Heteroepitaxy of Organic–Organic Nanostructures

Georg Koller,* Stephen Berkebile, Joachim R. Krenn, Falko P. Netzer, Martin Oehzelt, Thomas Haber, Roland Resel, and Michael G. Ramsey

Institute of Physics, Karl-Franzens-University, Universitaetsplazt 5, A-8010 Graz, Austria, and Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

Received March 21, 2006; Revised Manuscript Received May 8, 2006

ABSTRACT

Highly crystalline organic heteroepitaxial layers with controlled molecular orientations and morphologies are one of the keys for optimum organic device performance. With studies of molecular orientation, structure, and morphology, we have investigated the ability of oriented organic films to act as substrate templates for the growth of a second organic layer. Depending on the molecular orientation in the sexiphenyl substrate, crystalline sexithiophene nanostructures of either pyramidal or needlelike morphology, with either near vertical or parallel molecular orientations, respectively, grow.

The potential of organic semiconductors as active materials in devices such as organic light-emitting devices (OLEDs), organic field-effect transistors (OFETs), photovoltaic cells, and sensors has attracted basic scientific as well as technological interest.1,2 These devices often consist of a multiplicity of organic layers, thus making the understanding of the organic interface and organic-on-organic growth a scientifically and technologically important issue. On one hand details of the interfaces are important for charge injection, while on the other hand the film’s morphology and crystallinity together with the molecular/crystallite orientation determine charge transport and light emission/absorption characteristics. To optimize device performance, one must control these key factors because specific devices such as OLEDs, OFETs, and photovoltaic cells have different requirements. The understanding and tailoring of organic heterostructures is the challenge that needs to be met if organic devices are to achieve their technological potential.

Until now, most controlled studies of organic interfaces have concentrated on the organic/inorganic interface, with few investigations of organic heterostructures being available. The bulk of the latter deals with the electronic band alignment at the organic/inorganic interface,3–5 while few investigations of the geometric structure and morphology have been performed.6,7 A possible reason for this deficiency in controlled structural studies of molecular heterostructures is the difficulty in producing uniform crystalline organic substrates with different well-defined molecular orientations, which are a necessary prerequisite for such investigations.

Here we report the growth of epitaxial thin films of alphathexithiophene (α-6T: S_6C_2H_14) on crystalline surfaces of para-sexiphenyl (p-6P: C_36H_24). Sexithiophene and sexiphenyl are not only good model materials for controlled studies but they are also in themselves technologically relevant. α-6T was the active material in the first thin-film OFET with useful characteristics,8 while p-6P was the bases for the first blue light-emitting OLED, and both are currently investigated as constituents for photovoltaic applications.9–13 In these molecular solids, charge transport is effectively perpendicular to the molecular axes while visible light emission/absorption is polarized parallel to the molecular axis. Consequently, for electrooptical devices molecules oriented parallel to the contact would be desired while for OFETs molecules with perpendicular or edge-on orientations relative to the gate dielectric would be ideal. We have thus produced crystalline p-6P films where the molecules are either exclusively parallel or near perpendicular to the inorganic supports.14–16 These p-6P(20–3) and (001) crystalline films are then used as substrates for the p-6P/α-6T heterostructures. Here the geometric structure and morphology of these α-6T/p-6P heterostructures obtained from near-edge X-ray absorption fine structure spectroscopy (NEXAFS), X-ray diffraction (XRD), and atomic force microscopy (AFM) studies are reported. The results show that these highly crystalline-oriented p-6P films act as molecular templates for the growth of α-sexithiophene films. Not only does the orientation of the molecules in the first organic film determine the
orientation in the heterolayer but this second film is also crystalline with a well-defined epitaxial relationship.

