



	<b>Experiment title:</b> Temperature and humidity effects on mesophase silica-surfactant film growth at the air/water interface.	<b>Experiment number:</b> CH-1340
<b>Beamline:</b> ID10B	<b>Date of experiment:</b> from: 3/10/02 to: 8/10/02	<b>Date of report:</b> 21/2/03
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr Oleg Konovalov	<i>Received at ESRF:</i>
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### Report:

These experiments are part of a series aimed at studying the growth of surfactant-templated silica films at the air/solution interface. These films are formed by the spontaneous aggregation of silica-coated cylindrical micelles at the surface. Continuing silica polymerisation has the effect of freezing in the structure, resulting in a thin mesoporous composite film at the interface. The surfactant channels usually arrange themselves so the long axis are orientated parallel to the surface.<sup>1</sup> The intensity available at the ESRF allows us to follow the growth process *in situ*, by making diffuse reflectivity measurements in the z-direction. It is possible to collect a pattern in 60 seconds hence the evolution of the diffraction peaks, which correspond to the ordered mesophases within the system, can be monitored as a function of time.

Our most recent experiment was focused on the study of the effect of temperature and ambient humidity on the growth processes in these films. We designed and built an enclosed sample cell for use on Tröika II in which the temperature, and the humidity above the solution can be controlled. We measured film growth while varying the temperature from 25 to 40°C, and varying the humidity from 50% to 100% by flowing nitrogen gas through cell. The effect of changing the silicate precursor concentration under these conditions was studied, while keeping a constant surfactant concentration, in order to compare these results with our previous measurements taken under ambient conditions (25°C, ~40% RH).<sup>2</sup> In this case we used cetyltrimethylammonium bromide (CTAB) as a surfactant and tetramethylorthosilicate (TMOS) as an inorganic precursor.

Changing the temperature and humidity significantly altered the rate of film growth observed in the experiment and also the processes of structure-development in the films. For constant TMOS and surfactant concentrations, increasing the humidity slowed down film formation. However films grown at room temperature and high humidity do not develop sharp diffraction peaks as long as these conditions are maintained. Figure 1 shows a film grown at  $T = 25\text{ }^{\circ}\text{C}$  and  $\text{RH} = 100\%$ , with the cell closed. The graph shows a broad peak in the position

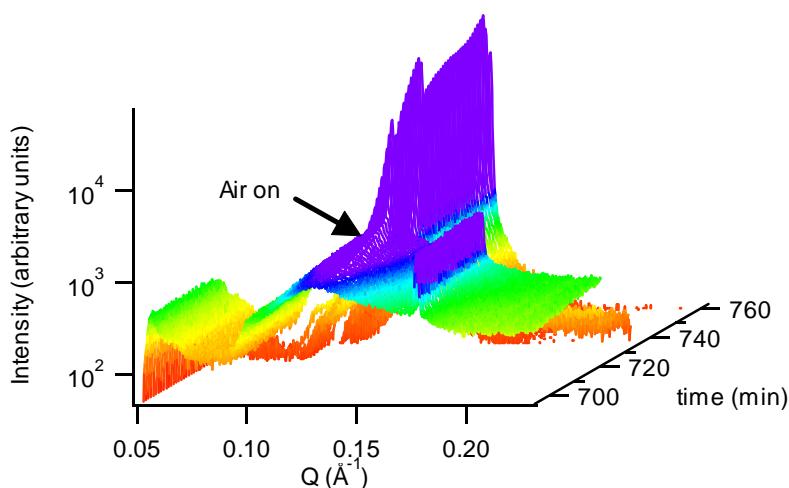


Figure 1: Rapid development of sharp diffraction peak from a disordered film grown at  $25^{\circ}\text{C}$  and  $100\%$  RH when gas flow to the cell was turned on.

of the first order diffraction peak, indicating a disordered system, in which the film formed very slowly. However, we then turned on the flow of gas through the cell. As the humidity decreased, the peak became sharper and grew rapidly in intensity indicating that the entire system became more ordered as the film lost water from its top surface. This result also shows the remarkable fluidity of the film – the silica condensation has not reached a point where the film structure is fixed, since it is still possible for an ordering transition to occur.

Increasing the temperature generally increases the rate of film growth at low humidity. It also alters the observed peak growth patterns. At room temperature our previous results showed that the peak widths were constant for intermediate concentrations, but at high and low TMOS concentration the peaks started out broad and became narrower.<sup>2</sup> At  $40^{\circ}\text{C}$  even at high and low TMOS concentrations, the peak widths are narrow and constant, increasing only in intensity as the film develops. At high concentrations however the peak does not develop the high intensity observed at other concentrations, possibly due to the presence of a disordered surface layer. This change in peak width behaviour indicates a change in film development from surface driven (where the peaks become narrower as the ordered film thickens) to bulk driven<sup>3</sup> (where the mesostructure forms in the bulk and particles containing the pre-formed mesostructure pack at the surface to form the film).

This experiment therefore shows that humidity and temperature have important effects on the mechanisms of self-assembly responsible for film growth and the degree of mesophase ordering. We are continuing analysis of this data and GID data on the in-plane structure of these films in the light of our other results, but clearly these results show that evaporation from the solution surface is required for ordered mesostructured film formation suggesting that dehydration and osmotic pressure are important factors in this self-assembly process.

## References

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