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ESRF

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://wwws.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.

ESRF	**Experiment title:** Nanographene nucleation and growth behaviour in inorganic-organic hybrid structures: real-time and in-situ X-ray scattering	**Experiment number**: SI- 2533
Beamline: ID 03	**Date of experiment**: from: 07. Feb. 2013 to: 12. Feb. 2013	**Date of report**:
Shifts: 15	**Local contact(s)**: Roberto Felici, Francesco Carlà	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The goals of studying nucleation density, critical cluster sizes and out-of-plane growth mode using real-time GISAXS and growth oscillation measurements were successfully completed. Due to technical difficulties (turbo pump failure) we had to use our backup UHV chamber and therefore not the molecule HBC but 6P and 6P-3,5-F2 was grown.

Experiments

We performed real time and *in-situ* investigations during the growth of 6P and 6P-3,5-F2 using a Dectris PILATUS 300K-W detector to simultaneously detect specular growth oscillations and diffuse GISAXS signals. The post-growth structure of the thin films was then measured by means of XRR and GIXD using a MaxiPix detector. The molecules were deposited on the substrate by OMDB (organic molecular beam deposition) inside our UHV chamber. The substrate temperature and the growth rate were varied for each run within 20-130°C and 1-15 A/min respectively.

Table 1: *Matrix of the parameters substrate temperature, rate and molecule grown during the beamtime.*

Tsub	Rate	Molecule
20	1,3	6P-F2
20	2,5	6P-F2
60	1,3	6P-F2
60	15	6P-F2
60	15	6P
100	1,3	6P-F2
100	1,4	6P
100	15	6P-F2
100	15	6P
130	1,2	6P-F2
130	15	6P

Real-time Investigation of layer coverage

By using the PILATUS 300K-W we measured *in-situ* growth oscillations in XRR geometry at $q_{anti\text{-}Bragg}= ½\, q_{Bragg}$. Independent of the substrate temperature and rate we observed that the weakly dipolar 6P-3,5-F_2 molecules are growing in smoother layers in comparison to the non-dipolar 6P molecules, were the island growth mode starts earlier. An example of one dataset for Anti-Bragg oscillations is shown in Fig. 2. We have been able to model these growth oscillations by using the Trofimov model (s. V.I. Trofimov *et al.*, Thin Solid Films, 1997). From the fits (red curves in Fig. 2) we obtained information about the critical layer coverages, the *in-situ* roughness evolution of the films and the downhill transport rates. In the case of 6P the growth oscillations were damped much earlier which shows that in this case the film is getting rougher much faster.

The layer coverage plots in Fig. 2 show the coverage of each layer as a function of time (i.e. film thickness during growth). Here *1* means that the layer is fully covered, while *0* stands for an empty layer. As can been seen from Fig. 2 the filling of each layer starts earlier in the case of 6P, i.e. the film roughens more quickly and 3d 'wedding cake' islands form. As already mentioned these findings are true independently of the chosen substrate temperature and growth rate and, thus, it can be assumed that there origin lies in the effect of the dipole moment of the molecule.

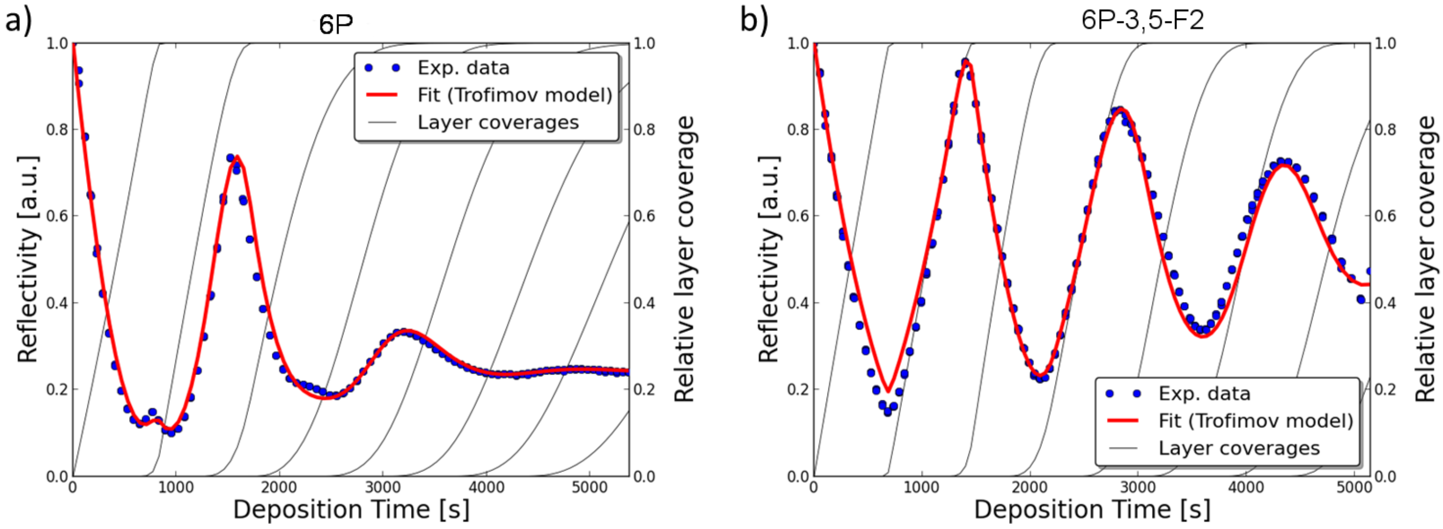

Fig. 1: *Growth oscillations obtained at the Anti-Bragg point of a) 6P and b) 6P-3,5-F2 at a substrate temperature of T=100°C and a deposition rate of 1.5 A/min. The oscillations were fitted using the Trofimov model (red curve). The grey curves in the background correspond to the layer coverage of each layer at each moment of the film growth. The larger damping of the oscillations in the case of 6P are due to a faster roughening of the film and indicate a growth mode change from layer-by-layer to island growth in comparison to 6P-3,5-F_2.*

