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ESRF

Experiment Report Form

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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

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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.

ESRF	**Experiment title:** **Time-evolution of surface correlation length related to interface doping by the organic semiconductor 1,3,4,5,7,8-Hexafluorotetracyanonaphtoquinodimethane grown in situ.**	**Experiment number**: SC-4220
Beamline: ID10	**Date of experiment**: from: 26.11.2015 to: 02.12.2015	**Date of report**: 23.03.2016
Shifts: 18	**Local contact(s)**: Giovanni Calogero li Destri Nicosia	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

1. Abstract

During this beamtime we performed two kinds of experiments employing organic semiconducting small-molecules.

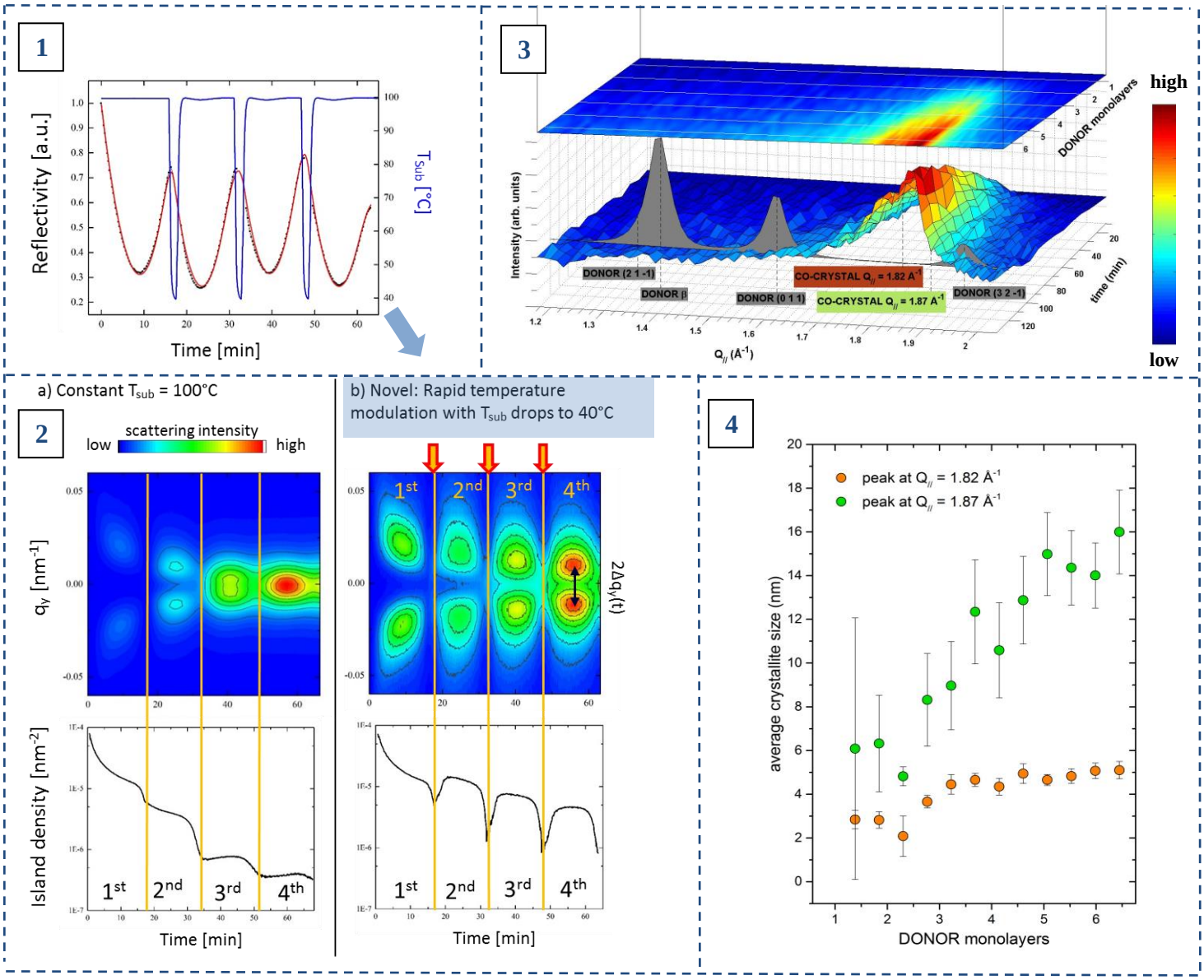
In the first part, using real-time and *in situ* GISAXS methods we studied the response of the nucleation behavior on rapid thermal cycles of the substrate temperature triggered at specified film coverages. The coverages were deduced from *in situ* monitored by anti-Bragg oscillations. We found a strong impact on the initial nucleation density, the growth-mode and layer smoothness.

