Growth of pentacene on α-Al$_2$O$_3$(0001) studied by *in situ* optical spectroscopy

Lei Zhang,[1,2,3] X. Fu,[2] M. Hohage,[3] P. Zeppenfeld,[3] and L. D. Sun[3,*]

[1]*School of Control Science and Engineering, Shandong University, Jingshi Road, 250061 Jinan, China*
[2]*State Key Laboratory of Precision Measuring Technology and Instruments, Tianjin University, Weijin Road, 300072 Tianjin, China*
[3]*Institute of Experimental Physics, Johannes Kepler University Linz, A-4040 Linz, Austria*

The growth of pentacene thin films on a sapphire α-Al$_2$O$_3$(0001) surface was investigated *in situ* using differential reflectance spectroscopy (DRS). Two different film structures are observed depending on the substrate temperature. If pentacene is deposited at room temperature, a wetting layer consisting of flat-lying molecules is formed after which upright-standing molecular layers with a herringbone structure start to grow. At low substrate temperature of 100 K, the long molecular axis of the pentacene molecules remains parallel to the surface plane throughout the entire growth regime up to rather large thicknesses. Heating thin films deposited at 100 K to room temperature causes the pentacene molecules beyond the wetting layer to stand up and assemble into a herringbone structure. Another interesting observation is the dewetting of the first flat-lying monolayer upon exposure to air, leading to the condensation of islands consisting of upright-standing molecules. Our results emphasize the interplay between growth kinetics and thermodynamics and its influence on the molecular orientation in organic thin films.

I. INTRODUCTION

The orientation of the molecules within organic thin films and at their interfaces with contacts is crucial for the performance of organic optoelectronic devices [1–4]. Because most of the organic molecules are highly anisotropic, their orientation will control the charge transport in the films as well as the direction and polarization of light absorption and emission [4,5]. Furthermore, the molecular arrangement at the interface strongly influences the subsequent thin film growth. In particular, whether a flat-lying monolayer (a wetting layer of molecules lying flat on the surface) is initially formed and how this wetting layer evolves during the further growth or upon exposure to air are issues relevant for the growth mechanism, stability, and other physical properties of the corresponding organic thin films [6–8]. For organic field-effect transistors (OFETs) where the transport channel is only a few monolayers thick, the orientation of the molecular layer buried at the interface with the gate dielectric becomes particularly important [9,10]. Great efforts have been devoted to investigate the molecular arrangement at the interfaces with dielectric substrates in order to understand the key factors which control the molecular orientation [6,7,11–20]. It has been demonstrated that the orientation of organic molecules depends strongly on the substrate, surface pretreatment, and the growth conditions [6,7]. On the other hand, the growth of organic thin films and its stability rely on the molecular self-organization driven by the interplay between thermodynamics and kinetics on the surface [12–15,19]. In order to control and manipulate the orientation of the molecules in organic thin films, it is thus essential to establish a fundamental understanding of the interface formation concerning both kinetic and energetic aspects.

Optical spectroscopy provides a powerful probe to monitor the adsorption of organic molecules and the growth of organic thin films [8,19,21–23]. The strong optical absorption of π conjugated molecules allows the study of nucleation and growth with submonolayer sensitivity. The polarization state and the spectral line shape related to the intramolecular electronic transitions reveal the molecular orientation and molecular conformation, whereas the spectral shift and the appearance of collective excitations provide detailed information regarding molecule-molecule and molecule-substrate interactions [19,20,24].

Pentacene has attracted notable attention as an active material for OFETs due to its high carrier mobility [9,10,25,26]. The orientation of the pentacene molecules on the SiO$_2$ gate dielectric has been investigated thoroughly [4,10,26]. It has been predicted that a flat lying pentacene molecule has to overcome a kinetic barrier to be incorporated into an upright-standing molecular layer. However, on both amorphous SiO$_2$ layers formed on silicon wafers as well as on single crystal quartz substrates, pentacene molecules exhibit exclusively upright orientation already in the first monolayer in direct contact with the substrate surfaces [6,7,14,27].

