Transferable Thin Films of Mesoporous Silica

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Synthesis of supported and free-standing thin mesoporous silica films from solution was investigated. It has been reported that the initial reactant concentration as well as the nature of the substrate affect the structure and symmetry of the resulting films. We found that by preparing the films on a polymer-coated substrate, one could de-couple the two parameters and control the structure of the resulting film exclusively via the concentration of reactants in solution. In addition, dissolution of the polymer layer in an organic solvent resulted in free-standing films, of hexagonal (MCM 41) or lamellar mesoporous phases, that could be transferred onto a target substrate. Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements were employed to characterize the films.

Introduction

Thin films of mesoporous silica have attracted considerable attention because of their potential use in the technologies of membrane filtration,[1] matrix preparation for heterogeneous catalysis,[2] medical applications,[3] and microelectronics.[4] In all of these examples, a thin film configuration is a technological necessity. Yet, mesoporous silica is a rigid solid which precipitates from a gel phase under conventional preparation procedure. At the postsynthetic stage, these materials cannot be easily shaped into thin films. Thus, the route for film formation involves deposition of the reaction mixture on a solid substrate[5−8] or formation of a free-standing film at the air−water interface.[7−9] The surface is introduced into the reactive mixture in the early stages of silica polymerization and thus may affect the final symmetry and *d* spacing of the obtained mesoporous thin film (MTF). The mesochannels of such films have been aligned on Si crystals,[9,10] graphite,[11] rubbing-

treated[12] and Lagmuir−Blodgett[13] polymer films, or by flow.[14,15] The aligned films could also be used to align guest polymer molecules.[16]

It was often found that a bulk synthesis procedure for a given symmetry leads to formation of film with substrate-dependent symmetry and pore orientation. It was suggested that specific interactions between the templating molecules and the substrate affect the symmetry and orientation of the resulting films.[17] For example, the symmetry of MTFs formed on Si(110) substrate differs from that of films formed on Si(111).[9,10] In this regard, several existing methods for preparation of mesoporous silica films were classified according to the nature of the support, symmetry, and orientation of pores.[18−20]

From a practical point of view, a method that will enable de-coupling of the symmetry and orientation of the film from the effect of the substrate is highly desirable. For example, in applications that utilize MTFs as humidity[21] or volatile organic compound[22]

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sensors, it is found that the sensing properties are strongly dependent on the mesoporous ordering, which among other parameters, is influenced by the substrate onto which the films are grown. Yet, the ability to control the pore geometry and alignment on a target substrate is limited.

In this paper, we focus on the preparation and characterization of transferable free-standing MTFs having either lamellar or hexagonal ordering. The films are spin-coated on an inert polymer support, and then floated off by selectively dissolving the polymer film in an organic solvent. The result is a free-standing film, which can be transferred onto a target substrate, circumventing surface effects on the MTF during its growth. In the following we describe the synthesis and structural characterization of these films.

Experimental Section

Materials. The synthesis reaction was carried out with tetramethyl orthosilicate (TMOS, >98%, Fluka), hydrochloric acid (1.043 N volumetric standard in water, Aldrich), methanol (99.8%, Frutaform), and cetyltrimethylammoniumchloride (CTAC, 25 wt % aqueous solution, Aldrich). Millipore water (resistivity 18.2 MΩ cm) was used as the source of water. Polystyrene (PS, M_n = 13.4 K, polydispersity index = 1.22, Polymer Source Inc.) and toluene (99.5%, Frutaform) were used for coating the substrates. All chemicals were used as received.

Few types of substrates were used: (a) one-sided polished (111) and (100) silicon wafers (P type 6–13 Ω/cm, 380 μm thickness, Institute of Electronic Materials Technology, Warsaw); (b) glass substrates (Corning micro slides of thickness 0.96 to 1.06 mm); (c) mica substrates cleaved from muscovite mica; and (d) gold-coated Si wafers prepared by evaporation.

Synthesis. Ogawa and co-workers have reported the preparation of mesoporous silica films using a sol–gel route. On utilizing different surfactants, hexagonal[23] and lamellar[24] films were formed by spin-coating on glass substrates. Free-standing films were also prepared[5] by varying the reactant composition, but the resultant phase was poorly ordered, as evidenced by only one peak in the SAXS spectra. Identification of the symmetry was thus not possible in this case. These films were in general 1–10 μm thick[5,25] and not suitable for most of the thin film applications.

