Self-organization of phthalocyanines on Al_2O_3 (11$\bar{2}$0) in aligned and ordered films

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We studied the self-organization process of F_{16}CuPc films (20–30 ML) on stepped Al_2O_3 (11$\bar{2}$0) substrates. X-ray diffraction measurements revealed a highly ordered layered structure with the molecules in a nearly upright configuration. The morphology, investigated by atomic force microscopy, consisted of long (several microns) and narrow (20–100 nm) needlelike terraces unidirectionally aligned along one of the main crystallographic directions of the Al_2O_3 (11$\bar{2}$0) surface. High resolution atomic force microscopy images revealed in-plane molecular order with the molecular stacking direction parallel to the needlelike terraces. Such anisotropic morphology is the result of a self-organization process of F_{16}CuPc in elongated crystallites driven to a preferential orientation by the interaction with the substrate. Spectroscopic ellipsometry showed that these films exhibit anisotropic optical properties correlated with the molecular arrangement.

I. INTRODUCTION

In the last decade it has been shown that organic molecules with extended π systems are a versatile and attractive alternative for the fabrication of electronic and optical devices. For the optimization of the electronic and optical properties, the control of growth and structure of the molecular assemblies is required.[1–4] One important advance has been the use of organic molecular beam epitaxy (OMBE) as a means to achieve control over the growth of organic films with extremely high chemical purity.[1] One of the key factors for the growth of ordered films is the interaction between substrate and molecules. This interaction provides a mechanism to order the first layers in correlation with the surface lattice. Thus, under the appropriate growth conditions, long-range ordered molecular monolayers can be successfully obtained.[5–7] With increasing film thickness, additional difficulties of achieving highly ordered molecular films can arise. Typical problems are the formation of polymorphic structures, roughening and island growth.[7–13]

For technological applications the formation of thin films with both, smooth surfaces and interfaces as well as high crystallinity is often desirable. Even when a highly ordered structure perpendicular to the surface can be obtained, it may still be difficult to achieve in plane orientation. The use of relatively strongly interacting substrates can cause in-plane molecular ordering. The disadvantage is that it can result in an abrupt morphology beyond a certain thickness due to the formation of islands for strain relief (dewetting structures).[9,7,14] The situation is rather different for more inert substrates (like NaCl, MoS_2, Al_2O_3, etc.) where the weaker molecule–substrate interaction largely avoids strain and may lead to the growth of thick and flat films. However, weak substrate interaction implies that the molecular arrangement is only weakly affected by the substrate and frequently the

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crystalline domains grow essentially randomly oriented in the plane of the surface.[6]

Thus, it is still challenging to find systems where the balance between intermolecular forces and interaction with the substrate leads to the formation of layered films with defined in-plane orientation.[15–17] A previous study has shown that the growth of $F_{16}CuPc$ on Al_2O_3 ($11\bar{2}0$) stepped substrates results in in-plane ordered organic layers.[17] Moreover, $F_{16}CuPc$ is particularly interesting because it is n-conducting with high electron mobility and also relatively stable.[18]

In this work we show that $F_{16}CuPc$ self-organizes on Al_2O_3 ($11\bar{2}0$) forming unidirectionally aligned needles. The $F_{16}CuPc$ films exhibit high out-of-plane order, probed by x-ray scattering measurements, and homogeneous thickness (of tens of layers). High-resolution atomic force microscopy (AFM) measurements reveal the molecular alignment. This study, performed with Al_2O_3 ($11\bar{2}0$) substrates with different stepped morphology, reveals that the preferential orientation is related to the crystallographic directions of the Al_2O_3 ($11\bar{2}0$) surface. The $F_{16}CuPc$ films exhibit strongly anisotropic optical properties whose spectral features measured by spectroscopic ellipsometry are connected to the molecular arrangement.

II. EXPERIMENTAL

Al_2O_3 ($11\bar{2}0$) substrates with different miscut direction (azimuthal orientation of the miscut) and magnitude (between 0.26° and 1.8°) have been used. The substrates have been annealed in air at 1300–1400 °C for 10–40 h to produce a regular stepped surface. The magnitude and azimuthal orientation of the miscut angle as well as the annealing time determine the stepped morphology. The miscut and its orientation have been determined by x-ray diffraction measurements.

