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Introduction

Organic semiconductors qualify to be used in sophisticated devices such as flat-panel displays,¹ radio-frequency identification tags,² integrated circuits or biological and medical applications.^{3,4} Apart from their mechanical flexibility and potential low-cost fabrication, this is mainly due to the achievable high charge-carrier mobility.⁵ In general, the charge-carrier mobility and, therefore, the performance of organic electronic devices is strongly influenced by the crystalline quality, the specific molecular packing, and the morphology of the organic film employed.^{6–9} However, film formation can be highly complex for organic

Reversibility of temperature driven discrete layerby-layer formation of dioctyl-benzothienobenzothiophene films[†]

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Film forming properties of semiconducting organic molecules comprising alkyl-chains combined with an aromatic unit have a decisive impact on possible applications in organic electronics. In particular, knowledge on the film formation process in terms of wetting or dewetting, and the precise control of these processes, is of high importance. In the present work, the subtle effect of temperature on the morphology and structure of dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT) films deposited on silica surfaces by spin coating is investigated *in situ via* X-ray diffraction techniques and atomic force microscopy. Depending on temperature, bulk C8-BTBT exhibits a crystalline, a smectic A and an isotropic phase. Heating of thin C8-BTBT layers at temperatures below the smectic phase transition temperature leads to a strong dewetting of the films. Upon approaching the smectic phase transition, the molecules start to rewet the surface in the form of discrete monolayers with a defined number of monolayers being present at a given temperature. The wetting process and layer formation is well defined and thermally stable at a given temperature. On cooling the reverse effect is observed and dewetting occurs. This demonstrates the full reversibility of the film formation behavior and reveals that the layering process is defined by an equilibrium thermodynamic state, rather than by kinetic effects.

semiconductor thin films. For example, initial layer-by-layer growth in the vicinity of the substrate is frequently followed by three-dimensional growth and islanding. Typically, the molecular assembly during layer formation depends on a variety of parameters including the type of substrate used, the deposition method and rate, the solute concentration or temperature.¹⁰ In particular, just the presence of the substrate surface itself can have a decisive impact on the molecular assembly during thinfilm growth. This can result in an interfacial structure which can be significantly different compared to the bulk phase - such phases are referred to as surface-mediated polymorphs.¹¹ Accordingly, various key-properties of such films can be very different for the different polymorphs. For instance, charge transport within the thin-film polymorph of pentacene is known to be considerably increased compared to the bulk phase based on band-structure calculations.^{12,13} For organic singlecrystal field-effect transistors, the impact of polymorphism on the device performance has even been demonstrated experimentally.¹⁴ In recent years, alkylated oligothiophenes like dioctylterthiophene,¹⁵ dihexylterthiophene¹⁶ or benzothienobenzothiophenes (BTBT) like 2,7-dioctyl-BTBT (C8-BTBT) have attracted considerable interest.5,20 The formation of their crystalline phases together with liquid crystalline mesophases allows studying the impact of deposition conditions, substrate properties

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and post-deposition treatments (temperature, solvent annealing) on the layer formation in detail.^{6,17–19}

Complementing the fundamental interest in organic thin-film growth, such information is crucial for rationalizing and improving the applicability of organic semiconductors in organic electronics. With charge carrier mobilities of above 1 cm² V⁻¹ s⁻¹¹⁸ as readily achievable, and values up to 170 cm² V⁻¹ s⁻¹ recorded,⁵ BTBT derivatives have turned out to be amongst the most promising candidates for low-cost and flexible electronic applications in recent years.²⁰

In the present study, the thermal response of C8-BTBT molecules deposited on silica-surfaces is investigated *in situ* by X-ray scattering methods and *in situ* atomic force microscopy. While the thermal response of the C8-BTBT monolayer has already been discussed in detail,^{21,22} the effect on multilayers has not been reported before and is of interest as the additional volume of C8-BTBT may lead to an enhanced stabilization of films up to device relevant thicknesses in the range up to 15 nm.²⁰

Experimental

The investigations were performed using 2,7-dioctyl[1]benzothieno[3,2-*b*][1]benzothiophene (C8-BTBT), a molecule consisting of a conjugated core and two terminal alkyl chains (see inset Fig. 1). Bulk C8-BTBT shows a complex thermal phase behaviour with two clear phase transitions.²³ Differential scanning calorimetry (DSC) of bulk C8-BTBT at a heating rate of 10 K min⁻¹ revealed a transition from crystalline to the liquid crystalline smectic A phase (SmA) at 382.5 K and a transition to the isotropic phase at 398 K (Fig. 1).

