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Strong optical anisotropies of F_{16}CuPc thin films studied by spectroscopic ellipsometry

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We have used spectroscopic ellipsometry to measure the optical functions of F_{16}CuPc (copper-hexadecafluoro-phthalocyanine, $C_{32}F_{16}N_8Cu$) films grown by organic molecular beam deposition simultaneously onto MgO(001), SiO_2/Si, and *A*-plane $(11\bar{2}0)$ sapphire substrates. The latter allows one to produce, under suitable conditions, highly ordered films with interesting anisotropic optical properties. These films are shown to be oriented with two principal axes of the dielectric tensor on the film surface, with one of them almost aligned with the c axis of the substrate. The main spectral features, corresponding to the strong Q- and B-band absorptions of phthalocyanines, are polarized along the other in-plane axis which is perpendicular to c. The Q band contains a particularly sharp excitonic peak near 1.55 eV whose intensity variations point to different molecular stackings in the films. © *2003 American Institute of Physics.*

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I. INTRODUCTION

The optical response of molecular solids is largely determined by the interplay between the optical properties of a single molecule and the local environment of the molecule in the solid. The detailed structure of a sample including crystalline phase, domain size, and distribution of crystallite orientations determines many characteristics of its optical properties. Single crystals of organic optoelectronic materials are commonly optically anisotropic due to their crystal symmetry, which frequently is monoclinic. When deposited as thin films good crystallinity, large domains, and smooth surfaces are not easy to obtain.[1,2] In addition, the nature and strength of the molecular interactions favors the occurrence of polymorphism. Therefore, a very fundamental issue is the correlation between optical and structural properties in these systems. In this work, we address this question by a systematic evaluation of the ellipsometric spectra of structurally well-characterized films of F_{16}CuPc deposited by organic molecular beam deposition simultaneously onto MgO(001), SiO_2/Si, and *A*-plane $(11\bar{2}0)$ sapphire substrates at different growth conditions. This conjugated π-electron macrocyclic compound is particularly interesting among other halogenated phthalocyanines because it is n-conducting with high electron mobility and also relatively stable.[3] This suggests that F_{16}CuPc can become practically useful to develop organic bipolar devices such as transistors or electroluminescent diodes, where knowledge of both structural and optical properties is relevant. In particular we measure strongly anisotropic optical responses and obtain the associated dielectric tensor components of those films. The optical functions are connected to structural issues such as average degree of order, preferential orientation, and molecular stacking arrangements.

II. EXPERIMENTAL DETAILS

All measurements were done using a spectroscopic ellipsometer with rotating polarizer. The available spectral range is from 0.7 to 5.2 eV, using a 75 W high-pressure Xe arc lamp as light source. Two detection setups are used: From 1.4 to 5.2 eV with a resolution of about 1 meV with a double prism/grating monochromator of 750 mm equivalent focal length plus a multialkali photomultiplier tube. Below 1.4 eV down to 0.7 eV a single spectrometer of 300 mm focal length and a GaInAs photodiode are used. The angle of incidence of

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the optical beam on the sample surface is usually chosen between $\varphi=60°$ and 70° whereby the vertical arc lamp spot results in an illuminated area of about $2\times2\,\mathrm{mm}^2$ at the sample surface position. Spectral data are recorded as a function of energy every 2 meV or larger (frequently 20 meV), depending on the sharpness of the observed electronic transitions and the required level of detail.

The studied film samples were deposited with different thicknesses between 5 and 45 nm (monitored with a quartz crystal microbalance calibrated by x-ray reflectivity), and substrate temperatures from −150 to 250 °C. Their structural characterization was published elsewhere.[4] The film morphologies and structures were found to depend on the substrate used, its temperature, and also on the layer thickness. We study the influence of these parameters on the optical properties of two groups of samples: films of the same thickness (20 nm) formed at different temperatures and films of varying thickness grown at the same temperature (230 °C).

