

Structural Rearrangements During the Initial Growth Stages of Organic Thin Films of F₁₆CuPc on SiO₂

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We present an experimental study on the first stages of the thin film growth of the organic molecule F₁₆CuPc (hexadecafluoro-copper-phthalocyanines) on SiO₂. By means of in situ X-ray reflectivity, in situ grazing incidence X-ray diffraction (GIXD), and ex situ atomic force microscopy (AFM), we provide a detailed picture of the film growth mode and its structural evolution at the nanometer scale. We discovered the formation of a low-density layer of molecular aggregates with heights between 5 and 10 Å at the interface with the SiO₂ and show that, on top of this interfacial layer, the nucleation and two-dimensional growth of elongated islands of upright standing molecules take place. Structural changes are observed, pointing to significant relaxations of the lattice parameters within the first layers of standing molecules.

I. Introduction

The development of electronic devices based on organic semiconducting films has become an attractive and competitive alternative to the traditional silicon-based devices for applications in which large scale areas or low production costs are required. In addition, their low processing temperature and compatibility with flexible substrates open new fields of applications. In the last years, enormous progress has been made in growing organic thin films with a wide range of exciting new properties.^{1–6} Among the various organic materials, planar aromatic molecules, which can be grown in highly ordered films, have emerged as potential candidates for the fabrication of organic field effect transistors (OFETs), solar cells, or organic light emitting diodes (OLEDs). In turn, the investigation of growth, assembling, and ordering mechanisms of organic thin films has become a topic of high interest in both fundamental and applied research.^{1–7} In contrast to inorganic semiconductors, whose physical principles of growth have been solidly established and successfully exploited to control the fabrication of desired morphologies and structures, the present-day knowledge on the growth of ordered organic films is still very poor. It is evident that more complex growth scenarios can emerge for organic molecules inherent to their anisotropy, and thereby with orientational degrees of freedom, and due to the van der Waals nature of the intermolecular interactions (less directional and weaker than covalent bondings).

F₁₆CuPc is a promising candidate material for organic electronics, since it is one of the few air-stable semiconducting molecules that show n-type behavior.⁸ Previous studies have shown that F₁₆CuPc forms highly crystalline films when prepared by organic molecular beam deposition (OMBD) on dielectrics which are relevant for electronics, such as SiO₂,^{9,10} functionalized SiO₂,¹⁰ or Al₂O₃.^{11,12} On all of these substrates,

a layered structure of molecules which stand upright is formed. This molecular orientation is the most favorable for those applications where transport within the surface plane is required, as is usually the case for OFETs, because the charge carrier transport in organic semiconducting films takes place preferentially along the overlapping direction of π -orbitals (i.e., perpendicular to the molecular plane).

Previous studies of F₁₆CuPc on SiO₂ were focused on mesoscopically thick films of typically tens of monolayers. However, as is known today, the charge transport in OFETs is essentially confined to the first layers of the organic films in proximity of the dielectric.^{3,13–15} Thus, the structure and morphology of the first layers are issues not only of high academic interest but of primary importance for the performance of OFETs as well. In this article, we provide, by means of in situ X-ray reflectivity, in situ grazing incidence X-ray diffraction (GIXD), and ex situ atomic force microscopy (AFM), a detailed picture of the early stages of the film growth and its morphology. Despite the low molecule–substrate interaction expected on SiO₂, we show that significant structural changes occur within the first F₁₆CuPc layers. We further disclose the formation of a low-density molecular layer at the SiO₂ interface.

