on Si(100) wafers covered with native SiO_x (thickness of ~ 15 Å) in ultra high vacuum (UHV) with a constant deposition rate of ~ 2 Å/min. The growth behavior was investigated for substrate temperatures of 35 and 90 °C. Prior to deposition, the substrates were cleaned in an ultrasonic bath with standard solvents and by annealing in UHV to desorb water and possible organic contaminants. Specular and grazing incidence x-ray diffraction (GIXD) measurements were performed *in situ* using a portable vacuum chamber (base

pressure of 10^{-8} mbar) at the synchrotron source Angströmquelle Karlsruhe (ANKA) of the Karlsruhe Institute of Technology (KIT) with a wavelength of $\lambda = 1.24$ Å. For specular x-ray reflection, the vertical resolution was 0.0032 Å $^{-1}$. For the GIXD measurements, the horizontal and vertical resolution were 0.019 Å $^{-1}$ and 0.076 Å $^{-1}$, respectively. The film morphologies were measured by a commercial Nanotec atomic force microscope (AFM) in air operating in contact mode and analyzed using the software WSXM [16].

The most remarkable feature of DIP growth is a morphological transition from layer-by-layer to rapid roughening at a critical thickness of a few monolayers. In agreement with previous studies of DIP grown at 120 °C, this scenario is also found for lower growth temperatures (35 and 90 °C). In what follows, we analyze in detail the growth at room temperature and present a comprehensive understanding of the microscopic origin of the rapid roughening phenomenon. Figure 1 displays AFM images for selected thicknesses. Single monomolecular terraces and islands corresponding to different molecular layers are visible with associated step heights of 17.0 ± 1.5 Å, in good agreement with previous studies [14]. Beyond a critical thickness of ~ 3 monolayers (ML), nucleation and growth of a new layer occur before total completion of the underlying layer and, in turn, the surface roughens anomalously fast: two layers (3rd and 4th layer) are partially exposed for a thickness of 2.4 ML while 7 incomplete individual layers are observed for a 9.3 ML thick film. Indeed, beyond a thickness of 2 – 3 ML, the roughness increases with a power law exponent of $\beta \sim 0.8$ [Fig. 2(a)]. We note here that a similar growth exponent is found for different growth temperatures ($\beta = 0.84$ at 35 °C, $\beta = 0.80$ at 90 °C, and $\beta = 0.77$ at 120 °C [13,14]).

A key observation is that the *in situ* x-ray structure analysis reveals noticeable changes during the first stages

of the growth. First, the shift of the (00 l) Bragg reflections in the specular x-ray diffraction data [Fig. 2(d)] discloses a fast decrease in the distance between molecular layers during the first stages of the growth giving evidence for an increase of the molecular tilt with respect to the surface vertical [17]. The fastest increase of molecular tilt occurs during the first stages of the growth with an angle increase from 3° (2 ML) to 21° (4 ML) [Fig. 2(b)]. Concomitant with the molecular tilt, there is an anisotropic change of the in-plane unit cell. The in-plane unit cell of the DIP thin-phase structure consists of a rectangular lattice with two molecules in the unit cell [schematically depicted in Fig. 2(b)] [18]. *In situ* GIXD measurements reveal a

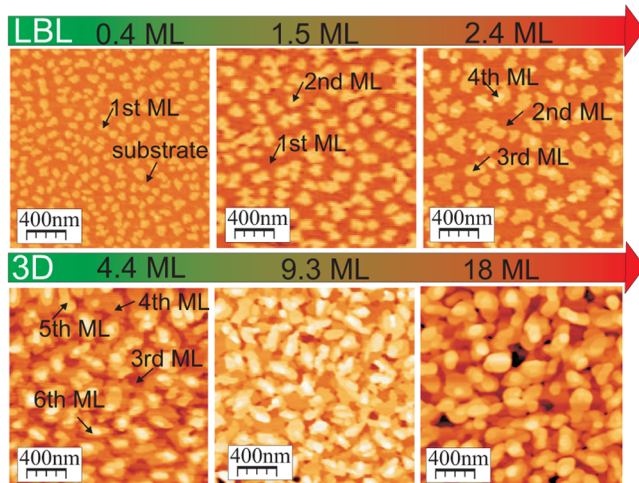


FIG. 1 (color online). AFM topographic images for different film thicknesses, illustrating the morphological transition from layer-by-layer (LBL) to 3D growth.

