EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:**<br>*In situ* X-ray reflectivity and GISAXS measurement of the influence of SuperCritical $CO_2$ on $CO_2$-philic and $CO_2$-phobic surfactant templated silica and titania thin film | **Experiment number**:<br>**SC-3686** |
| **Beamline**:<br>ID10 | **Date of experiment**:<br>from: 07 May to: 14 May | **Date of report**:<br>16.03.15 |
| **Shifts:**<br>15 | **Local contact(s)**:<br>Oleg Konovalov | *Received at ESRF:* |

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

Name: CHAVEZ Elvia, BEUVIER Thomas, GIBAUD Alain

Adress: IMMM, Université du Maine, Av. Olivier Messiaen, 72000 Le Mans.

## Report:

**Abstract :** Surfactant templated silica thin films were self-assembled on solid substrates by dip-coating using a partly fluorinated surfactant $F(CF_2)_8C_2H_4(OC_2H_4)_9OH$ as the liquid crystal template. The aim was twofold: first we explored the phase diagram to determine the domain of existence of highly ordered crystalline phases and second we exposed the films to sc-$CO_2$ to foster the removal of the surfactant. The films were characterized by *in situ* X-Ray Reflectivity (XRR), Grazing Incidence Small Angle X-ray Scattering (GISAXS) under $CO_2$ pressure. GISAXS patterns reveal the formation of a 2–D hexagonal structure at a molar ratio FSN/Si equal to 0.1. We further evidence that the extraction of the template using supercritical carbon dioxide can be successfully achieved since fluorinated surfactants are $CO_2$-philic in nature. Very surprisingly the 2D rectangular structure was well preserved after depressurization of the cell and removal of the surfactant.

**Methods:** For measurements, the film was placed inside a high pressure cell that was thermo regulated at 34°C ± 0.1°C. Pressure was automatically adjusted via a electromechanical pressure controller with a precision better than 0.1 bar. Specifications about the pressure cell are given in reference[1]. All measurements made on these films were carried out at a constant temperature of 34°C. In-situ XRR and GISAXS experiments were performed as a function of $CO_2$ pressure at the ID10B beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a monochromatic x-ray beam of energy 22 keV. The high energy X-rays are required to minimize the absorption of the beam going through the diamond windows of the cell (1 mm) and 35 mm of $CO_2$ in gas or sc- state. The time scale between each measurement was 30 min. The depressurization process was achieved in 1h.

**Results:**

The experimental results obtained during the pressurization up to 100 bars are presented in Fig. 1. The experiment was carried out on a fresh film which was not yet stabilized. First, it is noted that XRR curves are not very affected by the elevation of pressure. Below 50 bars, a small increase in *d*-spacing is observed shown

by the shift of the Bragg peak towards lower $q_z$ values. This result suggests that $CO_2$ is penetrating inside the film causing a slight expansion of the structure. However, when the pressure is raised above 50 bars, we observe a contraction of the silica matrix concomitant to an increase of the intensity of the Bragg peaks. To make the story simple, in the framework of Born approximation we can expect that the intensity of the Bragg peaks should be proportional to the electron density contrast $\boldsymbol{I} = (\rho^{e-}_{\boldsymbol{wall}} - \rho^{e-}_{\boldsymbol{pore}\,\text{or micelle}})^2$ . Therefore an increase in intensity of the Bragg peaks as a function of $CO_2$ pressure can be associated with the progressive extraction of the surfactant. After the depressurization of the cell, the intensity increases by about 1 order of magnitude compared to the the intensity at 0 bar before $CO_2$ exposure. If we consider that the initial intensity at 0 bar is proportional to $\boldsymbol{I}_0 \approx (\rho^{e-}_{\boldsymbol{wall}} - \rho^{e-}_{\boldsymbol{micelle}})^2$ while the final intensity after the depressurization is proportional to $\boldsymbol{I}_f \approx (\rho^{e-}_{\boldsymbol{wall}} - \rho^{e-}_{\boldsymbol{pore}})^2$, we obtain a ratio of about 13 which is close to the observed ratio of 10. The small difference between these two values can be explained by a change in pore size. The fairly good agreement between the change of intensity before and after removal of the surfactant is the sign that the surfactant was fully removes after depressurization.

| | |
|---|---|
| $\rho^{e-}_{\boldsymbol{wall}}$ | 0.559 $e^-/Å^3$ electron density of the [Layer1] obtained after fitting data at 0 bar |
| $\rho^{e-}_{\boldsymbol{micelle}}$ | 0.404 $e^-/Å^3$ electron density only for the fluorinated part of FSN (density = 1.39 g/cm $^3$) |
| $\rho^{e-}_{\boldsymbol{pore}}$ | ≈0 $e^-/Å^3$ |