II. Experimental Section

A. Film Growth. Thin F₁₆CuPc films have been prepared by organic molecular beam deposition (OMBD) on Si(100) wafers covered by their native oxide. The substrates were cleaned ultrasonically with acetone and ethanol and then dried with nitrogen gas. Subsequently, they were annealed under ultrahigh vacuum (UHV) above 500 °C for 12 h and slowly cooled to the growth temperature. The molecules were purchased from Sigma-Aldrich Chemie GmbH and purified twice by gradient sublimation before use. The film coverage and growth rate were controlled by means of a calibrated quartz crystal monitor (QCM).¹⁶

All X-ray and AFM measurements were performed on F₁₆CuPc films grown under similar conditions and on the same Si wafer. The substrate growth temperature was $T = 195$ °C, which

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results in well ordered F₁₆CuPc films on SiO₂,^{9,10} and the growth rate was 3 Å/min. A lower growth rate of 1 Å/min was employed for the films measured in situ by AFM under UHV conditions, leading to very similar results. The films used for the AFM characterization were grown under a base pressure of 10⁻¹⁰ mbar, and those grown in the portable UHV chamber for the in situ X-ray experiments, at 10⁻⁹ mbar.

B. AFM Studies. The growth evolution was studied ex situ under ambient conditions in amplitude modulation mode (tapping AFM) with a Digital Instruments NanoScope III SPM instrument. In addition, higher resolution AFM measurements were performed under UHV conditions in frequency modulation mode (NC-AFM) with an Omicron system. Low-resistivity silicon cantilevers with a spring constant of $K \sim 40$ N/m were used. The height of the different layers, together with its standard deviation, was determined statistically from numerous topographical profiles. The fraction of area covered by each layer was obtained by binary maps which show the percentage of area above a certain height.

C. X-ray Studies. In situ X-ray reflectivity and diffraction measurements have been performed in a specially designed portable UHV chamber, equipped with a beryllium window, a QCM, a Knudsen cell, and a heatable sample holder. The X-ray reflectivity measurements were carried out at the MPI Surface Diffraction Beamline in the synchrotron radiation source ANKA (Karlsruhe) with a wavelength of $\lambda = 1.2398$ Å. The reflectivity profiles have been obtained by specular $\theta - 2\theta$ scans. The diffuse background was eliminated by additional offset scans (offset of $\Delta\theta = 0.025^\circ$) and rocking scans (transverse scans) at certain q_z positions along the reflectivity curve. The purely specular intensity has been fitted with the Parratt algorithm,¹⁷ employing a multilayer model in which each individual layer is characterized by its thickness, electronic density, absorption coefficient, and the root-mean-square (rms) roughness of the associated interfaces. The data associated with the bare substrate are fitted with a layer for Si and another for SiO₂. Electron densities of $0.720 \text{ e}/\text{\AA}^3$ for the Si and $0.642 \text{ e}/\text{\AA}^3$ for the SiO₂ are obtained, in good agreement with literature values. The oxide thickness and roughness derived from the fitted model are 14 and 4.3 Å,¹⁸ respectively. The substrate parameters have been kept unchanged during the fitting of the F₁₆CuPc film. Additional layers were added whenever necessary to obtain satisfactory fits. The fit parameters for a certain thickness were used as the starting parameters for the subsequent fits. The height of the different molecular layers as well as its standard deviation has been calculated averaging over the values obtained for all samples. The fraction of area covered by each layer has been determined dividing the electronic density of the layer by the mean electronic density of a complete layer ($\delta = \rho/0.58$).

The GIXD measurements were carried out at the ID-10 beamline at the ESRF (Grenoble) using a wavelength of $\lambda = 0.7232$ Å. For the measurements of the in-plane powder structure of the F₁₆CuPc films, detector scans have been performed in the surface plane with the grazing incidence angle fixed at the critical angle value of the substrate ($\alpha_c = 0.1^\circ$). The observed Bragg peak widths, Δq_B , are related to the domain size, $\xi_{||}$, through $\xi_{||} = 2\pi/\Delta q_B$, allowing the determination of the mean lateral domain size, $\xi_{||}$, along the corresponding crystallographic direction.

III. Results

In what follows, we describe the coverage in terms of the equivalent thickness, D , of a close packed film with the same mass as the deposited film. Alternatively, we normalize the

thickness by the height of a layer of standing molecules, $d_z = 14.3$ Å, previously measured by X-ray diffraction in thicker films.^{9,10} The resulting fractions of a monolayer of standing molecules, Θ , and the equivalent thickness, D , are then related through $\Theta = D/14.3$.

