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Structure, morphology, and optical properties of thin films of F_{16}CuPc grown on silicon dioxide

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Abstract

Thin films of hexadecafluorophthalocyanine (F_{16}CuPc) were grown by organic molecular beam deposition (OMBD) under ultra high vacuum (UHV) conditions on oxidized Si(0 0 1) substrates. The film thicknesses ranged from 120 to 450 Å and the substrate temperature was varied from −150 to 300 °C. X-ray diffraction and atomic force microscopy (AFM) were used to characterize the structure and morphology of the layers. Spectroscopic ellipsometry was employed to determine the dielectric properties and to locate characteristic transitions between 1.4 and 3.7 eV. The correlation of the electronic properties with the molecular packing in the films is discussed. The results are compared to the case of F_{16}CuPc films grown on stepped sapphire surfaces, which differ in their lateral ordering behavior.

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1. Introduction

Thin films of organic semiconducting molecules continue to attract a significant degree of attention due to their optical and electronic properties and the possibility to modify these by changing specific functionalities of the molecules. Phthalocyanines are model systems of this interesting feature, since by changing the central atom, e.g., the gap in the electronic spectrum can be modified [1,2]. In addition, hexadecafluorophthalocyanines have attracted interest as a possible n-type organic semiconductor with good stability characteristics [3]. It has been realized, however, that similar to the case of inorganic semiconductors, the electronic performance depends strongly on the structural integrity of these systems. Moreover, besides the need of a thorough structural characterization for device optimization, it has also become clear that the growth of these films exhibits characteristics specific for organics [4,5] with their additional

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degrees of freedom, such as their orientation (tilt angle) and their inherent anisotropies (see, e.g., Refs. [6–10]).

In this paper, the structure, the morphology, and the resulting optical properties of $F_{16}CuPc$ thin films on silicon dioxide are studied using X-ray scattering techniques, AFM, and spectroscopic ellipsometry. Oxidized silicon wafers were used as substrates, since they are widely used in prototype organic electronics, such as organic field-effect transistors (OFET), where the oxide layer serves as the insulating layer between one electrode (typically the gate) and the electronically active (semiconducting) film. The data obtained for the films studied here are compared to results from a recent study of $F_{16}CuPc$ grown on stepped sapphire substrates [11,12].

2. Experimental

Thin films of $F_{16}CuPc$ were evaporated in UHV following similar procedures to the ones described in Ref. [11]. The film thickness was varied from 120 to 450 Å and several films of 200 Å were investigated as a function of the growth temperature (T_g) in the range from −150 to 300 °C. All samples were prepared with a growth rate of 4 Å/min. Atomic force microscopy was performed in UHV in a commercial system (Omicron). Specular X-ray reflectivity was used to characterize the electron density profile, $\rho_e(z)$, along the surface normal. The reflectivity data were analyzed using the Parratt formalism [13], which takes into account multiple scattering effects. Grazing-incidence X-ray diffraction (GIXD) [14] was used to determine the in-plane structure and degree of epitaxial alignment of the film. Spectroscopic ellipsometry measurements were done with a rotating polarizer ellipsometer in the spectral range from 1.4 to 5.2 eV with a resolution of around 1 meV, and at an angle of incidence of 70° [15].

3. Results and discussion

Fig. 1(a) shows a typical specular scan of a 200 Å thick film deposited at $T_g = 230$ °C with a fitted curve using the Parrat formalism. At momentum transfer q_z below about 0.2 Å^{-1} well-defined Kiessig interferences corresponding to the total film thickness are visible, whereas at $q_z = 0.42$ Å^{-1} the first order out-of-plane Bragg reflection is seen with its associated Laue satellites (interference fringes due to the finite thickness of the film lattice). It should be noted that the thickness deduced from the Laue oscillations is identical to that deduced from the Kiessig interferences, implying that the out-of-plane order is high and coherent over the entire film thickness. This high out-of-plane order is further seen from the rather narrow width (0.02°) of the rocking scan (Fig. 2), which is a