In the current study, we have chosen pentacene on sapphire, namely α-Al$_2$O$_3$(0001), as a model system to investigate the details of the growth of π-conjugated molecules on crystalline insulating substrates. The combination of its favorable chemical and physical properties make sapphire a preferred material for high performance optoelectronic devices. Al$_2$O$_3$ thin films are also widely used as advanced dielectric layers in the electronic devices based on organic semiconductors [28]. To this end, differential reflectance spectroscopy (DRS) [24], a technique that is extremely sensitive to the adsorption and interaction of organic molecules on surfaces, has been used to monitor the growth *in situ* and in real time. We will demonstrate that the details of the growth process can be unraveled based on the evolution of the optical reflectance during growth. In particular, by studying the dependence of the molecular orientation on the substrate temperature, we will explore the kinetic and thermodynamic aspects of the pentacene thin film growth on α-Al$_2$O$_3$(0001).

*Corresponding author: lidong.sun@jku.at

II. EXPERIMENT

The experiments were carried out in a UHV chamber with a base pressure of 1×10^{-10} mbar. The α-Al_2O_3(0001) substrate used in our experiments has a rough backside which suppresses interference fringes in the optical reflection. The α-Al_2O_3(0001) substrate was mounted on a sample plate made of Ta, which can be heated up to 900 K by electron beam bombardment from the backside and cooled down to 100 K with a continuous flow liquid nitrogen cryostat. Before the deposition, the α-Al_2O_3(0001) substrate was heated to 900 K in order to desorb the residual adsorbates on the surface. During the deposition of pentacene the substrate temperature was fixed at either room temperature or 100 K. Moreover, the sample could be subsequently heated with constant heating rates using a high-accuracy temperature controller (Eurotherm). Pentacene molecules were evaporated from a thoroughly degassed Knudsen cell. The evolution of the optical properties was monitored *in situ* using a home built differential reflectance spectrometer. The DR spectra were recorded in a normal incidence configuration, using a super quiet Xe lamp (Hamamatsu) as light source and a QE65000 spectrometer (Ocean Optics) as detector. With an integration interval of a few seconds, a spectrum with high signal-to-noise ratio and high energy resolution can be obtained. The differential reflectance spectra are calculated using the following equation:

$$\frac{\Delta R}{R} = \frac{R(d) - R(0)}{R(0)}, \tag{1}$$

where $R(0)$ and $R(d)$ denote the reflectance of the bare surface and the one covered by an adlayer with a nominal thickness d. The so obtained DR signal $\Delta R/R$ thus represents the change of the optical reflectivity relative to the bare substrate as a function of the nominal film thickness d. The morphology of the pentacene thin films were characterized *ex situ* using atomic force microscopy (AFM, Dimension 3100, Brucker).