X-ray investigations showed that out-of-plane ordering exists in all samples with a Bragg reflection that corresponds to a spacing of about 15 Å, being close to the size of the molecule, consistent with molecules that adopt a standing up arrangement in the films as was also found in Ref. 3. However, azimuthal ordering has only been obtained on sapphire substrates,[4] and using suitable growth parameters. This azimuthal order and the associated optical anisotropy can be detected and characterized by ellipsometry.

III. DATA ANALYSIS

Suitable anisotropic models must be applied to ellipsometric measurements in order to deduce the film's optical properties. This analysis is done by least-squares fitting of a model describing the sample to the experimental ellipsometric spectra. For fitting we have used the MINUIT package[5] and the connection between experimental measurements and sample properties is described in the following.

The general relationship between Jones vectors of incident (E_{ip},E_{is}) and reflected (E_{rp},E_{rs}) light beams is given by[6]

$$\begin{pmatrix} E_{rp} \\ E_{rs} \end{pmatrix} = \begin{pmatrix} R_{pp} & R_{ps} \\ R_{sp} & R_{ss} \end{pmatrix} \begin{pmatrix} E_{ip} \\ E_{is} \end{pmatrix}. \tag{1}$$

The nondiagonal elements of the reflection matrix lead to a mixing of s and p polarizations. These elements vanish $(R_{sp}=R_{ps}=0)$ in isotropic media and for symmetric orientations of the dielectric tensor in anisotropic cases. In these particular situations, the experimentally measured quantities $\tan\Psi$ and $\cos\Delta$ or complex reflectance ratio ρ can be written as

$$\rho=\tan\Psi e^{i\Delta}=\frac{R_{pp}}{R_{ss}}, \tag{2}$$

where the reflection matrix elements are related to the angle of incidence φ of the light beam and the optical functions $\varepsilon=N^2\equiv(n+ik)^2$ and thicknesses of the different materials in the multilayer.

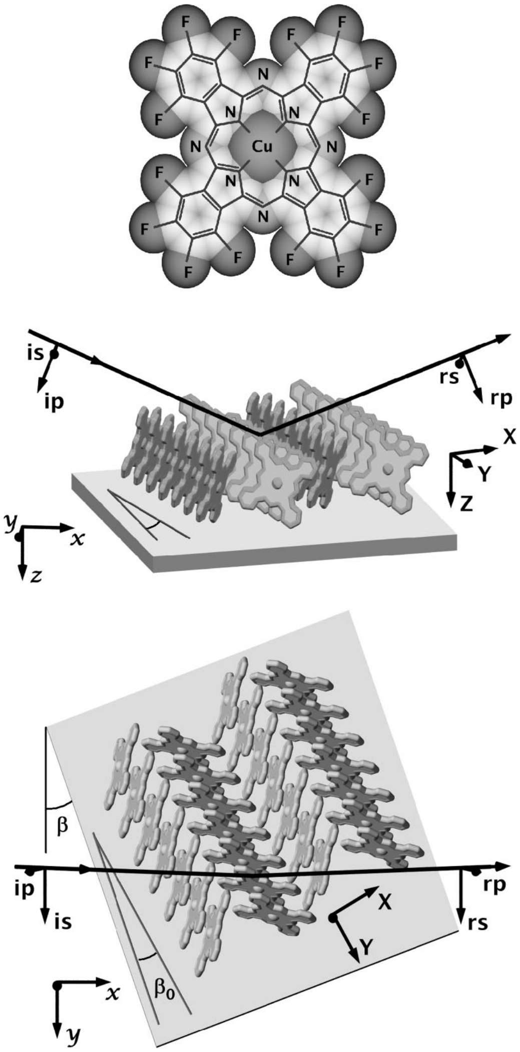

FIG. 1. (Top) Chemical structure of a molecule of F_{16}CuPc. (Bottom) Schematic representations of one layer of a typical Pc crystalline structure on a substrate, indicating our measurement configuration and the definitions of the principal axes of the tensor (X,Y,Z), laboratory axes (x,y,z), and the angle β.

