

Derivation of Cubic and Hexagonal Mesoporous Silica Films by Spin-coating

Jia Hong Pan and Wan In Lee*

*Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: wanin@inha.ac.kr*

Received September 22, 2004

By introducing spin-coating method to the evaporation induced self-assembly (EISA) process, a simple and reproducible route in controlling the mesophase of silica thin films has been developed for the first time in this work. When a comparatively solvent-rich Si-sol (The atomic ratio of TEOS : F127 : HCl : H₂O : EtOH = 1 : 0.006 : 0.2 : 9.2 : 30) was used as coating solution, the mesophase of resultant silica films was selectively controlled by adjusting the spin-on speed. The cubic mesophase has been obtained from the coating at a low rpm, such as 600 rpm, while the 2-D hexagonal mesophase is formed at a high rpm, such as 2,500 rpm. At a medium coating speed, a mixture of cubic and hexagonal mesophase has been found in the fabricated films. The present results confirm that the evaporation rate of volatile components at initial step is critical for the determination of mesopore structures during the EISA process.

Key Words : SiO₂, Thin films, Mesoporous structure, Mesopore, EISA

Introduction

Surfactant-templated mesoporous silica thin films with tailored mesopore structures and high surface area have attracted great interest due to their new possibilities of applications, such as nano-filters, photonic devices, low-*k* dielectrics, support materials for catalysts, encapsulation, sensors, etc.¹⁻⁵ So far various strategies have been exerted to tailor new class of mesopore structures, to develop more convenient route to syntheses, and to understand formation mechanisms.⁶⁻¹²

The so-called evaporation induced self-assembly (EISA) process, initiated by Brinker's group, has realized a facile fabrication of mesoporous silica thin films.^{6,7} The selective control of the mesophase for those thin films would be a greatly important issue, since the properties of the prepared films depend critically on their mesopore structures. Fundamentally the hexagonal mesopore structure is considered to be an ideal form for those purposes, since it has straight pore channels favorable to efficient mass transfer for the materials in the pore. However, those pore channels are apt to be aligned parallel to the substrate plane, and thus the entrances of mesopores are not appeared on the surface of the mesoporous film as a result. Hence, the cubic mesoporous structure would be more plausible form at this moment for the purpose of applications mentioned above, since the pore channels are open to the surface of film regardless of structural orientation.

In general, the hexagonal or cubic mesophase can general be predicted by adjusting the ratio of inorganic component to surfactant. By using cationic-type surfactants,^{6,11,13} such as cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC), or nonionic-type block copolymers [*e.g.* Pluronic P123 (EO₂₀PO₇₀EO₂₀), F127 (EO₁₀₆PO₇₀EO₁₀₆), and Brij 58 (C₁₆H₃₃EO₂₀)]^{10,14,15} as structure-directing reagents, a number of highly ordered mesoporous SiO₂ films with hexagonal and cubic mesophase

have been selectively synthesized from the silicon alkoxide derived acidic sol. Recently, Sanchez's group reported the similar control could also be achieved by adjusting the evaporation rate of solvent during the EISA process.^{12,16-19}

So far, most of mesoporous SiO₂ films were prepared by dip-coating method. However, the rapid evaporation of volatile components followed by dip-coating step will lead to severe concentration gradients across the film. As a result, the mesophase often varies across the films and the calcined films are apt to peel off. Those problems might be overcome to a certain degree by introducing spin coating method. So far, only a few studies have been reported for the preparation of mesoporous films by spin-coating method. Moreover, all of their films were only the hexagonal phase.^{13,20-22} In the present study, we report for the first time that the hexagonal and cubic mesophase can selectively be controlled from the same Si-sol by adjusting the condition of spin coating. That is, the spin speed in the spin-on procedure is a crucial factor in determining the mesostructure for SiO₂ thin films.

