



	<b>Experiment title:</b> Real-time simultaneous study of optical spectra and film structure of organic semiconductors during growth	<b>Experiment number:</b> SI-1936
<b>Beamline:</b> ID 10B	<b>Date of experiment:</b> from: 20/01/2010 to: 25/01/2010	<b>Date of report:</b> 02/08/2010
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## Report:

### 1. Introduction

As described in the proposal, the purpose of the experiments at ID10B was to study the relationship between optical and structural properties of organic semiconductor thin films, especially from sub-monolayer coverage. Both properties are crucial for organic devices, such as organic photovoltaic cells and organic light-emitting diodes, and also are of great fundamental interest because they are often strongly coupled to each other. The experiment was performed using our new home-made portable UHV chamber which allows simultaneous X-ray and optical measurements.

The *in situ* real-time measurements of X-ray reflectivity (XRR) and differential reflectance spectroscopy (DRS) were performed on perfluorinated copper phthalocyanine ( $F_{16}CuPc$ ) and  $H_{16}CuPc$  thin films deposited on a  $SiO_2/Si$  wafer. The DRS technique, which determines the light absorption of the films with sub-monolayer sensitivity [1], was combined with real-time XRR measurements [2]. The materials are typical examples of n- or p-type semiconductors, respectively. The molecules proposed for this beamtime, i.e. perfluorinated pentacene and pentacene, were replaced by the two phthalocyanine derivatives, because test experiments with  $F_{16}CuPc$  on  $SiO_2$  had shown unusual spectral changes, that might be related to structural transitions accessible via real-time XRR.

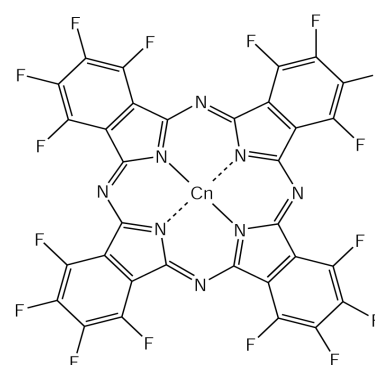
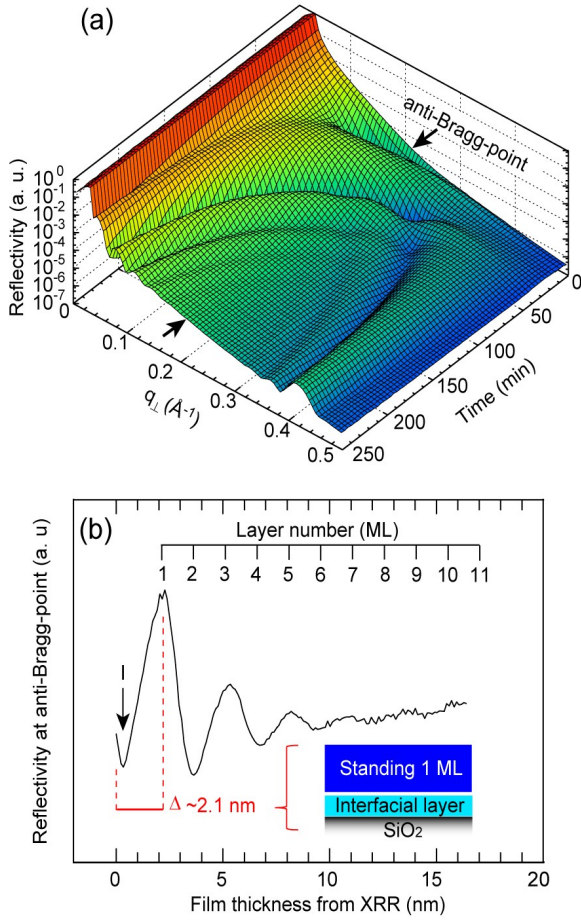


Fig. 1 Chemical structure of  $F_{16}CuPc$

Below we give a short summary of the results for one of systems, namely  $F_{16}CuPc/SiO_2$ , obtained in the beamtime (SI-1936) at ID10B.

## 2. Real-time X-ray reflectivity measurements of $F_{16}CuPc/SiO_2$



Real-time XRR data of  $F_{16}CuPc$  deposited on  $SiO_2$  at 303 K are shown in Fig. 2(a). In the post-growth reflectivity data we observe the well-known first-order Bragg peak at  $q_{Bragg}=0.42 \text{ \AA}^{-1}$ , which corresponds to a lattice plane spacing of 1.50 nm and essentially standing  $F_{16}CuPc$  molecules. From the real-time results the reflectivity at the anti-Bragg point, i.e. at  $q_{Bragg}/2$ , can be extracted. The data are shown in Fig. 2(b) as a function of the film thickness, which we determined separately by fitting the XRR data.