A typical monoclinic crystalline structure of a metallophthalocyanine is indicated schematically in Fig. 1. In general, our films are composed of crystallites with anisotropic optical properties. Our measured spectra carry averaged information of their dielectric response, that is, we must consider that the films behave as effective dielectric media, which can be represented by a general dielectric tensor. Hence, this tensor bears information both about the nature of the crystallites and their distribution. Corresponding to the observed optical response, the investigated samples can be classified in two different groups: azimuthally isotropic and anisotropic.

The first group is composed by the films grown on MgO(001) and SiO_2/Si. Since, according to results of x-ray diffraction, all samples are ordered in the out-of-plane direction, we must regard these films as uniaxially anisotropic with optic axis perpendicular to the sample surface. The possible difference between in-plane and out-of-plane dielectric functions can be tested by comparing spectra measured at various angles of incidence.[6] Note that in this special case a

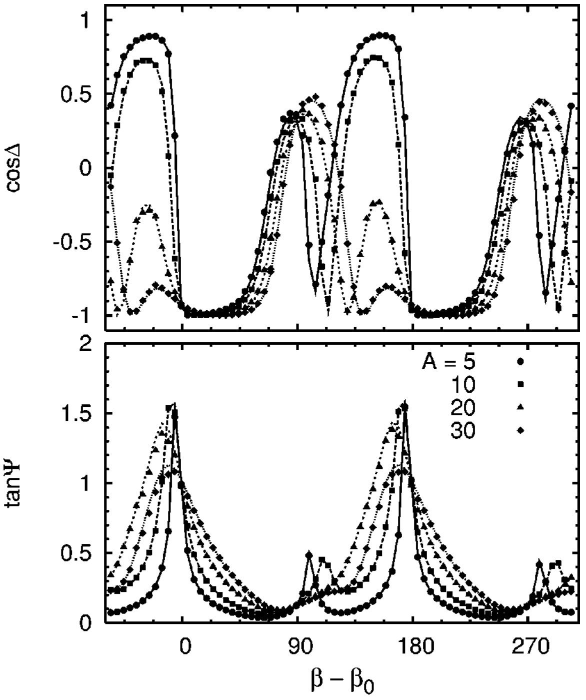

FIG. 2. Beta scan measurements at 1.5 eV of the sample with the thickest film on Al_2O_3 $(11\bar{2}0)$. Scans at other energies are of course different but show the same symmetry properties, namely: Four crossings at intervals of 90° and periodicity of 180°, indicating that two principal axes of the dielectric tensor are on the film surface. Points are measured and lines the best fit calculated with a biaxial model. The effective dielectric tensor is characteristic of orthorhombic symmetry. The true symmetry of the crystallites, expected to be monoclinic (but unknown) could average to orthorhombic due to some misalignment or mosaicity.

small anisotropy is hardly detectable: The contribution of the out-of-plane component in the measurement is generally small,[7] but it increases with the angle of incidence (as the incident light is further away from normal incidence $\varphi=0$). However, we found no dependence other than the geometric angle factor, which seems to indicate that the out-of-plane dielectric response is similar to that in-plane. Thus, the optical spectra of the deposited films can be deduced from the measured data by using standard isotropic multilayer models to fit both their effective dielectric function and layer thickness. We call the so obtained isotropic effective dielectric function $\varepsilon_{\mathrm{iso}}$.