Experimental Section

Preparation of silicate sol. The initial Si-sol was prepared based on the original report of Zhao *et al.*¹⁰ The tetraethylorthosilicate (TEOS, Aldrich) was added to the mixed solution of HCl, ethanol, and H₂O, and the solution was heated at 60 °C for 2 hr, while stirring. This pre-hydrolyzed solution was then added dropwise to the Pluronic F127 (Aldrich) dissolved in ethanol solution. In a typical experiment, the molar ratio for the chemical composition of Si-sol was as follows. TEOS : F127 : HCl : H₂O : EtOH = 1 : 0.006 : 0.2 : 9.2 : 30.

All the prepared initial sols were aged with stirring at room temperature for 3 hr, before they were spin-coated on a Pyrex glass. The spin speeds were adjusted to 500-3000 rpm with spinning time of 4-20 s. The coated films were then aged at 25 °C for three days in a closed chamber under 60%

relative humidity (RH), which was controlled with saturated salt solution. The surfactant removal was carried out by heating at a rate of 1 °C/min to 300-500 °C in air and holding for 4 hr at the peak temperature.

Characterization of silicate films. Small-angle X-ray diffraction (XRD) patterns for the SiO₂ films were obtained by using a Rigaku Multiflex diffractometer with a monochromated high-intensity Cu K α radiation operated at 40 kV, 20 mA. The diffraction patterns were scanned at a rate of 0.1°/min over the 2 θ region of 0.7-5°. For the observation of the prepared mesoporous thin films with TEM (Philips CM30 transmission electron microscope operated at 250 kV), the films were scratched off from the substrate, and the collected flakes were gently dispersed in methanol. The suspension was then dropped on a holey amorphous carbon film deposited on Ni grid (JEOL Ltd.).

Results and Discussion

For the fabrication of mesoporous silica thin films by spin-coating method, a comparatively solvent-rich Si-sol was applied in order to compensate an excessive solvent evaporation that might happen during the spinning step. That is, the molar ratio of TEOS : F127 : HCl : H₂O : EtOH was adjusted to 1 : 0.006 : 0.2 : 9.2 : 30. Also, the coated films were aged at 25 °C under a relatively high humidity.

In order to investigate the effect of spin speed on the formation of silica mesophase, first of all, the Si-sol was

coated at a low spin speed, typically at 600 rpm for 10 s, and the coated films were subsequently aged under a humid environment. During this aging step the F127 would be gradually self-assembled to form ordered cylindrical bundles with the evaporation of volatile components, and at the same time the Si-sol could be slowly hydrolyzed and condensed to form silicate structure. Then, the aged films were heat-treated at 150, 300, 400, and 500 °C in air for 4 hr. The XRD patterns in Figure 1 indicate that the prepared films are a cubic mesoporous structure. The ordering of mesostructure was improved with the increase of heat-treatment temperature up to 400 °C, while the further increase of heat-treatment temperature deteriorated its ordering. That is, the mesoporous films heat-treated at 150 °C show a strong (200) peak with tiny (220) and (400) peaks, whereas the films annealed at 400 °C clearly present (100), (110), (200), (211), and (220) peaks. We found from the thermal gravimetric analysis that the most of volatile component in the Si-sol was evaporated at around 150 °C, and the triblock copolymer used for the liquid-crystal template was removed at 250-350 °C. Thus it is deduced that the arrangement of mesopores is still going on even after the complete evaporation of solvent above 150 °C. For the three

