EUROPEAN SYNCHROTRON RADIATION FACILITY

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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 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:** Secondary Templating of Mesoporous Silica Films	**Experiment number**: CH-1022
Beamline: ID10B	**Date of experiment**: from: 30/5/01 to: 5/6/01	**Date of report**: 23/08/01
Shifts: 18	**Local contact(s)**: Dr. Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The current experiment is the continuation and development of CH-912 and SC-630 [1]. We aim to study the growth and structure of surfactant-templated films formed at the air/solution interface using both specular and off-specular reflectivity. Specular measurements are highly sensitive to the electron density of the film normal to the interface, and the roughness of the surface so allow us to examine the properties of the formed film. Off-specular patterns can be taken every 60 seconds (using a position sensitive detector) throughout the induction and film formation process, hence the evolution of the diffraction peaks, corresponding to the ordered mesophase within the films, can be monitored as a function of time. In this study we have been particularly interested in the effects of changing the silica precursor concentration on the structure and surface texture of the film and the effect of an insoluble monolayer at the solution surface.

The films were grown at room temperature at the air/solution interface at the surface of a raised meniscus in a Teflon trough with a surface area of ca 63cm^2. The films were grown from an acidic subphase (0.2M HCl) using tetramethoxysilane (TMOS) as the silica source and cetytrimthylammonium bromide (CTAB) as the surfactant template. The molar ratios were 1 water : 3.63×10^{-3} HCl : 1.52×10^{-3} CTAB, and the TMOS varied between 0.005 and 0.019. Film formation occurs after an induction period of 200 to 300 mins depending on TMOS concentration. Insoluble monolayers of perfluorodecyltriethoxysilane and PS-PEO diblock copolymer were spread at the solution interface, to act as secondary templates.

Typical specular and off specular measurements are shown in Figures 1 and 2 for 1 water : 3.63×10^{-3} HCl : 1.52×10^{-3} CTAB, 0.016 TMOS. The specular reflectivity exhibits Fresnel decay which is modified by a broad fringe due to the surface film. Superimposed on this profile are three diffraction peaks which correspond to a repeat distance of ca 40Å; this is consistent with the size of cylindrical CTAB micelles (~35Å) [2]. Analysis of this data, for films grown with and without secondary templates, is in progress using standard Parratt fitting procedures.

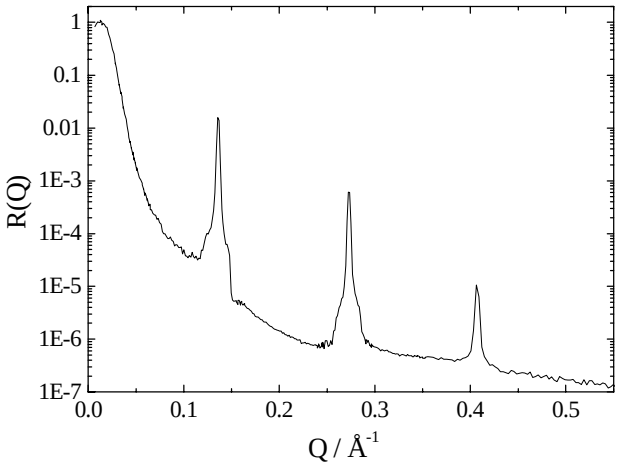

Figure 1 The specular reflectivity from 1 water : $3.63x10^{-3}$ HCl : $1.52x10^{-3}$ CTAB : 0.016 TMOS.