III. RESULTS AND DISCUSSION

A. Pentacene thin film growth at room temperature

We deposited the pentacene films at a rate of about 0.022 ML per minute on the sapphire substrate at room temperature. Here we define the unit ML as one monolayer of upright standing pentacene with a surface molecular density of the thin film phase which is approximately 4.48 nm^{-2} [26,29]. In order to obtain a detailed understanding of the evolution of the molecular orientation at different stages of the growth, let us have a closer look on the changes of the DR spectrum at the very beginning of the deposition (Fig. 1). At the initial stage of the growth up to a nominal coverage of 0.1 ML, the features c and d, which are due to the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) electronic transition and its first vibronic replica, respectively [5,8,30], rise linearly with pentacene coverage. However, the most pronounced peak appears at 4.2 eV and its amplitude is proportional to the pentacene coverage, too. Furthermore, the energetic position of this feature is very close to the electronic transition from HOMO to LUMO+2 of isolated pentacene molecules in a Kr matrix [31]. Therefore, we attribute the peak e to the
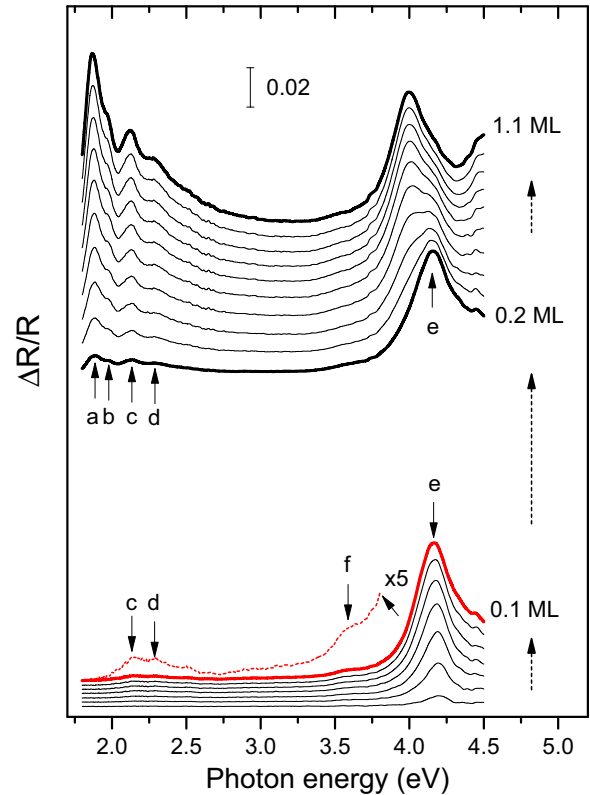

FIG. 1. DR spectra recorded during the deposition of pentacene on the bare α-Al_2O_3(0001) surface at room temperature. The lower panel shows the evolution of the DR spectrum up to the completion of the dilute flat-lying phase which is equivalent to a nominal thickness of 0.1 ML of up-right standing molecules. The upper panel presents the DR spectra recorded during the further growth of the pentacene thin film up to a nominal thickness of 1.1 ML which corresponds to the completion of the first up-right standing layer in addition to the dilute phase containing flat-lying pentacene molecules. For clarity, subsequent spectra in the lower and upper panels are shifted vertically by 0.001 and 0.01, respectively.

HOMO to LUMO+2 transition of pentacene molecules. Due to the fact that the corresponding transition dipole moment is oriented along the long molecular axis of pentacene [32], the formation of a pronounced peak at 4.2 eV indicates that, during the initial stage of the growth, the pentacene molecules are flat lying with their long axis parallel to the α-Al_2O_3(0001) surface. Following the same argument, the shoulder, which appears at about 3.6 eV, can be assigned to the HOMO to LUMO+1 transition whose transition dipole moment is also parallel to the long molecular axis. Actually, the DR spectrum of the pentacene film with a nominal coverage below 0.1 ML on the α-Al_2O_3(0001) surface is very similar to the absorption spectrum of isolated pentacene molecules in a Kr matrix regarding both the spectral line shape and the energetic positions of the main peaks. This indicates that the pentacene molecules in direct contact with the α-Al_2O_3(0001) surface experience rather weak interactions with the substrate and between each other. Furthermore, the complete absence of any feature related to the Davydov components [30] at this growth stage corroborates our interpretation. According to our definition of the ML, a nominal coverage of 0.1 ML

corresponds to a surface number density of $\sim$0.45 nm^{-2} for pentacene molecules. This is indeed quite small compared to full monolayer coverage of 0.85 nm^{-2} observed on Cu(110) where the long axis of the pentacene molecules is also parallel to the substrate surface [33,34]. Actually, a similar surface number density ($\sim$0.48 nm^{-2}) is only observed for flat lying pentacene on Au(110) [35]. Therefore, on the α-Al$_2$O$_3$(0001) surface, the flat lying pentacene forms a rather dilute phase. Above the threshold coverage of 0.1 ML, the DR spectrum evolves in a different manner: (1) The amplitude of the peak e stops to increase and its energetic position shifts to 4 eV. (2) The Davydov components a and b [30] set in and their amplitudes increase with pentacene coverage. These two observations reveal the onset of the growth of a molecular phase containing upright standing pentacene molecules. Actually, the absence of any further growth of peak e indicates that the long molecular axis of the newly deposited pentacene molecules is now aligned close to the surface normal. The red shift of peak e can be explained by the change of the dielectric environment of the flat lying phase due to the growth of the upright standing pentacene layer next to it. The formation of the exciton states evidenced by the appearance of the Davydov components a and b confirms the formation of a herringbone structure [36] in the upright standing pentacene layer.