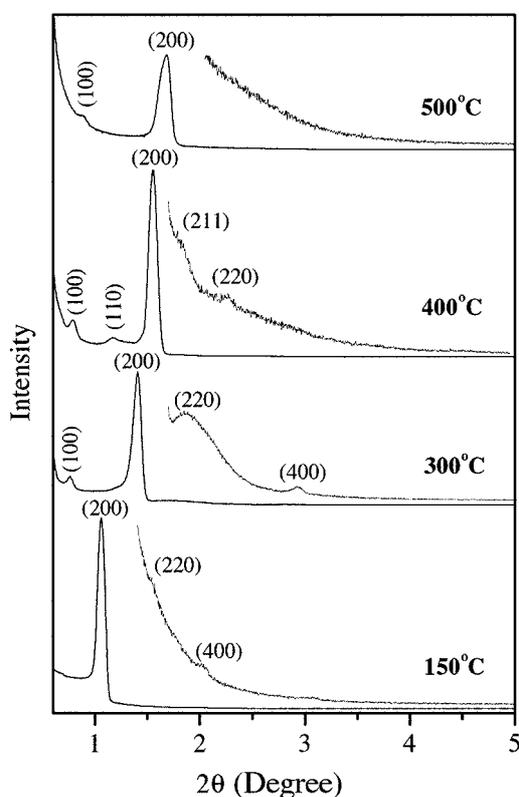


Figure 1. Small angle X-ray diffraction patterns of cubic mesoporous SiO₂ films annealed at 150-500 °C. The films were spin-coated at 600 rpm for 10 s.

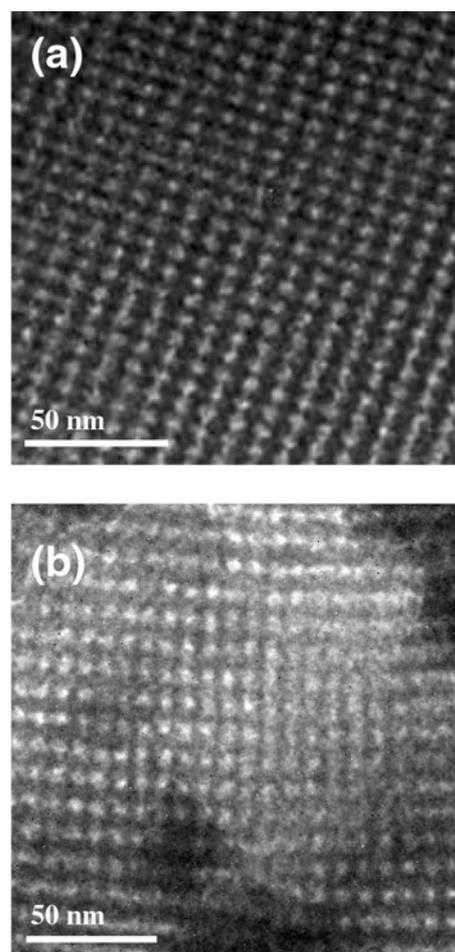


Figure 2. Plan-view TEM micrographs of cubic mesoporous SiO₂ films annealed at 400 °C. The films were spin-coated at 600 rpm for 10 s. (a) (100) orientation; (b) (110) orientation.

diffraction peaks of the films heat-treated at 150 °C or 300 °C assumed to be (200), (220), and (400), the *d*-value ratio was determined to $1 : 1/\sqrt{2} : 1/2$. Therefore, the position of (220) peak is a clear evidence for the formation of cubic mesophase.

Figure 2 shows plan-view TEM images of the cubic mesoporous SiO₂ films heat-treated at 400 °C. Most of flakes scraped from SiO₂ film were in (100) orientation, but some of them were in (110) direction, as indicated in Figure 2(a) and 2(b), respectively. This is consistent with the overall orientation of cubic mesopores determined from XRD, and also corresponds to the previous studies on block copolymer-templated SiO₂ or TiO₂ thin films prepared by dip-coating.¹³⁻¹⁵

The same Si-sol solution was also applied for the fabrication of hexagonal mesoporous SiO₂ films. That is, the Si-sol was spin-coated at a high rpm, such as 2,500 rpm for 20 s, while the post-treatment was carried out at the same condition applied to the formation of cubic mesophase. Noticeably, the prepared SiO₂ films heat-treated at 400 °C present highly ordered 2-D hexagonal mesoporous structures, as indicated by the plan-view TEM images shown in Figure 3. The mesopore channels were formed straight, and regularly arrayed parallel to the Pyrex substrate. The wall-