The growth and evolution of the different F₁₆CuPc layers have been monitored by AFM and in situ X-ray reflectivity. Topographical AFM images are shown in Figure 1, for nominal film thicknesses ranging from 0.2 to 1.6 ML. At a coverage of $\Theta = 0.2$ ML (Figure 1a), the molecules nucleate in elongated islands, forming an incomplete first layer. The anisotropic shape of the islands is characteristic of the growth of standing F₁₆-CuPc molecules.⁹⁻¹² As the coverage increases to $\Theta = 0.4$ ML (Figure 1b), the islands of the first layer grow predominantly in length (anisotropic two-dimensional growth). Upon further increase of the molecular deposition up to 0.7 ML, the film growth remains confined mainly to the first monolayer, although few nucleation sites of the second layer are already present for the lowest coverages (brightest islands in Figure 1a–c). The anisotropic growth and the elongated shape of the crystallites prevent the complete coverage by coalescence, giving rise to the nucleation of new islands to fill the space between the existing islands. These new crystallites display smaller island sizes as a consequence of the lower amount of free space (Figure 1c). Note that, as a result of the poor packing of the film, the boundaries between individual islands are still clearly distinguished in the first layer. Better resolution images obtained by NC-AFM under UHV in a sample with a coverage intermediate between those of parts b and c of Figure 1 reveal that the domain boundaries serve as nucleation sites for the next layer. This is illustrated in Figure 2. Upon further deposition, the second layer grows (Figure 1d) and also the nucleation of the third layer starts before the second monolayer is completed (Figure 1e). We have determined that the average length of the F₁₆CuPc islands is of 150, 350, and 400 Å for the first, second, and third layers, respectively.

The experimental X-ray reflectivity data (symbols) are shown in Figure 3a together with their corresponding fits (solid lines) for film thicknesses ranging between 0.6 and 24 Å. This corresponds to a coverage, Θ , between 0.04 and 1.68 monolayers. The inset shows a rocking scan performed at a q_z value of 0.177 \AA^{-1} , evidencing the excellent data quality and the narrow peak width of 0.01° . The development of the electron density of the molecular layers as a function of coverage can be followed in Figure 3b, in which, as a guide for the eyes, the color boxes denote the different layers. The vertical dashed line marks the mean electronic density of $\rho = 0.58 \text{ e}/\text{\AA}^3$ obtained for thick films and, thus, the value expected for a complete compact layer of the organic material. It agrees perfectly with the electronic density estimated from the monoclinic bulk unit cell ($a = 20.018$ Å, $b = 5.106$ Å, $c = 15.326$ Å, and $\beta = 111.83^\circ$) containing two molecules.¹⁹ The growth behavior of each layer versus the total deposited film thickness, as obtained from AFM and X-ray reflectivity (Figure 4a), clearly shows that the film growth deviates from an ideal layer-by-layer growth (Figure 4b illustrates, as a control of internal consistency, the X-ray and AFM total coverage plotted versus the QCM coverage).

In addition, the X-ray reflectivity data give unambiguous evidence for the formation of an interfacial layer between the SiO₂ and the first layer of standing molecules (Figure 3b). The height of the interfacial layer, according to the reflectivity data, is about 3 Å for the first stages of the growth (0.2 ML) and increases to 6.5 ± 0.6 Å for higher coverage. When the total