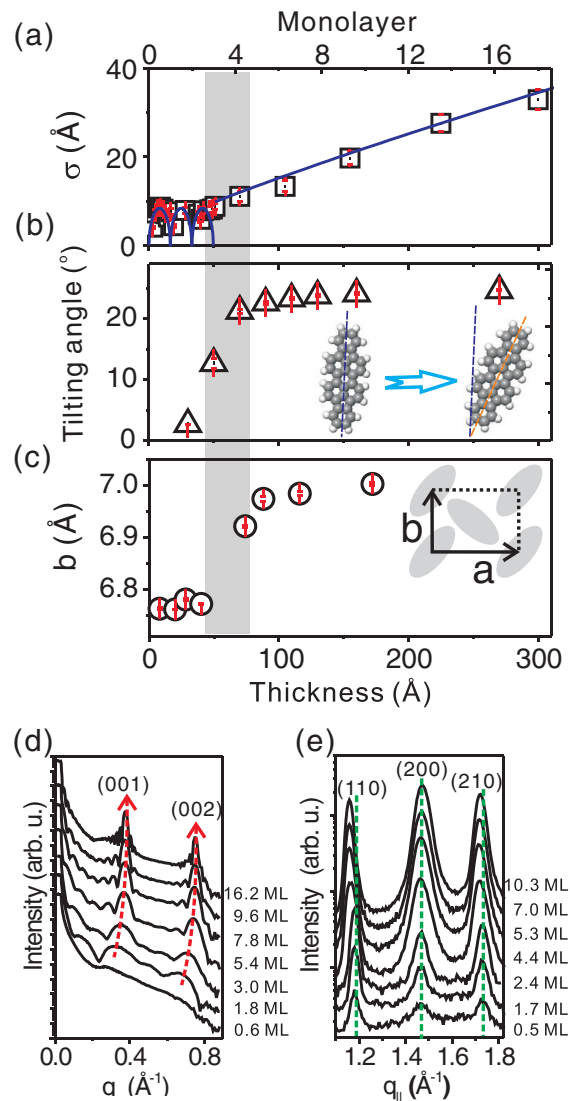


FIG. 2 (color online). Evolution of the root mean square roughness (a), the tilting angle with respect to the surface normal (b), and the in-plane lattice parameter b (c) of the DIP film with increasing thickness, showing a similar transition as function of thickness. The corresponding x-ray reflectivity and GIXD data are plotted in (d) and (e). Continuous line in (a) corresponds to the oscillatory behavior of a perfect layer-by-layer growth.

strained structure with a compression of -3.4% along the b -axis for the first DIP layer in contact with SiO_2 [Fig. 2(e)] [19]. A noticeable shift in the peaks position shows that the strain of the first layer is progressively released during the growth of approximately four layers [Fig. 2(c)]. The calculated increase of the b lattice parameter is plotted in Fig. 2(c). The variation of the a lattice parameter is not shown since it is less than 1% [20]. Quantitatively similar structural changes have been determined for the growth at 90 and 120°C (initial compressive strain of $\delta b = -3.0\%$ at 90°C and of $\delta b = -4.0\%$ at 120°C [14]). Since no heteroepitaxial relationship is expected on the amorphous SiO_2 surface, the formation of a denser structure for the first DIP layer is possibly attributed to the minimization of the organic-substrate interfacial energy [20].

To understand the origin of the growth front roughening, we have performed a careful analysis of the morphological AFM images to quantify the evolution of coverage θ_n for the various layers n and, therewith, the interlayer transport. The distribution of the layer coverage has been evaluated for several stages of the growth, i.e., for certain thicknesses Θ , and compared to the evolution in complete absence of interlayer transport, i.e., random deposition (Fig. 3). Experimentally, this is accomplished by evaluating the layer coverage for a total thickness of Θ and upon a small increase of coverage $\Delta\Theta$ (in the range of 0.2 – 1 ML). Then, the distribution of layer coverage for a total thickness $\Theta +$

