Simultaneous *in situ* measurements of x-ray reflectivity and optical spectroscopy during organic semiconductor thin film growth

T. Hosokai,[1] A. Gerlach,[1] A. Hinderhofer,[1] C. Frank,[1] G. Ligorio,[1] U. Heinemeyer,[1] A. Vorobiev,[2] and F. Schreiber[1,a]

[1]*Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, Tübingen 72076, Germany*
[2]*ESRF, 6 Rue Jules Horowitz, Boîte Postale 220, 38043 Grenoble Cedex 9, France*

Simultaneous *in situ* real-time measurements of x-ray reflectivity and differential reflectance spectroscopy were conducted during deposition of perfluorinated copper-phthalocyanine thin films on SiO_2/Si. We found a continuous spectral change coinciding with structural changes from submonolayer coverage, to standing $\beta_{bilayer}$-phase and to β-phase for thicker films. This combined measurement enables us to study the relationship between structural and optical properties of organic semiconductor thin films. © *2010 American Institute of Physics*. [doi:10.1063/1.3478450]

Understanding the relation between structural and optical properties of organic semiconductor thin films is of fundamental interest because of the often complex coupling mechanism between them.[1–7] So far, both properties have been studied individually by either postgrowth measurements or *in situ* real-time measurements. The latter has the great advantage of being able to detect possible time-dependent/transient film structures and also to allow monitoring the evolution of those properties all in one sample.[8–10] However, determining the structure after the optical spectra or vice versa, involves problems of comparability. Therefore, in order to study the correlation between the properties directly, simultaneous *in situ* real-time measurements of optical and structural data during growth are desirable.

In this letter, we present the realization of such an experiment for perfluorinated copper phthalocyanine ($F_{16}CuPc$) thin film growth. Oteyza *et al.*[11] have reported that the thin film shows a thickness-dependent structural transition on SiO_2 surfaces (flat-lying amorphous bilayer film → standing $\beta_{bilayer}$-phase films → β-phase films). While the optical spectra of $F_{16}CuPc$ multilayer films have been intensively studied by variable angle spectroscopic ellipsometry[12,13] the behavior in the few monolayer (ML) regime is not yet clarified. We use x-ray reflectivity (XRR) and grazing incidence x-ray diffraction (GIXD) measurements, which provide information on the out-of-plane and in-plane structures, respectively. By measuring real-time XRR intensity oscillations at the anti-Bragg point ($q_{Bragg}/2$), we can deduce information on the growth mode.[10] Differential reflectance spectroscopy (DRS)[14] compares the light reflectance of the bare substrate R_0 with the reflectance $R(d)$ of the same substrate covered with a deposited thin film of thickness d. The DRS signal, which is defined as $DRS=[R(d)-R_0]/R_0$, is related to the dielectric function of the thin film. In good approximation, it reflects the imaginary part, i.e., the absorption of the film at low coverage.[2,5,7,14] While other optical techniques, such as a reflection anisotropy spectroscopy,[15] can be also used to determine the optical spectra *in situ* and in real-time, the very simple DRS setup is suitable to be combined with x-ray scattering techniques.

All experiments were performed at beamline ID10B at the ESRF in Grenoble (France), using a home-built portable UHV chamber[16] newly equipped with a DRS setup at x-ray wavelength of 0.919 Å. The chamber design and experimental geometry are depicted in Fig. 1(a). $F_{16}CuPc$ was purchased from Aldrich Chemical Co. and purified by gradient sublimation twice before use. As substrate Si(100) wafers covered with their native oxide were cleaned ultrasonically with aceton, isopropanol, and ultrapure water, followed by heating to 700 K in the UHV growth chamber. The DRS data were acquired with a DH-2000 deuterium tungsten halogen light source and a fiber optics spectrometer (Ocean Optics, USB2000) in the energy range of 1.4–3.0 eV, measured at normal incidence and averaged over several thousand spectra to reduce the noise. The simultaneous real-time measurements were performed starting from the bare substrate with an accumulation time of 2 min, using a deposition rate of 0.1–0.2 nm/min. After the deposition postgrowth XRR and GIXD measurements were also conducted.