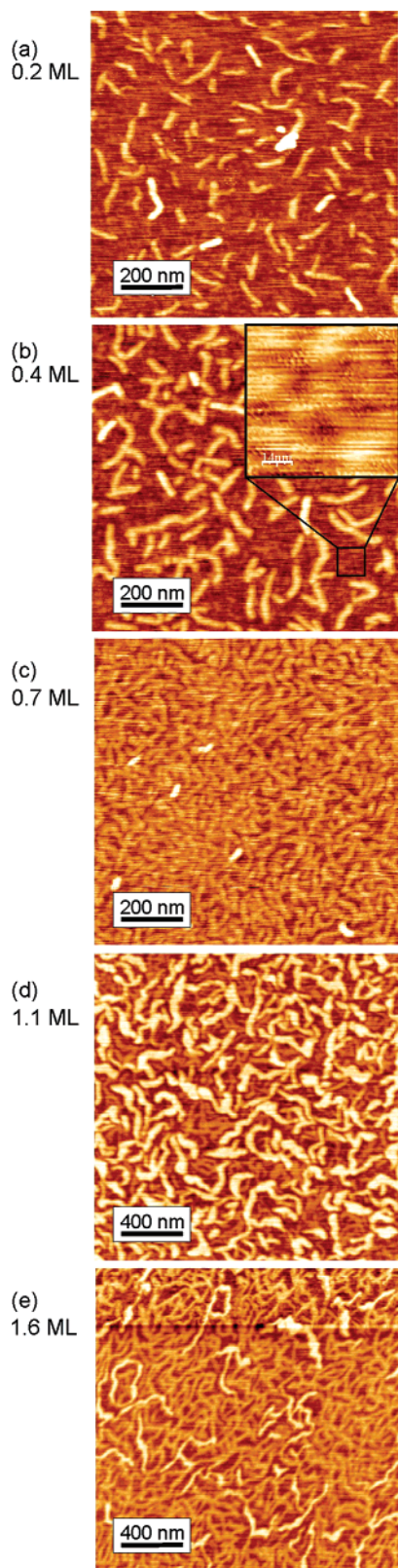


Figure 1. AFM topographic images of $F_{16}CuPc$ films on SiO_2 with a nominal coverage of 0.2 (a), 0.4 (b), 0.7 (c), 1.1 (d), and 1.6 ML (e), respectively. $F_{16}CuPc$ nucleates in a standing configuration and forms anisotropic islands. The inset in part b shows a zoom into the areas between the islands, revealing the existence of molecular aggregates.

coverage exceeds 0.77 ML (11 \AA), the electronic density of this layer reaches a saturation regime and increases only very slightly with further deposition. Surprisingly, the saturation value of $\rho = 0.35 \text{ e/\AA}^3$ is only 60% of the value expected for a closed

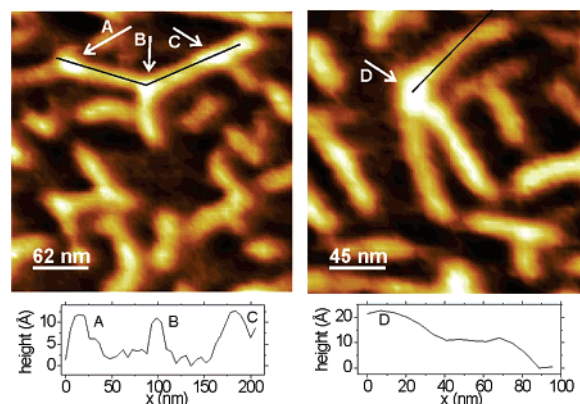


Figure 2. AFM topographic images showing the preferred nucleation sites for the second layer (brighter spots marked with labeled arrows) at the grain boundaries of the underlying first layer in two different areas, together with profiles taken along the crystallites as shown on the images. The nominal coverage corresponds to 0.34 ML.