$\Delta\Theta$ is compared with the calculated one considering one-step deposition of $\Delta\Theta$ incoming molecules randomly deposited on the morphology observed with Θ . Histograms in Fig. 3(a) depict the layer coverage experimentally measured for a certain film thickness of Θ (light gray) and upon deposition of $\Delta\Theta$, experimentally (dark gray) and calculated value (striped). The analysis has been performed for five stages of the growth. Note that an exclusive downward interlayer transport occurs for the first stages of deposition resulting in the perfect layer-by-layer growth. For a film thickness of $\Theta = 2.4$ ML and $\Delta\Theta = 0.2$ ML, the nucleation of the 4th layer on an incomplete 3rd layer can be observed, identifying an inefficient interlayer downward transport that leads to a gradual buildup of roughening. The same scenario persists for a film thickness of $\Theta = 4.2$ ML. However, for higher thicknesses in the multilayer regime (shown here for a coverage of $\Theta = 8.7$ ML and $\Theta = 9.3$ ML), the coverage of the last layers is larger than the calculated one without interlayer transport which can only be explained by an upward diffusion of molecules. From the experimental analysis of the layers coverage distribution, we have quantified the hopping-down and hopping-up rates within a modified mean-field model for the multilayer growth. A fraction $k_{n,\text{down}}$ of the molecules which arrive per unit time on top of the n th layer (being proportional to the exposed area), diffuses to the $n - 1$ layer, while another fraction $k_{n,\text{up}}$ jumps up to the $n + 1$ level. The modified rate equation is

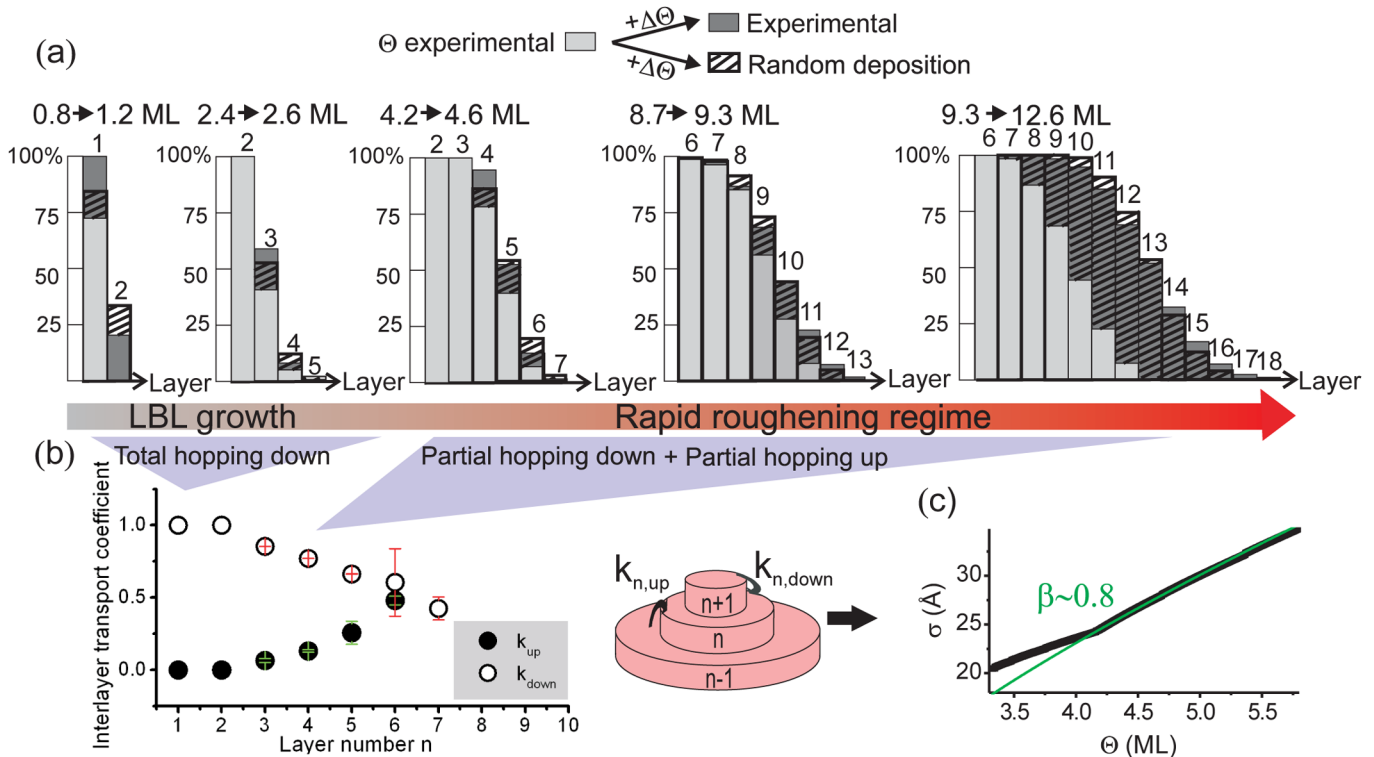


FIG. 3 (color online). (a) Histograms comparing the evolution of the layer coverage with film thickness (experimentally obtained) to the calculated one assuming one-step random deposition. (b) Calculated interlayer transport coefficients as a function of layer number. (c) Simulated roughness by using the hopping rate values from (b).