Oteyza *et al.*[11] have observed the thickness-dependent structural transition at a substrate temperature of 463 K during deposition. To confirm this under our deposition conditions, i.e., deposition at room temperature (303 K), we measured real-time GIXD using a MarCCD area detector. Figure 1(b) shows the final charge coupled device (CCD) image of $F_{16}CuPc$ (12.2 nm)/SiO_2, where the in-plane scattering intensity at $q_\perp \sim 0$ obtained with a point-detector is also shown. As previously reported,[11] diffraction peaks derived from the $\beta_{bilayer}$- and β-phase can be found. Interestingly, we identify a weak (01),(11) powder ring of the β-phase, indicating that the β-phase domains exhibit a very large mosaicity. It should be noted that the film thickness, at which the β-phase is observed, is significantly smaller than the reported 20.0 nm in Ref. 11. Figure 1(c) shows the intensity profile at $q_\perp \sim 0$ between the arrows in Fig. 1(b) as a function of the deposition time. A gradual shift in the $(01)\beta_{bilayer}$ peak to larger $q_\parallel$ is observed. This demonstrates the structural rearrangement of the $\beta_{bilayer}$-phase due to a small rotation of the molecules around the (10)-axis perpendicular to the molecular plane.[11,17] These results show that the thickness-dependent structural transition ($\beta_{bilayer}$-phase → β-phase) occurs even for deposition at room temperature.

a)Electronic mail: frank.schreiber@uni-tuebingen.de.
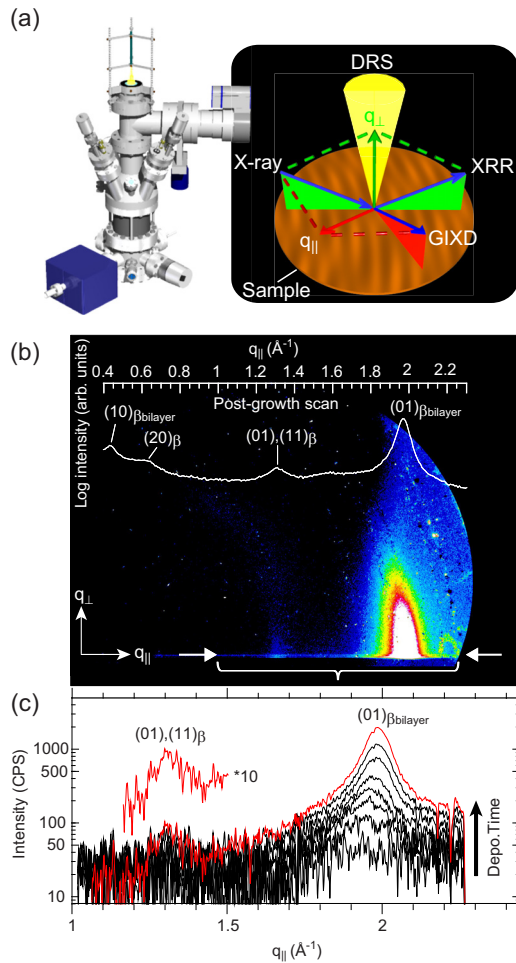
(a)

(b)

(c)

FIG. 1. (Color online) (a) Design of the DRS/XRR chamber and experimental geometry. (b) GIXD reciprocal-space map measured with a MarCCD area detector and a point-detector after deposition of $F_{16}CuPc$ (12.2 nm) at 303 K on SiO_2. The background of the CCD image is subtracted using the first frame of the time series (bare substrate). The peak assignment follows Ref. 11. (c) Time-dependent GIXD at $q_\perp \sim 0$ extracted from the real-time CCD measurement by taking line profiles between the arrows indicated in (b) [The top red curve is extracted directly from (b)].

(a)

(b)

FIG. 2. (Color online) (a) Evolution of XRR as a function of time (or film thickness) during $F_{16}CuPc$ film growth on SiO_2 at 303 K. (b) Thickness-dependent reflectivity at the anti-Bragg point ($q_{Bragg}/2$) extracted from (a). The film thickness was obtained by fitting the reflectivity curves using Parratt's formalism. The inset in (b) is a schematic of the film structure at a thickness of 2.1 nm as suggested in Ref. 17.

Figure 2(a) shows the real-time XRR of $F_{16}CuPc/SiO_2$ deposited at 303 K. Postgrowth we observed a Bragg peak at $q_\perp = 0.42$ Å^{-1}, which corresponds to a lattice spacing of 1.50 nm of standing $F_{16}CuPc$ molecules. From the real-time data, the XRR at the anti-Bragg point is extracted and shown in Fig. 2(b) as a function of film thickness. Above 2.1 nm we observe damped intensity oscillations with a periodicity of ~1.50 nm, which indicate that the molecules form layered films of standing molecules with significant roughness.[10] Obviously, the offset value of 2.1 nm is larger than the lattice spacing of standing molecules. This early growth regime can be related to the formation of a standing monolayer (1.50 nm) on an interfacial wetting layer, consisting of flat-lying molecules with 2 ML coverage corresponding to ~0.7 nm, as discussed in Ref. 17.