The samples grown on sapphire are all optically anisotropic to a higher or lesser degree. The orientation of the principal axes of the general dielectric tensor can be obtained, without solving the ellipsometric equations, from β-scan measurements.[8] All samples investigated in this work display anisotropy patterns like that illustrated in Fig. 2. The exact values of $\tan\Psi$ and $\cos\Delta$ depend on each sample, as well as on the measurement energy and angle of incidence, but we always obtain a 180° symmetry and crossings at four azimuthal positions every 90° as displayed in Fig. 2. These measurements demonstrate that these anisotropic films behave in principle as optically biaxial media with two principal axes of the dielectric tensor on the film surface. The angular positions of these axes are read at the crossing points, which coincide with the symmetric positions where $R_{sp}=R_{ps}=0$. In a bare sapphire substrate the maximum anisotropy of the measured $\tan\Psi$ is $<1\%$ of the total observed in most of these $F_{16}CuPc$ films. Besides, there are no electronic transitions of sapphire in the measured spectral range. Therefore, the observed structures and their large detected anisotropies stem from the $F_{16}CuPc$ films, and their optical spectra can be numerically obtained from the measured data by neglecting the comparatively small substrate's anisotropy and reducing the problem to the readily solvable equations of a biaxial layer on an isotropic substrate in an isotropic ambient.[6]

The diagonal reflection matrix components are written for this case following Ref. 6 as a function of the complex refractive indices of the ambient N_0, film N_{1X}, N_{1Y}, N_{1Z}, and substrate N_2, and the film thickness d_1. Taking the z axis perpendicular to the sample surface and defining the plane of incidence together with x, the overall three-phase diagonal reflection coefficients are

$$R_{pp}=\frac{r_{01pp}+r_{12pp}e^{-2i\phi_p}}{1+r_{01pp}r_{12pp}e^{-2i\phi_p}}, \tag{3}$$

$$R_{ss}=\frac{r_{01ss}+r_{12ss}e^{-2i\phi_s}}{1+r_{01ss}r_{12ss}e^{-2i\phi_s}}, \tag{4}$$

with phase thicknesses

$$\phi_p=2\pi\left(\frac{d_1}{\lambda}\right)\left(\frac{N_{1x}}{N_{1z}}\right)(N_{1z}^2-N_0^2\sin^2\varphi_0)^{1/2}, \tag{5}$$

$$\phi_s=2\pi\left(\frac{d_1}{\lambda}\right)(N_{1y}^2-N_0^2\sin^2\varphi_0)^{1/2}. \tag{6}$$

The angle of incidence from the ambient is φ_0 and λ is the free space light wavelength. The different interface reflection coefficients are as follows:

$$r_{01pp}=\frac{N_{1x}N_{1z}\cos\varphi_0-N_0(N_{1z}^2-N_0^2\sin^2\varphi_0)^{1/2}}{N_{1x}N_{1z}\cos\varphi_0+N_0(N_{1z}^2-N_0^2\sin^2\varphi_0)^{1/2}}, \tag{7}$$

$$r_{12pp}=\frac{-N_{1x}N_{1z}\cos\varphi_2+N_2(N_{1z}^2-N_2^2\sin^2\varphi_2)^{1/2}}{N_{1x}N_{1z}\cos\varphi_2+N_2(N_{1z}^2-N_2^2\sin^2\varphi_2)^{1/2}}, \tag{8}$$

$$r_{01ss}=\frac{N_0\cos\varphi_0-(N_{1y}^2-N_0^2\sin^2\varphi_0)^{1/2}}{N_0\cos\varphi_0+(N_{1y}^2-N_0^2\sin^2\varphi_0)^{1/2}}, \tag{9}$$

$$r_{12ss}=\frac{-N_2\cos\varphi_2+(N_{1y}^2-N_2^2\sin^2\varphi_2)^{1/2}}{N_2\cos\varphi_2+(N_{1y}^2-N_2^2\sin^2\varphi_2)^{1/2}}, \tag{10}$$

where $N_0\sin\varphi_0=N_2\sin\varphi_2$.