Figure 2(a) shows the evolution of the DR spectra during the growth of the first 10 upright standing monolayers. Due to the formation of an initial wetting layer of flat-lying pentacene molecules, there is an offset of 0.1 ML for all the thickness indicated in Fig. 2. The evolution of the optical properties with increasing film thickness is very similar to the growth of pentacene on quartz(0001) [24]. The position of the lower Davydov component a as a function of the film thickness is plotted in Fig. 2(b). As we have shown in our previous work on the growth of pentacene thin films on quartz(0001) [24], the onset of the continuous red shift of peak a is associated with the completion of the first monolayer containing upright standing pentacene molecules. This fact allows us to calibrate the film thickness and determine the deposition. Furthermore, the spectral position of peak a beyond the first upright-standing monolayer can be fitted nicely using:

$$E = E_b + \Delta E \frac{d_{\mathrm{ML}}}{d}, \qquad (2)$$

where E_b is the absorption energy of bulk pentacene, ΔE represents the difference between the optical absorption energies of the first monolayer and bulk pentacene, d_{ML} and d are the nominal thickness of a single upright standing monolayer and the thickness of the growing thin film, respectively. The best fit of Eq. (2) to the experimental data (open circles) is obtained for $E_b = 1.85$ eV and $\Delta E = 32$ meV [solid blue line in Fig. 2(b)]. Similar to the growth on quartz(0001), the characteristic spectral shape and its dependence on the film thickness reveals that after the completion of the first upright-standing monolayer, the pentacene multilayers crystallize in the thin-film phase forming (001)-oriented 3D islands consisting of nearly upright-standing molecules. On the other hand, the continued presence of peak e demonstrates that the flat-lying phase remains intact even after the condensation of the upright standing molecular layers.
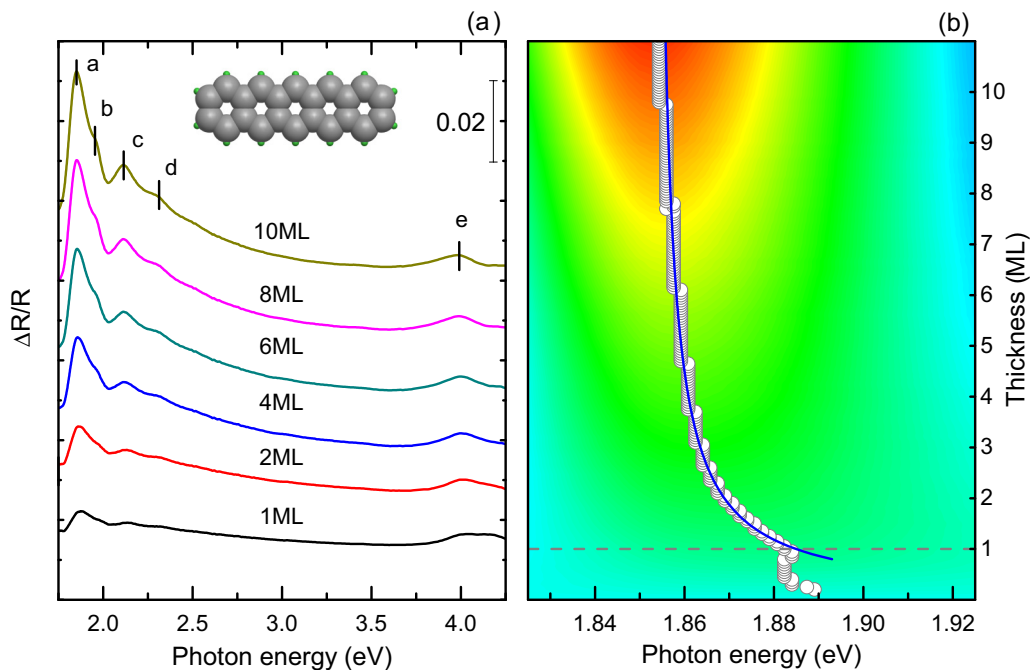