Films of C8-BTBT were prepared onto Si-wafers covered with a 150 nm thermally grown silicon oxide layer provided by Siegert Wafers (Aachen, Germany). Prior to film fabrication, the pre-cut wafers were cleaned in an ultrasonic bath with acetone and then isopropyl alcohol solutions and finally dried under a nitrogen stream. The oxide thickness and the surface roughness of the substrates was determined by X-ray reflectivity, values of 150 nm and 0.3 nm were obtained, respectively. The surface energy of the substrate was determined by the method of Owens and Wendt.²⁴ The contact angle measurements using water and diiodo-methane resulting in a value of 49.8 mJ m⁻²



Fig. 1 Differential scanning calorimetry curve of C8-BTBT, the chemical structure of the molecule is shown as an inset.

with 25.4 mJ m⁻² for the dispersion part and 24.4 mJ m⁻² for the polar part.

C8-BTBT films were prepared by spin coating using a 5 mg ml⁻¹ tetrahydrofuran solution at a spin speed of 1000 rpm for 9 s followed by 1500 rpm for 30 s, respectively. At this concentration, multilayer thick C8-BTBT films form (for comparison, in a previous experiment using the same deposition conditions,²² the formation of a single monolayer was obtained using a solution concentration of 0.27 mg ml⁻¹). The samples were stored under ambient conditions for several hours prior to the experiments.

X-ray reflectivity (XRR) measurements were performed on a Panalytical Empyrean Reflectometer using Cu Ka radiation (wavelength $\lambda = 0.15418$ nm). At the primary side a multilayer mirror for generating a parallel beam was used and at the secondary side, a receiving slit, a Soller slit and a PANalytical PIXCEL3D detector were employed. The angular scans (2Θ) have been recalculated to scattering vector notation using $q_z = 4\pi/\lambda \times \sin \Theta$. XRR data were fitted using the software X'Pert Reflectivity 1.3 (PANalytical, Netherlands).^{25,26} The samples were modelled (according to previous similar investigations)^{15,22,27} such that a single C8-BTBT layer consists of three regions of distinct electron density modulation. The high electron density of the conjugated core is embedded in between lower electron density regions of the alkyl chains which represents a triple layer sequence for a single molecular layer. This building block was vertically stacked with a surface roughness of 1 nm per layer in order to fit films consisting of multiple layers.

Grazing incidence X-ray diffraction experiments (GIXD) were performed at the beamline W1 (DESY-HASYLAB, Hamburg, Germany) using a wavelength of $\lambda = 0.11801$ nm in order to assess the in-plane structure of the samples. The incident angle was set to $\alpha_i = 0.15^\circ$ which corresponds to an angle slightly below the critical angle of total external reflection of silica. The diffracted intensities were collected with a one-dimensional position sensitive Mythen 1K detector (Dectris) oriented in the out-of-plane direction. The experimental intensities are integrated along the out-of-plane part of the scattering vector (q_z) from 0 to 3 nm⁻¹. The experimental intensities are finally presented as a function of the in-plane part of the scattering vector q_{xy} . Data processing, visualization and indexation were performed using the in-house developed software package PyGID.^{28,29}

The sample environment and temperature were controlled using a Domed-Hot-Stage (DHS900) heating stage³⁰ from Anton Paar Ltd (Graz, Austria) under He-atmosphere to minimize sample degradation.³¹ Samples were heated at rates of 5 K min⁻¹ and 1.5 K min⁻¹ and cooled at natural cooling rate of the set-up. Measurements were performed at constant temperatures measured at the heating plate of the temperature attachment.