Using Eqs. (2)–(10), we have performed numerical fits of groups of spectra measured at different angles of incidence at the four symmetric azimuths (see Fig. 2) with x either along X or Y. The seven fitted parameters are the unknown three complex (six real) components of N_1 and the layer thickness d_1. The layer thickness can be best determined in the region of transparency of the phthalocyanine layer[9] or by analogy with the side-by-side grown isotropic layers and kept constant in the subsequent fitting process. The procedure is facilitated by MINUIT features such as inside-fit fixing and releasing of parameters as well as parameter scanning for best value within an interval. The layers

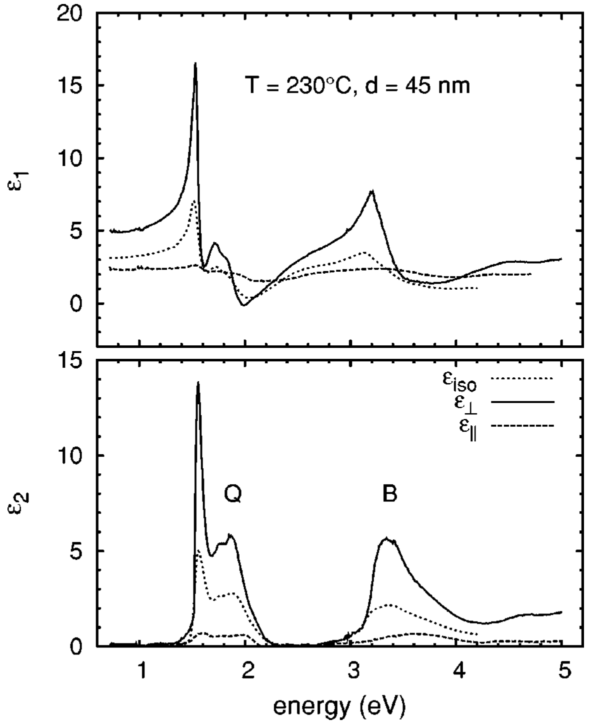

FIG. 3. Fitted components of the complex dielectric tensor $\varepsilon_1 + i\varepsilon_2$ for two films of the same growth run. The two in-plane components of the film on Al_2O_3 are denoted $\varepsilon_\parallel$ (component parallel to sapphire's *c* axis) and $\varepsilon_\perp$ (perpendicular component). The isotropic $\varepsilon_{\mathrm{iso}}$ is that fitted for the corresponding film on MgO.

can be considered transparent below 1.4 eV and in the region around 2.5 eV (see Fig. 3). Our typical error in fitted thickness is around 0.5 nm and the obtained values do not deviate significantly from the target thicknesses controlled with the quartz crystal monitor. Slight differences (below 5%) between simultaneously deposited films may occur, therefore we display our results using target thicknesses. For the fit of dielectric tensor, at each energy we have typically eight independent measurements (two orientations per two angles of incidence). From the three values of N_1 it is clear that the two in-plane components N_{1X} and N_{1Y} will produce the main contributions to our measured signal, whereas the out-of-plane component N_{1Z} will contribute less. In spectra from these azimuthally anisotropic layers, for a given orientation, we observe a distinct dependence on angle of incidence which is due to anisotropy. However, this effect is not directly attributable to different contributions of N_{1Z} alone since the detected proportions of N_{1X} and N_{1Y} vary as well. In fact, we have found that the spectra of N_{1Z} cannot be unambiguously fitted from the data. The fit quality was rather insensitive to its particular value within a certain range. We found that a good working procedure was to assume that the layers are actually uniaxial, with optic axis on the surface. Then the best fit is obtained when this axis is almost aligned with the sapphire *c* axis, with a difference $\beta_0 \simeq 4°$, determined by comparison with measurements on a bare substrate of the same batch. To reflect this fact, we denote the fitted components in reference to the substrate's *c* axis: $\varepsilon_\parallel = N_\parallel^2$ is the tensor component along the *c* axis and $\varepsilon_\perp = N_\perp^2$ is the perpendicular component, both in-plane and out-of-plane.