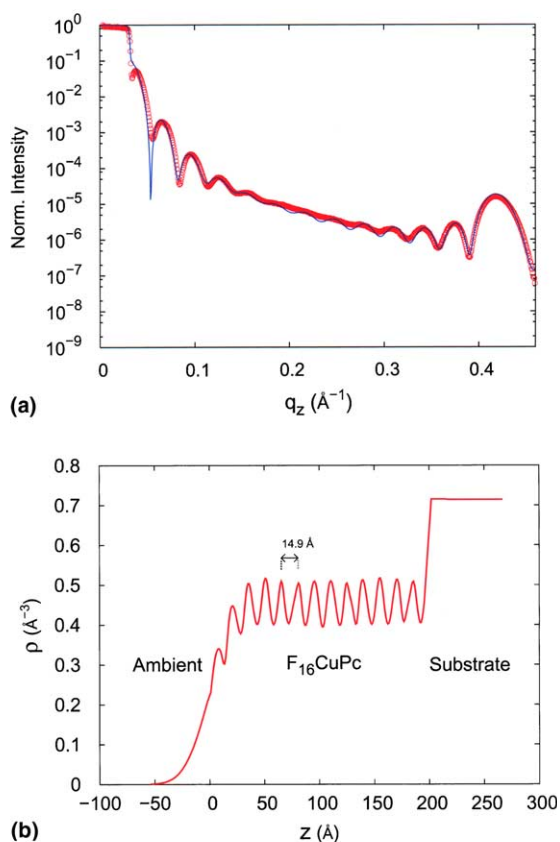

Fig. 1. (a) X-ray diffraction scan along the specular rod with a fitted curve following the Parrat formalism of a $F_{16}CuPc$ film with a thickness of 200 Å deposited at a substrate temperature of 230 °C. (b) First order approximation of the electron density profile along the surface normal ρ_z. The variations of the electron density in the organic layer are simulated with a 14.9 Å periodic sine function.

measure of the distribution width of the orientation of the lattice planes about the normal.

The electron density profile used in the fit of Fig. 1(a) is shown in Fig. 1(b). Note that if the data are limited to the first Bragg reflection a sinusoidal electron density profile is fully sufficient. Further refinement (on a shorter real-space length scale) would require the analysis of additional Bragg reflections, which is not in the focus of the present study.

It is important to note that the high order only develops at high substrate temperatures ($T_g > 100$ °C) during growth, while for decreasing growth temperature the order decreases (a rocking width of 0.1° is obtained when the substrate is kept at −150 °C during growth). Also, for increasing thickness, the root mean square roughness increases from $\sigma_{rms} = 0.6$ nm at a thickness of 13 nm to $\sigma_{rms} = 2.8$ nm at a thickness of 45 nm. Given that the roughness is still moderate even for thicker films grown at high temperatures (i.e., for growth not too far from equilibrium), this is suggestive of the films displaying wetting as opposed to dewetting behavior on this substrate, a finding similar to the results on sapphire [11]. Also the AFM measurements (see below and Fig. 4) show a wetted morphology, the F_{16}CuPc layers are closed and smooth.

Also, the out-of-plane lattice parameter $a_\perp$ (measured in each case at room temperature), which in this system is a measure of the molecular tilt, depends on the growth temperature, as for the films on sapphire [11], suggesting that the growth mechanism (with its presumably kinetically controlled "untilting" during growth) is similar. In Table 1 the values of the out-of-plane lattice parameter $a_\perp$ are shown together with the growth temperature T_g used in each case. As can be observed there is an increase of $a_\perp$ from 14.54 Å for $T_g = 45$ °C to 15.2 Å for $T_g = 250$ °C. However, when the substrate is maintained at $T_g = -150$ °C the value of $a_\perp$ is again 15.2 Å.

As for the in-plane structure, the analysis is somewhat limited by the azimuthal averaging on this isotropic substrate. Nevertheless, from the radial width of the in-plane diffraction spot shown in Fig. 3 we can deduce that the in-plane crystallite sizes are in excess of 200 Å.

Fig. 4 shows typical AFM images after the growth of the films. The surface morphology is characterized by needle-like features randomly oriented in the film plane, with a length of up to

Table 1
Dependence of the out-of-plane lattice parameter $a_\perp$ as a function of the deposition temperature T_g

T_g (°C)	−150	45	150	170	230	250
$a_\perp$ (Å)	15.2	14.5	14.6	14.9	15.0	15.2

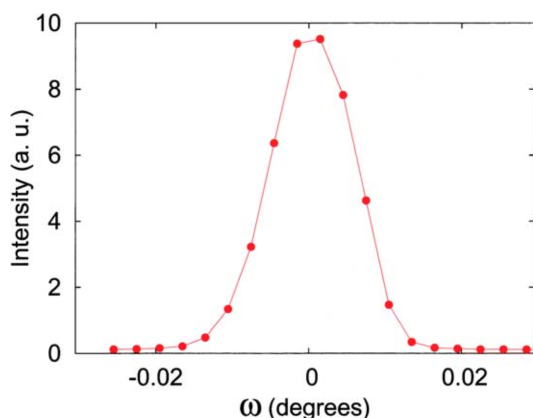

Fig. 2. Rocking scan over the first order Bragg reflection of Fig. 1. The full width half maximum (FWHM) of the peak is 0.02°.

