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.

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:** Rubrene-based molecular electronics: Real-time and in-situ study of rubrene thin film growth	**Experiment number**: SC-1723
Beamline:	**Date of experiment**: from: 06/07/2005 to: 11/07/2005	**Date of report**: 31/08/2005 *Received at ESRF:*
Shifts: 17	**Local contact(s)**: Dr. Leide Cavalcanti	

Names and affiliations of applicants (* indicates experimentalists):
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Report:

The experiments were performed along the lines of our proposal, focussing on the growth of the organic semiconductor rubrene *in situ and in real time*. Since the experiments are only 4 weeks ago and the data analysis is still in progress, we can only report the most important findings. Details will be seen in a careful fit of the experimental results.

In in situ and real time X-ray scattering provided information on the microscopic structure of the rubrene molecules as well as information about the film morphology. Anomalous growth with a delayed rougheneing during growth (that is delayed roughening with thickness) was found.

Structure of rubrene thin films:

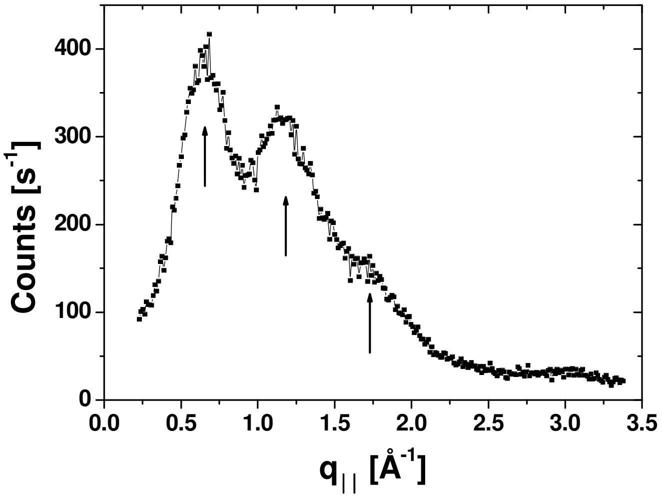

Fig. 1 Grazing incidence scan on a 384 Å rubrene film, showing in-plane (parallel to the sample surface) correlation lengths of about 10 Å for rubrene.

Figure 1 shows a GID scan on a 384 ± 2 Å thick rubrene film, probing the structure in the plane of the thin film. The absence of sharp Bragg reflections indicates that there are no crystallites in the film. This is consistent with the relatively low charge carrier mobility in thin film devices of rubrene. Only broad features can be seen, with a typical length scale of 10 Å indicating some degree of local order, but an otherwise largely disordered structure.

Morphology of the rubrene thin films:

The post-growth specular reflectivity of the same film, shown in Figure 2, again shows no sharp Bragg reflections but slight enhancements in reflectivity again around q⊥ = 0.65 Å-1 (as in GID). This confirms the above conclusions that there are no crystalline regions but at best some degree of short-range order.

Importantly, the specular reflectivity shows pronounced finite thickness oscillations (Kiessig fringes). This is due to a very low film roughness of 10 ± 2 Å, as determined from a fit to the data using the Parratt formalism (see Fig. 2, inset).

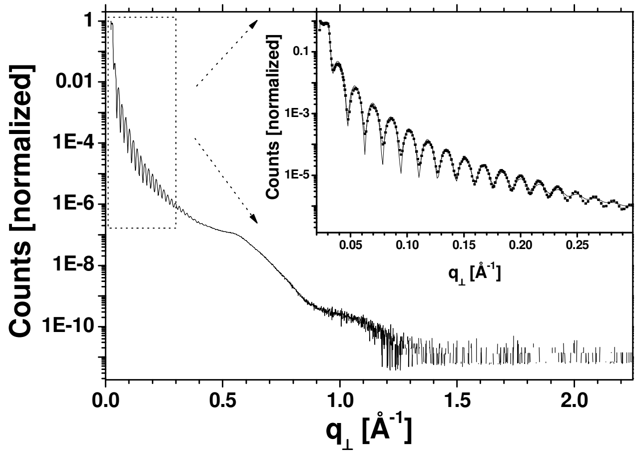

Fig. 2 Post growth X-ray reflectivity scan of a 1280 Å rubrene film. Pronounced finite thickness oscillations at low q indicate a very smooth surface (Inset: Zoom for low q range, solid line is a fit to the data).

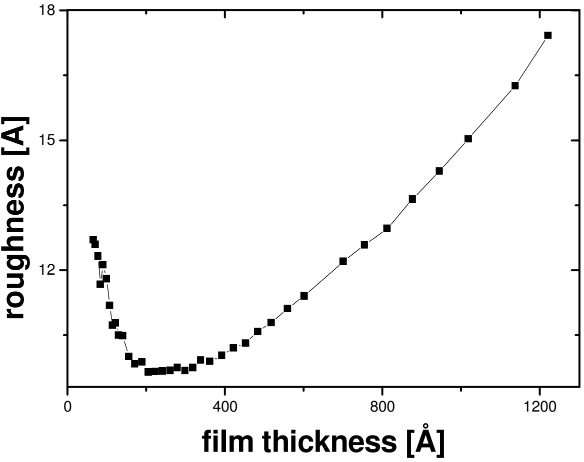

Fig. 3 Evolution of the root mean square roughness with film thickness during OMBD growth of rubrene at 10 °C substrate temperature. The absolute error bar is ±7 Å, while the relative uncertainty is ±2 Å. The film is very smooth and only starts to get rough at around 400 Å.

The evolution of the film roughness with film thickness is shown in Figure 3. As we have only part of the specular reflectivity for fits, the absolute value of the roughness can only be determined with an accuracy of ± 7 Å. Importantly the relative uncertainty between successive fits of ± 2 Å, which is the relevant quantity for our analysis, is significantly smaller though.

As seen in Figure 3 the roughening of the rubrene film shows a delay, with an increasing roughness starting only at around 400 Å. Figure 3 even suggests a certain degree of smoothening (that is a reduction of roughness with time) in the initial stage of the growth. In our experiments this behaviour of delayed roughening is universally found for a variety of growth conditions from 10 to 80 °C substrate temperature and for unpurified as well as purified rubrene. For substrate temperatures of 100 °C we find relatively rough films, possibly due to a dewetting tendency.

The most important finding, however, is the delayed roughening or even smoothening at $T \leq 80$ °C in the initial stage of the growth. This is in stark contrast to most other growth

scenarios, where the roughness σ exhibits a monotonic increase with thickness D, and the difference between different systems is “only” the slope of σ(D). The comparison to a detailed study of another organic semiconductor diindenoperylene where even enhanced (rapid) roughening was found makes the present finding even more remarkable.
The anomaly of delayed roughening, or even smoothening, in the beginning of rubrene growth may be related to structural or conformational changes of rubrene. According to a recent study by Käfer et al. [1] the energy required to bring rubrene from its twisted state to the planar state in which it crystallises, prevents the molecules to form crystallites near the surface. After a critical film thickness of 120 Å the molecular conformation changes, which may then start to induce roughening.

We are presently preparing a publication in Appl. Phys. Lett. We expect to publish other results later.

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[1] **D. Käfer and G. Witte, Physical Chemistry Chemical Physics 7, 2850 (2005).**