

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Growth and annealing of doped thin films of organic semiconductors followed in situ and in real-time. F6TCNNQ-doped Pentacene: a system relevant for device applications.	<b>Experiment number:</b> SC-4454
<b>Beamline:</b> ID03	<b>Date of experiment:</b> from: 28.06.2017 to: 04.07.2017	<b>Date of report:</b> 28.02.2018
<b>Shifts:</b> 18	<b>Local contact(s):</b> Linus Pithan	<i>Received at ESRF:</i>
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## Report:

### 1. Abstract

During this beamtime we performed two kinds of experiments employing organic molecular semiconductors.

In the first part we employed *in situ* real-time X-ray reflectivity (XRR) to monitor the roughness evolution of F6TCNNQ-doped diindenoperylene (DIP) films. The content of F6TCNNQ was increased in each film. The time evolution of the reflectivity at specific  $Q_z$  values was modeled using the kinematic approximation for X-ray scattering in combination with a “birth-death” growth model [1] and the surface width was extracted as function of the total film thickness.

In the second part we demonstrate that employing a very low growth temperature and then performing a slow annealing it is possible to obtain highly crystalline DIP films where the molecular semiconductors adopt a lying down orientation in conditions (at room T and on  $\text{SiO}_x$ ) where they would normally adopt a standing up orientation [2]. The data relative to this second part have been evaluated only partially and therefore will not be presented here. However, the data evaluated so far look promising and we are confident will lead to a publication within this year.

Below we report the results concerning the first part of the experiments.

### 2. Experimental Results

For this experiment we grew three films *via* co-deposition of DIP and F6TCNNQ starting from a DIP:F6TCNNQ 6:1 molar ratio, then up to 4:1 and finally 2:1. The films were grown in a custom-made portable vacuum chamber [3] and XRR *in situ* and in real-time during film growth was measured in order to extract film roughness as function of thickness. We optimized the  $Q_z$ -range as well as the point density and integration time for a single XRR scan such that we could achieve sub-

monolayer resolution for the growing films. Additionally, our approach is to measure full XRR curves (up to slightly beyond the first DIP Bragg peak) instead of measuring time-scans at one single  $Q_z$  (typically the anti-Bragg point): in this way we can fit the time-dependent reflectivity at several  $Q_z$  points simultaneously, an approach already used in refs. [4,5]. In Fig. 1a, the evolution of XRR curves as function of time for the 2:1 mixture is shown. We modeled the XRR curves using the kinematic approximation for the reflectivity from a multilayer system:

$$I_{refl}(t) = \left| A_{substr}(q_z) \cdot e^{i\Phi(q_z)} + f(q_z) \cdot \sum_n \theta_n(t) \cdot e^{i \cdot n \cdot q_z \cdot d} \right|^2 \quad (1)$$

where  $A_{substr}$  and  $\Phi(q_z)$  are respectively the scattering amplitude and phase of the substrate,  $f(q_z)$  is the scattering amplitude of the organic material,  $\theta_n(t)$  is the partial layer coverage for the  $n$ -th layer and  $d$  is the interlayer spacing of the growing molecular layers. The parameter  $q_z$  is set depending on the point of the reflectivity curve along which the cut is being fitted. In order to model  $\theta_n(t)$  we used the “birth-death model” of growth as in ref. [1], where it holds:

$$\frac{d\theta_n}{d(t/\tau)} = (\theta_{n-1} - \theta_n) + k_n(\theta_{n+1} - \theta_{n+2})(\theta_{n-1} - \theta_n) - k_n(\theta_{n-2} - \theta_{n-1})(\theta_n - \theta_{n+1}) \quad (2)$$

In Eq. (2) the parameter  $k_n$  denotes the effective jumping rate to the  $n$ -th layer. Therefore, fitting  $k_n$  leads to a set of time-dependent  $\theta_n$  curves, which then can be used to calculate the interface width (i.e. the film roughness) as function of film thickness according to:

$$interf. \ width = d \cdot \sqrt{\sum_n (\theta_n - \theta_{n+1})(n - \bar{d})^2} \quad (3)$$

Where  $\bar{d}(t) = \sum_n \theta_n(t)$  is the average relative thickness. In Fig. 1b,c we show for the 2:1 mixture an example of fits and the extracted layer coverages, respectively.

Finally, we show in Fig. 1d the calculated interface width as function of film thickness for the three DIP:F6TCNNQ mixtures studied: the step occurring for the three curves comes from an artefact of the fits, but we assume that it does not affect the comparability of the results. We summarize our results as follows.

- 1) Increasing the content of F6TCNNQ leads to an improved layer filling mechanism: as shown in the inset of Fig. 1d, the 6:1 mixture is the roughest and the layers do not close completely (shallower dips).
- 2) In the 2:1 mixture, the closure of a single molecular layer is delayed compared to the 4:1 mixture, although it is more effective (deeper dips, see also inset of Fig. 1d). We suggest that for the 2:1 mixture the presence of growing DIP:F6TCNNQ co-crystallites [6] significantly affects the roughness evolution.
- 3) Overall, employing a 4:1 mixing ratio one obtains the smoothest film.

In Fig. 1d we also show sketches of the suggested growth scenarios for the different mixtures.

We relate here to the comment of review committee C09 to the main proposal. Unfortunately we could not grow nominally equivalent samples due to some time and equipment constraints related to the preparation of the experiment. However, Atomic Force Microscopy scans (AFM) of similar samples reveal no difference in the morphology between spots several mm apart from each other, revealing the homogeneity of these samples over the whole substrate.