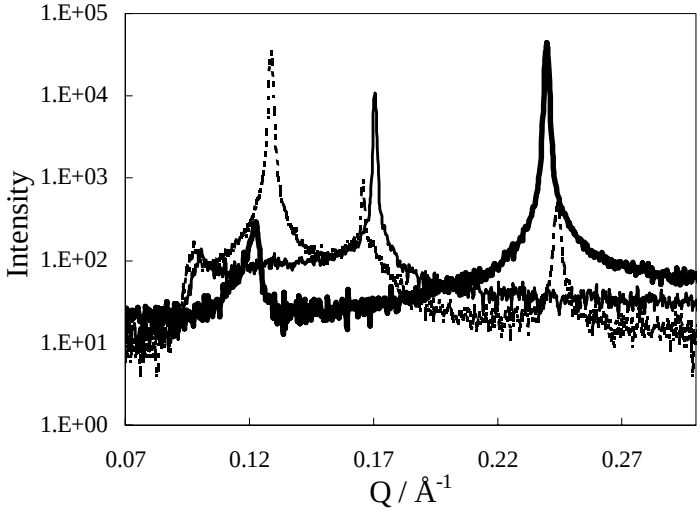

Figure 2 The off specular reflectivity recorded 188 mins (thin line), 288 mins (dashed line) and 368 mins (bold line) after spreading

The central peak ($0.17Å^{-1}$) in the off-specular reflectivity profile (Figure 2) corresponds to the specular reflectivity peak; its position is seen to move slowly with time, due to evaporation of the solution. The specular peak is flanked by the 1st order diffraction peak ($0.13Å^{-1}$) and the 2nd order diffraction peak ($0.24Å^{-1}$). The peak situated at $0.1Å^{-1}$ is the Yoneda wing which probes the changing surface roughness with time. Figure 2 shows how these peaks evolve with time. The intensity of the specular peak decreases, while the first and second order peaks only become significant when the film begins to form (>270 mins). Surprisingly, the intensity of the 1st order peak reaches a maximum and then begins to decrease. This can be seen clearly in Figure 3 (the open diamonds), which also shows for the first time that the growth mechanism of the film is concentration-dependent. At the lowest silica precursor concentration, the 1st order diffraction peak is found to grow in slowly, and remain at its maximum intensity indefinitely. As the silica concentration is increased, the maximum peak intensity increases; however almost as soon as it reaches its maximum intensity the peak starts to decay. Similar trends are seen in the 2nd order diffraction peak. We are currently modelling this data assuming the growing film can be approximated to a layer of particles, having alternating silica and surfactant layers, which appear at the surface during the film formation [1].

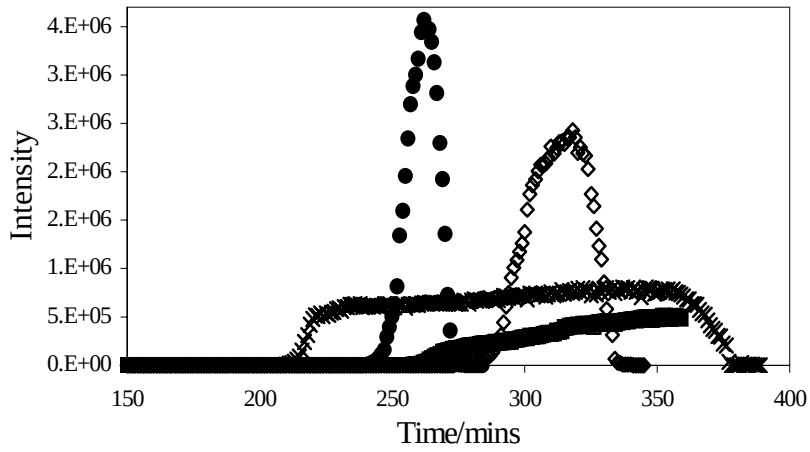

Figure 3. The intensity of the 1st order difraction peak as a function of time for 1 water : $3.63x10^{-3}$ HCl : $1.52x10^{-3}$ CTAB, X TMOS, where X is 0.005 (open squares), 0.011 (crosses), 0.015 (closed circles) and 0.016 (open diamonds).

References

[1] K.J. Edler, A. Goldar, A.V. Hughes, S.J. Roser, S. Mann, Microporous Mesopourous Materials 44-45. (2001) 661.

[2] A. S. Brown, S. A. Holt, T. Dam, M. Trau, J. W. White Langmuir, 13, (1997) 6363.