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Phase transformation during cubic mesostructured silica film formation

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The structural evolution taking place during CTAB/TEOS based solvent evaporation-induced thin film formation has been followed by *in-situ* time-resolved SAXS; this shows that the final *Pm*3*n* cubic structure is formed *via* the formation of lamellar and hexagonal intermediate structures within the water rich evaporation regime.

The preparation of porous oxide thin films has undergone a major improvement since mesoporous materials showing large surface area and narrow pore size distribution can be prepared by surfactant templating methods.[1] Nowadays thin SiO_2,[1–5] TiO_2,[6] ZrO_2[7] films can be synthesised with porous frameworks (i) exhibiting from 30 to 60% porosity, (ii) composed of well-organised interconnected or not interconnected spherical or cylindrical pores with tailored diameters (20–100 Å), (iii) arranged in various organised or disorganised structures (worm-like, compact 2D and 3D hexagonal, cubic). One of the most studied systems is based on the self-assembly of TEOS (tetraethoxysilane) derived oligomers and CTAB (cethyltrimethylammonium bromide) surfactant micelles during dip-coating. By carefully adjusting the initial solution composition, the coating parameters, and the treatment conditions, a discontinuous *Pm*3*n* cubic mesoporous thin film can be synthesised by dip-coating.[8] Previous detailed characterisation of such a film showed that the whole film, of optical quality, is formed of large organised domains that have a preferential orientation with respect to the substrate surface. The pore dimension was deduced to be between 20 and 25 Å. The self-assembly requires the spontaneous organisation of the material, *via* electrostatic interactions at the CTAB/silica solution interface, induced by the rapid evaporation of solvent associated with dip-coating.[9] The rigid mesoporous film is thereafter obtained by thermal degradation of the surfactant. Even if the sol–gel chemistry of silica and the mesophase behaviour of CTAB in aqueous/alcoholic media are well known,[10] the self-assembly process taking place during thin film formation remains only partly resolved because of the very low quantity of mater and the rapid kinetic of organisation that made chemical and physical investigations difficult to perform. We recently succeeded in following the structural evolution of the system by SAXS (small angle X-ray scattering) during the first minutes that followed the deposition.[11] This was made possible by using synchrotron radiations (Austrian high-flux SAXS beamline of the 2 GeV electron storage ring ELETTRA, Trieste, Italy). Concerning the CTAB/silica system, it was reported that the mesostructures form close to the drying line and are not only highly dependent on the solution composition but also on the solution age[8] (*e.g.* silica species condensation). With the aim of completing this study, additional investigations were performed and the results are presented here. The experiments were focused on the precise structural transformations that take place during the *Pm*3*n* cubic film formation. The initial solution was prepared as detailed previously and contained 1 TEOS : 20 EtOH : 0.004 HCl : 5 H_2O : 0.14 CTAB (molar ratio) and was aged for five days prior to deposition.[8] For such an experiment, the initial solution container was lowered while the substrate remained fixed in order to analyse the same film region during evaporation (Fig. 1). Substrates were placed at an angle of 0.18° with respect to the incident X-ray beam direction. Structures were deduced from the diffracted patterns collected every 1 s with a 2D-CCD detector (see Fig. 1). The use of such a detector has proved to be greatly advantageous as it confirms the assumptions previously reported[8] (same experiment with a linear detector) in addition to new information on the transformation sequence detailed now.

A selection of *in-situ* 2D-SAXS patterns recorded at various times after deposition (acquisition time = 1 s) are shown in Fig. 1. The scheme shown on the upper right depicts the geometry used for this experiment. The displayed patterns correspond to the dashed framed area on the CCD detector (the diagrams have been rotated of 90° for clarity). The intensity profiles corresponding to the in-plane diffraction between the two ◆ points shown on the 10 s pattern are also given for the other patterns. The in-plane black line labelled S on the 13 s pattern is present

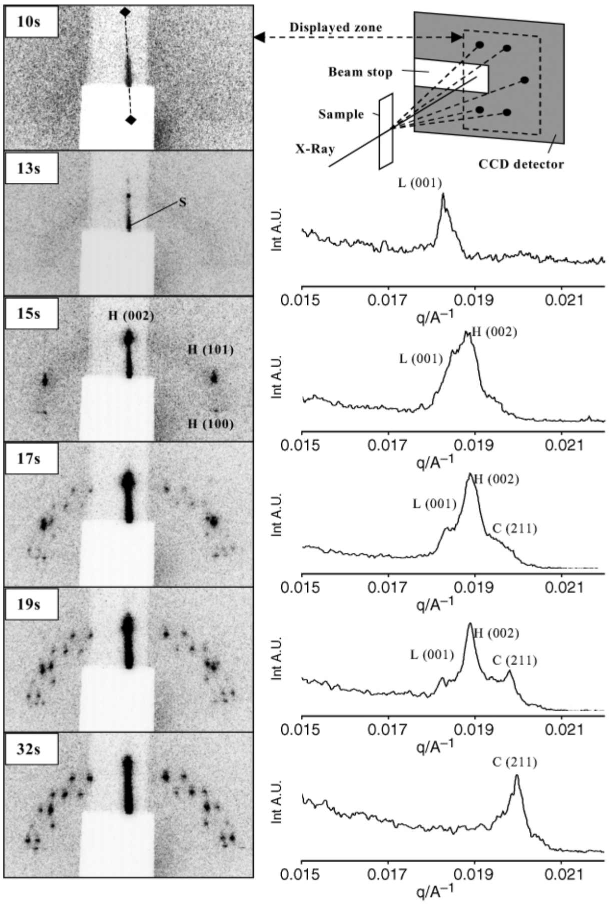

Fig. 1 Two- and one-dimensional SAXS patterns showing the structural evolution of the film during solvent evaporation. Upper right: scheme of the SAXS geometry used.