We have used a modified sol–gel method to generate both hexagonal and lamellar films on different substrates as well as in free-standing format. In our methodology, preparation of thin films involves few steps, as follows.

1. Bulk Reaction. The following molar ratios were used to synthesize the different mesoporous phases. Hexagonal phase (method A): TMOS/H_2O/HCl/CH_3OH/CTAC = 1:5.2:0.06:5:0.25. Hexagonal phase (method B): TMOS/H_2O/HCl/CH_3OH/CTAC = 1:13.2:0.06:5:0.25. Lamellar phase (method C): TMOS/H_2O/HCl/CTAC = 1:13.2:0.06:0.5.

The reaction mixture other than the surfactant CTAC, was mixed in a covered (but not sealed) polypropylene beaker and reacted at room temperature for 1 h. Initially the mixture was opaque (because of the immiscibility of TMOS and water), but after few minutes it became transparent as the hydrolysis reaction proceeded. Following 1 h of reaction, an aqueous solution of CTAC was added to the reaction mixture and the content was stirred and reacted for one additional hour.

Comparing the structure of films prepared by methods A, B, and C we found that the concentration of the surfactant and the type of solvent determine the structure of the films: either hexagonal or lamellar phases could be prepared by

tuning the above parameters. Similar observations were reported by Honma et al.[26] and Ogawa et al.[27]

2. Film Formation. (a) Solid Supported Films. Two hours from the initiation of the reaction, the reaction mixture was spin-coated (or dip-coated) on various substrates: Si(111) or (100) wafers, glass, mica, and gold-coated Si wafer. Prior to coating, the substrates were cleaned by CO_2 snow-jet and dried with nitrogen. Films of different thicknesses were prepared by coating at speeds ranging from 2000 to 10 000 rpm. Unless otherwise noted, we relate to samples cast at 2000 rpm. Dip-coated films were prepared at a substrate withdrawal speed of about 10 cm min^{-1}.

(b) Free-Standing Films. A thin film of polystyrene (PS) was spin-coated from a toluene solution (50 mg/mL) at 2000 rpm on a clean substrate. Subsequently, the reactive solution from step 1 was spin-coated onto the PS layer at the required speed (Figure 1).

To remove the MTF from the substrate, the substrate was slowly dipped into toluene, leading to dissolution of the PS layer, followed by detachment and floating of the MTF film at the air–toluene interface (Figure 1). The free-standing film could be furthermore deposited on a target substrate. The sequence of steps is shown schematically in Figure 1.

3. Postsynthesis Film Treatment. This step is intended to enhance condensation resulting in a more rigid and denser silica matrix. Films were aged in an oven at 100 °C for different time intervals (12–72 h).

4. Calcination. Following step 2 or 3, the templating surfactant was removed by calcination. The film was annealed in an oven under atmospheric pressure at a rate of 1 °C min^{-1} up to 300 °C, incubated for 2 h at 300 °C, further annealed at the rate of 1 °C min^{-1} up to 500 °C, with a final incubation time of 2 h at 500 °C.

Analysis Techniques. *Small-Angle X-ray Scattering.* (a) Reflected beam. Scattering curves of the thin films were measured by a Rigaku Rotaflex X-ray diffractometer with an attachment for thin films. The measurements were done at 50 kV, 150 mA in the θ–2θ mode with a scanning rate of 0.30 ° min^{-1} and an angular resolution of 0.02° in the diffraction angle of 2θ. An X-ray source of wavelength 0.154 nm (Cu Kα) and a graphite monochromator was used. The film was mounted vertically in the attachment and data were collected in a reflective geometry. The presence of Soller slits for both the incident and diffracted beams ensured that the collected spectra were not smeared, even at low angles.

(b) Transmitted Beam. The scattering curves of liquid-phase reaction mixtures were obtained from a combination of Ni-filtered Cu Kα radiation of 0.154 nm at 40 kV, 40 mA (Seifert ID3000 generator), evacuated compact Kratky camera (Antonn Paar), and a linear position sensitive detector (MBraun). The liquid sample was injected into a 1.5-mm-diam. thin-glass capillary, which was subsequently sealed by epoxy glue. Data were collected for 20 h. A direct method of beam-height correction[28] was used for desmearing the raw data, which is smeared due to the use of rectangular source geometry of the X-ray.

