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Organic Electronics 5 (2004) 291–297

Organic Electronics

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The anisotropic dielectric function for copper phthalocyanine thin films

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Received 12 August 2004; received in revised form 6 October 2004; accepted 12 October 2004
Available online 5 November 2004

Abstract

Copper phthalocyanine (CuPc) thin films were prepared by organic molecular beam deposition (OMBD) in high vacuum and ultra-high vacuum on passivated Si(1 1 1) using β-phase CuPc as source material. The substrates were kept at room temperature during the deposition. The IR peak positions indicate that the films consist mainly of α-phase CuPc, while the relative intensities suggest that the films are anisotropic. The anisotropic dielectric function for these CuPc layers was determined from ellipsometric spectra using uniaxial models in the range from 0.73 to 5 eV.

Keywords: Ellipsometry; Infrared spectroscopy; Optical anisotropy; Organic molecular thin films; Copper phthalocyanine

1. Introduction

The phthalocyanines (Pcs) are a class of materials which exhibit a high thermal and chemical stability and also high optical absorption in the visible range. Due to their blue or green colour the Pcs were largely used in industry as dyes [1], and more recently due to their semiconducting properties they have proven their applicability in electronic devices such as organic photovoltaic cells [2,3], organic field effect transistors (OFETs) [4], organic light emitting diodes (OLEDs) [5] and gas sensors [6].

The copper phthalocyanine (CuPc) is one of the most extensively studied Pcs by means of ellipsometry [7–11], infrared spectroscopy [12–15] and X-ray diffraction [15–18]. Even though the CuPc molecule has an intrinsic optical anisotropy due to its planar structure, in the reported dielectric functions or optical constants derived from ellipsometriy spectra the CuPc layers are considered as being isotropic [8–11]. In one previous analysis Debe [7] tried to approximate the anisotropic dielectric function of CuPc by investigating two different types of oriented films—with the *b*-axis (the molecular stacking

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doi:10.1016/j.orgel.2004.10.001

axis) perpendicular and respectively parallel to the substrate surface. For each film only the in-plane components of the dielectric function were determined. In other reports [19,20] the optical anisotropy of the CuPc layer was taken into account but these studies were limited to single wavelength ellipsometry at one angle of incidence. The experimental data in [19] was modelled assuming an isotropic layer for thicknesses below 100 nm and an isotropic inner layer plus an anisotropic outer layer for thicknesses higher than 100 nm. However, the anisotropic dielectric function of CuPc was not reported in the literature so far.

Therefore the aim of this work is to present the dielectric function for CuPc films over a wide spectral range (0.73–5 eV) obtained from simulating ellipsometry spectra using anisotropic model approaches. The implementation of new mathematical algorithms [21] based on a 4 × 4 transfer matrix formalism developed by Berreman [22] is a promising approach to tackle the problem. As reported previously for metal-free phthalocyanine [23] and for perfluorinated vanadyl phthalocyanine [24], the determination of the anisotropic dielectric function from spectroscopic ellipsometry does not only yield physically reliable values, but also allows the orientation of the molecules with respect to the substrate to be determined.

2. Experimental

Organic thin films of CuPc were grown by OMBD in high vacuum (HV—8×10^{-7} mbar) and ultra-high vacuum (UHV—6×10^{-10} mbar) on hydrogen passivated Si(1 1 1). The substrates were kept at room temperature during the deposition. The CuPc source material used for HV deposition was β-phase CuPc with 97% purity, supplied by Aldrich. For the UHV deposition higher purity (99%) β-CuPc was used. The Si(1 1 1) substrates were cleaned with isopropanol and deionised water. The hydrogen passivation was performed using HF (40%) etching for 2 min. After passivation the substrates were immediately transferred into the deposition chamber. The thickness of the organic material was monitored by a quartz crystal micro-balance which was located in the vicinity of the samples. The change in the resonant frequency of the quartz is proportional to the film thickness. The deposition rate was kept constant at approximately 0.3 nm/min.