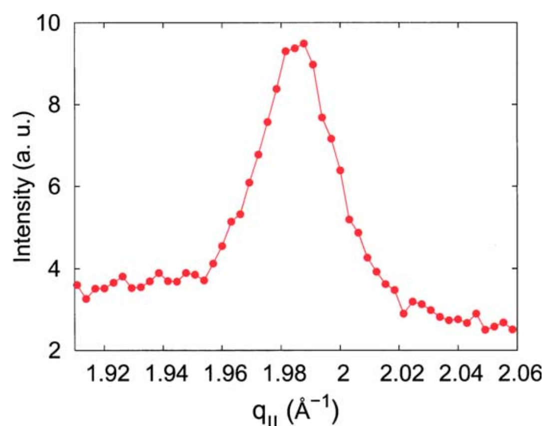

Fig. 3. In-plane reflection at $q_\parallel = 1.982$ Å^{-1}. The FWHM of the peak is about 0.028 Å^{-1}, which implies a domain size of ~220 Å. The thickness and deposition temperature of the film are 450 Å and 230 °C, respectively.

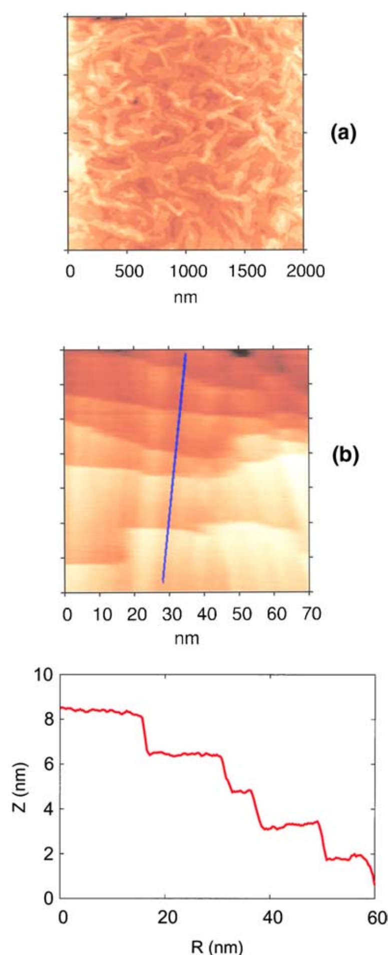

Fig. 4. Contact-mode AFM images of a 200 Å $F_{16}CuPc$ film on SiO_2 deposited at $T_g = 230$ °C. (a) shows a wide-range scan and (b) a zoom of an edge of the needles with a line scan showing the monomolecular steps.

several 100 nm and an aspect ratio (length: width) around 10:1. Planar terraces on the needles are visible. The line scan in Fig. 4 reveals regular steps between these terraces of ~1.5 nm, which is close to the out-of-plane periodicity determined by X-ray scattering. This regular step pattern is suggestive of essentially upright-standing molecules with a regular stacking sequence, fully consistent with the X-ray data. The line scan has been deliberately performed over an area where the deepest depression of the surface has been found. In this particular area five open layers are found. However, in general only the four top layers are not closed for this film, which is completely compatible with the electron density profile derived from the X-ray data (see Fig. 1(b)).

While the out-of-plane order of the films on silicon dioxide in terms of their crystallinity appears to be similar to that found for films on sapphire [11] the morphology obviously exhibits significant differences. The sapphire surface induces an in-plane alignment of the crystalline structure, which in turn can change the appearance of the morphology beyond simple alignment of the needles.

