Polymorphism of dioctyl-terthiophene within thin films: The role of the first monolayer

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ARTICLE INFO

ABSTRACT

The origins of specific polymorphic phases within thin films are still not well understood. The polymorphism of the molecule dioctyl-terthiophene is investigated during the presence of a silicon-oxide surface during the crystallisation process. It is found that a monolayer of molecules forms two-dimensional crystals on the surface. In the case of thicker films crystalline islands are formed, a comparison of the three polymorphic phases observed within thin films and the thermodynamically more stable single crystal phases reveals distinct differences which can be related to an adaption of the molecular packing with the flat surface of the substrate.

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1. Introduction

The molecular organisation of thin films of organic semiconductors has been a topic of intense investigation in recent years [1]. The detailed knowledge of the crystal structure of a film in contact with a substrate (a dielectric for example) is of pivotal importance since it, in general, strongly influences the performance of organic electronic devices [2]. However, new polymorphic phases may appear due to the presence of a substrate surface during the crystallisation process [3–5]. This is an interesting fact, since the presence of different phases are important in several areas like organic electronics or pharmaceuticals. Such type of polymorphism is mainly observed in very thin films (<50 nm). For instance, pentacene shows a change of the triclinic unit cell as the thickness is decreased below a critical value of about 50 nm [6,7]. Also, the presence of a substrate-induced phase in semiconducting liquid crystals has been observed for alkylcyanobiphenyl and for dioctylterthiophene (DOTT) [8–10]. Recently, we have observed a coexistence of

two crystalline phases in thin films of DOTT, which we have called s- and b-phase [10]. Both phases are mediated by the substrate during thin film formation under conditions far from equilibrium [11]. A deeper understanding of the organisation of the film as the thickness is reduced to the monolayer level could be relevant for the understanding of the evolution of the different crystalline phases. Therefore, we performed an X-ray study, using both reflectivity and grazing incident diffraction techniques, on the organisation of DOTT films as the thickness is reduced to a single layer. We have clearly observed a new monolayer phase, different from the s- or b-phases, upon which, as the thickness of the film increases, both s- and b-phases develop. The crystal structures of these three substrate-induced phases are solved. Comparison with single crystal structures determined at room temperature and 100 K reveals differences in the conformation and packing of the molecules to the crystal structures formed within thin films.

2. Methods

The molecule DOTT shows three different smectic phases in between the isotropisation temperature (360 K) and the melting temperature of the crystalline state (335 K) [10,12]. Samples were

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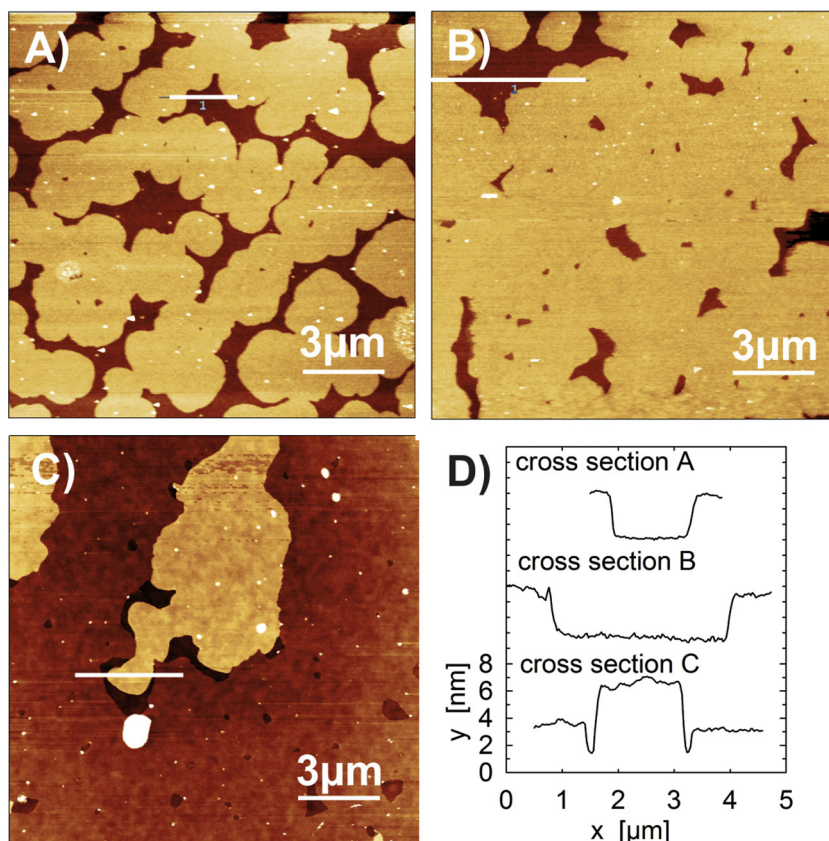
Figure 1. Atomic force microscopy images of three different thin films prepared by spin coating from different concentrations of the molecule DOTT in the solvent tetrahydrofuran (z-scale: 9 nm): 0.26 g/l (A), 0.33 g/l (B) and 0.43 g/l (C). For each micrograph a single line scan across the terraced morphology is given (D).