The thin film morphologies were investigated by atomic force microscopy (AFM) in tapping mode using an Asylum Research MFP-3DTM AFM equipped with an *xyz* closed-loop scanner and a PolyHeaterTM heating stage. Standard NSG01 silicon cantilevers by NT-MDT with a force constant of 5.1 N m⁻¹, a tip-cone angle of 17° and a guaranteed tip radius of less than 10 nm were used. Height information was analysed using the Gwyddion software package.³²

Results

The structure of the as-prepared film

The organic thin film is investigated in terms of morphology and crystallographic properties after film preparation at room temperature. Rod-like molecules typically arrange with an upright-standing orientation on silica-substrates forming layered, structured films with monomolecular steps.^{33,34} In the present case, C8-BTBT films showing islands of well-defined layers with a terrace-like structure are observed in the AFM height image (Fig. 2a). The layers show reduced coverage as the distance from the surface is increased, resulting in steps being visible within the AFM image; a step height of about 2.9 nm is observed which is consistent with the length of a single molecule in an uprightstanding orientation. The deltoid-like shape of the pyramid base shows similarities with the morphology of single crystals of C8-BTBT which were previously studied.¹⁷

The separation and size of the islands strongly varies which indicates that the nucleation probability of these islands is statistically poorly defined. Such a behavior is typically found for thick films prepared by solution processing, while, in contrast, vapor deposition of such compounds results in more defined island morphology.³⁵ The terrace-like structures are better observed in a phase-contrast image as shown in Fig. 2b. Considering the phase-contrast information, most of the surface has a similar mechanical response to the AFM tip (darker areas) corresponding to the organic compound. The areas with higher phase contrast (brighter areas) correspond to the bare silica surface, indicating that the substrate surface is not fully covered upon spin-coating.

To gain crystallographic information on the film, specular X-ray reflectivity was performed. An XRR curve from an as-prepared



Fig. 2 Representative atomic force microscope height image (a) and high-resolution phase contrast image (b) of a spin coated C8-BTBT multilayer film in the as-prepared state at room temperature. The micrographs are taken from two different sample positions.

multilayer film is shown in Fig. 3a, allowing the structure perpendicular to the substrate surface (z-direction) to be evaluated. The curve shows a typical XRR trajectory with the total external reflection plateau up to $q_z = 0.31 \text{ nm}^{-1}$ providing information on the critical angle and, with increasing scattering vector, a strong decrease in the reflected intensity. Thickness oscillations of the 150 nm thermal oxide are clearly observed, but no Kiessig fringes indicative of a highly rough C8-BTBT film are present.

The absence thereof can be explained by the large surface roughness of the film as observed by AFM (see Fig. 2). At $q_z =$ 2.16 nm⁻¹, an intense diffraction peak arises. This peak is identified as the 001 Bragg peak of the known monoclinic crystal structure of C8-BTBT with unit cell dimensions of a = 0.5928 nm, b = 0.788 nm, c = 2.918 nm and $\beta = 92.443^{\circ}$.³⁶ Its dominance reveals a strong preferred orientation of crystallites with the 001 plane parallel to the substrate surface.

Within this crystal orientation, the triple layer building blocks (sheets of octyl chains – sheets of the conjugated cores – sheets of the octyl chains) are arranged along the *z*-direction (perpendicular to the substrate). To gain further insight into the structural properties, fitting of the experimental data was performed consisting of such triple layer building blocks.^{15,22}



Fig. 3 X-ray reflectivity curves of a C8-BTBT film as a function of temperature from room temperature (RT) to 378 K (a). Time evolution of the X-ray reflectivity pattern keeping the temperature at 378 K (b).

The procedure shows that crystals consisting of 22 layers (~ 63 nm) is required to fit the experimental XRR curve, where the density of each additional layer was reduced representing the decreasing layer-coverage as the distance from the surface increases. This is in excellent agreement with the AFM investigation of the terraced crystallites.

