

Real-Time Observation of Structural and Orientational Transitions during Growth of Organic Thin Films

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We study kinetically controlled orientational and structural transitions of molecular thin films during growth *in situ* and *in real time*, using diindenoperylene (DIP) as an example. By time-resolved surface-sensitive x-ray scattering (out of plane and in plane), we follow the organic molecular beam deposition of DIP on silicon oxide, on stepped sapphire, and on rubrene as an organic model surface. We identify transitions for the few-monolayer (ML) regime, as well as for thick (several 10's of ML) films. We show that the differences in the interaction of DIP with the substrate change the thickness as well as temperature range of the transitions, which include (transient) strain, subtle changes of the orientation, as well as complete reorientation. These effects should be considered rather general features of the growth of organics, which, with its orientational degrees of freedom, is qualitatively different from growth of inorganics.

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The understanding of growth phenomena is of obvious relevance for many technical applications including very diverse systems from single crystals to thin films and surface coatings to nanostructures of various materials. At the same time, growth offers many fundamental challenges for theory as well as experiment [1,2]. While for “atomic” systems a certain level of sophistication has been reached, the growth of molecular systems exhibits important qualitative differences [3–5], which are not included in the established approaches. Probably the most important difference is related to the orientational degrees of freedom, which imply that the problem is generally anisotropic, and that not only the positional adsorption state of a molecule, but also its orientation must be considered. Since the orientation may change from one layer to the next or even within a given layer, one is faced with an additional source of disordering during growth which, in turn, can affect, e.g., electronic transport [6]. Together with vibrational and conformational degrees of freedom [7], these features of organic materials can introduce qualitatively new effects in the growth, for which we are only beginning to develop an understanding [3–5,7–10].

Probably the clearest manifestation of the orientational degrees of freedom is the issue of the lying-down (λ) vs standing-up (σ) configuration. During growth the system can undergo a structural transition, possibly involving changes of the tilt angle, which will depend on temperature, rate, and the strength of the interactions. This complication of different orientations on differently interacting substrates may become particularly relevant for organic semiconductors grown on lateral metal-insulator heterostructures like organic field effect transistors [6]. In this Letter we present an x-ray scattering study of the kinetically controlled structural and orientational transi-

tions of molecular thin films during growth *in situ* and *in real time*.

We focus on diindenoperylene [DIP; a red dye, $C_{32}H_{16}$; see Fig. 1(a)] as a model for van der Waals systems, which we have already structurally characterized in detail (“post-growth”) [9,11,12]. For growth “near equilibrium” (high T , i.e., ~ 130 °C substrate temperature) by organic molecular beam deposition (OMBD), DIP orders very well [12]. In addition, promising charge carrier mobilities (measured in thin-film transistor geometry) were found [6].

The experiments were performed at beamline ID10B at the ESRF in Grenoble, France, in a small UHV chamber dedicated to OMBD studies, equipped with a Be window, effusion cells, thickness monitor, etc. [13], at x-ray wavelengths of 1.082 and 0.903 Å. Reflectivity measurements provide information on the out-of-plane structure (q_{\perp} denotes the out-of-plane momentum transfer). Grazing incidence diffraction (GID) probes the in-plane structure (q_{\parallel} denotes the in-plane momentum transfer). To study the influence of the substrate on the growth behavior, we used silicon wafers with a native oxide layer as a rather smooth surface, sapphire (A-plane, average terrace width well below 1000 Å) as a substrate with a relatively high step density and a slightly higher van der Waals interaction with the adsorbate, and an organic film (amorphous rubrene, thickness 384 Å, rms roughness 10 ± 2 Å [7,14]) as weakly interacting substrate.

In what follows, we present our results organized according to different thickness (time) regimes; first we follow structural transitions in the beginning of growth [few monolayer (ML) regime] including the dynamic transition from layer-by-layer growth to rapid roughening and secondly we describe transitions (σ to λ in particular) at later stages (thick films ≥ 10 ML).

