Journal of the European Ceramic Society **19** (1999) 1361–1364
© 1999 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(98)00435-X
0955-2219/99/$ - see front matter

Synthesis of Oriented Meso-structure Silica Functional Thin Film

H. S. Zhou,* D. Kundu and I. Honma

Energy Division, Electrotechnical Laboratory, 1-1-4, Umezono, Tsukuba, 305, Japan

Abstract

We report the synthesis of oriented silica meso-structure films by surfactants such as hexadecyl-trimethylammonium bromide (C_{16}TMA) or 11-ferrocenylundecyl-ammonium bromide (Fe-TMA) surfactant on a sol–gel method by spin coating. X-ray diffraction of the film showed that the film oriented in a lamellar, hexagonal or cubic structure, just depending on C_{16}TMA's concentration. In the case of lamellar oriented film by Fe-TMA, linear temperature dependent conductivity properties were observed. © 1999 Elsevier Science Limited. All rights reserved

Keywords: sol–gel processes, microstructure-final, porosity, electrical conductivity, SiO_2.

1 Introduction

Mesoporous materials invented by scientists at Mobil Corp. have attracted considerable interest since 1992[1,2] because of applications in molecular sieves, catalysis, and adsorbent materials. These materials contain large, uniform cages and channels in the mesopore size (15–100 Å) which can be controlled by the synthesis conditions. The morphologies of these mesoporous materials are hexagonal, lamellar, and cubic phases. Efforts to create electronic and photonic function devices, based on ordered molecules, have been inspired by these self-assembled mesoporous materials.[3,4] Conducting polyaniline filaments have been synthesized in a mesoporous channel[5] system for electronic functional devices. However, for electronic and photonic application, it is very important to control the materials phase from powder to thin film. Now, successful syntheses of self-organized mesorporous thin films make functional devices[6–10] possible. Here we report that the morphologies of silicate mesoporous film can be controlled from lamellar, cubic to hexagonal phases by silica-to-surfactant ratio in spin coating, and a conductive oriented silica meso-structured film can be synthesized by a dye bound surfactant (11-ferrocenylundecylammonium bromide: Fe-TMA) in a spin coating method.

2 Lamellar, Hexagonal, Cubic Meso-Structure Silica Film

Silica sols with different SiO_2:C_{16}TMACl ratios were prepared in the following way. The required amount of TEOS was mixed with 1-propanol and stirred for several minutes. The TEOS was hydrolysed via the addition of a solution of previously mixed HCl and water, then 2-butanol was added into the hydrolysed TEOS sol and stirred. The surfactant solution was prepared separately with a variation of concentration and then slowly added under stirring into the previously prepared sol. The sol was then stirred for another 60 min and finally used for the deposition of films on glass by spin casting. After spin casting, the coated glass substrates were heated at different temperatures (100 and 400°C) in air for 60 mins.

Figure 1 shows XRD patterns of thin films with different C_{16}TMA/TEOS ratios which were heat treated at 100°C. The mesophase structure has been systematically transformed by the increase of the surfactant concentration from (a) to (d). Figure 1(a) shows a very broad fundamental diffraction peak at around 2·2° in 2θ, which indicates the film is an amorphous mesostructure when formed from a low C_{16}TMA/TEOS ratio (about 0·062). The C_{16}TMA/TEOS molar ratios in the casting solution were (a) 0·062, (b) 0·093, (c) 0·156 and (d) 0·25, respectively.

Figure 1(b) and (d) shows very intense fundamental peaks with d values at 38·0 and 36·9 Å, respectively. This intense peak is associated with a weak second order reflection for both compositions (shown in the insert). Although the lamellar as well as an oriented hexagonal mesostructure film can

---

*To whom correspondence should be addressed. Fax: +81-298-54-5805; e-mail: hszhou@etl.go.jp