Infrared (IR) measurements were performed using a Bruker FTIR spectrometer IFS-66. All samples were measured in reflection at 20° and at 60° using s- and p-polarized light. KBr pellets containing crystallites with random orientation of the β-phase CuPc were also prepared. These pellets were measured in transmission.

The ellipsometric measurements were carried out using a variable angle spectrometric ellipsometer (VASE, J. A. Woollam Co. Inc.). In order to determine the film thicknesses and the energy dependence of the optical constants ellipsometric spectra were recorded at different angles of incidence (65°, 70°, 75°) in the range of 0.73–5 eV with a 0.02 eV step for each sample.

Ellipsometry measures the changes in the polarization state of the light upon the reflection on the sample surface [21,22,25]. The relation between the amplitudes of the reflected E_r and incident E_i electric field can be written in the Jones matrix formalism as

$$\begin{pmatrix} E_{rp} \\ E_{rs} \end{pmatrix} = \begin{pmatrix} r_{pp} & r_{sp} \\ r_{ps} & r_{ss} \end{pmatrix} \begin{pmatrix} E_{ip} \\ E_{is} \end{pmatrix}$$

The diagonal elements of the Jones matrix represent the change of amplitude and phase of the p- and s-components, while the off-diagonal elements describe the transfer of energy from the p-component to the s-component and vice versa. For isotropic samples or anisotropic uniaxial samples with in-plane isotropy the off-diagonal elements of the Jones matrix are zero. In this case the change in the polarization state can be described in terms of the ellipsometric parameters Ψ and Δ. The ellipsometric parameters are related to the ratio of Fresnel reflection coefficients r_{pp} and r_{ss} by

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan\Psi \exp(i\Delta)$$

For the evaluation of the ellipsometry spectra a model which describes the interaction of light with a specific material has to be taken into consideration. Afterwards a complex numerical fitting procedure is used to simulate the experimental spectra. The mean-square error (MSE) which provides the differences between the model and the experimental points is defined as follows:

$$\mathrm{MSE} = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}}-\Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}}\right)^2+\left(\frac{\Delta_i^{\mathrm{mod}}-\Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]}$$

where N is the number of the experimental points, M is the number of fit parameters and σ is the standard deviation for each point. The standard deviation is used to weigh the contributions of each data point to the mean-squared error during the fitting process, such that very noisy data points are effectively excluded from the fit. A detailed description of the ellipsometry principles and theory can be found in [25].

3. Results

The first assessment of the ellipsometric spectra revealed that all films are in-plane isotropic. This was checked by measuring the ellipsometry spectra for various azimuthal angles. Consequently the possibilities are reduced to isotropic or uniaxial anisotropic samples.

3.1. Infrared spectroscopy

In order to decide which model is more appropriate the IR spectra of the samples were analysed. The spectra for the films prepared in the same condition have similar features regardless of the thickness. This leads to the conclusion that the structure of the CuPc films is preserved in this thickness range. Fig. 1 shows the IR spectra of the samples prepared in HV in comparison with the ones prepared in UHV. The spectra were normalised with respect to the reflection of the Si(1 1 1) substrate and the 722 cm^{-1} peak. The IR spectrum of the CuPc pellet is also shown.

The peak positions for all samples indicate that the films consist of α-phase CuPc while the CuPc in the pellet exhibits β-form characteristics [14,15]. According to Debe [7] the 722 cm^{-1} and 750 cm^{-1} peaks correspond to out-of-plane vibrations of the CuPc molecule while the peak at 753 cm^{-1} and all bands above 800 cm^{-1} are due to molecular in-plane vibrations.

Considering s-polarization the relative intensity ratios of the peaks for the samples prepared under HV condition are very different when compared with the ones of the samples prepared in UHV and the ones in the transmission spectrum of the pellet. Especially the peak at 722 cm^{-1} is more intense for samples prepared in UHV. This indicates that the molecular arrangement is different for the two types of films. For the samples prepared in UHV the molecules adopt a standing configuration with respect to the substrate surface, i.e. the molecular plane has a large tilt angle, while for the HV samples the molecules obviously adopt a different orientation.