In-situ **measurement of the island size evolution**

In addtion to the investigation of the growth oscillations by using specularly reflected beam on the PILATUS detector, with its high dynamic range we were able to simultaneaously record the weak, diffuse *in-situ* GISAXS signal during the growth of the films. This in turn allows us to monitor the temporal evolution of the island formation. In Fig. 3 examplary GISAXS images corresponding to the above Anti-Bragg oscillations at the early stage of the film growth are shown for both molecules. In case of 6P-3,5-F2 we observed a larger peak splitting in comparison to the one in the case of 6P. This shows that the islands are smaller in the dipolar 6P-3,5-F2 molecular film (~300nm vs. > 1µm).

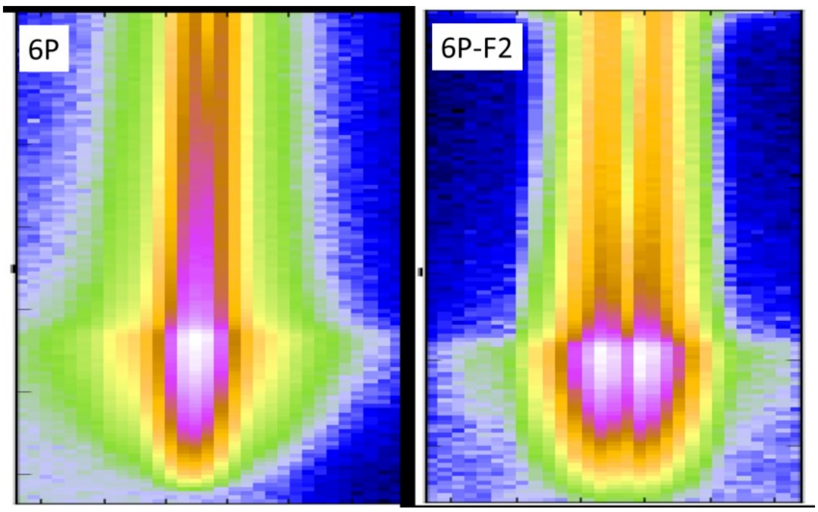

Fig. 2: *GISAXS at the beginning of the film growth of a)6P and b) 6P-3,5-F2. The larger peak splitting in the case of 6P-3,5-F2 indicates smaller islands. By analysing the GISAXS images at each moment of the growth the evolution of the island formation can be understood.*

Combining results from specular and diffuse scattering investigation

By combining the results obtained from the GISAXS and the Anti-Bragg oscillations one can schematically illustrate the growth of the two molecules (Fig. 4). From the results above it follows that 6P forms bigger islands and rougher films. In contrast, 6P-3,5-F_2 films are smoother and the topmost islands are smaller and start to grow only when the underneath layer is almost fully covered.

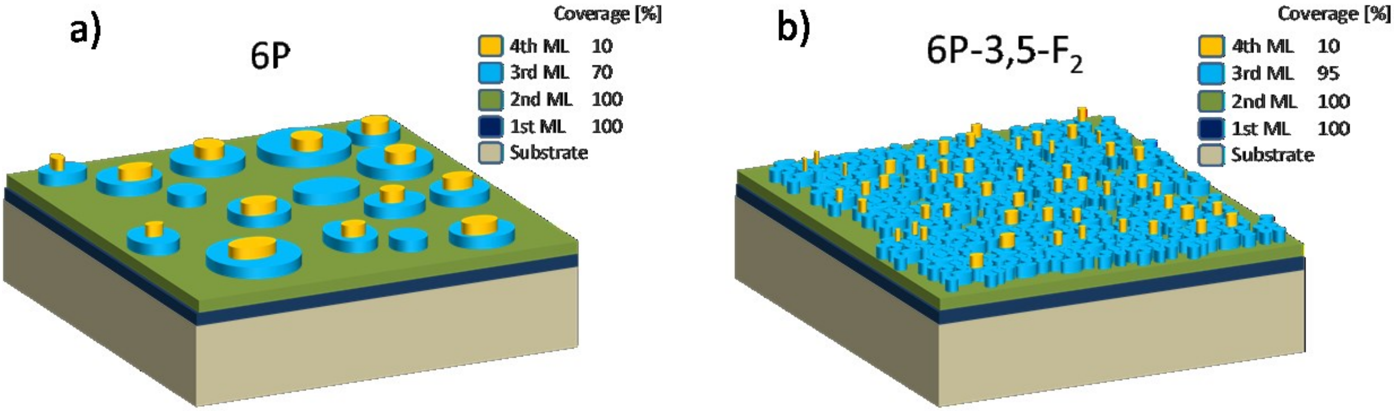

Fig. 3: *Sketch of the growth of a)6P and b) 6P-3,5-F2.*

Outlook

The obtained results of the study are of high significance for further possible optoelectronic applications as well as for fundamental science where a molecular design with a dipole moment may help to positively influence the grown structure, e.g. to obtain smooth films. We are currently finishing the analysis and fitting of the whole dataset (i.e. for the full temporal evolution of GISAXS and for all growth conditions) and expect to submit a manuscript by the end of 2013.

We gratefully thank the local contacts Roberto Felici and Francesco Carlà and the whole staff of ID03 for the excellent and helpful support.