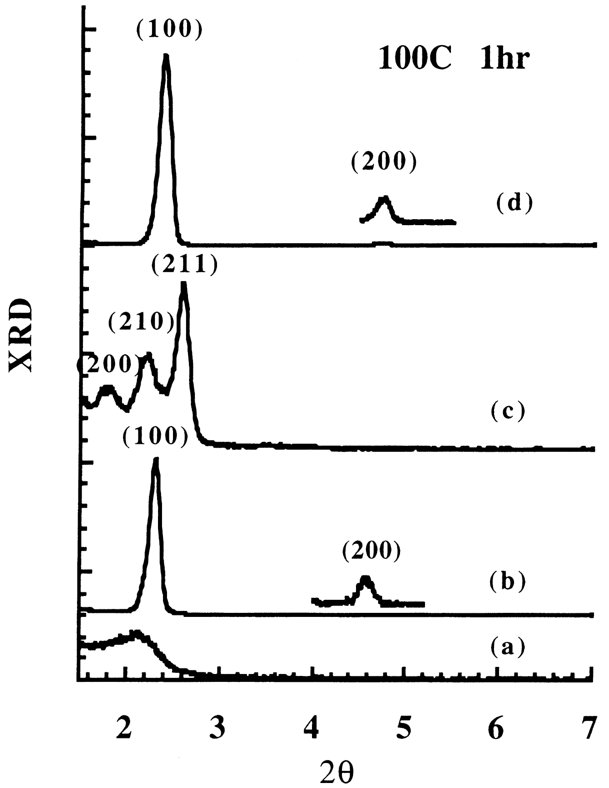

Fig. 1. X-ray diffraction patterns (XRD) of the spin casted film on the glass substrate with a systematic change of the solution composition. The surfactant (C_{16}TMACl)/TEOS molar ratios in the casting solution were (a) 0·062, (b) 0·093, (c) 0·156 and (d) 0·25, respectively. However, the other composition was kept constant; the ratio of H_2O/TEOS = 10 and HCl/TEOS = 0·01 are used. The mesoporous structure of the film has been systematically changed from (a) amorphous, (b) one-dimensional hexagonal (1-dH), (c) bicontinuous cubic to (d) lamellae by increasing C_{16}TMACl/TEOS ratios.

produce the same XRD pattern,[7,8] the absence of any peak for sample (d) after heat-treatment at 400°C, shown in Fig. 2(d), suggests the formation of a lamellar (L) mesostructured silica in the as-deposited thin films. The removal of surfactants resulted in collapsing the lamellar structure to an amorphous one.

Figure 1(c) shows a bicontinuous cubic mesophase's XRD pattern of novel amphiphilic polyhydroxy compounds. Although the similar XRD pattern has been reported for micellar cubic mesophase (Cub_{II}, Pm3n or P43n) of novel amphiphilic polyhydroxy compounds,[11–13] the diffraction indexes can be labeled to indicate bicontinuous cubic phase formation of Pn3m structure with the primitive cubic lattice unit cell of 83A. The calculated data for cubic Pn3m lattice spacing with unit cell size of 83A are agreeable to the data extracted from Fig. 2. The other cubic phase found in mesoporous silicate in the past literatures are also bicontinuous mesophase such as Ia3d structure, however, a direct formation of bicontinuous cubic mesophase as a silicate thin film is observed for the first time in the present spin casting method.

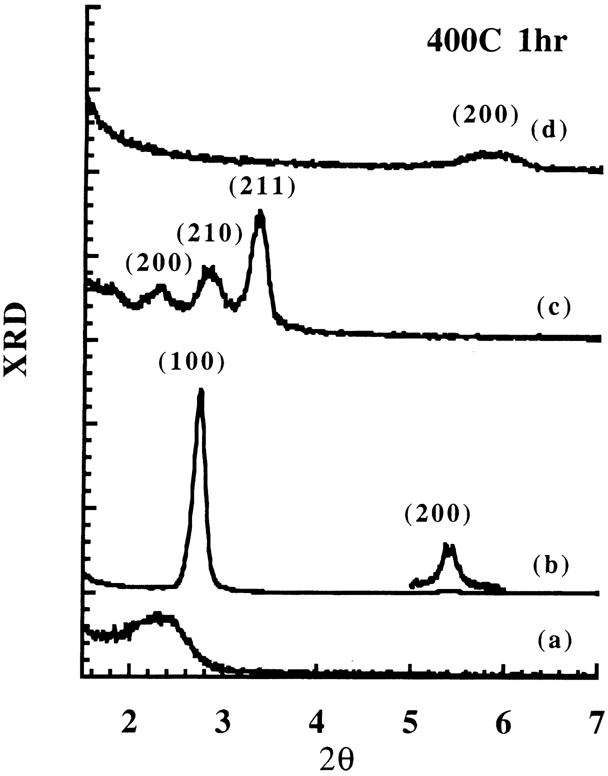

Fig. 2. XRD pattern of the film annealed at 400°C for 1 h in air. Although the lamellae phase, after the surfactant removal, has collapsed by annealing as shown in (d), other phases of (a) amorphous, (b) one-dimensional hexagonal (1-dH) and (c) cubic phases are thermally stable up to 400°C with a shrinkage of the unit cell size. The films become 'mesoporous' with different pore continuity by the surfactants removal.

Figure 2(a)–(d) shows the XRD pattern for the same film samples as in Fig. 1 after annealing at 400°C for 1 h. Figure 2(b) shows (100) and (200) reflections are still remaining after surfactant removal with a shrinkage of the pore diameter from 38 to 32 Å, indicating that the film structure is one-dimensional hexagonal (1-dH), where the cylindrical mesochannels stack parallel to the substrate surface. So, the film is stable during calcination because the honeycomb framework stands as a pillared block to sustain the hexagonally packed mesopores.