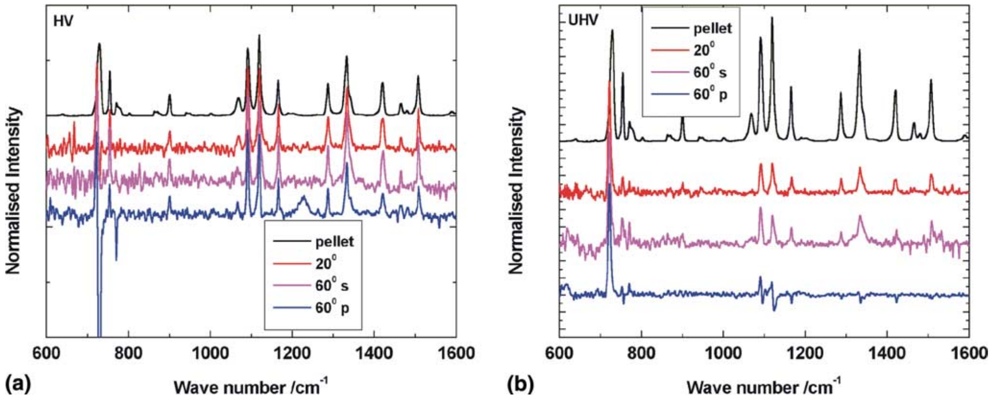

Fig. 1. (a) Reflection IR spectra of the CuPc sample HV-1. (b) Reflection IR spectra of the CuPc sample UHV-1.

Table 1
Thickness and surface roughness of CuPc films on Si(1 1 1) substrates determined from ellipsometry

UHV			HV		
Sample nr.	Thickness/nm	Surface roughness/nm	Sample nr.	Thickness/nm	Surface roughness/nm
UHV-1	49 ± 0.6	10 ± 0.8	HV-1	46 ± 0.5	2 ± 0.6
UHV-2	105 ± 1	11 ± 0.9	HV-2	78 ± 0.3	3 ± 0.5

Considering p-polarization, as can be seen in Fig. 1, the 722 cm^{-1} and 750 cm^{-1} peaks have derivative like shapes, or are pointing downwards for the HV films. This indicates that the displacement of atoms for these oscillations is in the z-direction of the films (perpendicular on the film surface). Consequently the average angle of the molecular plane with respect to the substrate surface is less than 45°. This can explain the higher coupling of the p-polarization with the out-of-plane vibrations of the molecule, while for s-polarization the IR spectra are similar to that of the bulk. For the UHV films the in-plane vibrations of the molecules exhibit derivative like bands in p-polarization indicating that the average molecular orientation is at a higher angle that 45° with respect to the substrate surface.

3.2. Ellipsometry

In order to obtain the optical constants from spectroscopic ellipsometry the film thicknesses have to be accurately determined. This can be done in the absorption-free range of the films where the light is coherently reflected by the substrate. In this case the refractive index n can be approximated with a Cauchy dispersion relation:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where λ is the wavelength, and A, B, C are parameters during the thickness fit. For a uniaxial anisotropic material two different Cauchy relations have to be used to simulate the in-plane refractive index of the film (x, y direction) and respectively out-of-plane refractive index of the film (z-direction). Table 1 summarises the thicknesses and the values for the surface roughness obtained from fitting the experimental ellipsometric spectra with a uniaxial model in the range of 0.73–1.1 eV. The surface roughness is simulated using an effective medium approximation consisting of 50% film material and 50% voids. The values obtained are in very good agreement with the ones obtained