In order to determine the lateral crystalline properties within the layers Grazing Incidence X-ray diffraction (GIXD) experiments have been performed. A diffraction pattern characteristic



Fig. 4 In situ grazing incidence X-ray diffraction pattern of the C8-BTBT film as a function of temperature in the crystalline state from room temperature (RT) up to 373 K (a) and in the smectic and isotropic state (b). The data is plotted as integrated intensity *versus* in-plane component of the scattering vector q_{xy} , curves are vertically shifted for clarity.

of fibre-textured crystallites with the (001) plane parallel to the substrate surface (two-dimensional powder) is found.

All experimentally observed Bragg peak position (q_z and q_{xy}) and intensities are well explained on the basis of the known crystal structure of C8-BTBT with 001 oriented crystallites (see ESI,† Fig. S1).³⁶ The integrated diffraction pattern collected at room temperature (RT) is depicted in Fig. 4a. The observed strong intensities at $q_{xy} = 13.3 \text{ nm}^{-1}$, 15.9 nm⁻¹ and 19.4 nm⁻¹ are the characteristic fingerprint for the herringbone packing of the aromatic units.

Film structure and morphology below 373 K

The effect of increasing temperature up to 373 K on the film structure is investigated in situ by atomic force microscopy and X-ray reflectivity/diffraction. Note that within this temperature range the film is solely crystalline. At a temperature of 303.5 K, a deltoid shape of the islands is observed (Fig. 5a). With only a moderate temperature increase of 15 K the morphology of the islands starts to change. The in situ AFM images show islands growing along the substrate z-direction, which consequently leads to a reduced lateral island size (Fig. 5). The initially "smooth" deltoids start to develop jagged edges beginning at a temperature of 318 K, which indicates migration of the molecules at temperatures far below the crystalline/smectic transition temperature. With increasing temperature, the edges become more irregular in shape, which shows an upward diffusion of the molecules (see Fig. 5b-d). The lateral size of the C8-BTBT crystals continuously reduces, indicating that the organic molecules tend to minimize their contact with the substrate surface. Increasing the temperature further to 363 K (Fig. 5e), a complete change of the morphology is observed. Drop-like structures are formed, where the lateral arrangement of the islands has considerably changed in comparison to the deltoids which were initially present. Please note that all of the AFM micrographs of Fig. 5 are taken at the same sample position.



Fig. 5 In situ atomic force microscopy height images of a C8-BTBT film at various temperatures starting at 303.5 K up to 378 K. The maximum height of the images (*z*-values) vary from 30 nm (a–d), to 50 nm (e), up to 110 nm (f). The micrographs are taken at the same sample position. Arrows show the appearance of a molecular monolayer.

The increase in the island height is in good agreement with our XRR investigations (Fig. 3a), where the vertical growth of the crystallites is deduced from decreasing width (*i.e.* sharpening) of the Bragg-peak as the temperature is increased. Fits of the reflectivity data show that at a temperature of 363 K, 50 layers (≈ 150 nm) are present *i.e.* the islands are now more than doubled in height compared to the initial 22 layers (~ 63 nm) in the case of the as-prepared film. GIXD patterns do not show a change in the peak shape for temperatures up to 373 K (see Fig. 4a). The shift in q_{xy} of the Bragg peaks is associated with thermal expansion of the crystalline lattice. An anisotropic expansion takes place with the crystallographic *b*-axis increasing most. The temperature dependence of the lattice constants is given in the ESI‡ (Table S1).

The *in situ* AFM together with the XRR investigations show that migration of the molecules detectably starts at moderate temperatures of around 318 K. With increasing temperature, the molecular diffusion at the thin film surface is accelerated, resulting in a complete change of the thin film morphology from regular deltoid shaped islands to drop-like mounds.