FIG. 2. (a) DR spectra recorded during subsequent pentacene deposition at room temperature for coverages beyond the completion of the dilute phase containing flat-lying molecules. The five most pronounced peaks are marked by a, b, c, d, and e, respectively. (b) False-color contour map of the DR spectra recorded in steps of 0.05 ML. The vertical axis indicates the total thickness of the upright-standing molecular layers excluding the flat-lying molecules. The changing energetic position of peak a is highlighted with open circles. The best fit to Eq. (2) is shown with the blue solid line.
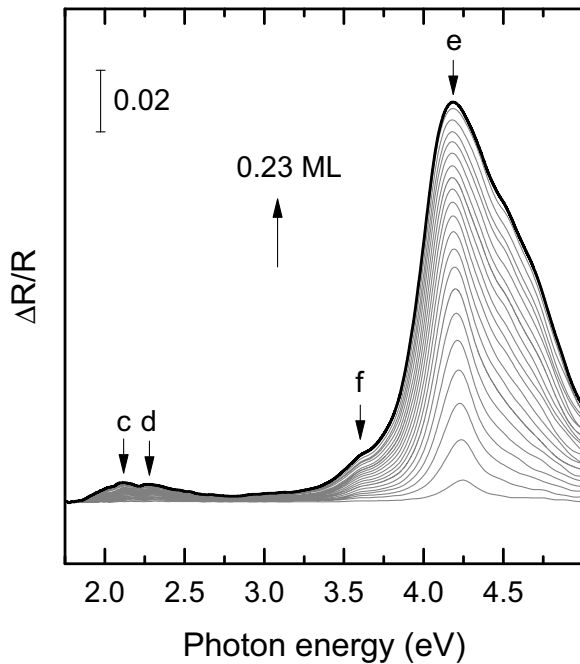
FIG. 3. DR spectra recorded during the deposition of pentacene on the α-Al$_2$O$_3$(0001) surface at 110 K. The pentacene coverage was increased in steps of about 0.01 ML up to a final thickness of around 0.23 ML.
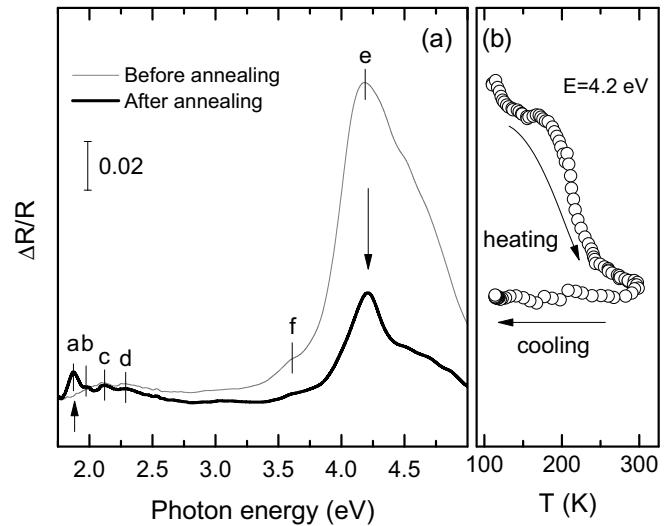

FIG. 4. (a) DR spectra of a 0.23 ML thick pentacene layer after deposition at 110 K (thin solid line) and after subsequent heating to 300 K at a rate of 0.2 K/s (thick solid line). The five peaks marked by *a, b, c, d,* and *e,* respectively, are defined in the same way as in Fig. 1. The decay of peak *e* and the concomitant increase of peak *a* are indicated by the vertical arrows. (b) Evolution of the DR signal at 4.2 eV as a function of temperature during heating and cooling.

