

## 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 using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

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

Reports can now 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.

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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.


**Experiment title:**

Kinetically Driven Orientational Transition in Organic Thin Film Growth

**Experiment number:**

SC - 1306

**Beamline:**

ID 10 B

**Date of experiment:**

from: 4 Feb 2004 to: 10 Feb 2004

**Date of report:**

1 March 2004

**Shifts:**

18

**Local contact(s):**

Leide Cavalcanti

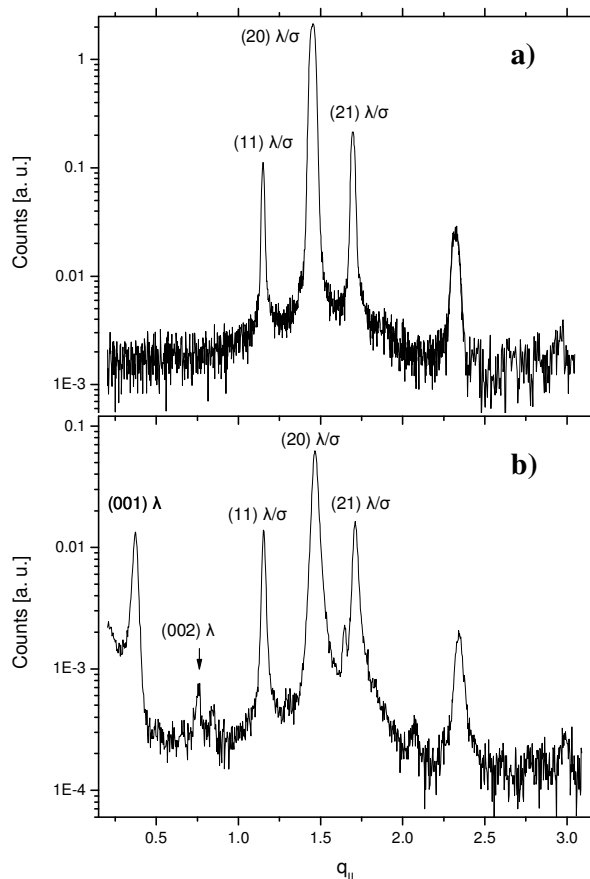
*Received at ESRF:*
**Names and affiliations of applicants (\* indicates experimentalists):**

 \*Frank Schreiber<sup>1</sup>, \*Alexander Gerlach<sup>1</sup>, \*Stefan Sellner<sup>1,2</sup>, \*Stefan Kowarik<sup>1</sup>
<sup>1</sup> Physical and Theoretical Chemistry Laboratory, Oxford university, OX1 3QZ, UK

<sup>2</sup> Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

**Report:**

As described in the proposal we performed a temperature and rate dependent study of the kinetically controlled orientational transition of molecular thin films. The experiments were performed during growth *in situ* and *in real time*. The analysis of the data is still in progress, and the results are preliminary. In this report we summarize our key findings: we could observe growth anomalies for the first DIP layers due to a substrate induced orientational transition; further we could show that in later growth stages the  $\lambda$ -phase of DIP is developing on top of the  $\sigma$ -phase.

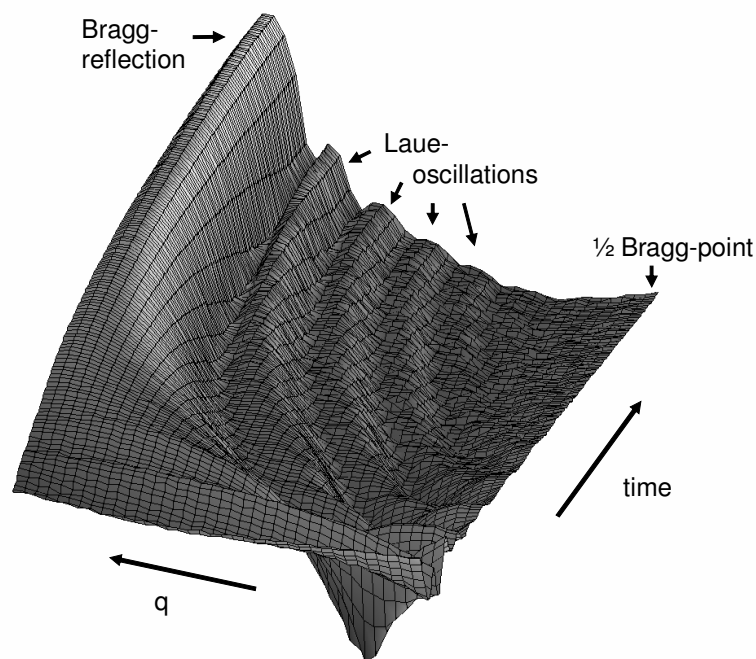


In grazing incidence X-ray diffraction the  $\sigma$ -phase (molecules standing up, cf. [1]) and  $\lambda$ -phase (molecules lying down) each show characteristic Bragg reflections. While a film grown at 130 °C (cf Fig. 1a) displays peaks that can all be attributed to the  $\sigma$ -phase, a reduction in growth temperature leads to new peaks. For a film grown at 35 °C (not shown) and even more so for a film grown at -7 °C (Fig. 1b) additional peaks that correspond to molecules lying down flat appear. By changing the penetration depth of the evanescent field we could further establish that the  $\lambda$ -phase is growing on top of the  $\sigma$ -phase.

The determination of the degree of phase coexistence as a function of growth temperature (that is the mobility of molecules on the surface), will allow us to correlate the growth kinetics of the two phases with the diffusivity / mobility of the DIP molecules.

