

EUROPEAN SYNCHROTRON RADIATION FACILITY



DUTCH-BELGIAN BEAMLINE AT ESRF

Experiment Report Form

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.

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DUBBLE	Experiment title: Template-controlled growth of alizarin	Experimentnum-ber:26-02-240
Beamline: BM 26 Shifts: 29	Date(s) of experiment: From: 01.09.2004 To: 12.09.2004 Local contact(s): Dr. Wim Bras	Date of report : 19.10.2004
Names and affiliations of applicants (* indicates experimentalists): S. Graswinckel*, D. Kaminski*, I. Shah*, R. Algra*, M. In 't Veld* and E. Vlieg*		

Report: (max. 2 pages)

When growing crystals, a precise control of the growth process and thus of the resulting crystals is usually required, because the crystals may need to have a well-defined size or morphology, be very pure, have a low defect density or need to have one specific crystallographic structure out of a set of possibilities (polymorphs). We have recently started a research program to investigate crystalline templates as a means to influence crystal nucleation and growth, because it induces long-range ordering with a controlled length scale and allows tailoring of the interaction with the crystal.





Epitaxy of inorganic materials has received a lot of attention, mainly because of the importance of semiconductors. We focus our attention on the epitaxial growth of organic crystals, an area that has been much less extensively studied, but that is rapidly gaining importance because of the developments in nano(bio)technology and organic semiconductors [1,2].

The organic dye alizarin (1,2-dihydroxy-9,10-anthraquinone, see Figure 1) has been found to form epitaxially oriented crystals on a cleaved NaCl (100) substrate. More recently, we found by atomic force microscopy that a monolayer of alizarin is often formed in addition to bulk crystals. The aim of the experiment was to determine the 2D and 3D structure of alizarin on a NaCl (100) substrate. For this, we used our specially designed experimental cell with temperature control for the crystal surface as well as for the alizarin doser. A monolayer of alizarin is easily formed on the surface; Figure 2 shows the specular profile before and after deposition.



Figure 2: The specular profile before and after alizarin deposition.

Figure 3 shows an azimuthal scan after long deposition. The $(\overline{2}02)$ Bragg peaks belong to epitaxially oriented alizarin crystals grown on the surface. However, the four equivalent orientations with respect to the NaCl substrate are not equally favorable, as can be seen from the different height of the alizarin bulk peaks. We speculate that this is due to the specific orientation of the cleavage steps on the surface.



Figure 3: Azimuthal scan for the bulk $(\overline{2}02)$ *alizarin reflection.*

Data acquisition was relatively straightforward because of the good quality of the NaCl substrates. Several surface preparations were performed to get the best results. Our data consist of specular scans for different conditions and additionally (11) and (02) rods for the alizarin monolayer. The first analysis indicates that a thin film without measurable in-plane ordering is formed, in which the 3D crystals slowly nucleate. These crystals grow at the expense of the film. After deposition the surface appears to be still covered with a monolayer of alizarin. However, water from the surroundings is in competition with this monolayer. At moderate relative humidity the monolayer is replaced by a layer of water [3]. This takes place at around 40% R.H. Unfortunately, the ambient humidity during the experiment was quite high (about 66% R.H.), which gave rise to problems.

The analysis is still in progress; to understand the role of the monolayer in the epitaxial growth of alizarin, a full computer modeling has to be done.

References

1. Hooks, D.E., T. Fritz, and M.D. Ward, *Epitaxy and molecular organization on solid substrates*. Advanced Materials, 2001. **13**(4): p. 227–241.

Whitesides, G.M., *The 'right' size in nanobiotechnology*. Nature Biotechnology, 2003. 21: p. 1161–1165
Arsić, J., Kaminski, D.M., Radenović, N., Poodt, P., Graswinckel, W.S., Cuppen, H.M., Vlieg, E., *Thickness-dependent ordering of water layers at the NaCl(100) surface*. Journal of Chemical Physics, 2004. 120(20): p. 9720–9724.