With the structural studies we confirmed that the film growth at room temperature is similar to that reported in Ref. 11, except for the rather low coverage at which the β-phase is formed. This is strongly supported by the real-time DRS spectra: Fig. 3(a) shows the Q-band region of the DRS spectra of $F_{16}CuPc/SiO_2$ at selected layer thickness (ML) and the interface layer (I) as marked in Fig. 2(b), respectively. As
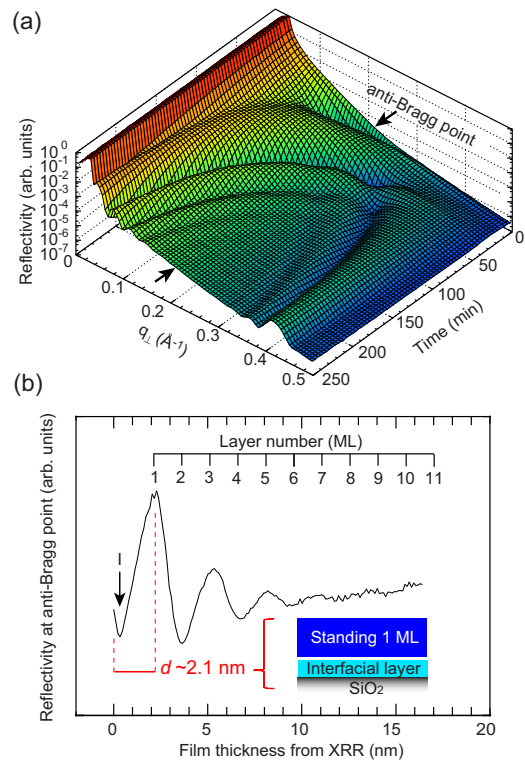
expected from the structural transition, a thickness-dependent change in the DRS spectra is observed, especially below 2 ML. For the interface spectrum, an absorption feature A and a broad shoulder B exist around 1.82 and 1.96 eV, with feature B dominating at 1 ML. Remarkably, an additional absorption feature C appears above 1 ML coverage around 1.59 eV, which becomes stronger with further deposition.

The absorption spectra of $F_{16}CuPc$ thin films have been discussed in terms of molecular exciton theory.[13] The characteristic feature C is observed in case $F_{16}CuPc$ is forming a β-phase crystalline film, in which molecules orient with ring-over-ring (eclipsed) stackings and an inclined alignment of transition dipoles. However, this is not seen for the α-CuPc columnar structures with parallel transition dipole moments.[18] These configurations of transition dipole moments correspond to the $\beta_{bilayer}$- and β-phase structures determined in Ref. 11 [Fig. 3(b)]. On the other hand, for $F_{16}ZnPc$ on glass substrates Schlettwein *et al.*[19] have argued that because absorption feature A occurs at an energy close to that observed in solution, it is related to an amorphous fraction in the $F_{16}ZnPc$ film. Taking these considerations into account, the change in the DRS spectra can be reasonably explained with the structural transition as follows: First, the molecules take preferentially a lying down orientation and form an amorphous bilayer film, so that the spectra show mainly feature A. Upon this layer, the molecules form a $\beta_{bilayer}$ film (standing molecules), in which the transition dipole moments are nearly parallel,[11] causing the increase in feature B. On the $\beta_{bilayer}$ film, the β-phase grows and yields feature C. Again, we note that the β-phase can form already
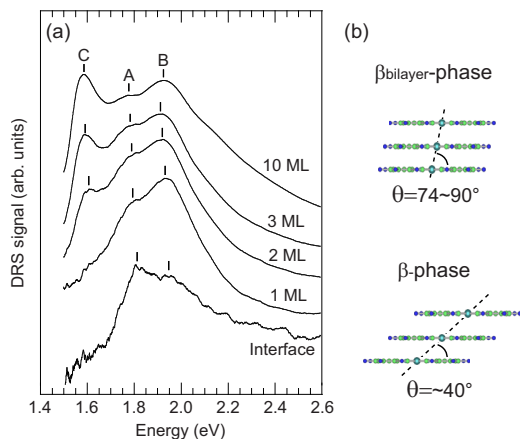
FIG. 3. (Color online) (a) Selected DRS spectra of F_{16}CuPc (16.2 nm)/SiO_2, which are corresponding to the film thickness shown in Fig. 2(b). The DRS signal is normalized and each spectrum is offset for better comparison. (b) A schematic of the molecular structure with the angle θ between the transition dipole moments and the columnar stacking of the $\beta_{bilayer}$- and β-phase as established in Ref. 11. The relation between θ and the spectral shift is discussed in Ref. 1.

above 1 ML coverage, indicating that the film growth in the first few monolayers is influenced by the chosen substrate temperature during deposition.

In conclusion, we are able to explain the thickness-dependent absorption spectra of F_{16}CuPc thin films deposited on SiO_2 observed during growth with the help of *in situ* real-time XRR. We studied the thickness-dependent structural transition of F_{16}CuPc and identified the correlated absorption spectra starting in the monolayer regime. We demonstrated that simultaneous *in situ* real-time XRR/DRS measurements are a powerful approach to understand the direct relation between structural and optical properties of organic thin films.

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