The upright (001)-oriented sexiphenyl substrate film was grown by depositing 80 Å p-6P on an oxidized Al(111) surface at room temperature. The growth mode of this system is Stranski–Krastanov, with a wetting monolayer of standing molecules being formed at ~30 Å coverage. High-resolution C1s-NEXAFS spectra have been recorded to confirm the molecular orientation within this p-6P substrate film. In the p-6P NEXAFS spectra (Figure 1a), the C1s → π* resonance is strongest in normal incidence (θ = 0°) but rather weak at grazing incidence (θ = 80°), indicative of upright molecules. To determine the molecular tilt angle, in Figure 1a we show the calculated intensity ratio plots I(θ = 0°)/I(θ) as a function of π*-orbital vector tilt angle (α) and for various X-ray incidence angles (θ) together with the experimentally determined C1s → π* transition ratios. The resulting tilt angle of the molecular planes of α = 77° ± 5° with respect to the surface plane, indicated by the dashed line, is compatible with a p-6P(001)-oriented film of the given crystal structure of p-6P, which would yield a tilt angle of 73°. Such an orientation represents the thermodynamic equilibrium state and is prevalent in films grown on weakly interacting and disordered substrates. α-6T was then deposited on this p-6P substrate in a stepwise fashion while monitoring both the C1s and S2p XPS and NEXAFS signals. The surface-sensitive spectroscopies show the α-6T signals becoming dominant for coverages >1.5 nm, suggesting the growth of an upright first layer of α-6T on p-6P. After depositing 165 Å of α-6T the spectral fingerprint is pure α-6T, but the polarization behavior of the NEXAFS spectra, as shown in Figure 1b, remains; that is, C1s → π* orbital transitions are a maximum for normal incidence and are very weak at glancing incidence. The molecular tilt angle was determined to be 75° ± 5°, which is markedly larger than one expects for the low surface energy α-6T(001) of 66°. This angle is, however, very close to the tilt angle of the p-6P(001) substrate film (73°), which suggests that the on top deposited α-6T molecules have adopted the orientation of the p-6P substrate.

The morphology of this 165 Å α-6T/80 Å p-6P organic heterostructure is displayed in the ex situ AFM images of Figure 2a–c and the structural model of Figure 2d. As shown in Figure 2a, the surface primarily consists of angular-shaped stepped pyramidal islands with a base width of typically several hundred nanometers and an average height of 20 nm. These pyramidal structures, shown in the higher magnification image of Figure 2b, have step heights of typically around 2.8 ± 0.3 nm and 2.2 ± 0.3 nm, as indicated by the line scan of Figure 2c. These values are in good agreement with expected step heights for (001)-oriented p-6P (2.6 nm) and α-6T (2.2 nm), respectively. It should be noted that these interlayer spacings are slightly smaller than the molecular lengths because of the tilt angle of the molecules in their crystalline structure (Figure 2d). The statistical analysis performed on the angles observed between the terrace edges of the pyramids (indicated in Figure 2a) yields values of 106° ± 5°, 114° ± 5°, 128° ± 5°, and 70 ± 10°, with angles greater than 100° being more frequent. Such values are expected between close-packed facets of 6P(001) and 6T-(001)-oriented crystallites and are thus clear indications of the crystallinity of these pyramids.

Although this is a good example of a well-defined crystalline organic heterostructure, the observed crystalline (001) orientation is the thermodynamic equilibrium structure one commonly obtains in organic film growth on dirty or disordered inorganic substrates. The real challenge that is significant for the future development of organic devices is growing films with controllable molecular orientations. We have developed strategies for growing crystalline p-6P films with the molecules parallel to inorganic substrates, for example, (21–3) or (20–3) oriented p-6P on Al(111), TiO$_2$-
For this study, we have used the p-6P(20−3) substrate grown on TiO$_2$ (110) at RT because it is the most highly defined, where all of the molecules are not only parallel to the substrate but they are also uniaxial. A typical AFM image of such a p-6P substrate is shown in Figure 3a. The long axis of the crystallites and the molecular axes are oriented parallel to the [1−10] and [001] azimuths of the TiO$_2$ surface, respectively. The deposition of sexithiophene on such a surface leads to a morphology that is completely different from the one observed for sexithiophene on upright p-6P. The AFM image of Figure 3b shows the morphology of a 40-nm-thick R-6T film on 40-nm-thick p-6P-(20−3). The surface appears highly anisotropic with worm-like structures following the general direction of the underlying sexiphenyl crystallites. The higher magnification image in of Figure 3c shows that typical dimensions of these R-6T structures are up to a few micrometers in length and 80 (10 nm in width. As well as being thinner in general, the R-6T structures are less regular than the underlying p-6P crystals. On close inspection, the elongated structures are seen to be segmented and often have a zigzag shape.