IV. RESULTS AND DISCUSSION

In order to establish the models for data analysis in Sec. III some results have been anticipated. From the azimuthal dependence (β scan) shown in Fig. 2 we have shown that very large anisotropies can be observed in these films, and that the corresponding dielectric tensor is oriented with two principal axes on the film surface. As the films are not one single domain, the expected monoclinic symmetry of the crystallites (see Fig. 1) is averaged to more symmetric effective tensors. The films on MgO and SiO_2/Si are at most uniaxial, with $\varepsilon_Z \simeq \varepsilon_X = \varepsilon_Y \equiv \varepsilon_{\mathrm{iso}}$ (almost isotropic). Notice that such Pc films are often termed oriented in the literature,[10] while azimuthally ordered films are rare.[11] On Al_2O_3, the films' dielectric tensor is at most biaxial, where one of the components $\varepsilon_Y \equiv \varepsilon_\parallel$ is very different from the other two $\varepsilon_Z \simeq \varepsilon_X \equiv \varepsilon_\perp$, giving a nearly uniaxial behavior. In these specific situations, with ε_Z perpendicular to the film surface and similar to the stronger in-plane component, it is not feasible to determine precisely this component. But it is important to notice that the determined ε_X and ε_Y are rather independent of the exact value of ε_Z within given bounds.

As already mentioned, for every growth run we can obtain three dielectric functions: $\varepsilon_{\mathrm{iso}}$, $\varepsilon_\parallel$, and $\varepsilon_\perp$. These are plotted in Fig. 3 for two films deposited on MgO and Al_2O_3 side-by-side at the given conditions: $T = 230\,°C$, $d = 45$ nm. As expected, $\varepsilon_{\mathrm{iso}}$ being a certain average of the other two, its value is in between. Moreover, all three spectra show similar spectral characteristics. The electronic bands observed in this range are $\pi \rightarrow \pi^*$ transitions characteristic of the phthalocyanine rings.[12] The structured band centered at 1.8 eV is identified as the *Q* band, and that at 3.4 eV as the *B* band or Soret band. The *Q* band has been measured for many phthalocyanine complexes[13] and is related to the formation of singlet excitons ($S_0 \rightarrow S_1$ transitions) in the Pc ring; the details of this band give some information about the relative positions of the molecules in the crystalline film structures.[14,15] The *B* band is less informative in this respect and has been considered bandlike absorption[16] involving hybridized states of both the ligand and the central metal. Looking at the *Q* band three distinct components are apparent: The two components usually reported in CuPc at about 1.75 and 1.95 eV[10,13] and an additional sharp extra peak at about 1.55 eV. Greater detail can be attained by performing a second derivative of the spectra.[9] Then the broad 1.95 eV structure is seen to be composed of two bands close to 1.9 and 2.0 eV. The exact four energy positions show slight variations from sample to sample. Beyond the precise interpretation of these bands, it is interesting to note that in the anisotropic samples these features are mainly associated with the component $\varepsilon_\perp$ of the fitted dielectric tensor while the component $\varepsilon_\parallel$ is less structured. If we think of a bulklike CuPc structure for these films, the observations are consistent with a monoclinic structure as represented in Fig. 1 where the monoclinic *b* axis is almost parallel to c_s of the substrate (except for the small β_0). Thus, the stacking direction of molecules is $\parallel c_s$, in-plane, with molecules basically standing upright, consistent with results from x-ray diffraction[4] and Raman scattering.[4,17] The similarity between ε_X and ε_Z (both associated with dipoles of the molecular