Film structure and morphology above 373 K

The morphology of the film when heating the sample from 373 K to the SmA state and into the isotropic phase is investigated. Approaching 378 K, the system shows a remarkable morphological change. The AFM images reveal that previously vacant areas at the silica surface are re-wetted and filled by a monolayer of the organic compound (see arrows in Fig. 5f). These monolayers have a lateral extension of several µm. The appearance of a monolayer is further supported by the XRR investigations (see Fig. 3a), where Kiessigfringes with a minimum around 0.8 nm⁻¹ and a maximum at around 1.4 nm⁻¹ are clearly observed. The spread of the monolayer across the entire substrate surface is a rather slow process; a time of about 30 minutes at a constant temperature is required for the formation of a complete monolayer (see Fig. 3b). Fitting of the XRR curve reveals a monolayer as a triple layer building block with an internal structure consisting of layers with alternating sheets of molecular segments with thicknesses/electron densities (and mass densities) of 0.9 nm/432 nm^{-3} (1.4 g cm⁻³) for the conjugated core and 1.0 nm/277 nm^{-3} (0.8 g cm⁻³) for the octyl chains. Please note that the monolayer is formed between the C8-BTBT islands which are still in a crystalline state, as evidenced by the still present Bragg peak at $q_z = 2.16 \text{ nm}^{-1}$. The AFM data clearly shows that the morphology of the thick multilayer crystals remain essentially unaffected (see Fig. 5f).

After the formation of this first closed monolayer at 380.5 K, XRR measurements were used to show the evolution of the film morphology as the temperature is further increased (Fig. 6). At a temperature of 383 K, two minima around 1.3 nm^{-1} and 2.0 nm^{-1} appear which can be identified as a bilayer structure (a second monolayer forms on top of the first monolayer). The continued presence of the strong Bragg peaks (001 and 002) shows that the bulk material with its large vertical extensions remains in the crystalline phase.

The formation of such discrete monolayer structures occurs together with the start of the transition from the crystalline



Fig. 6 In situ X-ray reflectivity measurements of a C8-BTBT film with increasing temperature, starting at a temperature of 363 K (bottom line) up to 403 K (top line). On the left, the number of stacked monolayers are shown, while the temperature of the measurement is given on the right, curves are shifted vertically for clarity.

state to the SmA state. From the X-ray reflectivity data, this phase transition occurs at a temperature of 383 K, where the diffraction peak of the SmA phase initially appears. At a temperature of 383 K, the 001 and 002 Bragg peaks of the crystalline phase are still clearly visible (Fig. 6). Thereafter at a temperature of 385.5 K and above the higher order Bragg peak (002) fully disappears and the 001 peak position significantly shifts from $q_z = 2.16 \text{ nm}^{-1}$ to 2.13 nm⁻¹ confirming that the phase transition to the SmA phase is completed. GIXD measurements at the same temperature show that the Bragg peaks transform into a broad halo (Fig. 4b) arising due to diffuse scattering from disordered molecules present in the SmA phase.

Surprisingly, during the phase transition to the SmA phase, the interfacial bilayer structure of the molecules at the substrate surface remains the same; this is clearly visible at the minimum at $q_z = 1.3 \text{ nm}^{-1}$ which is a characteristic feature of a double layer structure (see Fig. 6). Heating the sample further up to 390.5 K, which is now well above the phase transition temperature of the bulk material (383 K), the system starts to develop a third fully closed interfacial layer. Keeping the temperature constant reveals that a time of about 30 minutes is required to form a triple layer system which is completely spread over the substrate surface (see ESI,† Fig. S2). Increasing the temperature further allows the formation of additional layers: four layers are observed at 395.5 K and additional layers are found to form as temperature progresses. Finally at temperatures above 398 K, the Kiessig fringes of the interfacial layers completely disappear. This indicates that the layers formed at the surface interface might have become too "rough" and, therefore, constructive interference of the X-rays does no longer occur.

According to the DSC measurements the clearing temperature of the liquid crystalline state is at 398 K. At this temperature the diffraction intensity of the smectic phase is drastically reduced and it finally disappears fully at a temperature of 403 K (Fig. 6). In the GIXD data, the maxima of the diffraction halos change at the SmA – isotropic phase transition from 1.36 nm^{-1} to 1.42 nm^{-1} (see Fig. 4b). Optical microscopy clearly shows a homogenous spreading of the C8-BTBT melt, *i.e.* the surface is covered with C8-BTBT in its isotropic form (not shown).