**Fig. 1** GIXD measurements on DIP films grown at 130 °C (a) and -7 °C (b).

We could obtain more detailed information about the *kinetics* of growth, by monitoring *in real time* the reflectivity at the  $3/2$  Bragg point, and, in a separate growth run, the reflectivity in a finite region of  $q$ -space from  $q = \pi/d$  to  $q = 2\pi/d$  (where  $d$  is the DIP  $\sigma$ -phase lattice spacing). The counting statistics is very good even for a sub-monolayer film, allowing for sub-second acquisition times per  $q$ -space point. This time resolution allows to follow the growth at typical rates of about one monolayer every five minutes. These time resolved measurements allow us to monitor changes of the lattice parameter of the layers interacting with the substrate. Fig. 2 shows the time evolution of the growth run at high substrate temperature ( $130^\circ\text{C}$ ).



**Fig 2.** Evolution of the reflectivity curve with film thickness. The measurement comprises the region between the  $1/2$  Bragg peak (right hand side) and the first Bragg peak (left hand side). The reflectivity develops from a plain Fresnel reflectivity of bare silicon (front) to the film reflectivity showing the first Bragg peak and four Laue oscillations at a film thickness of  $300 \text{ \AA}$ .

The plot contains several pieces of information important for understanding the growth dynamics:

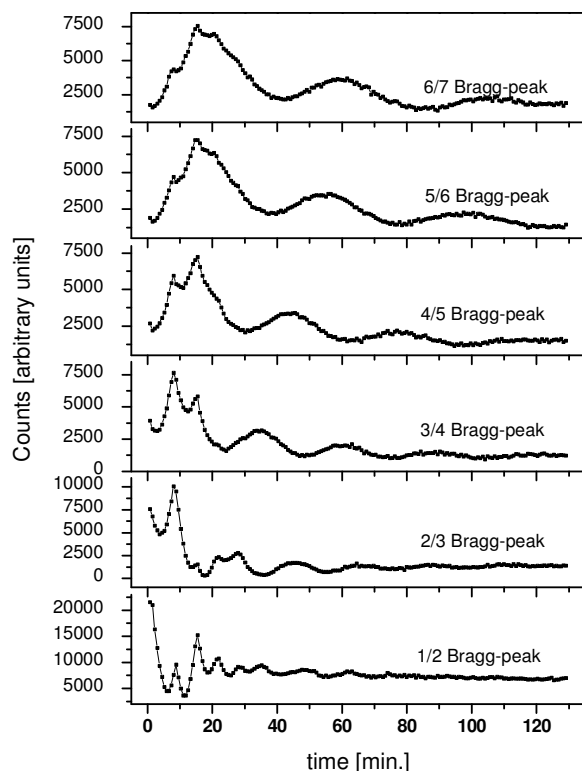
- With increasing film thickness the  $\sigma$ -phase Bragg peak grows stronger and its width decreases, Laue satellites form.
- The Bragg peak intensity does grow less than quadratic (i.e. sub-linear in the above log plot), so with increasing film thickness not all material is forming the  $\sigma$ -phase. This agrees with the complementary GIXD information about the development of the  $\lambda$ -phase growing on top of the  $\sigma$ -phase [1], and allows for a quantitative estimate.
- The region near the anti-Bragg peak is affected strongly by interference between the substrate and the film. This may allow us to determine the relative phase and therefore relative distance between substrate and film lattice planes.
- During the deposition of the first monolayer the time evolution does not follow the expected pattern. We are currently in the process of analysing this with a model in which the first layers are lying down flat on the substrate to maximize the van der Waals interaction. Scans at the  $3/2$  Bragg peak where the interference with the substrate is small, provide a means to distinguish between substrate interference effects and effects of molecular orientation.

From data such as shown in Fig. 2 it is possible to extract the time traces of the growth not only at the  $1/2$  or anti-Bragg peak, but also for the  $2/3$ ,  $3/4$ , ... up to the  $6/7$  Bragg peak. These time traces again show that during deposition of the first layers the molecules do not all adopt the standing up configuration.

After the first monolayers have grown, the time traces follow smooth oscillations. The oscillation period is changing with  $q$  as follows: at the  $\frac{1}{2}$  Bragg the oscillation period is the time until completion of 2 monolayers, at the  $\frac{1}{3}$  point up the time to complete 3 monolayers and so on. The different traces also show different damping constants: while the  $\frac{1}{2}$  point oscillations are damped out after the roughness of the crystalline layers reaches 2 ML, the time constant for the damping at the  $\frac{6}{7}$  point is equivalent to the time when the roughness has reached a value of 7 ML.

This data enables us to reconstruct the coverage of the individual molecular layers as a function of time, and thus the kinetically driven roughness. This allows to extract the associated growth exponents for the *dynamic equilibrium* during growth, as opposed to the post growth scenario (cf. [2]).

To conclude, we could follow for the first time the growth of a molecular thin film in real time over a broad  $q$ -range. This measurement could demonstrate the existence of an orientational transition of the first monolayers, showing that the growth dynamics of molecular systems contains qualitative new phenomena that require further investigation.



**Fig. 3** Real time trace for the growth of a 300 Å DIP film at 130 °C

We wish to acknowledge the excellent collaboration with the local contact L. Cavalcanti which made this challenging experiment a success.

#### References:

- [1] A. C. Dürr, F. Schreiber, M. Kelsch, et al., Journal of Applied Physics 93, 5201 (2003).
- [2] A. C. Dürr, F. Schreiber, K. A. Ritley, et al., Physical Review Letters 90, 016104 (2003).