The substrates have been cleaned in ultrasonication bath with repeated cycles of water with soap, acetone and ethanol and annealed at 750 °C in ultrahigh vacuum (UHV) for about 12 h. Although Auger electron spectroscopy has revealed traces of carbon on the Al_2O_3 substrates, similar morphologies have been obtained on other substrates where the carbon had been removed by sputtering. All the samples discussed and presented here have been grown on substrates without further treatment than the one explained above (i.e., no sputtering). [In a small number of samples we have obtained the formation of a dewetting film. It is not known yet what the reason for the formation of this structure is, but it is presumably related to the surface conditions].

Other parameters that can influence the growth have been kept fixed, like the substrate temperature (230 °C) and the evaporation rate (2–3 Å/min). The films have been grown in an UHV chamber with a base pressure of 10^{-10} mbar. The $F_{16}CuPc$ ($C_{32}F_{16}N_8Cu$) powder was purchased from Aldrich Chemical Co. (Munich, Germany) and purified twice by gradient sublimation prior to evaporation from a custombuilt Knudsen cell.

AFM in contact mode was performed in a UHV-AFM commercial system (Omicron, Mannheim, Germany) using rectangular cantilevers with a normal spring constant of 0.1 N/m. The x-ray measurements were performed using in-house x-ray stations with Cu K_α ($\lambda = 1.54$ Å) and Mo K_α ($\lambda = 0.71$ Å).

Spectroscopic ellipsometry measurements were performed with a rotating analyzer ellipsometer using a 75 W high-pressure Xe lamp as light source and a 750 nm equivalent focal lenght double prism/grating spectometer.[19] Data were taken at angles of incidence of 60° and 70°.

III. RESULTS

A. X-ray diffraction

In Fig. 1(a) we show a typical specular scan obtained from one of the films. The sample was oriented with the steps parallel to the beam to avoid misalignment between the surface reflectivity and the crystallographic planes. The x-ray reflectivity at low values of the perpendicular momentum transfer (q_z) shows Kiessig fringes charateristic of the interference between the film–substrate interface and the film surface. From the periodicity of fringes Δq_z, a thickness of 340 Å is obtained for this film according to the equation $D = 2\pi/\Delta q_z$.

To investigate the out-of-plane crystallinity, x-ray diffraction measurements along the specular rod have been performed on $F_{16}CuPc$ films with thicknesses between 230 and 390 Å. All the films exhibited a Bragg reflection that corresponds to a distance between molecular planes of $d = 14.14$ Å ± 0.05 Å. This is evidence for a configuration of molecules standing essentially upright. The error corresponds to the standard deviation of the values obtained of different samples. Figure 1(b) shows the higher-angle region from the same sample. The first-order Bragg reflection and two higher-order reflections can be observed. The peak has been assigned to the (001) orientation by comparison to bulk structure data.[20] A more detailed scan around the first order reflection is depicted in the inset of this figure. The oscillations around the first order Bragg peak (Laue oscillations) indicate that the film exhibits a well-defined and homogeneous coherent thickness. From the width of the Laue oscillations Δq_z, the coherent thickness D_{coh} can be estimated via the relation $D_{coh} = 2\pi/\Delta q_z$. It is found that the film is coherently ordered across 310 Å (~22 molecular layers), almost across the entire thickness.

Another evidence of the good crystallinity is found in the low mosaicity as probed by the small full-width half maximum (FWHM) of the rocking scans around 0.02°.