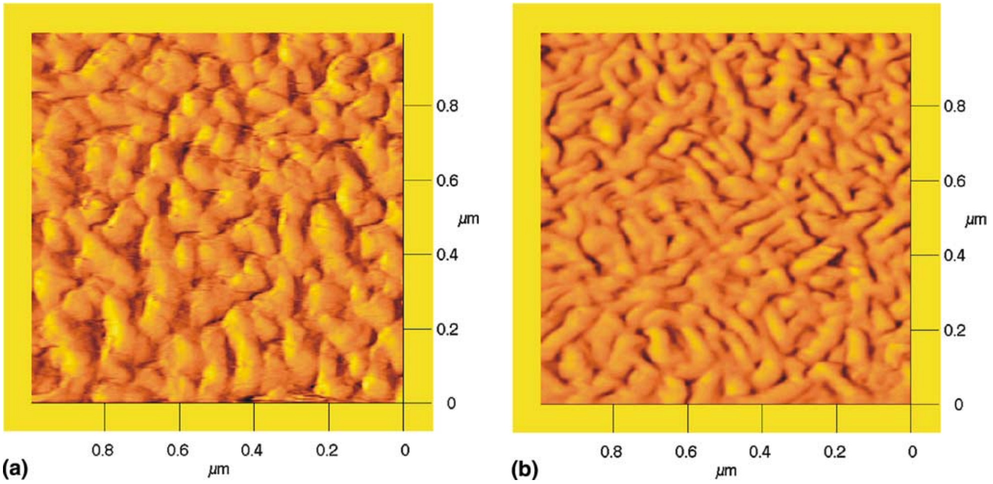

Fig. 2. (a) AFM images of surface morphology for sample HV-1 prepared in HV. (b) AFM images of surface morphology for sample UHV-1 prepared in UHV.

from an atomic force microscopy (AFM) scan. The surface morphology of the samples prepared in HV is different from the ones prepared in UHV as can be seen in Fig. 2. This can be related to the different growth mode of the CuPc molecules on Si(1 1 1) substrates depending on the pressure conditions.

For simulating the optical response of the films in the entire range from 0.73 to 5 eV more complex models have to be employed using WVASE™software. Initially a point-by-point fit was performed. In the point-by-point fit the refractive index *n* and the extinction coefficient *k* are found by fitting the experimental data at each wavelength. The overall result, however, is not always Kramers–Kronig (KK) consistent. In order to ensure the KK consistency a mathematical based model was used. In this model the shape of the imaginary part of the dielectric function ε_2 is simulated using Gaussian oscillators while the real part is solved applying KK consistency. For the uniaxial models two sets of oscillators were used—one for the in-plane direction (*xy*) of the film and one for the out-of-plane (*z*) direction of the film. Especially for the *z* component (normal to the surface) it is usually difficult to obtain reliable optical constants for thin uniaxial films. To overcome this problem we used a special multiple-sample analysis procedure [26]. In the multiple-sample analysis several films with different thicknesses, but the same optical constants can be coupled together in the fit. The films prepared in HV were coupled together in the same model as the IR revealed that the films show similar spectra regardless of the thickness.

