Molecular Reorganization in Organic Field-Effect Transistors and Its Effect on Two-Dimensional Charge Transport Pathways

Fabiola Liscio, Cristiano Albonetti, Katheina Broch, Arian Shehu, Santiago David Quiroga, Laura Ferlauto, Christian Frank, Stefan Kowarik, Roberto Nervo, Alexander Gerlach, Silvia Milita, and Fabio Biscarini

CNR—Istituto per la Microelettronica e Microsistemi (IMM), I-40129 Bologna, Italy, CNR—Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), I-40129 Bologna, Italy, Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, D-72076 Tübingen, Germany, Institut für Physik, Humboldt-Universität zu Berlin Newtonstrasse 15, D-12489 Berlin, Germany, and ESRF, 6 rue Jules Horowitz, BP 220 38043 Grenoble, France

**ABSTRACT**

Charge transport in organic thin film transistors takes place in the first few molecular layers in contact with the gate dielectric. Here we demonstrate that the charge transport pathways in these devices are extremely sensitive to the orientational defects of the first monolayers, which arise from specific growth conditions. Although these defects partially heal during the growth, they cause depletion of charge carriers in the first monolayer, and drive the current to flow in the monolayers above the first one. Moreover, the residual defects induce lower crystalline order and charge mobility. These results, which are not intuitively explained by electrostatics arguments, have been obtained by combining in situ real time structural and electrical characterization together with ex situ AFM measurements, on thin films of a relevant n-type organic semiconductor, \( N,N' \)-bis\((n\text{-octyl})\)-dicyanoperylene-3,4:9,10-bis dicarboximide grown by sublimation in a quasi-layer-by-layer mode at different substrate temperatures.

**KEYWORDS:** thin film growth · molecular organization · organic field-effect transistors · organic electronics · perylene derivatives

**S**ublimation of \( \pi \)-conjugated molecules in high vacuum is technologically important for growing active thin films in organic field-effect transistors (OFETs). In such devices the charge transport is confined within the first few monolayers grown on the gate dielectric, and it is two-dimensional (2D) in stacked molecular layers. The number of active molecular layers and the distribution of charge carriers across the stack may vary depending on the growth rate.

Molecular thin film growth is far more complex than atomistic growth described by classical growth modes. Organic semiconductor molecules have roto-vibrational degrees of freedom, anisotropic shape, and intermolecular interactions governed by dispersive forces. As high-vacuum sublimation is a nonequilibrium process, the energy barriers at the surface and in the film determine self-affine morphology with time- and space correlations.

The correlation between charge transport, molecular order, and morphology has been widely explored. A still open question concerns the nature of disorder generated during the early stages of growth, and how it affects charge transport in OFETs. Domain boundaries yield rapidly varying local electrostatic potential in the channel causing charge trapping and modulation of charge mobility by few orders of magnitude. Coexistence of islands of homeotropically oriented molecules and regions with a low-density layer of planar molecules was reported for sexithiophene, its occurrence being related to surface chemistry. The planar phase disappears in favor of the homeotropic orientation as growth proceeds. How these defects may affect OFET response is a matter of debate.

* Address correspondence to milita@bo.imm.cnr.it, f.biscarini@bo.ismn.cnr.it.

Received for review October 12, 2012 and accepted January 27, 2013.

Published online January 27, 2013 10.1021/nn304733w

© 2013 American Chemical Society
Here we focus on 3,4,9,10-bis(dicarboximide)-PDI8-CN2 molecule, which is an emerging n-type semiconductor with high charge mobility (0.16–0.6 cm² V⁻¹ s⁻¹) and high ambient stability in OFET operations.²²,²⁶,²⁷ PDI8-CN2 does not exhibit either polymorphism²⁸ or thin film phases,²⁹ and hence is suitable for studying the evolution of the molecular organization during the growth of the first monolayers (MLs) in an OFET. Films of PDI8-CN2 tens of nanometers thick deposited at high substrate temperatures, Tsub, exhibit enhanced crystallinity, morphology, and texturing, which yield an improved OFET response.²⁹

Here we demonstrate that structural differences exist in the first three MLs for low (25 °C) and high (120 °C) Tsub and that their evolution during growth determines which ML contributes most to the charge transport in the OFET. We have used a multitechnique approach including: in situ real time X-ray scattering techniques, which allow us to monitor the evolution of the surface morphology at the substrate surface from the early stages of growth,⁴,³⁰–³³ providing information on how MLs are filled and stacked; in situ real time electrical measurements which reveal the number of the active layers,⁷ quantitative ex situ AFM which gives us insights on the growth mechanism of the first MLs.