The sample of Figure 3 was grown in a stepwise fashion monitoring the core-level spectroscopies. Figure 4a shows NEXAFS spectra of the 400-Å-thick p-6P substrate for normal and grazing (80°) incidence with the X-ray polarization being parallel to the [001] and [1−10] surface azimuths of the inorganic TiO$_2$(110) support. The C1s → π* resonance displays little intensity variation with increasing incidence angle in the [1−10] azimuth, while in the [001] azimuth the intensity of the π* transition increases with the angle of incidence. For N. I. in [001] it is all but invisible, whereas in [1−10] it is quite distinct, indicating the uniaxial orientation of the molecules parallel to the TiO$_2$ [001] direction. Measurements of the π* intensity as a function of incidence angle Θ imply that the molecular planes are tilted by α = 36° ± 5° with respect to the TiO$_2$ surface plane as indicated by the dashed line in Figure 4a, which is in agreement with the p-6P(20−3) crystallite orientation determined via XRD (see below). Stepwise deposition of α-6T was followed with photoemission and X-ray adsorption spectroscopies. The C$_{K\pi}$-NEXAFS results for 40 nm of α-6T onto this surface are displayed in Figure 4b. In general, the X-ray polarization dependence of the α-6T NEXAFS is the same as that for the p-6P substrate, indicating that the α-6T molecular axis is aligned parallel to the p-6P molecules. The tilt angle α of the α-6T molecular plane of 33° ± 5° with respect to the TiO$_2$ surface plane is slightly smaller than that of 6P, which is in good agreement with the XRD results discussed below. It should be noted that the α-6T molecules were seen to remain parallel to the p-6P molecules from exposures equivalent to a lying monolayer (0.3 nm) up to 100 monolayer thickness. This is of particular significance given that the p-6P substrate film was exposed to air prior to the adsorption of the α-6T layer and orientational changes with thickness have often been reported for organic growth on less-defined or inorganic substrates. Both laboratory source XRD and high-resolution synchrotron GI-XRD measurements have been performed on this sample, and the results showing Θ/2Θ scans and XRD pole figures are summarized in Figure 5. The Θ/2Θ scan of Figure
5a shows only two peaks at 22.5° and 23°, which can be attributed to diffraction planes of the β-phase p-6P(20−3) orientation and the so-called low-temperature phase of α-6T(020), respectively. The latter implies that both the p-6P and α-6T molecules are all oriented with their axis parallel to the substrate and a tilt angle of the molecular planes of 33° (R-6T) and 35° (p-6P), respectively. Significantly, no diffraction intensity at around 4°, which would be indicative of standing sexithiophene molecules (α-6T-(001) orientation), is observed. A high-resolution specular

Figure 3. (a) AFM image of 40 nm p-6P on TiO₂ and (b) the heterostructure of 40 nm α-6T (a). The inset of a shows the molecular orientation within the p-6P substrate, which is also indicated in b. (c) A higher magnification AFM image of the heterostructure expressing the internal structure of the α-6T overlayer.