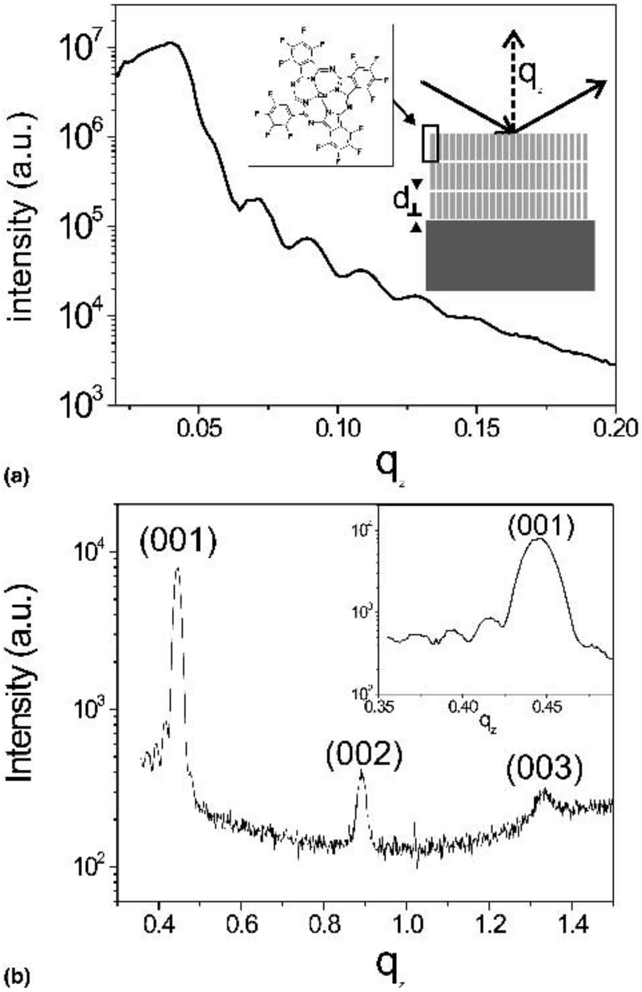

FIG. 1. (a) X-ray reflectivity data of a F_{16}CuPc thin film. The inset shows a scheme of the molecule and of the specular diffraction geometry. (b) X-ray diffraction along the specular rod showing the three first order Bragg reflections. Inset is the rocking scan in the (001) Bragg peak; Laue oscillations appear at the sides of the peak.

Although significant differences were found in some samples, the FWHM was less than 0.1° in all cases.

B. Morphology

The morphology and order in the plane of the films have been investigated by AFM. The images have been taken in contact-mode at low load to avoid damage to the films.

Figure 2 shows images of three different Al_2O_3 (11$\bar{2}$0) substrates. Due to the miscut angle, the Al_2O_3 (11$\bar{2}$0) substrates develop a stepped surface after annealing at 1300–1400 °C[21–23] with steps running mostly perpendicular to the miscut direction. The miscut angle is 1.8°, 0.3°, and 0.26° for the substrates shown in Figs. 2(a)–2(c), respectively. The main crystallographic directions of the Al_2O_3 (11$\bar{2}$0) surface, [0001] (parallel to the *c* axis) and [1$\bar{1}$00], are indicated. The steps of the substrate in Fig. 2(a) are parallel to the [1$\bar{1}$00] direction of the Al_2O_3 (11$\bar{2}$0) surface. In the other two substrates [Figs. 2(b) and 2(c)] the azimuthal direction of the miscut determines the formation of steps that do not follow any of the surface crystallographic directions. The step-height is of the order of magnitude of the molecular diameter (~15 Å). Line profiles are shown on the top part of Fig. 2.

Topographical images of the F $_{16}$CuPc films grown on these substrates are shown in Figs. 2(d)–2(f). The thicknesses, determined by x-ray diffraction, are 340, 235, and 270 Å, respectively. The x-ray data shown in Fig. 1 were measured in the film from Fig. 2(d). The films completely cover the substrate. Interestingly, parallel elongated molecular terraces are observed, unidirectionally aligned all over the sample. The length of the needles is several microns and the width varies from sample to sample between 20 and 100 nm (length-to-width ratio of up to 100).

We note that the alignment occurs along one of the main crystallographic directions of the Al_2O_3 (11$\bar{2}$0) surface, either along [0001] or along [1$\bar{1}$00], independent of the average step direction. This is evidenced for films grown onto those substrates where the average step edges do not follow any of the crystallographic directions like it is observed in Figs. 2(e) and 2(f). Similar needlelike morphologies have been observed in films from 50 to 380 Å and on substrates with different miscut angle and direction. As it is illustrated in the Fig. 2, we have not found any dependence of the films morphology with the terrace-width for the substrates used. It can be observed that the terrace-width of the Al_2O_3 (11$\bar{2}$0) surface does not limit the length of the molecular needles which extend across the steps. The terraces of the underlying substrate can still be distinguished in those films with small roughness like in Fig. 2(e). The data from different samples are summarized in Table I. A systematical variation of the mean width of the molecular needles with thickness has not been observed.