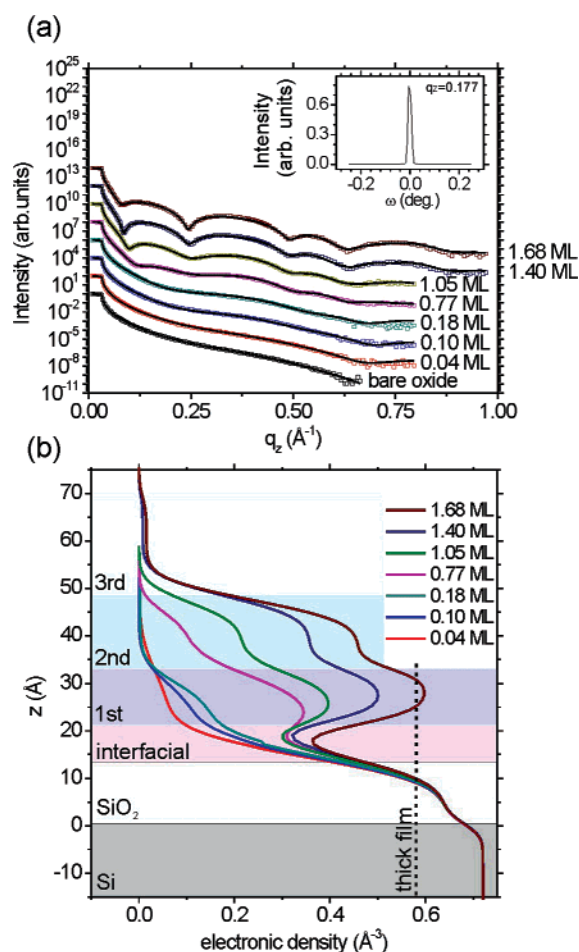


Figure 3. (a) X-ray reflectivity measurements of the clean substrate and $F_{16}CuPc$ films of 0.04, 0.1, 0.18, 0.77, 1.05, 1.40, and 1.68 ML thickness (symbols). The solid lines are fits to the data. The data sets are shifted for clarity. The inset shows a rocking scan performed at a q_z value of 0.177 \AA^{-1} . (b) Evolution of the electronic density profiles along the surface normal obtained from the fits for increasing coverage. The dashed line is the average electronic density of a thick $F_{16}CuPc$ film and thus the expected saturation value of the layers. The colored fringes represent a guide to the eye to distinguish the different layers of the film.

$F_{16}CuPc$ layer ($\rho = 0.58 \text{ e/\AA}^3$). The effect of the X-ray exposure onto the films has been carefully tested and gave no evidence for radiation damage during the X-ray reflectivity experiments.

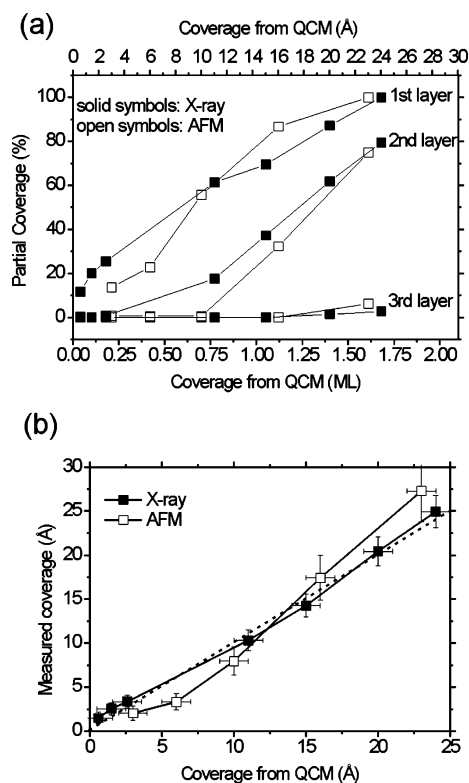


Figure 4. (a) Partial coverage of the first three layers of standing molecules as a function of the total coverage from X-ray (solid symbols) and AFM (open symbols) measurements, showing an excellent agreement between both techniques. (b) Estimated coverage as obtained from AFM (solid symbols) and X-ray (open symbols) data versus the nominal coverage obtained from the QCM during growth. The dashed line would indicate perfect agreement.

A closer inspection of Figure 1a and b shows that the region between islands is covered by some molecular aggregates. A topographic image of the area between islands is depicted in the inset of Figure 1b. This molecular film is inhomogeneous, with clusters of heights varying between 5 and 10 Å, resulting in an increased roughness ($\text{rms} = 4.2$ Å) compared to that measured on the bare SiO₂ ($\text{rms} = 1.6$ Å) in an area of 70 nm \times 70 nm. We correlate this molecular film to the interfacial layer observed by X-ray reflectivity.