RESULTS AND DISCUSSION

The growth dynamics is inferred from the analysis of the oscillations of X-ray reflected intensity vs deposition time recorded at the anti-Bragg (AB) position δ_AB = π/δ where δ is the interlayer spacing. For PDI8-CN2 films, ex-situ X-ray diffraction (XRD) on thin films (thickness from 5 to 50 monolayers) reveals that molecules are oriented with their long axis almost normal to the surface (edge-on configuration), and δ ≈ 2 nm.²⁹

In a kinematic approximation the scattering intensity at the AB position reads

\[ I_{AB}(t) = |A_{sub}e^{i\phi} + A_{film} \sum_{n=1}^{t} \theta_n(t)e^{i\phi_n}|^2 \]  (1)

Here A_{sub} and A_{film} are the scattering amplitudes of the substrate and of the molecular monolayer, \( \phi \) is the relative phase between waves scattered from substrate and molecular adlayer, \( \theta_n \) is the molecular coverage of the nth monolayer (\( \theta_n = 0 \) for an empty layer, \( \theta_n = 1 \) for full layer). Equation 1 shows clearly that the contributions of odd and even layers have opposite sign, odd layers interfering destructively and even layers constructively (assuming \( \phi = 0 \)). At the completion of each \( \theta_n \) the intensity exhibits minima or maxima. The oscillation intensity is modulated by the evolution of \( \theta_n \) that we describe using the Trofimov model.³¹,³³–³⁷

We first plot the AB intensity vs the nominal thickness \( D \) which is directly read from the quartz microbalance.³⁸ From the fit \( D = T_{sub} \phi \) the molecular flux \( \phi \) can be extracted. Plotting the relevant observables vs \( D \) instead of the time \( t \) allows us to compare different deposition temperatures which might change the effective deposition rate. From the fit of the AB intensity vs \( D \) using the Trofimov model, we extract the evolution of the molecular coverages \( \theta_n \) which yields the total coverage \( \Theta = \sum_{1}^{n} \theta_n \). A calibration curve of the effective thickness, expressed as total coverage \( \Theta \) in MLs, vs \( D \) can be constructed.

Figure 1a shows the experimental AB oscillations (dots) normalized to the maximum intensity vs \( D \). The best fit (continuous lines), obtained with Supporting Information eqs 1 and 2 and the parameters reported in Supporting Information Table 1, result in a good agreement with the exception of the first peak. The fact that identical parameters have been obtained by the simultaneous fitting of the intensity oscillations recorded at different q\_f values validates the model adopted (Supporting Information, Figure S1).

In Figure 1b (top) we show the evolution of the \( \theta_n \) obtained from the best fit vs \( \Theta \). At both Tsub the sublinear trend of \( \theta_n \), just above zero or in the proximity of 1 indicates the slight deviation from the ideal layer-by-layer growth mode. At 120 °C the deviation
from the ideal layer-by-layer growth is observed already at the first monolayer and is even more pronounced at the second monolayer with respect to the curves at 25 °C. These differences can be well represented from the evolution of root-mean-square roughness, $\sigma_{\text{rms}}$, which has been determined from the fitting of the AB oscillations. The minima of the $\sigma_{\text{rms}}$ oscillations in Figure 1b (bottom) correspond to the completion of a ML and the maxima to half ML, as typical of layer-by-layer growth. The smaller amplitude oscillation at 120 °C (dotted line) indicates the more marked deviation from the ideal layer-by-layer growth. Above 3 MLs the oscillations are damped and $\sigma_{\text{rms}}$ scales almost linearly vs thickness with a larger slope for the higher $T_{\text{sub}}$.

In Figure 1c we plot the actual film thickness as a function of $D$. At 25 °C the growth of the first two MLs is $1.3 \pm 0.1$ times faster than that of following ones. The growth speed for upper layers matches, within the accuracy of the data, that at 120 °C which is constant during the deposition. The apparent acceleration of growth, reported also in thicker organic films, hints to a lower density of the first MLs deposited at 25 °C. For the sake of completeness, we mention that there could be a contribution from molecular desorption, more pronounced at 120 °C.