In the second part we studied *in situ* and in real-time the formation of donor-acceptor co-crystallites in mixtures of organic semiconductors for different mixing ratios of the pristine compounds.

2. Experimental Results

a. First Part. Rapid T_{sub} modulation during growth

For this experiment we designed a setup that can perform rapid substrate temperature (T_{sub}) cooling cycles and at the same time allows specular and diffuse *in situ* x-ray diffraction experiments. Rapid T_{sub} cycles allow to increase the monolayer coverage by increasing the nucleation density in the initial stage of ML growth while keeping the ad-atom diffusivity constant (inspired by [1] and [2]) Following anti-Bragg oscillations [3, 4] we are able to monitor the current layer coverages online and trigger a fast cooling cycle whenever a new ML starts to nucleate (Figure 1).



Figures. **1.** Growth oscillations at the anti-Bragg point (red) and the T_{sub} profile (blue) triggered by the local maxima in the growth oscillations which correspond to maximal coverage in the topmost ML. **2.** Diffusely scattered intensity over time and the derived island densities. **3.** Real-time growth of the donor-acceptor co-crystal (color-scaled) compared to the spectrum of the pure donor (grey-filled). **4.** Extracted average crystallite size.

To have a measure for the nucleation density / island density we analyze the diffusely scattered intensity at small diffraction angles (GISAXS) [3]. Here we can relate the observed splitting in q_y to an average inter-island distance and from this distance calculate the island density $N = \frac{2}{\sqrt{3}} \left(\frac{\Delta qy}{2\pi}\right)^2$ as shown in Figure 2. For the film grown in the conventional fashion (T_{sub}=*const.)* the island density decreases significantly for each consecutive ML whereas a high nucleation density can be conserved also in upper MLs when the novel temperature modulated growth strategy is applied. Additinally the distict phases during ML growth - nucleation, lateral growth and coalescence of islands - are more pronounce in this case as can be seen from the evolution of the island density within the growth of each individual monolayer.

From analysis of anti-Bragg oscillations recorded simultaneously with the diffuse scattering (making thus full use of the 2D detector) we could quantify a decrease in surface roughness by means of the analytical Trofimov model [5], therefore assessing the success of this experiment.

b. Second part. Real-time growth of donor-acceptor co-crystals

For this experiment we co-evaporated two organic small-molecules acting as donor-acceptor pair and monitored in real-time the growth of the corresponding mixed crystal. Employing GIXD it is possible to follow the evolution of two features which are distinctive of the donor-acceptor co-crystal. In Figure 3 we show for a mixture with 2:1 donor:acceptor molar ratio the real-time evolution of the two peaks close to each other (color-scaled plot) and we compare them to the peaks of the pure donor molecule (grey-filled spectrum in Fig. 3). Since the pure acceptor molecule does not show any distinctive Bragg peak in this region, we conclude that the developing peaks are completely new features which appear only in the mixtures. Using the Scherrer formula $D = \frac{2\pi K}{\Delta Q}$ for evaluating the average crystallite size D from the FWHM of the single peaks, ΔQ, where K is a shape factor, despite the relatively large error bars it is possible to see that the two evolving textures exhibit qualitatively different behavior (see Figure 4): the crystals of one texture remain constantly smaller and stop increasing in size after a certain time stage.

3. Remarks on quality of measurements

We found the ID10 beamline particularly suited for our real-time experiments with weakly scattering organic materials. Despite we had to take some precautions in order to avoid beam damage on our samples (e.g. insertion of filters), we consider the obtained signal very good. In particular we would like to mention the excellent signal-to-noise of the diffuse scattering signal, thanks also to the installation of a 4m long evacuated flight path provided by the beamline which allowed to significantly reduce air scattering.

4. Status and progress of data evaluation

First part. We aim to submit a publication on this experiment during this year, once the dataset is fully analyzed.

Second part. We aim to include these data in a wider publication concerning charge-transfer interactions in donor-acceptor systems.

We thank O. Konovalov and G. Li Destri for the valuable support as local contacts during the beamtime.

5. References

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