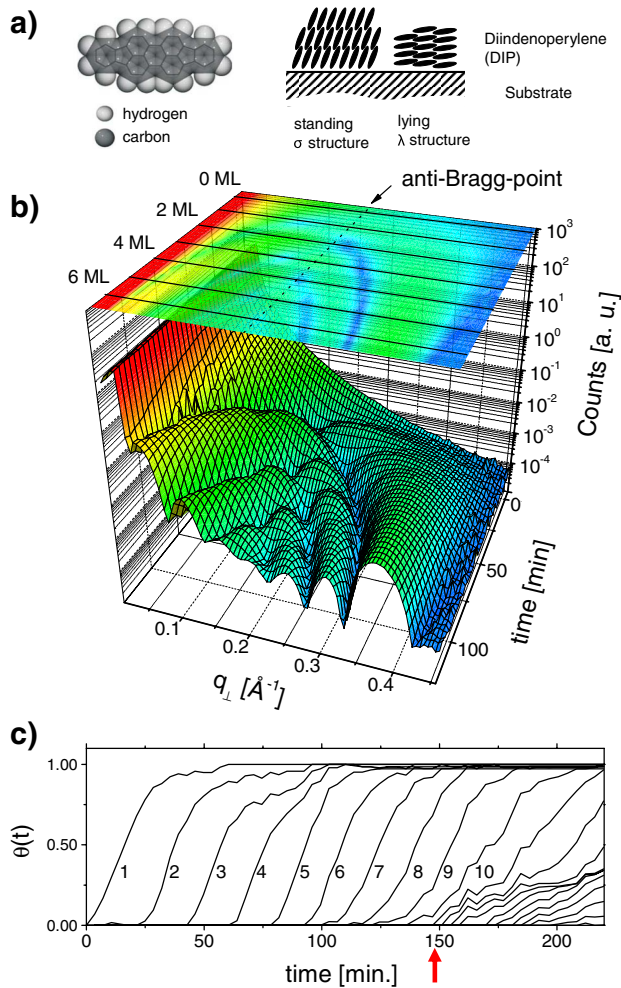


FIG. 1 (color online). (a) The DIP molecule and a schematic of standing (σ) and lying (λ) structures. (b) Evolution of the real-time x-ray reflectivity as a function of time (i.e., film thickness) during growth on silicon oxide (at 130°C). (c) Layer coverages $\theta(t)$ as obtained from fits to the above real-time data. A change from layer-by-layer growth to rapid roughening is clearly discernible after ~ 10 ML (see arrow).

For growth on silicon oxide at $T = 130^\circ\text{C}$ substrate temperature only reflections characteristic of the σ structure [Fig. 1(a)] are observed already for a laterally averaged coverage of $\leq 3 \text{ \AA}$, so the σ structure exists as islands at sub-ML coverage, as evidenced by both out-of-plane and in-plane data (see below). Therefore, a single adsorbed molecule must have a high translational and orientational mobility, staying in an upright orientation once it attaches to a σ island, while no λ islands nucleate at high T on silicon oxide.

To follow the *temporal evolution* of the σ structure we have measured x-ray reflectivity in real time during growth [Fig. 1(b)]. The scans were performed on a time scale of ≤ 3 min, which is well below the deposition time for 1 ML of the σ structure (~ 17 min, growth rate 1 \AA/s). The well-defined first order Bragg reflection including the

Laue oscillations show that the films are well ordered. From the temporal oscillations of the reflectivity at the anti-Bragg point ($q_{\perp} = q_{\text{Bragg}}/2 = 0.37/2 \text{ \AA}^{-1}$) with a period corresponding to 2 ML we can deduce the growth mode [15–17]. Since our data extend over a broad range in q_{\perp} , using the Parratt formalism [18] we can directly obtain the coverages $\theta(t)$ of the individual layers with high precision [Fig. 1(c)]. After initial layer-by-layer growth, the films roughen after ~ 10 ML. These data show in real time the onset of the rapid roughening, which had been deduced based on a series of post-growth measurements [9]. This change of growth mode is strongly temperature dependent, occurring earlier for lower temperatures. The data analysis shows that the first ML is slightly thicker than the following layers and has a lower electron density, consistent with a model of interdigitating layers. The following MLs grow strained with a lattice constant of 16.9 \AA which later reduces to 16.6 \AA for thick films. These (partly transient) strain effects during growth are believed to be important for rationalizing the transition in the growth mode.

To study the structural evolution in more detail, the in-plane lattice parameters were measured by real-time GID. From the position of the (11) in-plane GID reflection (using the notation from Ref. [11]) one can determine the in-plane lattice constant with high resolution. The shift in peak position in Fig. 2 shows that the lattice parameter parallel to the surface expands by 2% upon adsorption of the second and third ML. Note that the reflection moves as a whole with increasing thickness, indicating that the