Figure 4. Calculated intensity ratio plots $I(\Theta = 0°)/I(\Theta)$ as a function of $\pi^*$-orbital vector tilt angle, for various X-ray incidence angles and assuming twofold substrate symmetry, together with the experimentally determined C1s → $\pi^*$ transition ratios for an (a) 40-nm-thick p-6P film on TiO₂ and (b) after deposition of 40 nm α-6T. The dashed lines indicate the concluded tilt angle of the respective molecular planes. The corresponding NEXAFS spectra for normal and gracing incidence and in the [001] and [110] azimuths of the inorganic TiO₂ support are shown as insets.
scan of this film, performed at the ID 10B beamline of the ESRF using a photon energy of 11 keV and shown in the inset of Figure 5a, allows a clear separation and identification of the $R$-6T and $p$-6P diffraction peaks: the measured values of $16.46^\circ$ and $16.8^\circ$ are in excellent agreement with the values calculated for the known bulk structures of $16.476^\circ$ for the $R$-6T(020) and $16.807^\circ$ for the $p$-6P(20$^{-}$3) diffraction peaks, respectively. Rocking widths of the $p$-6P (20$^{-}$3) and $R$-6T (020) peaks measured in the directions parallel and perpendicular to the long axes of the crystallite structures are highly anisotropic: in the direction parallel to the long crystallite axis, the rocking widths are very narrow for organic films (1.31$^\circ$ for 6P and 1.41$^\circ$ for 6T) and comparable to rocking widths of metal single crystals (e.g., 0.5$^\circ$ for a Cu (110) crystal), whereas in the direction perpendicular to the crystallite axis the rocking widths of 2.29$^\circ$ for 6P and 4.87$^\circ$ for 6T are considerably larger. This indicates that the mosaicity along the direction of strong molecule–molecule interaction is considerably smaller than that in the direction across the cleavage plane (model in Figure 6a). It is suggested that this is caused by substrate surface roughness (p-6P(20$^{-}$3)), which is more readily accommodated across the crystal cleavage planes, leading to the high mosaicity (of the $\alpha$-6T crystallites) in this direction.

The epitaxial relationship between sexithiophene, sexiphenyl, and the inorganic support TiO$_2$ has been determined by a pole figure measurement around the TiO$_2$ (110) surface plane (Figure 5b). In the magnified quadrant of the polar scan, we find strong peaks symmetrically around the TiO$_2$ [−110] direction, which can be attributed to the $p$-6P(20$^{-}$3) substrate, and two weaker peaks, which can be assigned to a $\alpha$-6T(010)-oriented film. This again confirms that the $p$-6P(20$^{-}$3) and $\alpha$-6T(010) crystal planes are parallel with respect to each other; and, moreover, it implies that the sexithiophene and sexiphenyl molecules are uniaxial throughout the whole heterostructure. As shown in the model of Figure 6a, this crystal orientation leads to two symmetry-equivalent domains of $\alpha$-6T (010) on p-6P(20$^{-}$3), which explains the zigzag shape of the crystallites we observed in the AFM images. The intermolecular spacing of the p-6P and $\alpha$-6T molecules, indicated in Figure 6b, is with 5.57 and 5.52 Å very similar (mismatch < 1%). However, the lattice mismatch between the p-6P(20$^{-}$3) and $\alpha$-6T(010) unit cells (Figure 6a) is around 6% for all of the molecules being.
parallel to each other. High-resolution synchrotron diffraction experiments determined the angle between the \( \alpha\)-6T and p-6P unit cells to be 22.5°, implying that the axes of the sexithiophene molecules are rotated by 1° relative to sexiphenyl. This is interesting because this very small \( \alpha\)-6T to p-6P misalignment also leads to a better lattice match (mismatch \( \sim \)2%) in the p-6P(010) direction than if the \( \alpha\)-6T molecules were perfectly parallel to the p-6P molecules and suggests that lattice match may be an issue even for weakly interacting organic heterostructures.

Here we have contrasted two distinctly different crystalline surfaces of sexiphenyl, the near-upright p-6P(001) and the interacting organic heterostructures. This suggests that lattice match may be an issue even for weakly interacting organic heterostructures.

Films of purely lying molecules are difficult to grow on inorganic substrates because defects or contaminated regions lead to the thermodynamically most stable phase with upright molecules. The result of lying \( \alpha\)-6T on p-6P substrates is thus particularly significant because it shows that the organic substrate does not require the stringent UHV conditions necessary for inorganic templates. We therefore conclude that organic substrates are good templates for the self-assembly of orientationally controlled organic heterostructures. This ability to grow crystalline organic heterostructures with different molecular orientations will be very important for the future of organic electronic devices because the molecular orientation within the active organic film is one of the key issues for optimum device performance.

Acknowledgment. This work was supported by the Austrian Science Foundation (FWF). The able assistance of Florian Pfumer and Denis Vyalikh at the RG-BL of BESSY II is gratefully acknowledged. We also acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities, and we thank Oleg Konovalkov for assistance in using beamline ID 10B.

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(10) Kline, R. J.; McGehee, M. D.; Toney, M. F. Nat. Mater. 2006, 5, 222–228.