We should point out that the structure and morphology of the films are thermally stable up to approximately 260 °C when desorption takes place.

C. In-plane molecular order

At higher resolution it can be observed that the needles consist of elongated molecular terraces [Fig. 3(a)]. The height of the smallest molecular step is around 15 ± 1 Å, coinciding approximately with the height of the molecule as shown in the topographical profile of Fig. 3(c). This reflects the layered stacking with molecules standing essentially vertical in agreement with the x-ray data, as has been observed before for films on Al_2O_3[17] and on SiO_2.[24] Small-size images reveal that the molecules are long-range ordered. As shown in Figs. 3(b) and 3(d),

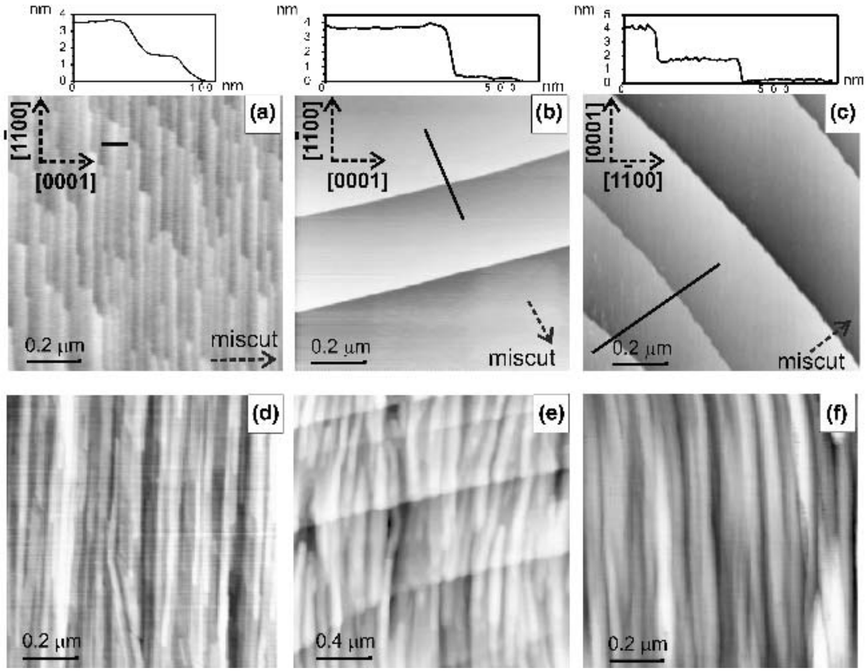

FIG. 2. AFM topographic images of Al_2O_3 (11$\bar{2}$0) substrates with a miscut of (a) 1.8° (b) 0.3°, and (c) 0.26°. The substrates in (b) and (c) show large terraces (about 400 nm) which are atomically flat and almost completely free of monoatomic steps. Line profiles are shown on top. Topographic images of the F_{16}CuPc films grown on these substrates are shown on (d), (e), and (f) with thicknesses of 340, 235, and 270 Å, respectively. The film morphology consists of needlelike structures oriented along the [1$\bar{1}$00] in films (d) and (e) and along the [0001] in film (f). The root-mean-square (RMS) roughnesses of the films are (d) 14 Å, (e) 25 Å, and (f) 39 Å. The RMS roughness of the bare substrates (measured onto an area of the same size) is (a) 4.5 Å, (b) 17.5 Å, and (c) 10 Å.

TABLE I. Selection of samples exhibiting needlelike morphology with different thicknesses and on Al_2O_3 (11$\bar{2}$0) substrates with different miscut magnitude and direction. The substrates labeled I, II, and III are those in Figs. 2(a), 2(b), and 2(c), respectively. The substrates type IV have a miscut angle of 0.3° and an average step direction deviated 40° from the [0001] direction. The films S6, S3, and S4 appear in the Figs. 2(d), 2(e), and 2(f), respectively.