Transmission Electron Microscopy. Film samples were scratched off of the substrates and the resultant powder was dispersed in acetone by sonication for 5–10 min. A drop of the dispersion was then blotted onto a holey-carbon TEM grid and examined under JEOL 2010 microscope in imaging mode.

Results

We describe the structure of supported (on Si(111)) and re-deposited MTFs following the synthesis before

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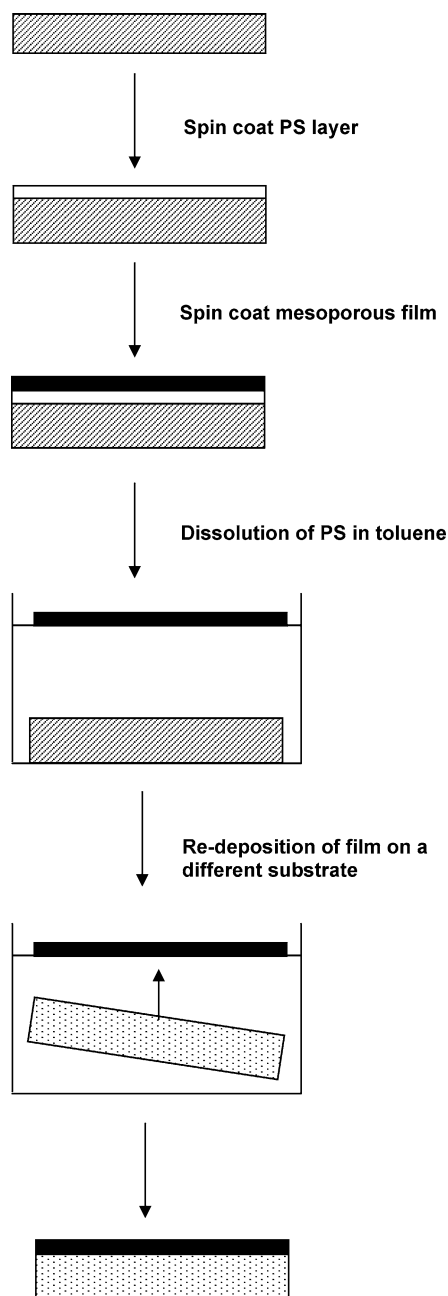(28) Singh, M. A.; Ghosh, S. S.; Shannon, R. F. *J. Appl. Crystallogr.* **1993**, *26*, 787.

Figure 1. Schematic representation of the process leading to the formation of a free-standing film and re-deposition.
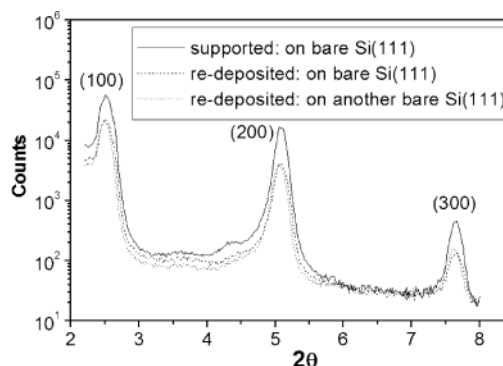

Figure 2. SAXS curves of spin-coated, lamellar, as-synthesized mesoporous films (method C): supported on bare Si(111) and free-standing films re-deposited on the same or on different Si(111) wafers.
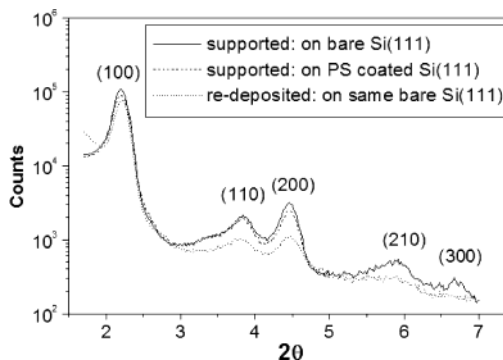

Figure 3. SAXS curves of spin-coated, hexagonal, as-synthesized mesoporous films (method A): supported on bare Si(111), on PS layer above Si(111), and free-standing, after PS was dissolved and the film re-deposited on Si(111).

aging or calcination, unless explicitly noted otherwise. These are referred to as synthesized films.