The heights of the different layers together with their standard deviation have been obtained statistically from the AFM and X-ray reflectivity measurements. The height values determined from AFM topographic profiles are 14.1 ± 2.6 , 16.1 ± 2.9 , and 17.9 ± 2.4 Å for the first, second, and third layers, respectively. As a local and “real space” probe, AFM is less sensitive to surface roughness and is more accurate than X-ray reflectivity (whereby the roughness of each molecular layer is convoluted with the electron profile of the F₁₆CuPc molecule).²⁰ The heights obtained for the two first layers agree, within the error bar, with the size of the F₁₆CuPc molecule (~ 14.5 Å). Although a larger height is observed for the third layer, this does not constitute conclusive evidence for a different structure due to the uncertainty of the height measurements. The occurrence of structural changes has been confirmed by an in situ GIXD study of the lateral ordering in the films performed for thicknesses between 0.63 and 10.49 ML. In Figure 5a, we show the evolution of the most intense in-plane Bragg reflection as a function of deposited film thickness. This peak has been previously found in the in-plane structure of thicker films of standing F₁₆CuPc molecules.^{9,10} Notice that the q_{\parallel} values of this

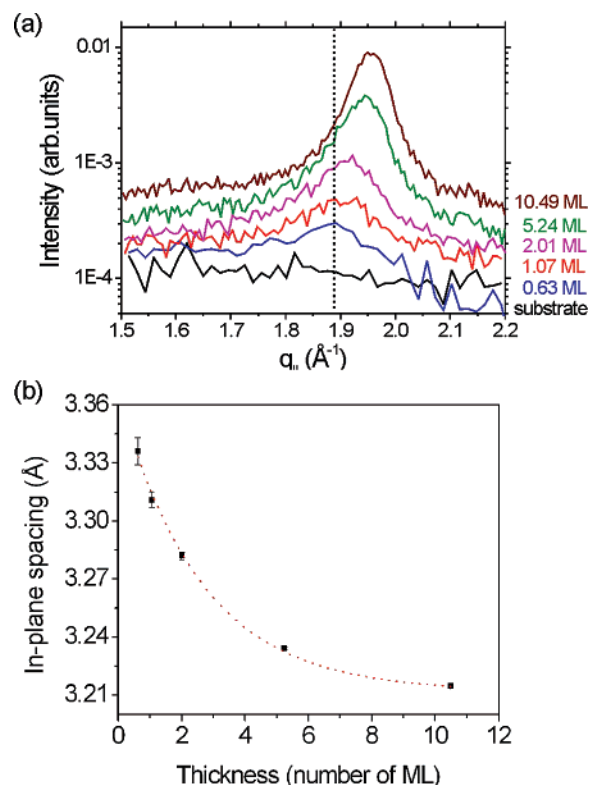


Figure 5. (a) In-plane scans of the F₁₆CuPc films for increasing coverage (0.63, 1.07, 2.01, 5.24, and 10.49 ML). The data for the clean SiO₂ is included. The scans are shifted for clarity. The dashed line is at the initial position of the reflection to make apparent the peak shift upon increasing film thickness. (b) Plot illustrating the change in in-plane spacing as a function of the thickness (in number of monolayers). This decrease can be fitted by an exponential decay (dotted line).

in-plane Bragg signal are close to $q_{\parallel} = 2\pi/3.22$ Å, associated with the lateral spacing of $d_{\parallel} \sim 3.22$ Å, which is similar to the distance between parallel molecular planes (as observed in the X-ray specular data for films of lying-down F₁₆CuPc molecules on other surfaces).²¹ The evolution of the lattice spacing with film thickness (Figure 5b) exhibits, in good approximation, an exponential decrease (dotted line) with a decay constant of 1/2.6 ML. This evidences that the major changes take place within the growth of the first three layers.