Reversibility of layer formation

To investigate the reversibility of the layer formation process just described, XRR experiments were performed in situ while the temperature was decreased (Fig. 7). Starting at a temperature of 390.5 K, the molecular material is still in the SmA phase with clear minima associated with Kiessig fringes of a complete triple layer at the substrate surface. This is essentially the same situation as found for the *in situ* investigations with increasing temperatures. In addition, the position of the Bragg peak at $q_z = 2.13 \text{ nm}^{-1}$ is in accordance with the expected value for the SmA phase. Upon further decreasing temperature, this peak position shows an abrupt shift to $q_z = 2.16 \text{ nm}^{-1}$ due to the SmA – crystalline phase transition at 378 K. Similar to the heating experiment, the layered structure remains unperturbed at the surface. However, the now slightly smeared minima, *i.e.* the reduced depth of the fringes, suggests a decomposition of the layered structure. At 373 K, the film-thickness oscillations change now showing only one single minimum at about 0.7 nm^{-1} .

At this point, only one single monolayer is present at the substrate surface. Importantly, no changes in peak-shape are observed for the Bragg peaks indicating that the large islands on top are not affected by the temperature decrease. At a temperature of 358 K, only a shallow minimum is present, which indicates the single monolayer to be nearly decomposed; at 348 K no indication of an interfacial monolayer is present. Overall, our experiments indicate that the layering behaviour at the interface is completely reversible in nature. To fully demonstrate the reversibility of the process, the sample was re-heated and cooled several times resulting in the same layer-formation behaviour which was observed during the first cycle.



Fig. 7 In situ X-ray reflectivity of a C8-BTBT film with decreasing temperature, starting at a maximum temperature of 383 K (top line) decreasing down to room temperature (bottom line). On the left of the curves, the number of interfacial layers are given, on the right the actual temperature, curves are shifted vertically for clarity.

However, the reversibility of multilayer formation is associated with a large change in the shape and size of the island structure. While in the as-prepared state the islands have a lateral size of a few μ m (Fig. 1 and 5), after heat treatment the island size increases up to 100 μ m with an elongated drop-like shape.

Discussion

The as-prepared spin coated films of the molecule C8-BTBT show irregular islands with a terrace like morphology. Increasing the temperature results in a strong dewetting of the molecular material from the substrate surface with increasing crystallite size in the *z*-direction. The observeed dewetting behaviour can be explained by the so-called spreading parameter, *S*, which is written as:

$$S = \gamma_{\rm s} - \gamma_{\rm l} - \gamma_{\rm sl}$$

with γ being the surface energies of the substrate (γ_s), the organic layer (γ_1) and the interface (γ_{sl}).³⁷ For values of the spreading parameter S < 0, the system typically favours dewetting (or partial wetting). Likewise, positive values ($S \ge 0$) favour wetting of the substrate.^{37,38} During our heating experiments, a temperature regime dominated by dewetting was observed up to 363 K. It follows that the energy of the crystalline C8-BTBT and the interface ($\gamma_{sl} + \gamma_l$) is higher than γ_s of the silica surface. Our experimental results give a value of $\gamma_s = 25.4$ mJ m⁻² for the bare silica surface. For simplicity, only the dissipative part of the surface energy is considered, since in the specific alignment of the molecules they expose only their octyl groups towards the substrate surface.

Upon further heating and approaching the transition from a crystalline to SmA, the behaviour changes and a defined formation of a monolayer is observed at 378 K, a temperature well below the bulk phase transition temperature of 383 K. The differences in temperature at which the phase transition (SmA to crystalline, and *vice versa*) occurs for the surface phase (interfacial layers) and the bulk material (islands) depends on the anchoring energy of the molecule with the surface (hence the surface energy) and the intermolecular packing.⁴⁰ Usually, small temperature differences are observed for transitions between different phases (surface and bulk). However, for the transition between a crystalline state and the SmA phase, values up to 13 K have been reported.⁴¹

The formation of closed monolayers across the entire substrate surface can also be explained by the spreading parameter. A value of about 21 mJ m⁻² is reported for smectic mesophases of molecules with terminal hydroalkyl chains (*i.e.* similar to C8-BTBT).³⁹ In addition, the surface tension γ_1 of the molecular material is known to be reduced in the smectic state by a factor of about 10%.⁴² Such a change is large enough to change the sign of the spreading parameter to positive, so that wetting of the smectic phase at the surface occurs.