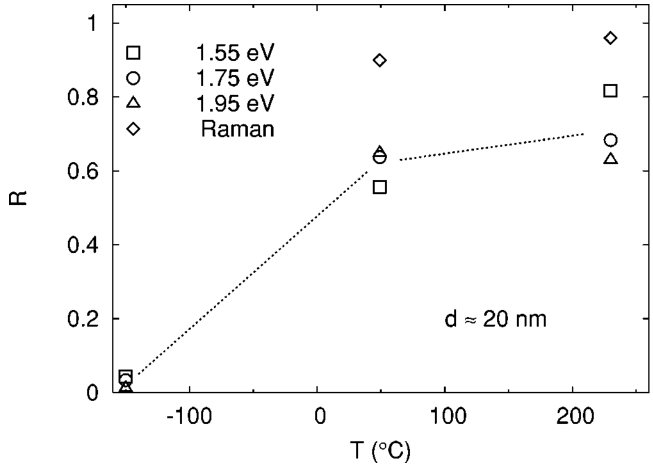

FIG. 4. Dichroic ratios of films of similar thicknesses ($d\sim 20$ nm) deposited at different substrate temperatures on Al_2O_3 (1120). Except for growth on a cooled substrate, a considerable anisotropy is always observed. The order parameters obtained from Raman measurements are given for comparison. The lines are displayed only as guides to the eye.

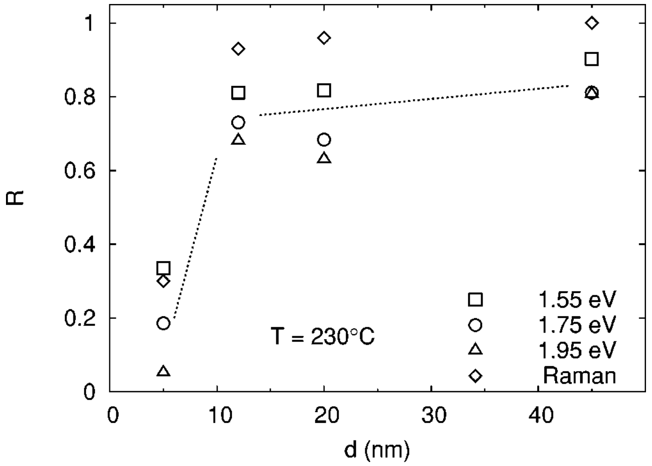

FIG. 5. Dependence of dichroic ratio and Raman order parameter on the thickness of films deposited at substrate temperature of 230 °C on Al_2O_3 (1120). The observed anisotropy increases with film thickness. Lines are meant to be guides to the eye.

planes) is reasonable for a structure composed of molecules with D_{4h} square symmetry. Such an ordered film is depicted in Fig. 1.

We find that the observed optical anisotropy depends mainly on the two growth parameters: Substrate temperature and layer thickness. To quantify the degree of anisotropy it is useful to define a dichroic ratio $\mathcal{R}$ as

$$\mathcal{R}=\left|\frac{\varepsilon_{2\perp}-\varepsilon_{2\parallel}}{\varepsilon_{2\perp}+\varepsilon_{2\parallel}}\right|. \tag{11}$$

Although $\mathcal{R}$ cannot be taken as an absolute measure of degree of order, in isotropic films $\mathcal{R}=0$ and $\mathcal{R}$ approaches 1 for very anisotropic films. The precise value depends on the energy where $\varepsilon_{2\perp}$ and $\varepsilon_{2\parallel}$ are read.

Considering the whole set of experiments, the most important factor influencing ordering is the growth temperature. On cooled substrates it is not possible to obtain ordered films, whereas ordering is achieved for growth on nonintentionally heated (room T) or heated substrates. This is illustrated in Fig. 4. Also, at a given temperature where ordering can be induced, some minimum layer thickness is necessary ($\sim$above 10 nm) to obtain a strong optical anisotropy, as displayed in Fig. 5. The ratio $\mathcal{R}$ shows similar tendency as the order parameters calculated from Raman measurements.[17]

The temperature not only influences the degree of order, it also affects the spectral behavior, and in particular the sharp excitonic peak observed around 1.55 eV. The intensity of this peak tends to increase with the growth temperature. Two extreme cases are shown in Fig. 6 where we compare the $\varepsilon_{2\perp}$ for two films of the same thickness grown at different T. Both samples show similar $\mathcal{R}$ values at the three energies (only slightly higher for the high T film, see Fig. 4) but the spectral behavior is obviously different. The differences must arise from different interactions between π-electron systems of neighboring molecules as a consequence of different local arrangement of the molecules. The Raman spectra of these samples also differ in some modes mostly related to vibrations of the outer atoms in the molecules, qualitatively supporting this interpretation.