In addition, the mean lateral domain size, ξ_{\parallel} , estimated from the width of the Bragg reflection is found to increase with increasing thickness, from $\xi_{\parallel} = 41 \pm 5$ Å for a coverage of 0.063 ML to $\xi_{\parallel} = 118 \pm 2$ Å for a coverage of 10.49 ML.²²

IV. Discussion

A. Interfacial Layer. The interfacial layer, with a height of 6.5 ± 0.6 Å, forms simultaneously with the first layer islands of standing molecules and reaches the saturation when the total coverage is about 0.77 ML. Since the distance between layers of flat lying F₁₆CuPc molecules is of ~ 3.15 Å,²¹ the observed height of 6.5 Å suggests the formation of a bilayer of molecules lying flat on the SiO₂. The presence of this interfacial layer is further supported by AFM.

Regarding the initial growth of F₁₆CuPc on SiO₂, two scenarios can be considered: (a) the growth of molecular clusters of lying molecules competing with the growth of ordered islands of standing molecules on the SiO₂ and (b) the growth of standing molecules taking place on top of the interfacial layer of lying molecules. The height of the first layer

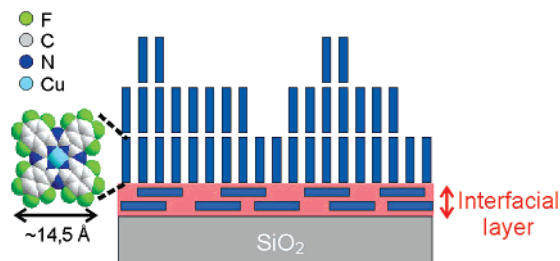


Figure 6. Simplified scheme illustrating the film structure. At the SiO₂ interface, an interfacial layer of lying F₁₆CuPc molecules forms on top of which the growth of standing molecules take place. At the left, the F₁₆CuPc molecular structure and its dimensions are presented.

of standing molecules measured by AFM relative to the upper part of the surrounding clusters (14.1 ± 2.6 Å) supports the scenario where the islands nucleate on top. Furthermore, the fact that the first layer does not replicate the topography of the clusters as observed at low coverage by AFM (with heights varying between 5 and 10 Å) suggests that the clusters eventually merge (leading to a more uniform interfacial layer) prior to the completion of the first layer of standing molecules. The existence of an underlying interfacial layer could provide an explanation of the large dispersion of heights obtained by AFM (with a mean square deviation of 2.6 Å) and of the high interfacial roughness obtained from X-ray reflectivity. The fact that the saturation value of the electronic density for this interfacial film is 60% of the value expected for a close packed F₁₆CuPc film seems to indicate a poor packing in the interfacial layer due to numerous vacancies and defects.²³ In fact, no evidence of ordering has been found by GIXD. A scheme illustrating the proposed scenario is shown in Figure 6.

The formation of a film of lying molecules is unexpected on a low-interacting surface as is the case of SiO₂. Previous structural studies on the first stages of the growth on SiO₂ of pentacene^{24,25} and diindenoperylene (DIP)²⁶ have not found any indication of a lying-down phase. Only for sexithiophene on SiO₂, the formation of a layer of lying-down molecules on the substrate in the submonolayer regime is observed, but these are no longer present when the first monolayer of standing molecules is formed.²⁷ A possible reason for the formation of such an interfacial layer in the case of F₁₆CuPc is the interaction of the fluorine atoms with the SiO₂ surface. A previous study of the electronic structure of F₁₆CuPc/SiO₂ by means of XPS has suggested that the strong interaction of F₁₆CuPc with SiO₂ leads to the breaking of the first F₁₆CuPc molecules, giving rise to the formation of a carbon-rich thin layer.²⁸