Lamellar Films − Supported and Re-Deposited. SAXS curve of MTF prepared on bare Si(111) is compared (Figure 2) with films prepared on PS-coated Si(111) and re-deposited onto the same or a fresh Si(111) wafer, respectively. All films display lamellar structure with associated (100), (200), and (300) reflections having 3.53 nm inter-lamellar distance calculated from the (100) reflection. Preparation of films on both bare and PS-coated glass and mica gave the same scattering pattern in SAXS (not shown).

We hence conclude that a lamellar film is formed on bare Si(111), glass, mica and PS, by applying method C. More importantly, the free-standing film retained the symmetry and d spacing upon removal of the PS layer and subsequent transfer and re-deposition on different

substrates − thus suggesting that the various stages of handling the film did not alter the structure.

Hexagonal Films − Supported and Re-Deposited. A similar investigation was carried out for hexagonal symmetry (method A). Figure 3 shows highly ordered hexagonal films, with up to 5 reflections, prepared on bare and PS-coated Si(111), as well as re-deposited on Si(111). All show identical d spacing of about 4 nm. Reproducible 4 nm hexagonal d spacings were obtained also for other PS-coated substrates (for example, glass or mica, not shown). The different steps of flotation, transfer, and re-deposition did not alter the symmetry and d spacing of the film.

We note that in this case, as well for the lamellar films, once transferred to the target substrate, the films showed good adherence to the substrate, as indicated by their homogeneous thickness and the absence of cracks.

Substrate Effect on Supported Hexagonal Films. The effect of different surfaces was investigated by comparing the structure of films formed on different bare substrates with that formed on Si(111). The SAXS patterns of films prepared by methods A and B are presented in Figure 4 panels a and b, respectively. A film prepared by method A (Figure 4a) on bare Si(111) showed perfect hexagonal structure, whereas when prepared on bare Si(100), it had an additional unaccounted peak. Films prepared by method B (Figure 4b) on both Si(111) and Si(100) showed the same unaccounted reflections, as seen previously for method A on Si(100) (see Figure 4a). More conspicuously, however,
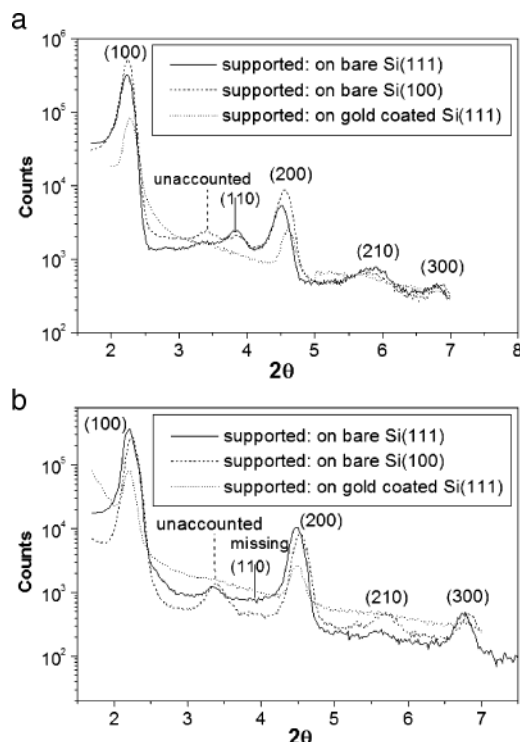
Figure 4. SAXS pattern showing the substrate effect (Si(111), Si(100), and gold) on spin-coated, as-synthesized, supported hexagonal films (a) method A and (b) method B.
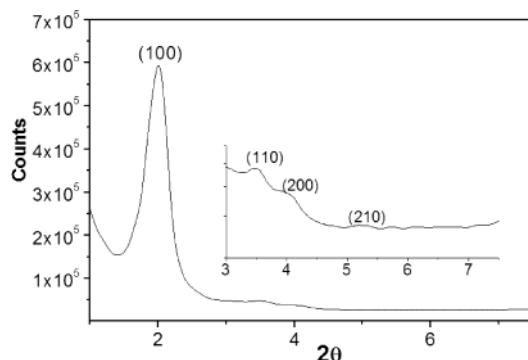