B. Pentacene thin film growth at 110 K

In order to gain more insight into the growth kinetics, pentacene was also deposited onto the α-Al$_2$O$_3$(0001) surface at a lower substrate temperature of 110 K. In fact, the growth at 110 K is quite different as compared to room temperature. As one can see in Fig. 3, the DR spectra maintain the line shape characteristic of the flat-lying phase at room temperature (cf. lower panel in Fig. 1) during the entire growth sequence: the DR amplitudes of peaks *c*, *d*, and *e* grow at a constant rate during the growth without changes of the spectral line shape. No exciton state related feature shows up, even for coverages far beyond the saturation of the flat-lying phase (0.1 ML) at room temperature. This observation reveals that, at 110 K, all the pentacene molecules adsorb in a flat-lying geometry on the surface and no herringbone structure of upright-standing molecules is formed during growth. Evidently, the substrate temperature influences the growth kinetics of pentacene thin films and thus affects the molecular orientation and crystalline arrangement. It has been suggested that there should exist an activation barrier between the pentacene molecule in flat-lying and up-right standing orientation [12,37]. The limited thermal energy available to the pentacene molecules at 110 K apparently reduces the possibility for pentacene molecules to overcome this barrier and condense into islands with up-right standing molecular orientation.

Indeed, after heating the sample up to 300 K, the DR spectrum changes drastically as one can clearly recognize in the DR spectra recorded before and after heating [see Fig. 4(a)]. The difference between the two spectra can be explained by the restructuring of the pentacene molecular layer. The amplitude of peak *e* drops gradually during heating [see Fig. 4(b)], indicating that an increasing fraction of the pentacene molecules have flipped from a flat-lying to an upright standing orientation. The simultaneous emergence of the Davydov components *a* and *b* reveals that the reoriented molecules condense into a molecular layer with herringbone structure. On the other hand, it is worth noting that peak *e* does not vanish completely. Closer inspection of Fig. 4(a) reveals that the remaining intensity of peak *e* is very close to that of the flat-lying phase formed at room temperature (see Fig. 1). This observation indicates the coexistence of a flat-lying phase with the upright standing molecular islands on the substrate surface. Consequently, upon heating to 300 K the pentacene molecular layer deposited at 110 K adopts the identical structure as the one grown at room temperature. The evolution of the DR transient at 4.2 eV [Fig. 3(b)] recorded during heating indicates that the structural rearrangement occurs most rapidly around 200 K (for a heating rate of 0.2 K/s).

C. Molecular reorientation upon exposure to air

In the previous sections, we have already provided evidence for the thermally activated transition from the flat-lying to an upright standing geometry of pentacene molecules and its influence on the growth of pentacene thin films. In the present section, we will show the importance of the surface free energy on the orientation of the molecules at the interface. For this purpose, an ultrathin pentacene film with a thickness of 0.04 ML was deposited at room temperature on the α-Al$_2$O$_3$(0001) surface in UHV. As we have shown in the previous section a pentacene film with this nominal coverage corresponds to a dilute phase of flat-lying pentacene molecules. This can be
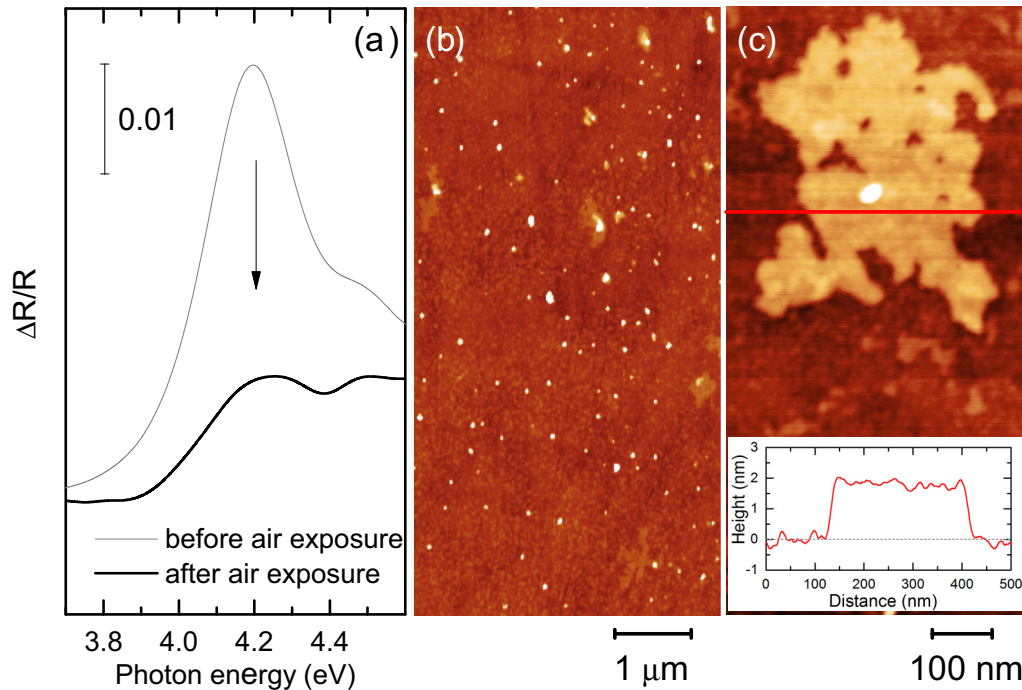
FIG. 5. (a) The DR spectra of a 0.04 ML thick pentacene molecular layer recorded in UHV directly after deposition (thin solid line) and in air (thick solid line). The quenching of the peak e at 4.2 eV is indicated by the arrow. (b) The overview surface morphology of the same sample revealed by *ex situ* AFM measurement in air (4 μm×8 μm). (c) The small scale AFM image (0.5 μm×1 μm) shows the details of a standing island. The height profile recorded along the red line in the AFM image is plotted in the inset of (c).