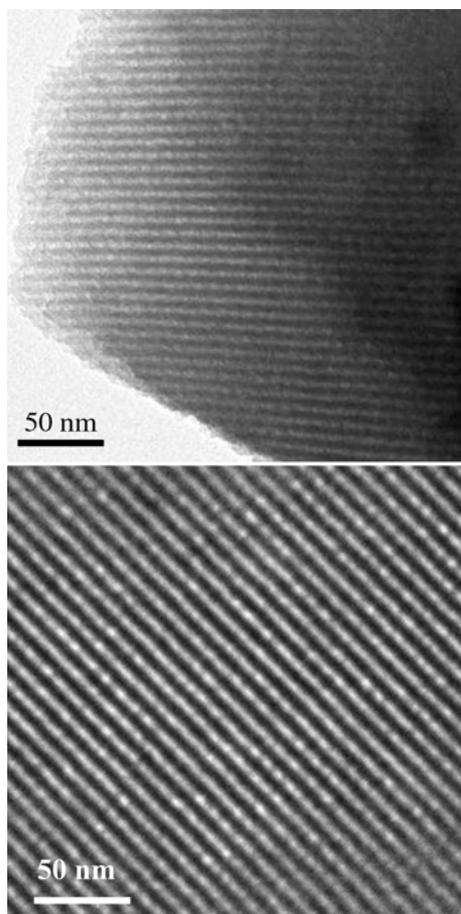


Figure 3. Plan-view TEM micrographs of 2-D hexagonal mesoporous SiO₂ films annealed at 400 °C. The films were spin-coated at 2,500 rpm for 20 s.

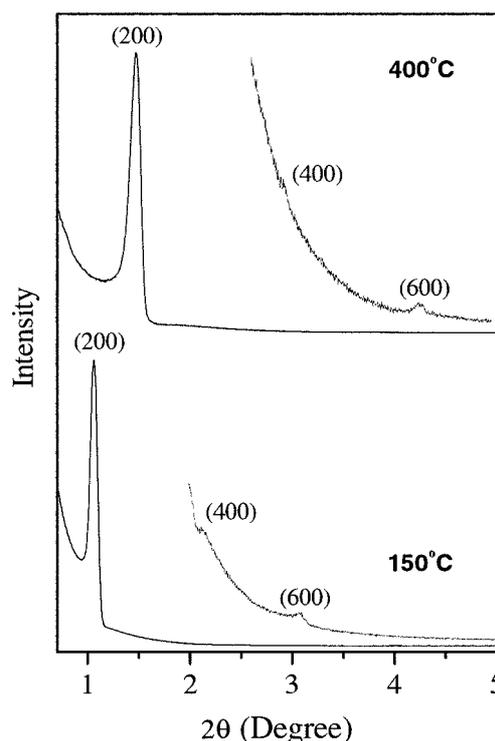


Figure 4. Small angle X-ray diffraction patterns of 2-D hexagonal mesoporous SiO₂ films annealed at 150 °C and 400 °C, respectively. The films were spin-coated at 2,500 rpm for 20 s.

to-wall distance was estimated to around 10 nm. The XRD patterns in Figure 4 show only the three peaks indexed as (200), (400), and (600), which are found reproducibly for all the films. This suggests that the hexagonal mesopores are ultra-uniformly 2-D arrayed parallel to the substrate throughout the film.

From above observations, we found that the mesophase of SiO₂ film is greatly dependent on spin speed during the spin-coating process. Then, we tried a spin coating with a medium speed between these two rpms, which have been used for the selective preparation of cubic or hexagonal mesoporous SiO₂ films. That is, the same Si-sol solution was spin-coated at 1,000 rpm for 10 s, aged at the same humidity, and finally heat-treated at 400 °C. Figure 5 illustrates XRD pattern and plan-view TEM image for the fabricated mesoporous SiO₂ film. TEM image shows a mixture of cubic and hexagonal mesoporous structures, and this mixed phase was formed repeatedly throughout the whole film. However, the worm-like structure (or local cubic structure) was not found at all. The XRD patterns for the films annealed at 400 °C show an intense (200) peak, as well as two weak bumps of (100) and (600), which have also been observed for cubic and hexagonal mesoporous films. In addition, a broad XRD peak in the range of 1.8-3° (designated to * in Figure 5(a)) has been observed, and we believe that this is indicative of mixed mesophases. At this medium-speed spin coating, the evaporation of volatile component in the coated film would be located in the boundary determining the cubic and hexagonal mesoporous