Figure 5. SAXS pattern of the liquid-phase reaction mixture used for hexagonal mesoporous film preparation (method A), at the end of step 1. The inset indicates the high ordering in the liquid.

for both methods, MTFs prepared directly on a gold-coated substrate did not exhibit the (110) peak at all. This indicates complete alignment of the hexagonal channels (the films do not collapse if calcined, which rules out lamellar phase) on the gold surface and manifests that interaction between the templating moieties and the surface play an important role in the formation of the film. The d spacing of the (100) peak in films on gold-coated surfaces were about 4 nm, similar to those of hexagonal films on other surfaces, indicating re-alignment but not major changes in channel dimensions.

The structure of the liquid reaction mixture was investigated by SAXS prior to spin- (or dip-) coating while preparing hexagonal MTFs (method A). Figure 5 shows a well-developed hexagonal ordering, as indicated by the presence of four reflections. The d spacing of the (100) peak is 4.34 nm. Ordering at such an early stage of MCM-41 is in agreement with observations in other
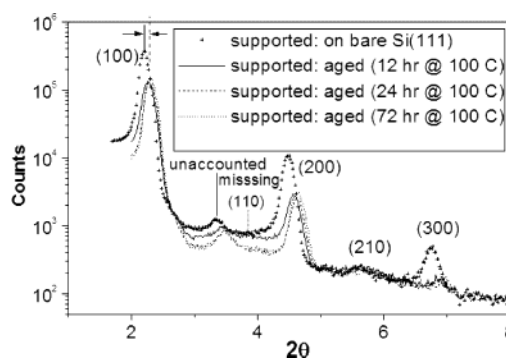

Figure 6. SAXS pattern showing the effect of aging on spin-coated, as-synthesized, supported hexagonal films on bare Si-(111) (method B). Note the missing (110) reflection and the additional unaccounted reflection (see text).

methods used for preparation of mesoporous materials.[29–35]

Effect of Aging on Supported Films. Some of the films were subsequently subjected to aging by heating at a temperature of 100 °C prior to high-temperature calcination. Figure 6 shows scattering curves of both as-synthesized and aged films on bare Si(111) prepared by method B. It can be seen that aging expectedly results in condensation of the silica network.[7] As a result, the inter-pore distances shrink (by 0.1–0.15 nm), as indicated by the shift in the hexagonal peak positions to scattering angles higher than those of the as-synthesized (un-aged) films. Longer aging period (of 72 h) does not alter the scattering, suggesting that further shrinkage in d spacing does not occur, as no further condensation reaction takes place in the matrix. Similar results were obtained for method A (not shown).

The two methods differ in an important aspect. Although the d spacing of the hexagonal phase remains the same for both methods A and B, we find indications for surface rearrangement of the hexagonal channels in method B. Whereas method A (Figure 3) generates films with perfect hexagonal symmetry, as indicated by the peak position and number (up to 5 peaks), in method B (Figure 6) the (110) reflection is shifted to a lower scattering angle (shown by a solid vertical line), from that expected of a perfect hexagonal lattice. The appropriate position of the (110) reflection expected in a hexagonal lattice is indicated by a broken vertical line in Figure 6. The shift in the position of the (110) reflection is attributed to alignment of the channels relative to the surface. For example, complete disappearance of this reflection would indicate that the channels are aligned parallel to the surface.[15] Note also that the unaccounted reflection follows the shift of the