Sample	Thickness	Needle direction	Needle width	Al_2O_3 (11$\bar{2}$0) type
S1	45	[0001]	44 ± 20	III
S2	45	[0001]	44 ± 20	IV
S3	235	[1$\bar{1}$00]	56 ± 14	II
S4	270	[0001]	56 ± 14	III
S5	270	[0001]	49 ± 10	IV
S6	340	[1$\bar{1}$00]	41 ± 12	I
S7	340	[1$\bar{1}$00]	43 ± 12	II

stripes running parallel to the needles are observed. The image in Fig. 3(b) was obtained in the area marked in Fig. 3(a). The average separation between rows is 9.5 ± 0.6 Å. Along the stripes another periodicity of 4.4 ± 0.6 Å can be distinguished. The error bar is obtained from the standard deviation of the periodicity determined in several tens of images.

A scheme of the structure is represented in Fig. 3(e). Since the bulk F_{16}CuPc structure has not been reported in the literature, the molecular arrangement has been depicted by analogy with the stable structure of the CuPc (β-form).[25] The CuPc (001) surface consists of molecular columns parallel to the surface as illustrated in the Fig. 3(e). The stripes observed on F_{16}CuPc films by AFM [Figs. 3(b) and 3(d)] can be recognized as columnar stacks of molecules where the direction of the stripes is the stacking direction (*b* axis).

Because the intercolumnar distance is smaller than the diameter of one F_{16}CuPc molecule (about 14.5 Å), it is inferred that the normal to the ring is tilted with respect to the staking direction as it occurs for CuPc [see Fig. 3(e)]. However the AFM data is not sufficient to determine whether molecules in adjacent columns are alternatively tilted as observed for CuPc.

D. Optical properties

We observed a strong in-plane anisotropy in the optical properties that is well correlated with the structural findings. Ellipsometry measurements for different azimuthal angles showed that two principal axes of the dielectric tensor are in the film plane and essentially aligned with the [0001] and [1$\bar{1}$00] substrate's directions. Moreover, these orientations showed no dispersion as a function of energy, as would be possible in monoclinic symmetry. Thus, the dielectric tensor components of the films can be obtained by considering the usual biaxial (orthorhombic-like) behavior. The particular orientation of the tensor is rather unfavorable to allow a precise