The complex refractive index of a 130 Å $F_{16}CuPc$ layer on SiO_2 is shown in Fig. 5(a). An isotropic model with four phases (ambient/ $F_{16}CuPc/SiO_2$/Si-substrate) has been used to numerically fit the experimental data. The strong anisotropy of the intrinsic optical properties of $F_{16}CuPc$ [11,15] (monoclinic unit cell) is averaged out due to the azimuthal spread of the crystallites. Thus, these films are at most uniaxial, with $\varepsilon_Z \simeq \varepsilon_X = \varepsilon_Y$. In Fig. 5(b), the second derivative of the imaginary part of the dielectric function is plotted (circles) together with a fit (solid line). Electronic transitions (marked with arrows) at the energies 1.57 (1), 1.76 (2), 1.90 (3) and 2.00 eV (4) (±0.01 eV) are observed. These positions are similar to those observed in films on Al_2O_3 and are $\pi \rightarrow \pi^*$ transitions characteristic of the phthalocyanine rings. These four transitions form the Q-band of $F_{16}CuPc$. The position of these excitons is linked to the stacking of the molecules inside the unit cell and is discussed elsewhere (Ref. [15]).

4. Summary and conclusions

OMBD growth of thin films of $F_{16}CuPc$ on oxidized silicon wafers results in films with a well-defined out-of-plane stacking of the molecular lattice planes and a narrow rocking width for growth temperatures above 100 °C. The films are coherently ordered across the entire thickness. In-plane crystallinity could be observed by GIXD with a domain size of the order of 200 Å, but on these flat amorphous substrates there is of course no overall azimuthal order.

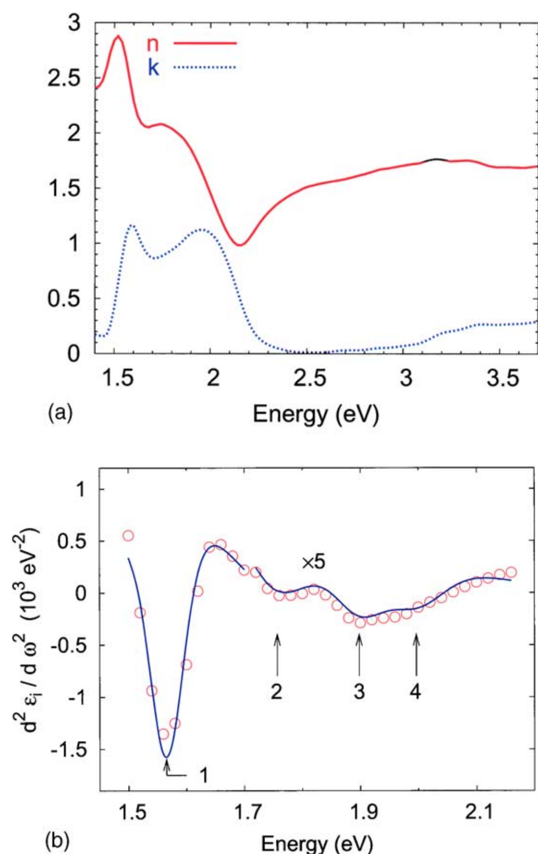

Fig. 5. (a) Ellipsometrically determined complex refractive index $N = n + ik$ from a numerical fit using an isotropic four-phase model (ambient/F_{16}CuPc/SiO_2/Si-substrate). The SiO_2 thickness was fixed to 30 Å (determined prior to growth) and the fitted film thickness is 130 ± 10 Å. The deposition temperature is 230 °C. (b) Second derivative of the imaginary part of the dielectric function. The experimental data are plotted as circles and the fit is shown by the solid line. The arrows show the observed transition energies. Note that for clarity reasons the data above 1.7 eV have been magnified by a factor of 5.

The AFM images exhibit a characteristic morphology with elongated features. At higher resolution, a needle-like substructure of the terraces becomes apparent. Obviously, these features are related to the inherently strong anisotropy of the F_{16}CuPc crystallites in structure and shape. However, the optical properties determined by spectroscopic ellipsometry are isotropic, due to the in-plane random orientation of the crystallites. Several electronic transitions in the Q-band could be identified by this method.

Generally, it can be concluded that in terms of their crystalline structure and quality the Fi_{16}CuPc films grown on silicon dioxide are similar to the ones grown on sapphire, at least in terms of the out-of-plane structure. Nevertheless, since the in-plane alignment found on stepped sapphire is missing on silicon dioxide, the morphology has a very different appearance, and of course also the strong in-plane anisotropy found in the optical spectra is averaged out. Both silicon dioxide and sapphire are rather inert substrates for F_{16}CuPc, which is probably the reason for the similar growth scenario in terms of the evolution of the out-of-plane lattice parameter and the related tilt angle as a function of growth temperature.

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