To test this hypothesis, we acquired AFM images of ultrathin films grown on thermal SiO$_2$/Si whose thickness was up to ~1 ML upon identical experimental conditions of the in situ experiments. The latter films were labeled by the amount of molecules that impinged on the quartz microbalance. Figure 2 shows the AFM images at 120 °C (a–d) and 25 °C (e–h).

A clear $T_{\text{sub}}$ dependence of the film morphology, as reported for thicker PDI8-CN2 films, is observed: elongated islands few micrometers long and grains a few nanometers diameter form at 120 °C and at 25 °C, respectively. To complete the first ML at 120 °C a larger amount of molecules ($3.8 \times 10^6$ molecules/μm$^2$) is required with respect to 25 °C ($3.1 \times 10^6$ molecules/μm$^2$). This is consistent with the apparent growth acceleration estimated at 25 °C by the in situ X-ray scattering analysis. The nucleation of the second ML occurs when $\theta_1 \approx 0.8$ ML at 120 °C (Figure 2d) and $\theta_1 \approx 0.95$ ML at 25 °C (Figure 2h), consistently with the marked deviation from layer-by-layer growth at high $T_{\text{sub}}$.

The analysis of the height distribution derived from the AFM images allows us to elucidate the evolution of the molecular arrangement of the first ML. At 120 °C (Figure 2i) two sharp peaks are observed: the first peak at 0.7 nm is contributed by the substrate and the peak at ~1.8 nm above is associated with the standing-up PDI8-CN2 molecules (edge-on) forming islands. When the first ML is complete, the integrated area of the first peak (substrate) decreases, whereas that of the second peak (first ML) increases. The thickest film exhibits a third peak at ~3.8 nm above the first one, which marks
the growth of the second ML where molecules exhibit the same orientation of the first monolayer.

The same trend is observed at 25 °C (Figure 2l) but the broadening of the first peak at 0.9 nm indicates an increased substrate roughness. This can be ascribed to a spatially inhomogeneous distribution of molecular mounds formed by face-on or bent/distorted edge-on molecules. By associating the second peak with the edge-on molecules forming islands, the separation between the two peaks (∼1.1 nm) is smaller than that observed at 120 °C. It can be explained by the presence of these inhomogeneous molecular mounds between islands. The coexistence of flat-lying molecules on the substrate was reported earlier for sexithienyl.24,39

Figure 3a,b show high-resolution AFM images, recorded with amplitude modulation mode in attractive regime,40 of a region between islands of standing molecules in submonolayer films grown with a low nominal molecular density (0.5 × 10⁶ and 0.7 × 10⁶ molecules/μm² at 25 and 120 °C respectively). The topography at 25 °C (Figure 3a) is inhomogeneous due to the presence of aggregates thinner than 2 nm; they contribute several peaks to the histogram in Figure 3c, the main peak centered at ∼0.9 nm, that is, ∼0.5 nm above the bare substrate. This value is consistent with molecules lying flat on the substrate. The shoulder to the larger height side of the main peak confirms the coexistence of several configurations of the molecules lying on the substrate. Conversely, the topography at 120 °C (Figure 3b) is flat and its height distribution exhibits only the symmetrical peak ascribed to the bare substrate roughness (∼0.4 nm).

To follow the progressive molecular arrangement we have assessed the topography from AFM images (Figure 4) of thicker films (~2MLs) obtained by depositing ~6 × 10⁶ (a,e) and ~7 × 10⁶ molecules/μm² (b,f) at the two T_sub.