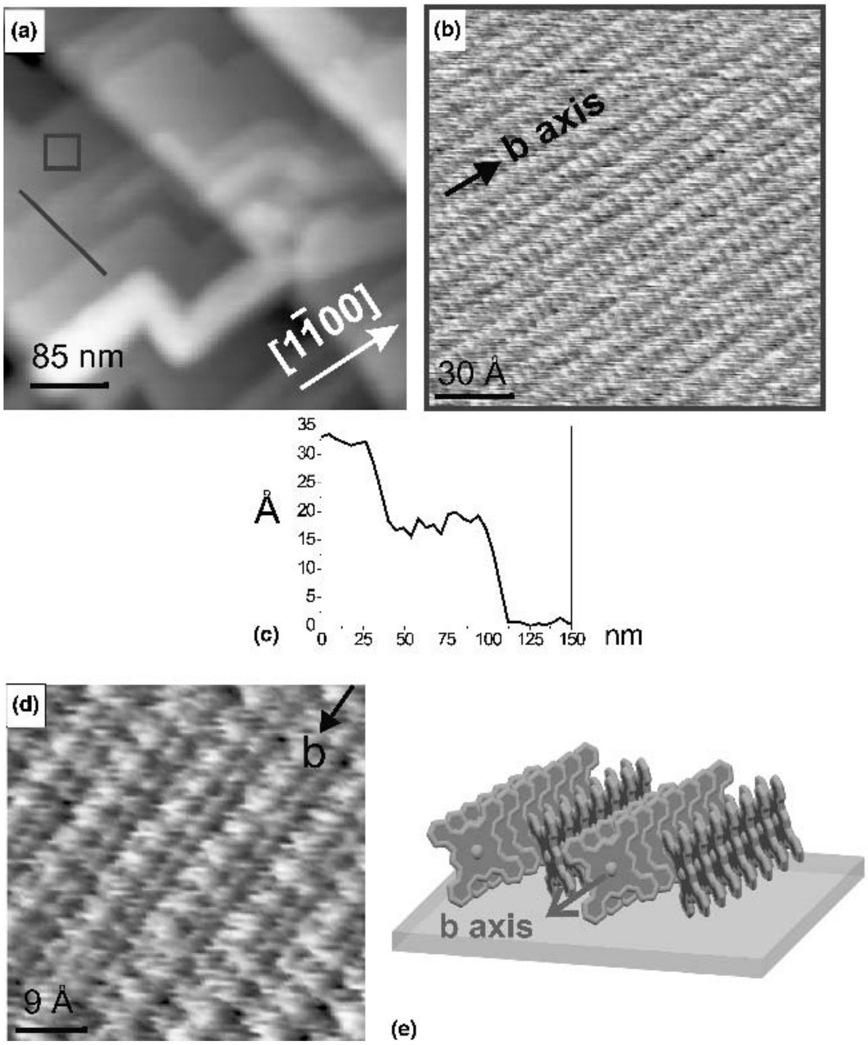

FIG. 3. (a) AFM topographical image in a film of 235 Å showing terraces of $F_{16}CuPc$ (one layer height). The steps of the underlying Al_2O_3 $(11\bar{2}0)$ substrate are also visible crossing the image diagonally. (b) A higher magnification image, taken on the marked area, shows the molecular arrangement in stripes parallel to the molecular terraces. The distance between stripes is 9.5 Å. A periodicity of 4.5 Å is observed along the stripes. (c) Line profile obtained in (a) showing molecular steps of around 15 Å in agreement with a configuration of molecules standing upright. (d) High resolution image of the molecular order (another sample). (e) Schematic model of the molecular arrangement by analogy with the stable structure of CuPc. The stripes observed by AFM correspond to the molecular stacking along the *b* axis.

measurement of the perpendicular component, especially because its value results very similar to one (the largest) of the in-plane functions. Therefore we considered a uniaxial behavior with ordinary components $\epsilon_Z = \epsilon_X$ and an extraordinary ϵ_Y one, obtaining a very good fit of the experimental results.[19] This procedure results in well determined in-plane ϵ_X and ϵ_Y, and approximate ϵ_Z. The fitted dielectric functions are depicted in Fig. 4(a) for one of the samples [that shown in Fig. 2(f)], evidencing the large in-plane anisotropy. A topographical image of the same sample is presented in Fig. 4(b) showing the characteristic morphology of aligned needles. The lower values of ϵ_Y, which imply a lower polarizability, are associated with the *b* axis orientation or stacks of molecules in phthalocyanine crystals. Accordingly, the *b* axis should be identified with the *Y* direction shown in Fig. 4(b), which is in agreement with the molecular needles being aligned along the sapphire [0001] direction. To illustrate the correlation between the structural features and the anisotropic optical response, an ellipsoidal representation of the dielectric tensor for this sample is depicted in Fig. 4(c), displaying a typical lentil-like shape at the energies of the main electronic transitions.

IV. DISCUSSION

The high crystallinity and large coherent thickness found for the out-of plane structure evidence a homogenous and well-layered structure with the molecules standing nearly upright. The morphology, observed by