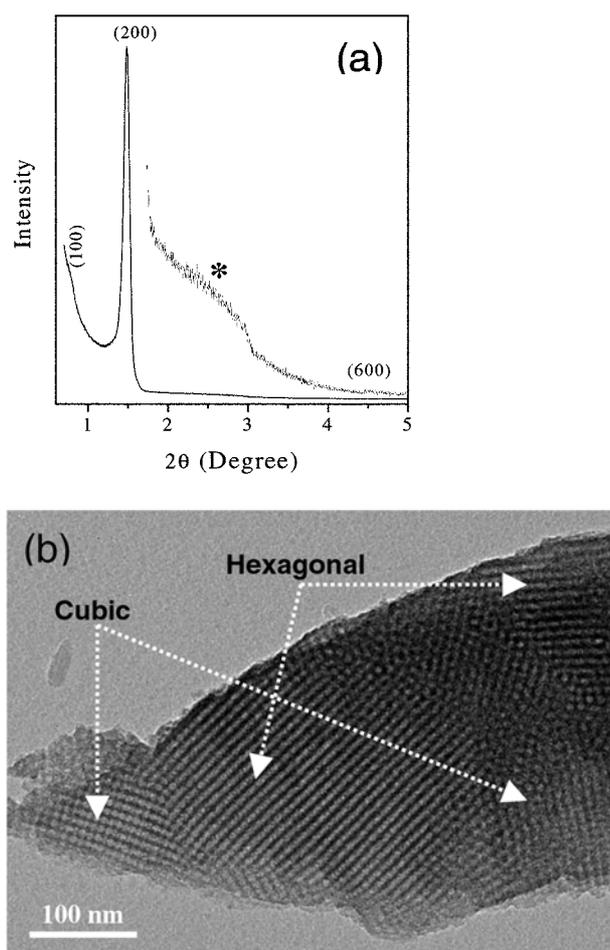


Figure 5. Small angle X-ray diffraction patterns (a) and TEM micrograph (b) for the SiO₂ films prepared by spin coating at 1,000 rpm for 10 s, and annealed at 400 °C.

phase.

Sanchez *et al.* reported that the evaporation rate of the solvent during the aging step is one of the key parameters that determine the final mesostructure.¹⁶⁻¹⁹ They have indicated that the hexagonal mesostructure is relatively favorable under ethanol-deficient condition. For the formation of cubic phase an ethanol-rich condition is necessary, and it is subtly related to the competition between the evaporation rate of solvent, the water diffusion, and silicate condensation. Similar trend was also observed by the early work in the formation of MCM series.^{23,24} That is, the mesophase of hexagonal MCM-41 and cubic MCM-48 was controlled by the surfactant packing parameter, $g = V/a_0l$, where V is the total volume of the surfactant chain plus cosolvent molecules between the chains, a_0 is the effective head group area, and l is the surfactant chain length. MCM48 was formed at a relatively high g , while MCM41 was obtained at a low g .

In our present work, we have demonstrated the selective control of mesophase by changing spin-coating speed. With the increase of spin-speed, the volatile ethanol will be evaporated considerably faster than other components, such as water or acid. Thus, the ethanol-deficient environment is

established in the coated film just after the spin-coating at high rpm, and this will lead to the formation of hexagonal phase. On the other hand, with the spin-coating at a low rpm an ethanol-rich condition can be formed in the coated film. The extreme case would be a dip coating process. In those cases, relatively abundant ethanol is remained in the coated film, and this provides an environment for the formation of cubic phase. Presumably, the individual mesophases are already determined by the condition of spin-coating, even though the actual mesophase gradually evolves during the aging step with slow evaporation of solvent, reorientation of surfactants and serial sol-gel reactions.

The other influence of spin coating process, differently from dip-coating, would be an application of relatively high shear pressure during the coating. Thus the coated films would be more tightly adhered to the substrate, and the block copolymer could be packed more efficiently. We believe that the prepared mesoporous structures of these thin films were relatively more highly ordered, and more robust compared with those prepared by dip-coating method. Also this process is a highly reproducible and very convenient, since the same sol solution is used for the control of cubic and hexagonal mesophase. Generalization of this process is now investigated in this group.