At low T_sub upon an increase of nominal density by 1.1 × 10⁶ molecules/μm², the morphology of the films appears unchanged (Figure 4a,b). However, the height distribution (Figure 4c) reveals the coexistence of two populations with different molecular orientation in the second ML: the weaker peak, 0.8 nm above the first ML, is related to the minority population of tilted/bent molecules; the stronger, ∼1.8 nm above the first ML, to the majority population. By increasing the thickness, the weaker peak disappears in favor of the stronger one indicating a rearrangement of the tilted/bent molecules of the second ML into a more stable configuration withstanding molecules. A similar phenomenon is
observed also for the molecules on the third ML, the height of which shifts from 2.7 nm (at $6.2 \times 10^6$ molecules/\(\mu\)m\(^2\)) to 3.7 nm (at $7.3 \times 10^6$ molecules/\(\mu\)m\(^2\)) above the first ML. The X-ray reflectivity (XRR) curves of the two samples are surprisingly similar (Figure 4d); their analysis\(^{41}\) evidences the same film thickness ($4.4 \pm 0.1$ nm, corresponding to $\sim$2MLs of molecules in edge-on configuration) and roughness ($0.4 \pm 0.1$ nm) with only a slight difference of mass density ($1.02 \pm 0.02$ g/cm\(^3\) for $6.2 \times 10^6$ molecules/\(\mu\)m\(^2\) and $1.13 \pm 0.02$ g/cm\(^3\) for $7.3 \times 10^6$ molecules/\(\mu\)m\(^2\)). The thickness value corresponds to the most intense peak in the height distribution in Figure 4c, which indicates that the majority of the molecules of the second ML stand up. The increased density of the thicker film is consistent with a closer packed molecular configuration. For the sake of clarity, we proved that XRR curves cannot be fitted by the same mass density, even releasing the other parameters (Supporting Information, Figure S12).

The evolution of the films deposited at 120 °C (Figure 4e,f) can be explained by the completion of the second ML followed by nucleation and growth of the third one. The height distributions (Figure 4g) indicate that the molecules of the second ML evolve only slightly to reach a more stable configuration. The analysis of XRR curves (Figure 4h) indicates a roughness decreasing due to the completion of the second ML.

Interestingly, the mass density of the film $\sim$2MLs thick ($\sim 6 \times 10^6$ molecules/\(\mu\)m\(^2\)) at 25 °C ($1.02$ g/cm\(^3\)) is lower than that at 120 °C ($1.49 \pm 0.02$ g/cm\(^3\)) (see Supporting Information, Figure S13). This confirms that, although at both $T_{\text{sub}}$ the crystallites are formed by PDI8-CN2 molecules standing up on the substrate, at 25 °C the molecular packing, averaged over the first two MLs, is less dense than that at 120 °C. The difference in mass density at the two $T_{\text{sub}}$ disappears when the film thickness is greater than 3MLs, as reported in Supporting Information, Figure S14. This confirms the fact that the molecular orientation/configuration differs for the two $T_{\text{sub}}$ just in the first MLs closer to the substrate. This has substantial consequences on the charge transport in a field-effect transistor when an ultrathin film is deposited, as discussed later. Although molecular reorganization takes place during the growth at 25 °C, in thicker films a crystalline order lower than the film grown at 120 °C is evidenced by XRD measurements (see Supporting Information, Figure S15a,b).

The presence of the edge-on/bent molecules at 25 °C demonstrates the lower layer density inferred upon fitting the AB oscillations. Density variation modifies the scattering amplitude of the first MLs, which instead is kept fixed in the Trotimov model. This approximation could justify why the shoulder appearing in the first oscillation around 2MLs of nominal thickness is not well reproduced. The maximum of the AB oscillation at around 1.6 MLs of nominal thickness could correspond to the complete coverage of the second monolayer with the coexistence of different molecular configuration; the shoulder at 2 ML of nominal thickness could correspond to the second completion of the second monolayer, where most of defects heal before the nucleation of the third monolayer.

The emerging scenario is schematically depicted in Figure 5. At 25 °C stable and metastable configurations coexist at the early stages of growth, then metastable molecular domains reorganize within each monolayer as the growth proceeds, increasing the size of stable crystalline phase domains. The coexistence of domains with different molecular configuration in the first monolayers at 25 °C represents a defect that dynamically heals, albeit not completely. At 120 °C the film grows in the more stable crystalline phase\(^{29}\) from the early stages, with only a slight rearrangement of edge-on molecules.