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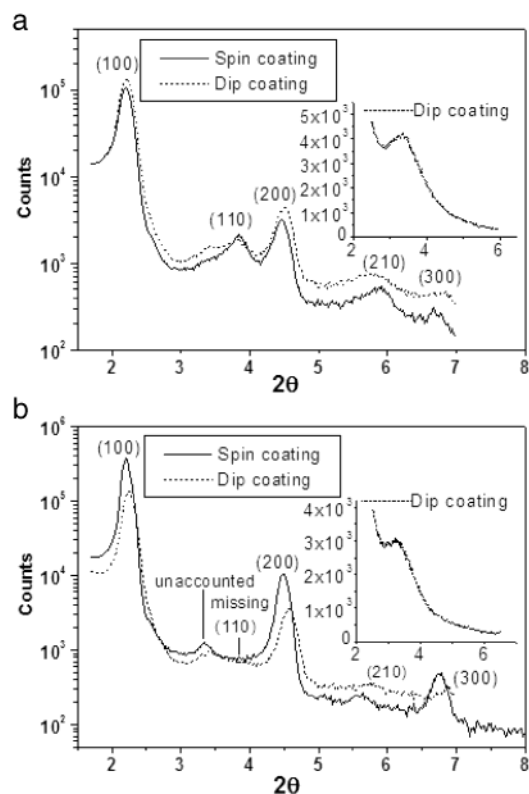
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Figure 7. SAXS pattern of as-synthesized hexagonal films supported on bare Si(111) made by spin- and dip-coatings for (a) method A and (b) method B. Inset: Calcined dip-coated film.

hexagonal peaks due to contraction of the spacing upon aging (Figure 6).

Dip-Coated Films. Comparisons between the scattering patterns of dip-coated and spin-coated films prepared by methods A and B are shown in Figure 7 panels a and b, respectively. The as-synthesized dip-coated films show the same highly ordered hexagonal structure with *d* spacing nearly identical to that of spin-coated films. We also observe here the phenomenon of surface-induced channel rearrangement in films prepared by method B, as well as in spin-coated films, as indicated by the shift of the (110) peak with respect to the expected position (Figure 7b). The method used for preparation of the film (spin- or dip-coating) thus does not affect the film structure. The scattering pattern of calcined film prepared by either method (Figure 7a and b insets) shows shrinkage of the structure, as indicated by a shift of the main peak to high scattering angle, as reported earlier.[8]

Figure 8 panels a and b show TEM images of dip-coated film (on bare Si(111)) prepared by method A at different magnifications. We see a hundreds-of-nanometers-sized ordered domain in Figure 8a; while pore-wall interfaces can be seen at higher magnification (Figure 8b). The inter-pore distances obtained by SAXS and TEM are in close agreement.

The thickness of the spin-coated films was controlled via the viscosity of the solution and the speed of coating, and was varied between 300 and 1000 nm.

Discussion

The main finding of this study is that it is possible to control the symmetry of MTFs exclusively via the
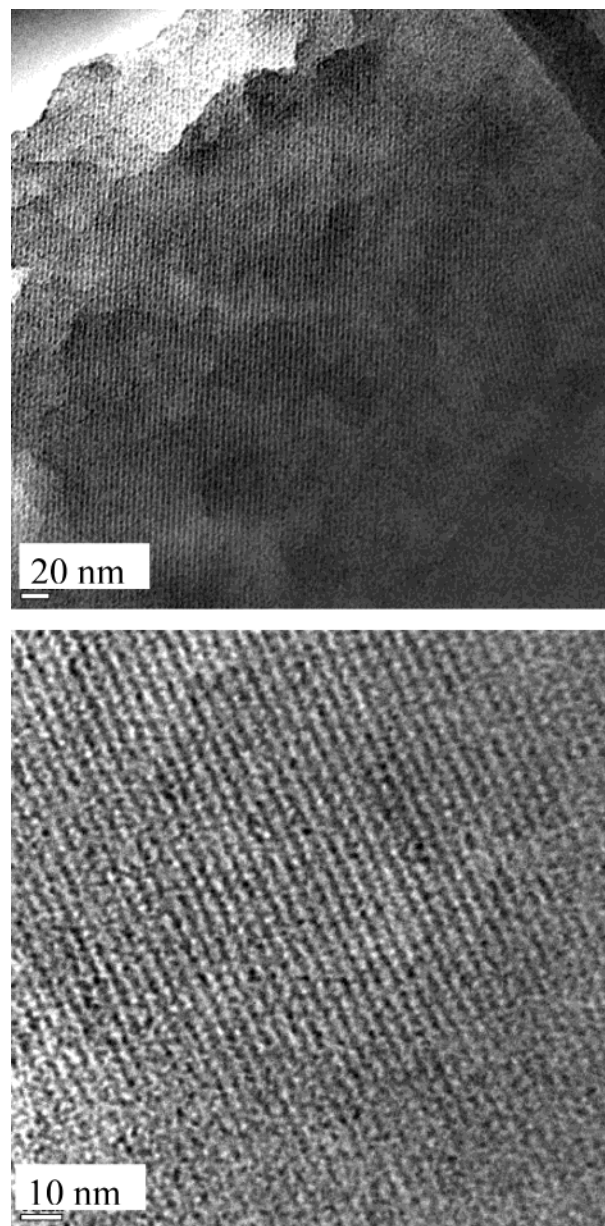