The observation of the peak at 1.55 eV is intriguing and unusual in the majority of Pc compounds.[13] In the frame of the molecular exciton model[18] the positions of these excitons are signatures of the particular polymorph.[19] The stronger band between 1.6 and 2.0 eV in the room T film basically coincides with that observed in the usual[10] CuPc columnar structures with ring-over-ring (eclipsed) Pc stackings and almost parallel transition dipoles. A further redshifted exciton is usually observed when there is a staggered (slipped) stacking involving inclined alignment of transition dipoles.[18] We cannot exclude the coexistence of different polymorphs in the films, in fact, some change in the Bragg peak position[4] indicates that certain structural differences exist between films grown at different temperature and the Raman spectra pointed also to such structural differences between films. However, we have found no evidence of polymorph mixtures, e.g., no splittings or duplicates of Bragg peaks are seen in these films. In particular, for the two samples of Fig. 6,

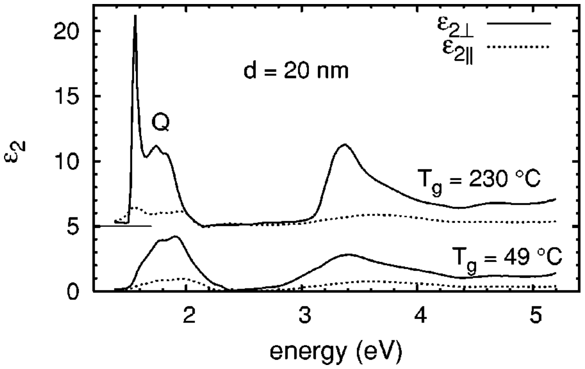

FIG. 6. Imaginary part of the two in-plane components of the dielectric tensor for two ordered films deposited at different substrate temperature. The origin is shifted in the upper curves as indicated on the left-hand side. The strong suppression of the sharp peak at $E\approx 1.55$ eV in the sample deposited at lower temperature suggests that the molecular stacking in these two films is different.

Raman data of the room *T* sample were consistent with a known CuPc-like structure, while the high *T* film structure could not be identified with a known polymorph. The electronic spectra are compatible with this, indicating that in the former sample a CuPc-like structure with rather eclipsed molecular stacks is preferred, while in the latter another structure with strongly slipped stacks is formed. The fact that the sharpest and most intense redshifted exciton is observed in the thickest high *T* film suggests that the latter is the most stable bulk structure grown at high temperature. Slipped structures with comparable absorption features have been reported[15,16] in crystals of nonplanar phthalocyanines. This is because slipping is a way of relieving the repulsion between adjacent monomers. For nonplanar molecules the repulsion has a steric origin, not possible in our case. Instead, slipping could be produced by repulsion between the highly electronegative F terminations and be stabilized by given growth conditions. In an analogous material, that is, films of perfluorinated planar molecules of F_{16}ZnPc, a band close to 1.55 eV was measured in the UV–vis absorption spectra[20] which could have the same origin. Finally, we mention that preliminary results on crystallized needles of F_{16}CuPc indicate similar optical spectra in the bulk.

V. CONCLUSION

In conclusion, spectroscopic ellipsometry is a very useful tool, when properly interpreted, for the characterization of these anisotropic layers. The optical anisotropy provides structural information such as an average degree of order and preferential orientation direction of the monoclinic *b* axis, whereas the spectroscopic details of the *Q* bands are related to the local arrangements of neighboring molecules. Highly aligned films of different polytypes with either eclipsed or slipped Pc stacking patterns are obtained depending on growth conditions. The latter, unusual in crystals of planar molecules, appears to be the most stable bulk structure grown at high temperature.

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