Table 1: Electron density

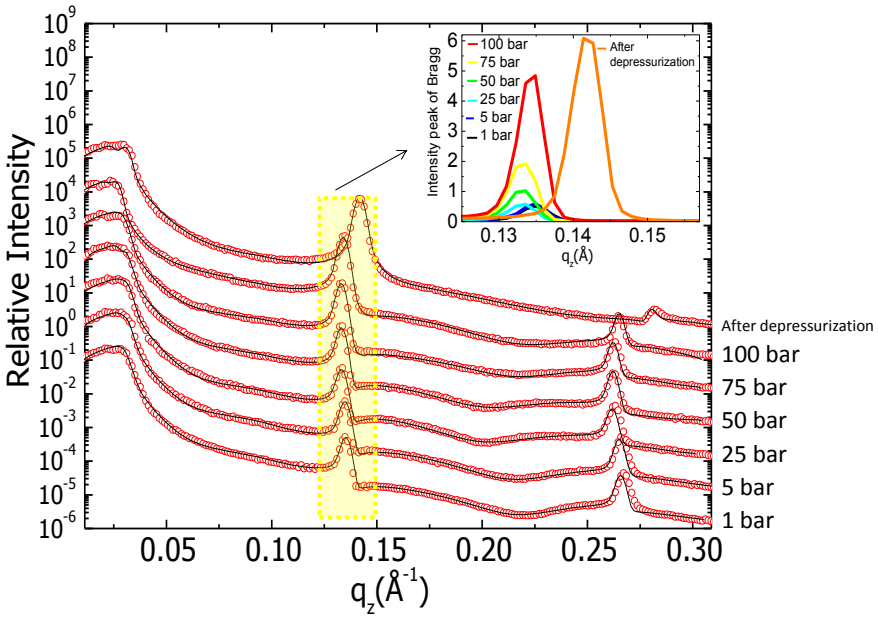


**Figure 1.** The evolution of in-situ XRR curves during pressurization of $CO_2$ in the cell. Curves are translated vertically for clarity (logarithmic scale). In the top inset, a zoom of the evolution of the intensity is shown in linear scale.

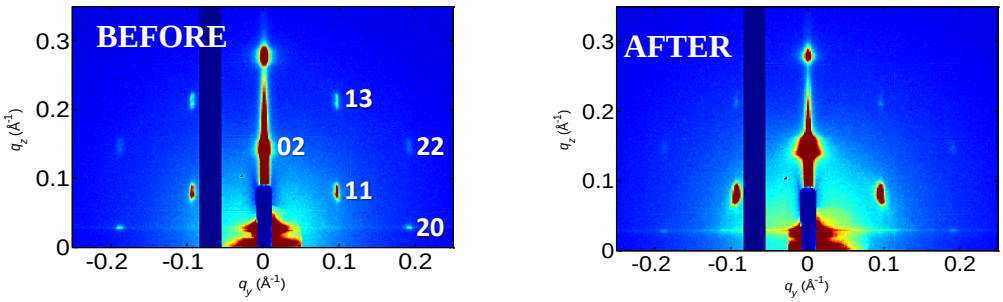


**Figure 2** GISAXS image of a FSN mesoporous thin film before and after the removal of the surfactant. This GISAXS measurement was performed at ID10 Beamline (ESRF) with 22KeV. The incident angle was 0.06$^{o}$.

The structural features of mesoporous thin films before and after the $CO_2$– treatment were studied by GISAXS measurements (see Figure 2). The GISAXS patterns show characteristic reflections of the 2D rectangular structure for FSN mesoporous thin film. These reflections can be indexed as reflections on the 11, 13, 20, 22, 02 scattering planes of the 2D centered rectangular unit cell. The GISAXS images show that the mesoporous structure is well preserved after the treatment of the film to sc-$CO_2$. The weaker reflections corresponding to planes 13, 22, 20 are hardly observed in the sample after the $CO_2$-treatment. The disappearance of these reflections can be assigned to a distortion of the pores due to the shrinkage of the sample on the process of the surfactant removal by sc-$CO_2$.

[1] Mattenet M, Lhoste K, Konovalov O, Fall S, Pattier B and Gibaud A 2010 An X-Ray Thermo-Pressure Cell For Carbon Dioxide . *AIP Conf. Proc.* **111** 68–72