We assess the impact of the presence of these dynamic defects on the charge distribution and the transport properties of a field effect transistor by monitoring in situ and in real time the evolution of the charge mobility $\mu$ during the growth. The trends of $\mu$ vs thickness extracted in the linear regime from the transfer characteristics are shown in Figure 6a,d. The values $\mu_{\text{sat}}$ in the saturation regime are shown in
CONCLUSIONS

We have demonstrated that PDI8-CN2, grown in a quasi-layer-by-layer mode at two different substrate temperatures, exhibits a marked difference in molecular organization, crystal order, and density, which also reflects in the distribution of charge carriers in a transistor. We have elucidated the nature of orientational defects at 25 °C, consisting of coexisting domains with either standing molecules or planar/tilted/bent molecules in the first PDI8-CN2 monolayers at the gate dielectric interface in working devices. Although these defects tend to heal dynamically, their formation at the early stages has an impact on the charge transport
properties of the device: they are the cause of depletion of charge carriers in the first monolayer, leading to the second monolayer being dominant in charge transport. This suggests that the defects effectively behave as shallow traps for electrons.

Conversely, at 120 °C the trend of charge mobility vs thickness is consistent with ideal 2D charge transport, where electron percolation occurs within each monolayer and no substantial charge transfer between adjacent monolayers occurs. In this case most of the charge carrier density is in the first monolayer. This highlights the complexity of the growth phenomena and their subtle effects on the device response, and how their control is technologically challenging.

EXPERIMENTAL METHODS

Materials. PD18-CN2 molecules were used as received from BASF.

In Situ and Real Time Measurements. Structural and electrical characterizations have been performed in situ and in real time during HV deposition of PD18-CN2 thin film on bare SiO2/Si wafers and on FET test patterns, respectively. The molecular flux Φ has been chosen to 0.1 ML/min, where 1 ML, defined by the deposition rate R, is approximately equal to 2 nm. This low flux minimizes the variation of the thin-film thickness between the beginning and the end of each characterization measurement and it enables real time investigations to be performed continuously, without interrupting the deposition. Depositions at low (25 °C) and high (120 °C) Tsub have been compared.

X-ray scattered intensities have been recorded in specular configuration at anti-Bragg (AB) position qAB in an in-house developed HV chamber (baseline pressure P = 10−8 mbar) designed to be compatible with in situ X-ray measurements. The chamber was installed on the 6-circle diffractometer at beamline ID10B at the ESRF (Grenoble-France). The X-ray energy was 13.45 keV and the maximum counting time was 120 s; at least 10 points have been recorded for each ML.

After each deposition 2D-GID images were collected using an incident angle of the X-ray beam, αs, close to the critical angle for total reflection of the organic film (i.e., 0.13°). The diffraction patterns were recorded by an in-plane scan of a linear detector oriented normal to the incident beam direction and equipped with soller slits (Δαs = 0.08°).

The test patterns (Fondazione Bruno Kessler, Trento, Italy) used for the electrical studies have channel lengths of 20 and 40 μm, and a width of 11200 and 22400 μm, respectively. Drain and source Au (150 nm)/Cr (3 nm) electrodes are lithographically defined by two vertical slits before a linear detector rotating in 0.13° steps up to 360° (that is, source Au/Cr/C0 and drain Au/Cr/C176) and equipped with soller slits (Δαs = 0.08°).

The boundary between the electrode and the channel.40,41 The transfer characteristic, that is, source–drain current, IDS vs gate voltage, VDS, has been measured in linear and saturation regimes (with VOSS = 5 V and VSS = 30 V, respectively) sweeping VDS continuously between -50 V and -30 V (forward and backward sweep) with a 1 V step. For each VDS value IDS has been measured with an integration time of 20 ms, corresponding to 1.6 s to record a complete transfer curve.

For each Tsub four devices have been measured, two in the linear and two in the saturation regime.

Ex Situ Measurements. A series of ultrathin films (from 0.5 to 3 ML) deposited on SiO2/Si, exactly in the same conditions reported above, have been characterized after deposition. The morphology has been studied by collecting AFM images in air in semicontact mode using a Sema NT-MDT microscope equipped with NGS10 cantilevers. The film thickness has been reported as the function of the amount of molecules deposited on the quartz microbalance.

Structural characterization by X-ray reflectivity measurements has been performed with a SmartLab-Rigaku diffractometer equipped with a rotating anode (Cu Kα, λ = 0.154 nm), followed by a parabolic mirror to collimate the incident beam, and a series of variable slits (placed before and after the sample position). XRD data in out-of-plane specular geometry have been recorded for selected thick films at beamline ID10B at the ESRF (Grenoble-France), with the X-ray energy fixed at 13.45 keV and defined by two vertical slits before a linear detector rotating around the normal axis of the film surface.

REFERENCES AND NOTES