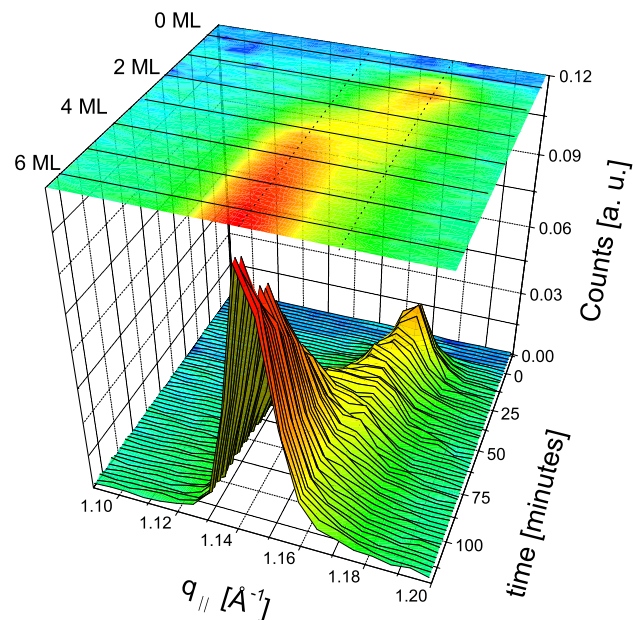


FIG. 2 (color online). In-plane structure: Real-time GID scans during growth of DIP on silicon oxide (130°C). The in-plane (11)-reflection of the σ structure shifts during growth of the second ML, showing that the first ML has to expand (time axis scaled to be comparable to Fig. 1(b)).

structure appears to change in a relatively collective fashion, i.e., not only in the newly growing layer (the top layer at a given point in time). These structural changes are associated with a broadening of the GID reflections: Δq_{\parallel} increases by 40% which may be partly due to residual strain or inhomogeneities, but also due to a decreasing lateral coherence length [decreasing from a lower limit of ≥ 500 Å (1 ML) to ≥ 300 Å (2 ML)]. Interestingly, for films >5 ML (when the structure is more “relaxed”) this value increases again to ≥ 500 Å.

The growth of DIP on sapphire ($T = 130$ °C) shows similar behavior. Again the (11) and (21) in-plane reflections shift in the first MLs, while the (20) reflection does not shift significantly. Since the ordering motif and symmetry are identical, this implies an expansion along the (01) direction. It is interesting to note that on a “soft” organic substrate (rubrene), DIP exhibits less strain. Note that on none of the substrates was a preferred azimuthal orientation of the crystallites found in GID.

The following structural model fits our observations on silicon oxide and sapphire ($T = 130$ °C): The structure of the first ML becomes strained upon adsorption of the (interdigitating) second ML. Further layers grow in a strained layer-by-layer mode until after ~ 10 ML rapid roughening and islanding sets in; the out-of-plane lattice parameter decreases with film thickness by 1.8%, possibly due to the molecules tilting slightly downwards. We note that for complex molecular materials several mechanisms may contribute to strain relief (e.g., changing molecular conformation, orientation, interdigitation).

It is important to note that only by measuring in real time during growth the structural transition in the first MLs can be accurately monitored. Stopping growth after 1 ML we find from the relative evolution of the partial coverages that there is significant interlayer mass transport from the first to the second ML on a time scale of minutes, changing post-growth results. The post-growth reordering demonstrates that the structure in this regime is kinetically limited.

We now turn to the later stages of growth, i.e., coverages $\gg 1$ ML. As described above, for $T = 130$ °C a well-defined structure is observed, with hardly any changes in the structure beyond a thickness of about 10 ML (apart from roughening). For lower T (≤ 35 °C), however, we find evidence for the nucleation of the λ structure. Figure 3 shows GID data of a 310 Å film grown at -5 °C on silicon oxide showing λ - as well as σ -structure reflections for different angles α_i of the incident beam, and therefore different penetration depths Λ of the evanescent x-ray field [18]. When probing only the near surface region (i.e., $\Lambda \lesssim 50$ Å) the (001)-reflection characteristic of the λ structure becomes stronger relative to those of the σ structure, showing that the λ structure grows on top. Following the GID signals in real time during growth [Fig. 4(a)], we find that the λ structure only starts to nucleate after a

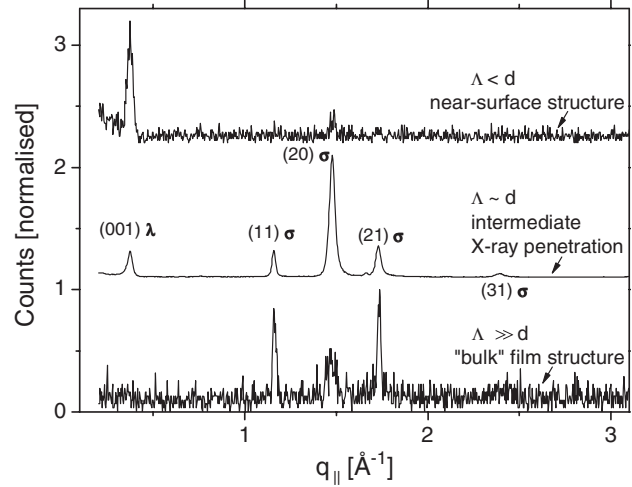


FIG. 3. GID for a $d = 310$ Å DIP film grown on silicon oxide at -5 °C (post-growth). The dependency of the (001) λ reflection on x-ray penetration depth Λ shows that the λ structure is growing on top of the σ structure.