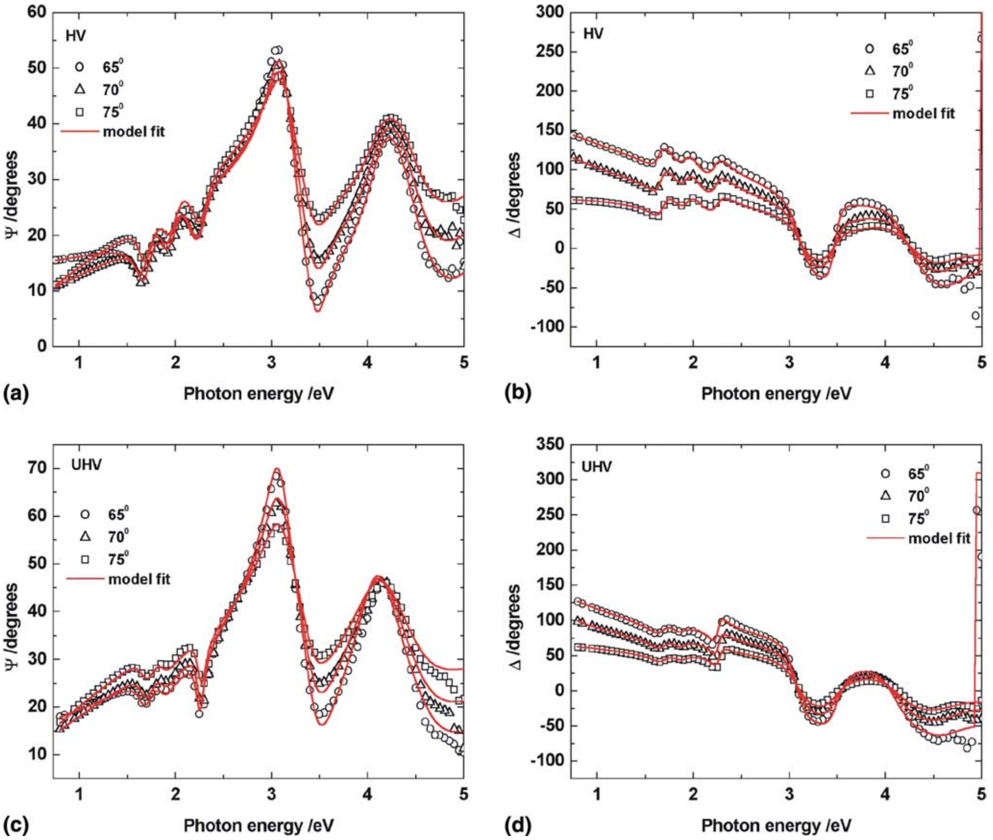

Fig. 3. Ellipsometric Ψ and Δ spectra at different angles of incidence for CuPc samples on Si (1 1 1) substrate. Open symbols are the experimental points and continuous lines the fits. (a) and (b)—sample HV-1 prepared in HV and (c) and (d)—sample UHV-1 prepared in UHV.

The same procedure was applied for the UHV films.

Fig. 3 presents the experimental Ψ and Δ values and the anisotropic fit for the HV sample HV-1 and also for the UHV sample UHV-1 as they have almost the same nominal thickness. The corresponding dielectric function is shown in Fig. 4. For the samples prepared in HV also an isotopic model was considered. In this case the MSE was 17.9 while using the anisotropic fit the MSE was lowered to 9. However, for the samples prepared in UHV the isotropic fit did not at all yield good agreement with the experimental data. Within the anisotropic fit all sample were coupled together giving a MSE value of 6.4. This indicates that the samples prepared in HV are only slightly anisotropic, while the films prepared in UHV have a more ordered structure with more pronounced anisotropic properties.

The shape of the ε_2 is typical for CuPc and is in agreement with previous works [8–11]. The absorption band centred at 2 eV is known as the Q band while the B band is centred around 3.6 eV [1]. Both are π–π^* transitions and are polarised in the molecular plane. For a random molecular orientation the in-plane and out-of-plane component of the dielectric function should be equal. A similar result should be obtained if the CuPc molecules would have an average 45° tilt angle with respect to the substrate.

Considering in a first approximation that the CuPc is planar and the overall absorption intensity is the result of a scalar product between the electric field vector and the transition dipole, an estimate of