As the temperature is further increased layer-by-layer growth with subsequent temperature-induced monolayers is observed. This is a known phenomenon at temperatures close to the phase transition temperatures of liquid crystals.^{43,44} Even growth of several layers in a discrete layer-by-layer process is already observed, but smooth surfaces are required for such discrete layer-by-layer growth.^{45–48}

However, there is a fundamental difference in the layer formation observed in this work, as compared to previous examples. While interfacial layers between the liquid crystal and substrate surfaces within individual domains are mainly reported in literature, in our case, the formation of free monolayers, separated from the crystalline domains, is observed. While the appearance of the first monolayer is well explained by the spreading parameter, it has been shown that the surface energy is not dependent on the number of layers within the smectic film.⁴⁹ Thus, the discrete nature of the layering process cannot be assumed to be an effect of further decreasing interfacial energy.

Frequently, the wetting of surfaces is a continuous process instead of first order. This means that the thickness of a wetting layer increases continuously with increasing temperature. The temperature dependence of the thickness depends on the range of the interactions of the wetting material with the substrate material: a logarithmic increase is observed for short range interactions, while an inverse temperature dependence is observed for long range interactions.⁵⁰ In our system, the molecules arrange with a defined orientation within the wetting layer. The monolayer is assembled in vertical direction by sheets formed by octyl chains followed by the conjugated cores and completed by a second sheet of octyl chains. As a consequence the molecules are "standing" at the substrate surface, with their long molecular axes approximately perpendicular to the substrate. The combination of a general wetting behaviour (increasing layer thickness with temperature), along with the defined monolayer thickness, could explain the observed effect: the stability of a discrete number of monolayers in a defined temperature range. However, the data quality of this work is not sufficient to determine the involved range of interaction (short or long range).

The time dependence of monolayer formation reveals that the reorganisation of the molecules is a rather slow process. The complete generation of a defined multilayer stack takes about 30 minutes. It is known from previous experiments that a single monolayer can be frozen due to rapid cooling from the smectic state down to room temperature.²² The hindered diffusion of the molecules at large cooling rates results in a kinetically determined thin film structure. Rapidly quenched multilayer structures could be of improved layer quality for applications in organic electronic devices.

Conclusions

The temperature dependence of the structural and morphological properties of a thick C8-BTBT film on thermally oxidised silicon substrates shows a transition from the crystalline state to a smectic A state (SmA) at 383 K and the transition from the SmA state to the isotropic state at 398 K.

The preparation of films by spin coating is far from thermodynamic equilibrium and results in a morphology of terraced islands. The islands are crystalline with a strong preferred orientation of the crystallites formed by "standing" molecules at the substrate surface. Annealing of the films at moderate temperatures results in dewetting of the substrate surface together with an increase of the vertical crystallite size from ~ 60 nm to \sim 150 nm. Close to the transition temperature from the crystalline to the SmA, at 378 K - a temperature slightly below the bulk phase transition temperature - a single monolayer of molecules with a smectic structure is formed at the interface with the substrate. This single layer is stable at this temperature, and it takes 30 minutes until the monolayer is completely developed. The process of monolayer formation appears already at temperatures slightly below the transition from the crystalline to the smectic phase due to surface ordering. The proposed process appears due to an enhanced migration of the molecules at the thin film surface with subsequent aggregation as monolayer at the uncovered silica surface. At increasing temperature a layer-by-layer formation (of up to five layers) is observed until the system passes towards the isotropic state. Decreasing the temperature shows the reverse effect by a discrete reduction of the number of layers.

The dewetting of the film at moderate temperatures and the rewetting by monolayer structures is explained by the surface energies and surface tension leading to a positive spreading parameter in the crystalline regime of the film and a negative spreading parameter in the smectic regime, where discrete monolayers are formed. The explanation of the changes in thin film morphology by using the spreading parameter together with the reversibility of the monolayer formation suggests that the temperature-induced assembly of the C8-BTBT molecules on silicon oxide can be understood as a process in thermodynamic equilibrium rather than being a kinetic effect.

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