$$d\theta_n = [(1 - k_{n,\text{up}} - k_{n,\text{down}})(\theta_{n-1} - \theta_n) + k_{n+1,\text{down}}(\theta_n - \theta_{n+1}) + k_{n-1,\text{up}}(\theta_{n-2} - \theta_{n-1})]d\Theta,$$

where θ_n is the coverage of n th layer and Θ is the total thickness in number of monolayers [21]. Two sets of experimental data were used to deduce the interlayer transport rates to account for the boundary conditions. The resulting hopping-down and hopping-up rates are plotted in Fig. 3(b) as a function of the layer number. The growth of the 1st and 2nd layer of DIP is a perfect layer-by-layer feature ($k_{2,\text{down}}$ is 1 and the interlayer transport from 2nd to 3rd layer $k_{2,\text{up}}$ is 0). Beyond the third layer, there is a continuous decrease of $k_{n,\text{down}}$ due to the emergence of a Ehrlich-Schwöbel energy barrier whose strength increases with the layer number. This is accompanied by an increase of $k_{n,\text{up}}$ showing that climbing up processes gain in importance. Hence, these experimental findings demonstrate a layer-dependent interlayer transport that includes the lowering of the energy barrier for molecules ascending steps. To check self-consistency, we have simulated the roughness evolution as a function of increasing film thickness by using the rate hopping values plotted in Fig. 3(b) and obtained a growth exponent of $\beta \sim 0.8$, in perfect agreement with the experimental value [Fig. 3(c)]. It is evident that the inclusion of such molecular ascending transport further enhances the traditional Ehrlich-Schwöbel barrier effect for kinetic roughening. However, we stress here that rapid roughening cannot be obtained in the simulation of the multilayer growth without a layer dependence of the hopping -down and -up rates.

The structural data, showing a strong decrease of tilt angle accompanied by an increase of the b in-plane lattice parameter during the first layers, provide a rationalization of the observed layer dependence of the step-energy barriers on the molecular level. The layer-dependent structure provides a thermodynamic driving force for upward molecular transport due to the different chemical potentials between layers. From a kinetic perspective, the activation energy encountered to ascend a step is expected to depend sensitively on the tilt angle and in-plane packing of the molecules in each molecular terrace. The present study evidences available molecular processes with low activation energy to climb up at steps, contrary to the standard assumption of irreversible attachment at ascending steps. Theoretical efforts are necessary to elucidate if the ascending process occurs via a place exchange mechanism (like for some metal surfaces) or by sliding or rolling over the edge. In a very recent work on sexiphenyl, Hlawacek *et al.* [3] have concluded a gradual increase of Ehrlich-Schwöbel barrier with thickness as origin of a strong trend toward mound formation, which was ultimately attributed to changes in the molecular tilt. Here, a bending of the molecule at the step edge is the mechanism proposed for step-down crossing. Although this mechanism cannot be generally valid for other molecules with a rigid aromatic core like DIP, their work coincides with our study in

underlining the relevance of the orientational degrees of freedom on the step-edge energy barriers for organic growth. We merely remark that the entire energy landscape of the kinetic processes is necessarily more complicated than implied above if competitive diffusion processes between molecules in lying-down and standing-up configurations (for instance, by the motion of more than one molecule) take place.

In conclusion, this experimental investigation on organic thin film growth provides unambiguous evidence for a layer dependence of the Ehrlich-Schwöbel barriers of descending and ascending molecular transport. We show that this variation of the interlayer transport with thickness is directly related to molecular reorientations during the first stages of the growth and is ultimately responsible for a morphological transition from layer-by-layer growth to surface rapid roughening. This study sheds light on our molecular-scale understanding of organic thin film growth and provides a valuable experimental input for the development of a new theoretical framework for organic materials, which might quantitatively predict morphologies.

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