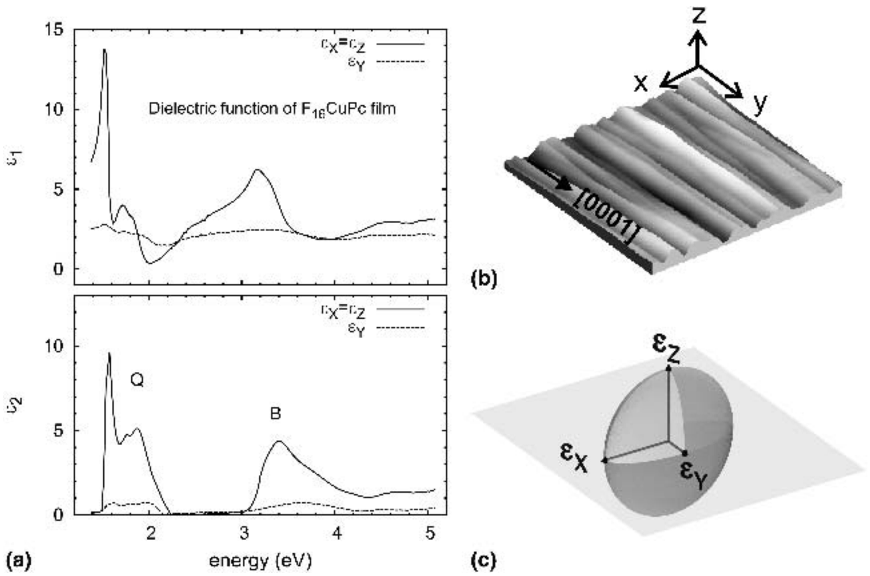

FIG. 4 (a) Fitted in-plane dielectric functions for one of the films denoted ϵ_X (component along substrate's [1$\bar{1}$00] direction, perpendicular to the wires) and ϵ_Y along [0001], in this case along the wires). (b) AFM topographical image of this film. (c) Scheme showing the indicatrix or real part of the dielectric tensor obtained for this sample at 3 eV.

AFM, consists of molecular needlelike terraces whose height corresponds to one or several layers. High-resolution images reveal that the molecules are long-range ordered in molecular columns parallel to the needles. A separation between columns of 9.5 ± 0.6 Å has been found with a molecular distance of 4.4 Å ± 0.6 Å within the columns.

The needlelike morphology reflects a self-assembling mechanism of F_{16}CuPc that drives to the formation of columnar stacks of molecules and leads to anisotropic two-dimensional growth of elongated molecular terraces. In fact, self-organization of F_{16}CuPc in needlelike structures occurs on SiO_2 as well.[24] However, in this case, elongated molecular crystallites are randomly oriented in the plane. Thus, the formation of anisotropic crystallites is an intrinsic property of the shape and intermolecular interaction of F_{16}CuPc molecules. Al_2O_3 (11$\bar{2}$0) substrates induce a preferential orientation of needles which is related to the crystallography of the surface, even for those substrates where the average direction of the steps does not coincide with one of the crystallographic directions. Spectroscopic ellipsometry shows that the films exhibit large optical anisotropic properties that are correlated with the morphology. Two principal axes of the effective dielectric tensor are found in the plane oriented along and perpendicularly to the needles, that is, along the [0001] and [1$\bar{1}$00] directions.

The driving mechanism for such anisotropic film growth has not been determined yet and the present data are not sufficient to attempt a detailed discussion. One possible mechanism responsible for the in-plane alignment might be the formation of a well-defined orientational relationship between the films and the substrate lattice interaction that is, epitaxial or quasiepitaxial structure. This can not be determined without more information of the in-plane molecular structure, especially for the first layer. However, it is puzzling that the alignment occurs along [0001] in some samples and along [1$\bar{1}$00] in others. Another mechanism of alignment might be due to the molecular interaction with facetted steps that is, steps whose edges are formed by low-index crystallographic planes. These facets develop at Å scale (defining a zigzag shape) along the edge of those steps whose average direction differs from one of the crystallographic directions.

Although the role of the steps is not entirely clear, it is plausible that they act as nucleation centers and contribute to the molecular alignment leading to enhancement of the inplane ordering for substrates when the miscut direction is near one of the crystallographic directions.[17] It is possibly the complex interplay of various factors (epitaxy, steps, miscut angle, and direction) that governs the azimuthal alignment.

V. SUMMARY

Well-defined layered F_{16}CuPc films with an interesting morphology of unidirectionally aligned needles can be grown on Al_2O_3 (11$\bar{2}$0). At molecular level, the unit cell is aligned parallel to the needles as revealed by the AFM images. Such anisotropic morphology is the result of a combined mechanism of self-organization and interaction with the surface. Spectroscopic ellipsometry measurements indicate that these films are oriented with two principal axes of the dielectric tensor on the film surface, with one of them essentially aligned with molecular needles.

Besides the interest derived from the anisotropic optical and electronic transport properties, the aligned needlelike structure of these F_{16}CuPc films is also attractive in that it may be exploited as template for inducing in-plane organization of subsequent films of other molecules.

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