High structural order in thin films of the organic semiconductor diindenoperylene

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We report extraordinary structural order along the surface normal in thin films of the organic semiconductor diindenoperylene (DIP) deposited on silicon–dioxide surfaces. Cross-sectional transmission electron microscopy (TEM), noncontact atomic force microscopy (NC–AFM), as well as specular and diffuse x-ray scattering measurements were performed to characterize thin films of DIP. Individual monolayers of essentially upright-standing DIP molecules could be observed in the TEM images indicative of high structural order. NC–AFM images showed large terraces with monomolecular steps of $\approx 16.5$ Å height. Specular DIP Bragg reflections up to high order with Laue oscillations confirmed the high structural order. A semi-kinematic fit to the data allowed a precise determination of the oscillatory DIP electron density $\rho_{\text{el},\text{DIP}}(z)$. The mosaicity of the DIP thin films was obtained to be smaller than 0.01°.

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Presently, organic semiconductors are receiving great attention due to their potential for cost-effective electronics and optoelectronics and due to the possibility to tailor the desired properties by chemically changing functional groups of a given molecule. Several devices including organic field effect transistors (OFETs), organic light emitting diodes, and organic solar cells have been demonstrated in the last few years. It has also been shown that the relevant physical parameters (e.g., charge carrier mobility) depend crucially on the structural order within the organic semiconductor. 1–5 For commercial applications, devices based on organic single crystals are not practical, rather, organic thin film devices are more likely to be used. Thus, it is necessary to find compounds which intrinsically exhibit the desired electronic properties and, at the same time, show high structural order in thin films. In this letter we report extraordinarily high structural order in thin films of the organic semiconductor diindenol[1,2,3-c.d.1’,2’,3’-l-m]perylen [C32H16 (DIP), Fig. 1(a)] on silicon–dioxide surfaces which, for example, can be used in OFETs as a gate insulator. Cross-sectional transmission electron microscopy (TEM), noncontact atomic-force microscopy (NC–AFM), and x-ray scattering were performed to highlight different aspects of the structural order.

DIP was purchased from Aldrich and purified by temperature gradient sublimation. All samples were prepared on oxidized (4000 Å) Si(100) substrates. DIP layers with varying thickness $70 \lesssim D_{\text{DIP}} \lesssim 1100$ Å were grown at a substrate temperature of $T = 145 \pm 5$ °C and at a rate of 12 $\pm 3$ Å/min under UHV conditions ($p \approx 2 \times 10^{-9}$ mbar during deposition). NC–AFM measurements were performed immediately after deposition in an UHV analysis chamber attached to the molecular beam epitaxy chamber ($p \approx 2 \times 10^{-11}$ mbar) without breaking the vacuum. TEM micrographs were taken by a JEOL FX4000 and a Philips CM200 microscope, at 400 and 200 kV, respectively. X-ray measurements were carried out at beamline ID10B at the ESRF in Grenoble, France, with a wavelength of $\lambda = 1.563(2)$ Å.

Figure 1(b) shows a cross-sectional TEM micrograph of a typical DIP layer. The image displays a closed film with homogeneous thickness, i.e., no island formation is observed. Remarkably, individual monolayers (ML) of the essentially upright standing DIP molecules (lattice constant $d_{\text{DIP}} = 16.5$ Å) can clearly be distinguished as pairs with dark-bright contrast. This implies a high degree of structural order otherwise the monolayer contrast would be smeared out.

In Fig. 2 the surface topology of a DIP film is displayed as probed by NC–AFM. The image shows a closed DIP film...
with large planar terraces extended to several 100 nm which are separated from each other by monomolecular steps of \(16.5 \text{ Å}\). These steps are particularly well seen at the left-hand side of the profile line, which follows the black solid line in Fig. 2. The surface roughness of this film is \(\sigma = 28 \pm 3 \text{ Å}\) which corresponds to less than 2 MLs of DIP.

In order to quantitatively determine the spatial coherence of the crystalline order, high-resolution x-ray diffraction measurements were performed. In the so-called “specular diffraction mode” the momentum transfer is perpendicular to the surface normal \(z\), i.e., \(\mathbf{q} = (0,0,q_z)\), see sketch in Figs. 3(a) and 3(b)], thus probing the electron density profile along the surface normal, \(\rho_\text{el}(z)\).

Figure 3(a) displays a typical scan along the specular rod for a DIP thin film \(D_{\text{DIP}} = 206 \text{ Å}\) prepared under the conditions described before. For all samples, Bragg reflections associated with the DIP film at least up to the seventh order are visible from which a lattice constant of \(d_{\text{DIP}} = 16.60 \pm 0.05 \text{ Å}\) is derived. The large number of Bragg reflections is evidence for high structural order in the DIP-films.