Above  $\Delta \approx 2.1 \text{ nm}$  we find the expected growth oscillations with a periodicity of 1.50 nm and a strong damping. Our data indicate that the molecules form layered films of standing molecules with a significant roughness. However, the observed  $\Delta$ -value is larger than the lattice spacing of standing molecules. This has been explained before [4] by the nucleation of one monolayer of standing molecules (1.50 nm) on an interface layer consisting of two layers of lying  $F_{16}CuPc$  molecules ( $2 \times 0.7 \text{ nm}$ ).

FIG. 2: (a) Evolution of the real-time XRR of  $F_{16}CuPc$  thin films as a function of time (film thickness) during 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 with Parratt's formalism.

## 3. Evolution of DRS spectra correlated to thickness-dependent structural transition

DRS spectra for selected film thicknesses with the corresponding numbers of molecular layers (ML) are shown in Fig. 3(a). Due to the structural transition of  $F_{16}CuPc/SiO_2$  a significant variation of the spectra – especially below 2 ML – is observed. An absorption feature A and a broad shoulder B, which becomes dominant at 1 ML, are observed at 1.82 eV and 1.96 eV, respectively. In addition, a third feature C around 1.59 eV appears at 1 ML and becomes more intense with increasing film thickness.

In the literature the absorption spectra of  $F_{16}CuPc$  thin films have been discussed based on molecular exciton theory [5]. Therein, peak C is attributed to the  $\beta$ -phase of  $F_{16}CuPc$ , that is characterized by ring-over-ring (eclipsed)  $\pi$ -orbital stackings and an inclined alignment of the transition dipoles, see Fig. 3(b).<sup>†</sup> Schlettwein et al. [7] have noted that for  $F_{16}ZnPc$  growth on glass substrates feature A is at similar energies as a peak found in solution spectra, suggesting that this feature could be related to an amorphous  $F_{16}ZnPc$  phase in the film.

With these information and on the basis of the XRR data taken during this beamtime the changes in the DRS spectra can be explained:

- Initially, the molecules prefer the flat-lying orientation and form an amorphous film with spectra showing mainly feature A.
- After completion of the interface layer the molecules build up the bilayer structure reported in Ref. [4] with nearly parallel transition dipole moments, causing the observed increase of feature B.
- Finally, the thin film  $\beta$ -phase of  $F_{16}ZnPc$  with the typical growth oscillations starts to nucleate. Above 2 ML the corresponding feature C appears in the spectra

<sup>†</sup> Peak C, in contrast, is not observed for the columnar  $\alpha$ -CuPc structure with parallel transition dipole moments [6].

## 5. Summary

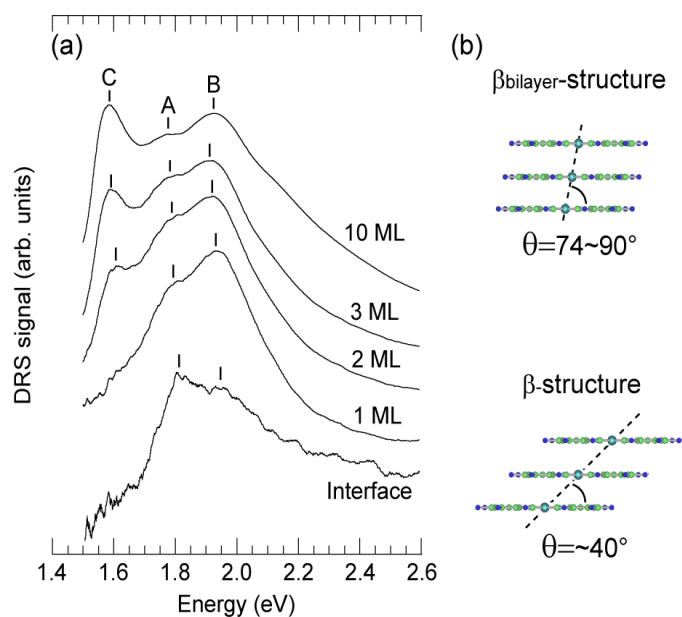


FIG. 3: (a) Q-band region for selected DRS spectra of  $F_{16}\text{CuPc}$  on  $\text{SiO}_2$ , which correspond to the film thickness given in Fig. 2(b). The intensity of the spectra was multiplied arbitrarily for a better of an evolution of the spectral shape. (b) A schematic of the angle  $\theta$  between the transition dipole moments in a molecular column of the bilayer-phase and -phase estimated in Ref. [4].

## 5. References

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We studied the thickness-dependent absorption spectra of  $F_{16}\text{CuPc}$  thin films deposited on  $\text{SiO}_2$  during growth simultaneously with measuring the real-time X-ray reflectivity. We confirmed the reported thickness dependent structural transition and determined the corresponding absorption spectra from the monolayer regime.

We demonstrated that simultaneous *in situ* real-time XRR/DRS measurements are a powerful approach to understand in which way the optical properties of organic thin films are related to the film structure and the growth behaviour.

A publication with the results for  $F_{16}\text{CuPc}/\text{SiO}_2$  will appear shortly [2]. – We wish to thank our local contact for the excellent support on ID10B.