recognized in Fig. 5(a), which shows the DR spectrum of this thin film recorded in UHV directly after deposition (thin solid line). The positive peak at 4.2 eV evidences the flat-lying molecular orientation and the peak amplitude confirms the targeted coverage of ∼0.04 ML (c.f. Fig. 1). Then, the UHV chamber was vented and the α-Al₂O₃(0001) covered by flat-lying pentacene molecules was exposed to air. The DR spectrum recorded afterwards [thick solid line in Fig. 5(a)] reveals a quenching of the peak e at 4.2 eV. This spectral change shows that the initially flat-lying pentacene molecules stand up upon exposure to air. AFM measurements carried out *ex situ* from this very sample confirm this interpretation. The AFM images presented in Figs. 5(b) and 5(c) recorded right after the exposure to air show islands with a height characteristic for upright standing molecules. Based on the DRS and AFM results, we can unambiguously conclude that the originally flat-lying pentacene molecules condense into 2D islands of upright standing molecules upon exposure to air. This *dewetting* of the flat-lying monolayer can be attributed to the adsorption of air molecules from the atmosphere, presumably water or oxygen. Obviously, upon contamination of the substrate the condensation of pentacene into islands of upright standing molecules becomes energetically more favorable on the α-Al₂O₃(0001) surface.

IV. CONCLUSION

In conclusion, we have shown that deposition of pentacene onto α-Al₂O₃(0001) at room temperature leads to the growth of upright standing layers with herringbone structure after the initial formation of a dilute phase consisting of flat-

lying molecules. On the other hand, depositing pentacene molecules onto α-Al₂O₃(0001) at a substrate temperature of 100 K prevents the pentacene molecules from standing up and the molecular orientation remains flat-lying during the entire growth far beyond the dense monolayer of flat-lying pentacene molecules. Most interestingly, subsequent heating to room temperature leads to the reorientation of the majority of the pentacene molecules and the formation of molecular layers composed of upright standing molecules ordered in a herringbone structure. These results provide evidence for a kinetic barrier between the flat-lying and upright standing molecular configuration. Furthermore, initially flat-lying molecules in the dilute phase were found to reorient and condense into 2D islands of upright standing molecules upon air exposure, emphasizing the influence of the surface free energy on the molecular orientation. Our work demonstrates that the molecular orientation on dielectric substrates, which is decisive for the electrical and optical properties of organic thin films, can be manipulated to a certain extent by adjusting the kinetic and energetic parameters of the growth.

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