prepared by spin-coating onto thermally oxidised silicon wafers. The substrates were cleaned with acetone, isopropyl alcohol and in an ultrasonic bath of acetone for 15 min. The spinning program was 1000 rpm for 9 s, followed by 1500 rpm for 30 s. Solutions of DOTT (in toluene or tetrahydrofuran) were deposited with concentrations varying from around 0.1 to around 2 mg/ml (corresponding to a sub-monolayer and 10 layer-thick films, respectively). Films deposited at elevated temperature are prepared by heating both, the substrate and the solution. No significant differences between the samples prepared from toluene and tetrahydrofuran solutions are observed.

X-ray reflectivity (XRR) studies were performed in-house using a PANalytical Empyrean Reflectometer with a wavelength of $\lambda = 0.154$ nm. The experimental data were fitted with the software 'X'Pert Reflectivity 1.3, PANalytical' using Parratt's formalism, surface roughness was implemented by the model of Nevot and Croce [13,14]. Grazing incidence X-ray diffraction (GIXD) was performed using the W1 Beamline at HASYLAB (Hamburg) with a wavelength of $\lambda = 0.118$ nm [15].

Atomic force microscopy (AFM) measurements were performed in tapping mode with an Asylum Research MFP-3D™ instrument equipped with an xyz closed-loop scanner. NSG30 cantilevers from NT-MDT have been used with spring constants of about 40 N/m. The applied force was minimised so that stable imaging was possible without squeezing the organic layers. The AFM topographic data were visualised and analysed using the Gwyddion SPM software v2.26. Optical microscopy was performed with an OLYMPUS BX51.

Molecular dynamics (MD) simulations were performed using LAMMPS in combination with the CHARMM General Force Field v. 2b7 [16,17]. Density functional theory (DFT) calculations were carried out using the Vienna Ab Initio Simulation Package (VASP) using PAW potentials with an energy cut-off of 345 eV [18–21]. The k-mesh was generated automatically by using a Monkhorst-Pack scheme.

Single crystals of DOTT were grown from toluene solution. Suitable crystals for X-ray structural analyses were selected and mounted on the tip of a glass fibre. Diffraction data were collected at 100 K and 296 K on a Bruker D8 Kappa diffractometer equipped with a SMART APEX II CCD detector. MoKα ($\lambda = 0.071073$ nm) radiation was used either from a sealed tube (1040724) or from a microsource (1040725). Solution of the crystal structures with direct methods and structural refinement was performed by SHELXS-97 [22]. The space group assignments and structural solutions were evaluated using PLATON [23]. The cif-files of all structures are given in the Supplementary Information.

3. Results and discussions

Figure 1 shows AFM images of films prepared from three different solution concentrations. At a concentration of 0.26 g/l, a submonolayer with a coverage of 80% is formed. The coverage increases to 91% at higher concentrations (0.33 g/l) and full coverage is reached at 0.37 g/l. Above this limit a second layer starts to form on top of the first closed monolayer, as shown in Figure 1c for a concentration of 0.43 g/l. Line scans reveal slight variations of the monolayer thickness between 2.9 nm (0.26 g/l) and 3.2 nm (0.33 g/l) which agree quite well with the length of an up-right standing DOTT molecule. A characteristic XRR profile of a monolayer is shown in Figure 2A. Pronounced Kiessig fringes are observed with maxima at 1.2 nm^{-1}, 3.3 nm^{-1} and 4.6 nm^{-1}, which are indicative of the presence of a monolayer. The fit of the reflectivity profile has been performed using a simple slab model including the silicon oxide layer on top of the bulk silicon substrate. The organic molecules