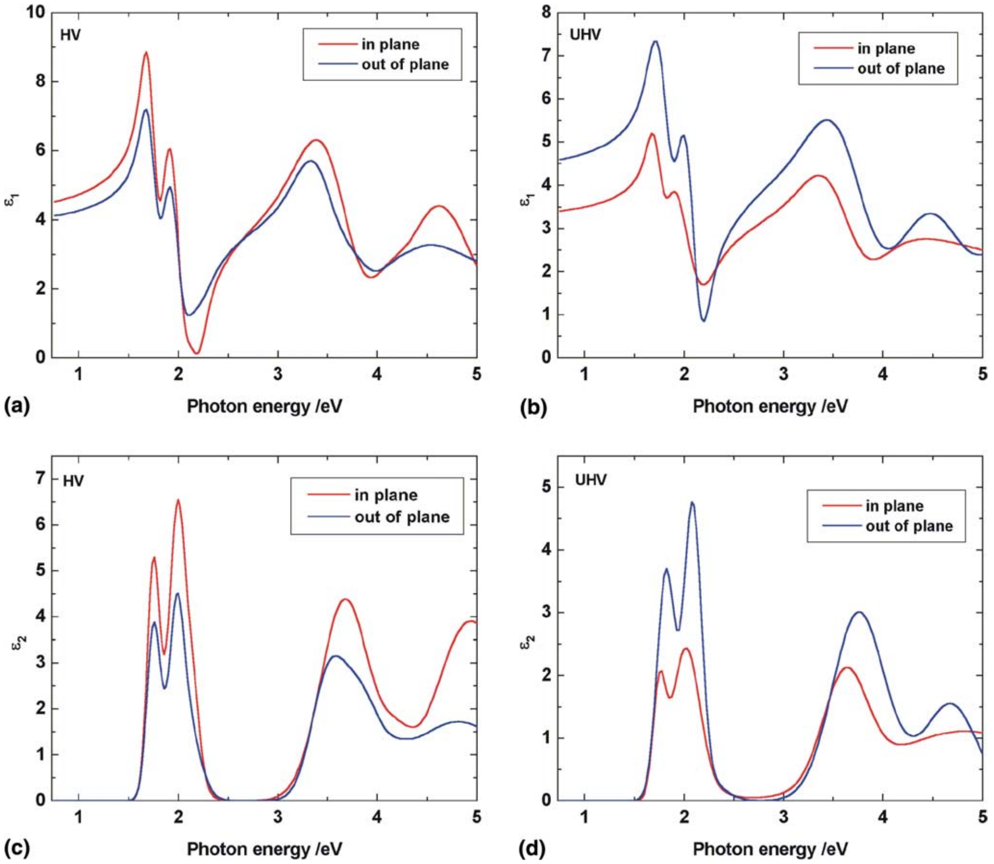

Fig. 4. Anisotropic dielectric function for CuPc; (a), (c) real part; (b), (d) imaginary part. (a) and (b) samples prepared in HV and (c) and (d) samples prepared in UHV.

the average orientation of the molecules with respect to the substrate can be obtained from the differences in the extinction coefficient between the *xy* and the *z* directions of the film. For the films prepared in HV the average molecular orientation with respect to the Si substrate is at ~40° while for the sample prepared in UHV the majority of the molecules are at ~53°. The differences may be correlated with the markedly different pressure during growth. However, an influence of the purity of the source material cannot entirely be ruled out. The explanation for the differences in the IR spectra between the two types of samples remains a future task. More complex calculations have to be performed taking into account also the refraction index of the CuPc film in the IR range. Further study of molecular orientation for such anisotropic materials can be of practical interest as the structural order can improve e.g. the charge transport in OFETs.

4. Summary

Several CuPc films were prepared by OMBD in high vacuum and ultra-high vacuum on passivated Si(111). Due to the intrinsic anisotropy of the CuPc molecule both types of films exhibit uniaxial anisotropy. IR spectra and ellipsometry show that the sample prepared in HV have an average orientation of the molecules with respect to the substrate surface at 40° while the majority of the molecules have a 53° angle with respect to the surface substrate for films prepared under UHV conditions. The small difference in the molecular tilt angle between the two types of films leads to pronounced differences in the dielectric functions of CuPc. This proves that ellipsometry and IR spectroscopy are very powerful tools for investigating the anisotropy of thin layers.

Acknowledgements

This work was financially supported by Deutsche Forschungsgemeinschaft, Graduiertenkolleg 829 “Akkumulation von einzelnen Molekülen zu Nanostrukturen”.

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