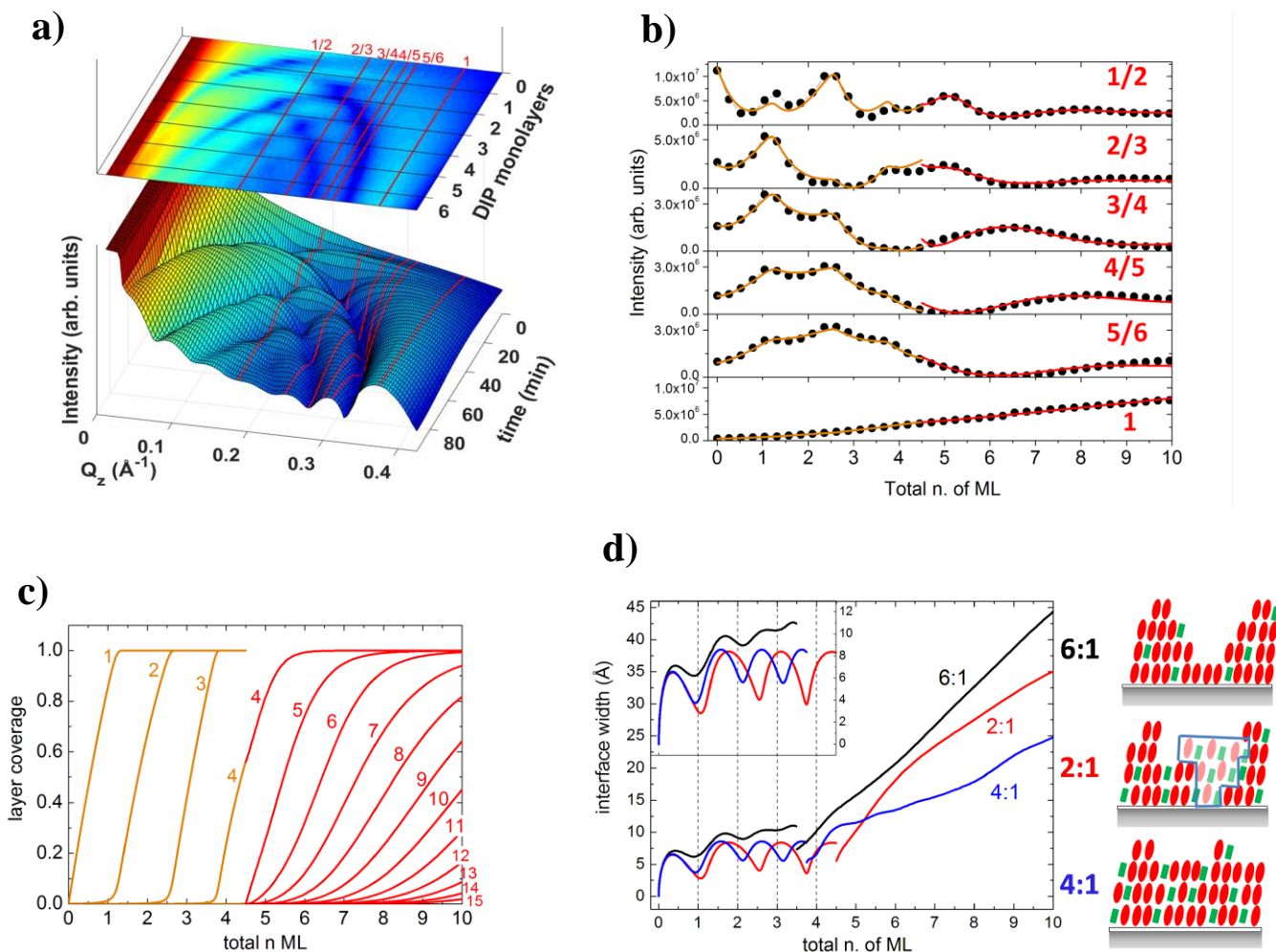
### 3. Remarks on quality of measurements

We found the ID03 beamline particularly suited for our real-time experiments with weakly scattering organic materials. The high beam flux allows very short integration times in the XRR scans and improves dramatically the time resolution of our experiment.

#### 4. Status and progress of data evaluation

We intend to fit the XRR data using two more models (Trofimov and Parrat) in order to strengthen the conclusions of this work. We aim to submit a publication containing the results of this experiment within this year.

We thank Francesco Carlà for the valuable support during the beamtime.



**Figure 1.** **a)** XRR scans in real-time during growth: cuts at fixed  $Q_z$  are highlighted in red. **b)** Simultaneous fits of the reflectivity at several  $Q_z$  (indicated by the red fractions in units of the Bragg peak position). **c)** Extracted layer coverages. Notice that data **a)** - **c)** are for the 2:1 mixture. **d)** Calculated interface widths for all investigated mixtures and sketches illustrating the suggested growth mechanism: for the 2:1 mixture a large co-crystal domain is highlighted.

#### 5. References

- [1] P. I. Cohen et al. Surf. Sci. 216 (1989), 222-248.
- [2] A. C. Dürr et al. Appl. Phys. Lett. 81 (2002), 2276.
- [3] K. A. Ritley et al. Rev. Sci. Inst. 72 (2001), 1453.
- [4] S. Kowarik et al. Eur. Phys. J. Special Topics 167 (2009), 11-18.
- [5] M. Sparanberg et al. Phys. Chem. Chem. Phys. 16 (2014), 26084.
- [6] G. Duva et al. *In preparation.*