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even when no film is deposited and corresponds to the residual specular reflection. In the present case, the drying line was observed at 22 s by interferometry, suggesting that the whole transformation process takes place in a non-totally dry system. One can clearly see that the formation of the cubic $Pm3n$ structure involves the formation of various intermediate phases for which recorded d-spacings are in the range of characteristic dimensions of CTAB micelles. 10 s after deposition, no diffraction is observed, suggesting that the film is not organised. After 13 s, a single well-defined peak starts to appear at q = 0.0183 Å^{-1} (55 Å). This peak, labelled L(001), corresponds to planes that are parallel to the surface and since no other diffraction are present it can be assumed that the phase is lamellar. A faint diffusion ring is also present, suggesting that randomly located and oriented micelles (average distance ≈ 60 Å) start to form at this stage. From 14 s, together with the diffusion ring and the lamellar phase peak, characteristic diffraction peaks corresponding to the H(002) (d_{002} = 53 Å), H(101) and H(100) reflections of the 3D-hexagonal $P6_3/mmc$ are recorded,[5] confirming that spherical micelles are present and organise in the latter compact structure. After 16 s, the characteristic diffraction pattern of the $Pm3n$ cubic structure begins to overlay the 3D-hexagonal and the lamellar ones, while the diffusion ring is not visible any longer. The characteristic C(211) diffraction is located at d_{211} = 50 Å and on the in-plane profile line, suggesting that the domains have their (211) planes parallel to the film surface. At this stage it can be assumed that the whole film is organised in three different mono-oriented mesostructures. At 20 s and at 21 s, the lamellar and the 3D-hexagonal phases respectively disappear, while the cubic structure remains the only phase present in the dry film. It is lost if the film is allowed to stay in an ethanol saturated atmosphere (within the sealed dip-coater) for more than 25 min.

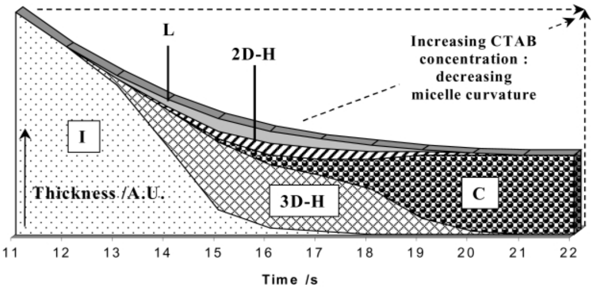

Fig. 2 Model of phase position during solvent evaporation.

In view of these results, it is clear that the formation of mesostructured CTAB/TEOS based films is a delicate and complex process involving intermediate phases. The critical parameter that influences greatly the phase evolution is the rapid evaporation of first ethanol and then water. A progressive concentration of non-volatile species (CTAB and silica oligomers) takes place at the air/film interface that induces a concentration gradient between both interfaces. This evaporation modifies the micelle morphology and organisation as less solvent molecules can take part in the charge density matching at the micelles interface. As the air/film interface is always more concentrated it should be the first area to undergo the micellisation. The initial lamellar phase may thus form at this interface, helped by the surfactant monolayer usually present there. The low intensity of the L(001) peak suggests that this interfacial lamellar phase is composed of relatively thin domains. Disorganised micelles are also present in the beginning as revealed by the diffusion ring. A compact 3D-hexagonal mesophase is then progressively formed by self-organisation of micelles, that is subsequently transformed in the final compact cubic structure through rearrangement. It is very unlikely that the intermediate 3D-hexagonal phase arises from a transformation of the lamellar domains as a surfactant smectic lamellar structure cannot turn into spherical micelles when the concentration increases. The 2D-hexagonal phase, composed of cylindrical micelles, may have formed in the described system and would have existed between the tridimensional phases (cubic and 3D-H) and the lamellar phase.[10] However, its presence could not be absolutely confirmed as its characteristic diffraction peaks could have been overlapped with the strong H (002) and H (101) peaks of the $P6_3/mmc$ structure. Therefore between 15 and 20 s, all the phases coexist in the system and it is likely that a depth profile during this period would be as shown in Fig. 2. The cubic phase forms for higher surfactant concentrations than the 3D-hexagonal one[12] and for lower concentrations than the 2D-H and the lamellar one, it is thought to be located between them. During the 15–20 s period, the L(001) and the H(002) peak progressively disappear due to the total transformation of domains that are close to both interfaces into the cubic phase.

In summary, we have shown that the formation by evaporation of a $Pm3n$ CTAB/TEOS based mesostructured film begins with the formation of a lamellar phase at the air interface. Spherical micelles then form underneath this phase and organise into a 3D-hexagonal phase that subsequently rearranges into the discontinuous cubic phase. This process progresses then towards the substrate interface. As previous TEM investigations of such a film profile showed only the $Pm3n$ structure, it is likely that the lamellar phase present at the film surface finally transforms into the cubic phase. In the present case, the whole process occurs within the water rich period range (before the drying line). During this process the location of the phases with respect to both interfaces concords with the general behaviour of surfactant in composition phase diagrams: isotropic $\longrightarrow$ arrangement of spherical micelles $\longrightarrow$ arrangement of cylindrical micelles $\longrightarrow$ lamellar, with increasing concentrations.

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