B. Growth Mode and Morphology. Since the lateral surface diffusion on amorphous SiO₂ is isotropic, the elongated shape of the islands (Figure 1) is due to an anisotropic sticking. Previous studies on F₁₆CuPc films have shown that the molecules stand upright and arrange into a cofacial columnar stacking, which finally leads to elongated crystallites or terraces with the long axis parallel to the stacking direction.^{10,11} It is the strong coupling of the electronic π -system which gives rise to this preferred anisotropic growth, and thus, also here the observed elongation direction is expected to be related to the stacking direction of F₁₆CuPc. With increasing coverage, the islands of the first layer grow and coalesce. As a consequence of the strong anisotropy, the first layer is formed with a large density of grain boundaries and vacancies and it is not completed before a total coverage of 1.6 ML is deposited (see Figure 4a). High-resolution images taken with NC-AFM in UHV (Figure 2) clearly show that the nucleation of the second layer takes

place mainly at grain boundaries between adjacent islands of the first layer. This suggests that, without experiencing a significant Schwoebel-type barrier, most of the molecules arriving on top of an island can diffuse to the lower layer at the initial growth stage (below the coalescence regime). In turn, at higher coverage, a fast growth of the subsequent layer occurs due to the higher abundance of grain boundaries that serve as nucleation centers. The similar morphology of the islands in the first and second layers suggests that the growth of the subsequent layer proceeds with the same alignment as that of the islands underneath.

The extended length of the islands together with the increase in the domain size for subsequent layers implies a higher lateral mobility of F₁₆CuPc on the standing F₁₆CuPc molecules than on the interfacial layer. The factors responsible for the reduced surface mobility of the first layer of F₁₆CuPc might be the higher roughness and inhomogeneity of the interfacial layer and/or an increased interaction of the molecules with the interfacial layer compared to the interaction with subsequent layers.

C. Structural Changes in the Layers of Upright Standing Molecules. The GIXD data give unambiguous evidence for noticeable structural changes during the growth. The observed decay of the in-plane lattice parameter must involve significant changes in the molecular orientation, either in molecular tilt or in angle between the molecular plane and stacking direction. This is an unexpected result, because the formation of strained structures or different phases of lying molecules in organic films occurs in general on substrates for which the molecule–substrate interaction dominates the intermolecular interaction, as is generally the case for organic film growth on metals.^{7,29–34} Although it is clear that, in comparison with metals, the molecule–substrate interaction for SiO₂ is rather weak, the present study shows that SiO₂ is apparently not so inert for F₁₆CuPc, causing the formation of an interfacial layer of lying molecules. It is plausible that the interaction of additionally deposited F₁₆CuPc layers with the substrate is sufficiently screened by the interfacial layer for the molecules, allowing them to arrange in a standing configuration, though being the molecular interaction with the interfacial layer strong enough to affect the molecular packing within the first layers.

We further note that, despite the built “strain” evidenced by the variation of the in-plane lattice parameter, a layered and continuous growth takes place. This is inherent to the flexibility derived of the van der Waals intermolecular interaction in organic crystals, allowing them to accommodate larger strain than inorganic semiconductors. A recent study on the growth of DIP on SiO₂ and on sapphire confirms that the formation of strained structures as well as structural changes during the growth may be a general feature of the growth of organic films.³⁵

V. Conclusions

By the combination of X-ray reflectivity, GIXD, and AFM techniques, we have elucidated the molecular assembly aspects in the initial growth stages of F₁₆CuPc on SiO₂. These results reveal a scenario that is more complex than what is expected on a low-interacting surface like SiO₂. It has been shown that an interfacial layer of around 6.5 Å is formed on the SiO₂, on top of which the nucleation and two-dimensional growth of long and narrow islands of upright standing molecules take place. Upon further deposition, subsequent layers start forming with a similar morphology but an increased elongation. Despite the similar morphology, the structural data reveal significant changes in the lattice parameters within the first layers, implying orientational and structural changes. The molecular interaction

with the F₁₆CuPc interfacial layer might be responsible for the formation of an initial standing phase with significant differences in the molecular packing.

This study gives clear experimental evidence that more complex growth scenarios have to be taken into account for organic semiconductors which are very different from those established for inorganic materials. Here, we have focused on those first layers which mainly contribute to charge transport in OFETs and thus are of great relevance for the understanding and further development of F₁₆CuPc transistors. Future studies are mandatory to determine the impact of the revealed structural and morphological properties on the evolution of the electron mobility in OFETs during the first stages of F₁₆CuPc growth.

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