Figure 8. TEM micrographs of dip-coated, supported hexagonal films on Si(111): (a) lower and (b) higher magnification of the same film.

composition of the reaction mixture, eliminating substrate effects. Variation of surfactant concentration results in either lamellar or hexagonal pore geometry in mesoporous thin films. Films can be prepared in a reproducible manner on various surfaces of different nature, for example, silicon (crystalline, hydrophobic), PS (amorphous, hydrophobic), and gold (crystalline, hydrophobic), as well as glass (amorphous, hydrophilic), mica (crystalline, hydrophilic) etc. The specific method used for thin film application − spin- or dip-coating − does not alter the hexagonal geometry. The geometry is retained due to the formation of a well-developed hexagonal phase in the reaction mixture itself (Figure 5), prior to the deposition of the films. This clearly establishes a route for tuning pore geometry in mesoporous films via initial surfactant concentration.

Although the film geometry remains grossly unaffected by the preparation technique, we do observe changes in orientation of pores of the hexagonal phase,

Table 1. Effect of Preparation and Coating Methods on the 110 Reflection of the Mesoporous Hexagonal Film[a]

support	method A		method B	
	spin-coated	dip-coated	spin-coated	dip-coated
Si (111)	UC	UC	N	N
Si (100)	N		N	
gold	R		R	

[a] N, new reflection replaces the 110 reflection. The 110 reflection is R, removed, or UC, unchanged.

for supported films prepared on different surfaces (Table 1). Gold, for example, completely oriented the cylindrical channels of the hexagonal phase along the surface for both methods A and B (Figure 4), while Si(100) substrate generated a new SAXS reflection in the hexagonal pattern indicating some re-alignment of channels (Figure 4), which we are unable to interpret.

It is in this regard that the suggested route for preparation of transferable films, by selective dissolution of a thin polymer layer, is very useful. Our results indicate that the symmetry of the ordered domain of either lamellar or hexagonal phase and the corresponding d spacings are preserved during the various stages of preparation, floating, and re-deposition of MTFs. We thus suggest that this method can be utilized to bypass surface effects on pore symmetry and orientation.[36]

We also found that d spacings of the ordered structure in the films are smaller than those measured in the solution phase (Figures 5 and 6, and Table 2). We suggest that evaporation of solvent during the formation and growth of the film has led to a reduction of the distance between the templating micelles. The intermicellar distance in the reaction mixture therefore constitutes the maximum inter-pore distance in any film made from a particular reaction mixture.

Conclusion

We have shown that mesoporous films can be made on an amorphous polymer substrate and re-deposit on

Table 2. Comparison Between the d Spacing (Obtained by SAXS Measurements) in the Liquid Phase (Figure 5) and in the Solid Film for Hexagonal Mesoporous Material (method A)

substrate	interpore (micellar) distance [nm]
Si (111)	4.55–4.63, 4.59[a]
Si (100)	4.55
glass	4.25
mica	4.47
gold	4.47
PS ($M_n = 13.4$ K)	4.25–4.71
liquid phase	5.01

[a] Dip-coated. All other films are spin-coated.

various target substrates without alteration of pore geometry, d spacing, and orientation. This route therefore may be utilized for preparation of mesoporous films with known structural features on different substrates preventing unwanted surface effects.

We have demonstrated that the formation of mesoporous silica film by solvent evaporation during spin- or dip-coating results in reproduction of the hexagonal phase formed in the liquid phase of the reaction mixture. Higher surfactant concentration in the same synthesis recipe resulted in lamellar films on few different substrates. We found that using the route of transferable films described above, one could circumvent the surface effects, which influence the orientation and geometry of MTFs. In addition, measurement of intermicellar distance in the reaction mixture provides an upper bound to the maximum interpore distance subsequently achievable in a film. Finally, we also observed that thickness of the film affects the structure and symmetry, in addition to the role played by the surface. The origin of this effect is yet to be studied.

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