Figure 3(b) shows a zoom into the small-\(q_z\) region of Fig. 3(a). The periodicity of interference fringes (“Kiessig fringes”) for \(q_z \leq 0.25 \text{ Å}^{-1}\), \(\Delta q_z,K\), is associated with the film thickness via \(D_{\text{DIP}} = 2\pi/\Delta q_z,K\). The almost undamped oscillations (“Laue oscillations”) around the Bragg reflections [Figs. 3(a) and 3(b)] are evidence for a laterally homogeneous coherent thickness, i.e., a well-defined number of
ordered monolayers. Their periodicity, $\Delta q_{z,l}$, is associated with the coherent thickness of the film via $D_{coh} = 2\pi/\Delta q_{z,l}$. For all inspected films, Kiessig fringes and Laue oscillations exhibit the same periodicity, which confirms the TEM observation that the DIP films are coherently ordered across their entire thickness ($D_{DIP} = D_{coh}$) quantitatively.

Within a semi-kinematic formalism the specularly scattered intensity reads \(^{8}\)

$$I(q_z) = I_0 G(q_z) R_F(q_z) \left| \frac{1}{\rho_{el,\infty}} \int_{-\infty}^{\infty} \frac{d\rho_{el}(z)}{dz} e^{iq_zz}dz \right|^2,$$

where $I_0$ is a normalization constant, $R_F(q_z)$ is the Fresnel-reflectivity of the substrate, $G(q_z)$ is a correction term accounting for geometrical effects and $d\rho_{el}(z)/dz$ is the derivative of the electron density of the sample with respect to $z$.

To model the electron density of the DIP in the thin film, $\rho_{el,DIP}(z)$, one can use the fact that each Bragg reflection corresponds to one Fourier component in the electron density. Thus, the DIP-electron density reads

$$\rho_{el,DIP}(z) = \rho_0 + \sum_{n=1}^{M} A_n \cos \left( n \frac{2\pi}{d_{DIP}} z + \phi_n \right),$$

where $M$ is the number of observed Bragg reflections, $A_n$ is the Fourier amplitude associated with the intensity of the $n$th DIP Bragg reflection, $d_{DIP}$ is the lattice constant of the DIP net planes (associated with the position of the set of Bragg reflections), and $\phi_n$ is the Fourier-phase of the $n$th Bragg reflection which actually reduces to $\pi$ or $2\pi$ due to the mirror-plane symmetry of the molecules in the present case. Using Eq. (1) with Eq. (2) as parameterization of the DIP electron density allows a fit of the complete specular rod with only few parameters (if the substrate-film and film-vacuum interfaces are properly taken into account). Based on the large number of Bragg reflections, the shape of the oscillatory DIP-electron density along the sample normal is obtained with high precision. Moreover, the electron density is obtained in absolute values since the fit includes the total reflectivity edge and thus provides a normalization value.

The inset of Fig. 3(a) shows a close-up of $\rho_{el}(z)$ for approximately 2 MLs of DIP as obtained by the fit. One can see that the DIP electron density exhibits pronounced oscillations around a mean value of $\rho_{el,0}^d = 0.367 \text{ e}/\text{Å}^3$ along 1 ML. The electron density in the DIP film along the $z$ axis exhibits a contrast between the highest and lowest value, $\rho_{DIP}^{max}/\rho_{DIP}^{min}$, of 1.79.

Rocking scans at a constant scattering angle of $2\theta$ at the position of Bragg reflections with varying angle of incidence, $\alpha_i$, probe the angular distribution of the lattice planes, i.e., the mosaicity [full width at half maximum (FWHM) of the rocking curve, $\Delta\alpha$]. For all inspected DIP films we found mosaicsities smaller than $0.014^\circ$ which is unusually small for thin films of organic semiconductors and which was found to be in the order of the substrate curvature. The best value was as small as $\Delta\alpha = 0.0087^\circ \pm 0.0003^\circ$ [for $D_{DIP} = 206$ Å, see inset of Fig. 3(b)]. Recently, it has been demonstrated that semiconductor transport properties in thin films such as the charge carrier mobility can depend strongly on the mosaicity of the film.\(^7\)\(^9\) This is thought to be a consequence of the electron transport mechanism in organic semiconductors. The mobility is limited by the slowest transport process in a given film which is a multiple-shallow trapping controlled “hopping transport” at grain boundaries as opposed to trap-free band-like transport in pure single crystalline grains where the $\pi$ orbitals of the molecules overlap efficiently.

In conclusion, we have shown in this letter that thin films of DIP deposited under suitable conditions (rate: $12 \pm 3$ Å/min, substrate temperature: $T = 145^{\circ} \pm 5^{\circ}$ C) on oxidized silicon wafers exhibit an outstanding crystalline order along the surface normal with the DIP molecules essentially standing upright and their $\pi$ orbitals overlapping parallel to the sample surface. In addition, these films are coherently ordered across their entire thickness. Because of these properties DIP is thought to be a prospective candidate for applications in electronic devices where high charge carrier mobility parallel to the substrate is desired (e.g., in OFETs). Moreover, the surface topology of DIP films shows large terraces (with lateral extensions up to several 100 nm) separated by monomolecular steps. Thus, the surface is well-defined and ideally suited as a template for metal deposition to study the interfacial morphology of metalorganic heterostructures.\(^6\)

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