Acknowledgment. The authors gratefully acknowledge the financial support of the Korean Science and Engineering Foundation (KOSEF R01-2003-000-10667-0).

References

1. Yang, H.; Coombs, N.; Sokolov, I.; Ozin, G. A. *Nature* **1996**, *381*, 549.
2. Frindell, K. L.; Bartl, M. H.; Popitsch, A.; Stucky, G. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 960.
3. Yang, C. M.; Cho, A. T.; Pan, F. M.; Tsai, T. G.; Chao, K. J. *Adv. Mater.* **2001**, *13*, 1099.
4. Coakley, K. M.; Liu, Y.; McGehee, M. D.; Frindell, K. L.; Stucky, G. D. *Adv. Func. Mater.* **2003**, *13*, 301.
5. Kim, K. Y.; Ahn, W. S.; Park, D. W.; Oh, J. H.; Lee, C. M.; Tai, W. P. *Bull. Korean Chem. Soc.* **2004**, *25*, 634.
6. Brinker, C. J.; Lu, Y.; Sellinger, A.; Fan, H. *Adv. Mater.* **1999**, *11*, 579.
7. Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soye, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364.
8. Alonso, B.; Balkenende, A. R.; Albouy, P. A.; Amenitsch, H.; Rager, M.-N.; Babonneau, F. *J. Sol-Gel Sci. Tech.* **2003**, *26*, 587.
9. Shen, S.; Tian, B.; Yu, C.; Xie, S.; Zhang, Z.; Tu, B.; Zhao, D. *Chem. Mater.* **2003**, *15*, 4046.
10. Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380.
11. Besson, S.; Ricolleau, C.; Gacoin, T.; Jacquiod, C.; Boilot, J.-P. *J. Phys. Chem. B* **2000**, *104*, 12095.
12. Gibaud, A.; Grosso, D.; Smarsly, B.; Baptiste, A.; Bardeau, J. F.; Babonneau, F.; Doshi, D. A.; Chen, Z.; Brinker, C. J.; Sanchez, C. *J. Phys. Chem. B* **2003**, *107*, 6114.
13. Honma, I.; Zhou, H. S.; Kundu, D.; Endo, A. *Adv. Mater.* **2000**, *12*, 1529.
14. Alberius, P. C. A.; Frindell, K. L.; Hayward, R. C.; Kramer, E. J.; Stucky, G. D.; Chmelka, B. F. *Chem. Mater.* **2002**, *14*, 3284.
15. Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C.

- Curr. Opin. Colloid Interface Sci.* **2003**, 8, 109.
16. Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Grosso, D.; Durand, D.; Sanchez, C. *Chem. Comm.* **2002**, 20, 2298.
 17. Grosso, D.; Cagnol, F.; Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Amenitsch, H.; Brunet-Bruneau, A.; Bourgeois, A.; Sanchez, C. *Adv. Func. Mater.* **2004**, 14, 309.
 18. Grosso, D.; Balkenende, A. R.; Albouy, P. A.; Amenitsch, H.; Babonneau, F. *Chem. Mater.* **2001**, 13, 1848.
 19. Soler-Illia, G. J. A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C. *J. Mater. Chem.* **2004**, 14, 1879.
 20. Yun, H.; Miyazawa, K.; Zhou, H.; Honma, I.; Kuwabara, M. *Adv. Mater.* **2001**, 13, 1377.
 21. Bae, J. Y.; Park, O.-H.; Jung, J.-I.; Ranjit, K. T.; Bae, B.-S. *Micropor. Mesopor. Mater.* **2004**, 67, 265.
 22. Cohen, Y.; Hatton, B.; Miguez, H.; Coombs, N.; Fournier-Bidoz, S.; Grey, J. K.; Beaulac, R.; Reber, C.; Ozin, G. A. *Adv. Mater.* **2003**, 15, 572.
 23. Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, 8, 1147.
 24. Gallis, K. W.; Landry, C. C. *Chem. Mater.* **1997**, 9, 2035.
-