“threshold-thickness” of ~ 170 Å (for 35 °C substrate temperature on silicon oxide).

A possible mechanism for the emergence of a λ structure could be that a given growing (top) layer of DIP has to “stand up” and newly form the σ structure. If, for laterally diffusing (and probably lying-down) molecules there is a finite probability for nucleation in the λ structure, depending on the substrate temperature and roughness of the layers underneath, this will at some point lead to nucleation of the λ structure. However, since this is a nonequilibrium phenomenon, we expect and do observe the coexistence of both structures, so that there is no laterally homogeneous interface between σ and λ . The λ nucleation may also be promoted by the increased roughness (and thus lower mobility and increased density of nucleation sites) for thicker films [9] and may be viewed as a kinetic instability, the characteristics of which change for low T or for interrupted growth.

For growth on sapphire at lower T we find qualitatively the same transition. Again the λ structure emerges in coexistence with the σ structure, but the λ structure starts to nucleate immediately without threshold and the fraction of λ molecules is higher than on silicon oxide [see Fig. 4(a)]. Furthermore for very low temperatures (-50 °C) the σ Bragg reflection disappeared completely from the reflectivity scans, and growth proceeded mainly in a λ structure, although with increased disorder. On sapphire both the disappearing σ structure at low T and the emergence of the λ structure without threshold thickness can be rationalized based on the stronger effective interaction with the substrate, due to the stepped sapphire surface and slightly higher van der Waals interaction.

It is interesting to compare these results with the growth of DIP on a metal (Au), for which the adsorbate-substrate

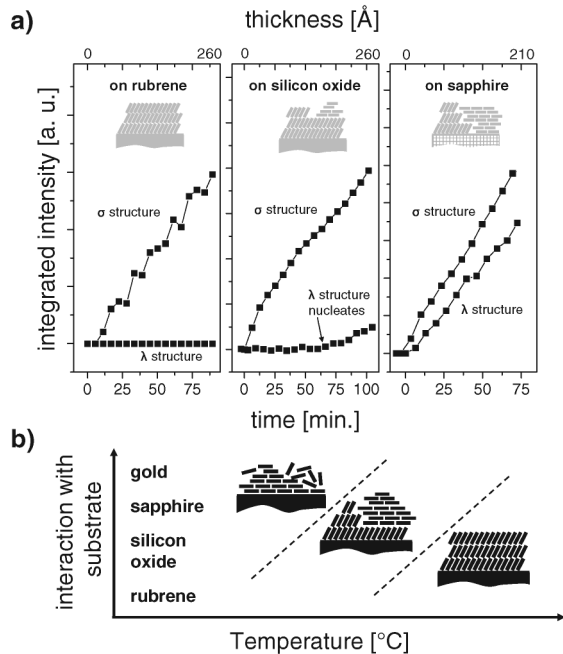


FIG. 4. (a) Evolution of the characteristic (100) λ and (11) σ reflections as a function of time (film thickness), for growth on rubrene (10 °C), silicon oxide, and stepped sapphire (both at 35 °C). Stronger interactions with the substrate promote earlier nucleation of the λ structure. (b) Schematic showing influence of substrate temperature and strength of interaction with substrate on the orientational transition from σ to λ structures.

interaction is still stronger, and where rather stable λ layers were observed in earlier work (post-growth) [11], consistent with our interpretation based on the strength of the substrate interaction having an impact on this transition. Growth data of DIP on a weakly interacting and smooth organic surface (rubrene) are consistent with this picture, as only the σ structure is observed even at intermediate temperatures, where DIP already forms λ structures on silicon oxide, sapphire, and gold.

The overall growth scenario is schematically summarized in Fig. 4(b). At high substrate temperatures we observe a σ structure only, apart from the structural changes during growth of the first MLs. Upon lowering T , i.e., for more kinetically limited growth, we find that the λ structure evolves on silicon oxide after a certain thickness. The growth on stepped sapphire follows a qualitatively similar scenario (both for the initial as well as for the later stage). We find, however, noticeable quantitative differences, namely, the stronger tendency on sapphire to grow lying down and therefore a higher temperature for pure σ growth. On the other hand, for DIP growth on the relatively weakly interacting surface of rubrene, we find pure σ growth for T down to at least 10 °C.

In conclusion, we have reported a real-time study of structural and orientational transitions during growth of

organic thin films. While the exact conditions such as temperature and thickness range depend, *inter alia*, on the specific substrate, we suggest that the occurrence of these transitions is a rather general phenomenon, and that similar transitions can occur, in principle, for other rodlike organic molecules [4]. For a coherent understanding of growth of organic thin films these transitions and their kinetics have to be incorporated into a theoretical description. This study is a step towards their experimental characterization in real time, including transient effects, which would be missed in post-growth measurements.

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