The lamellar pattern in Fig. 1(d) almost vanishes after calcination at 400°C as shown in Fig. 2(d); only a negligible broad diffraction peak remains at around 6°. This is because the simple lamellar structure of the mesostructured film collapses after surfactant removal. However, the XRD pattern, found in Fig. 2(c), of the micellar cubic phase[11] is thermally stable up to this temperature. The cubic mesophase survives after the calcination for surfactant removal, forming bicontinuous mesoporous structure in the casted thin film. The film structure of mesoporous cubic is quite interesting and useful for applications such as in separation membrane and/or sensors. Thus, the present experimental results provide a novel process for controlling the film mesophase structure systematically as amorphous (A)–one-dimensional hexagonal (1-dH)–cubic (C)–lamellae (L) when the surfactant-to-TEOS ratio in the starting solution increases. A tunable control of the mesophase in the spin casted mesoporous film has been proposed in this work for the first time while the homogeneous and continuous film can be easily produced on the substrate surface as an advantage for large area applications. The casted film becomes 'mesoporous' with different pore continuity by the surfactants removal.

3 Conductive Lamellar Silica Film

We chose 11-ferrocenyltrimethylundecylammonium (Fe-TMA) bromide as the surfactant because Fe-TMA surfactant has a ferrocenyl ligand at the lipid tail with a distance of eleven carbons to a head group of a trimethylammonium cation. So we can synthesize functional mesostructured films for optical or electronic device applications by Fe-TMA where the functional dyes are doped in the mesochannels by a direct self-organization process of surfactants,[3,4] not by external doping after the calcination of the channel.[5] The ferrocenyl TMA (I^0) and its oxidized form I^+ show that the surfactants form redox-active micelles. The isolated molecules have an absorption band at 440 nm which results in an orange color of the surfactants.

Silica meso-structure films templated by Fe-TMA were prepared in the following way; the required amount of TEOS was mixed with ethanol and stirred. The TEOS was hydrolysed via the addition of a solution of previously mixed HCl and water. The surfactant solution was separately prepared (Fe-TMABr in H_2O) and then slowly added under stirring into the previously prepared sol. The mole ratio is TEOS:H_2O:EtOH:Fe-TMA = 4:8:2:1. The hybrid sol was then kept under stirring for another 60 min and finally used for the deposition of films on glass by spin coating at 2000 rpm. After the spin casting, the coated glass substrates were heated at temperatures of 100°C in vacuum for 60 min to remove EtOH.

The Fe-TMA/SiO_2 mesostructure film was confirmed by XRD. Two strong peaks like those of lamellar C_{16}TMA/SiO_2 film were observed in the low-angle region with [100], and [200]. The interplanar distance $d_{100} = 36{\cdot}3$ Å. The structure of Fe-TMA/SiO_2 mesostructure film should be lamellar because it collapsed after a 2 h heat treatment at 400°C.[7,8]

Fe-TMA bilayers are intercalated in the silica layer as $\{/O\text{–}Si\text{–}OH_2^+/Br^-/N^+(CH_3)_3\text{–}Fe@Fe\text{–}(CH_3)_3N^+/Br^-/^+H_2O\text{–}Si\text{–}O/\}$ while all of the surfactants have functional ferrocenyl molecules at the end of their tails. The very strong and sharp [100] peak shows that orientation of SiO_2/TMA–Fe@Fe–TMA/SiO_2 lamellar structure is very good.

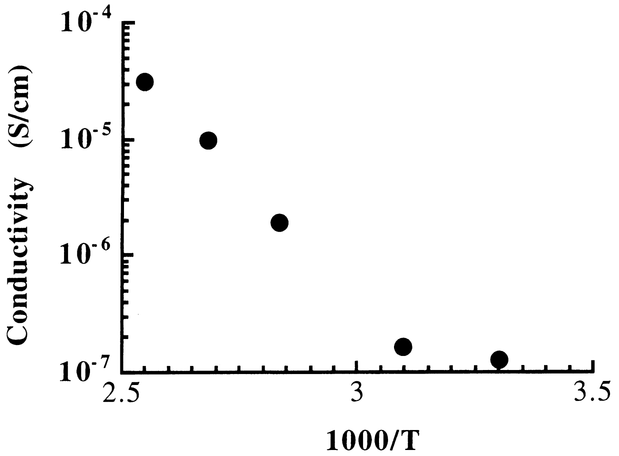

Fig. 3. The electronic conductive properties of Fe-TMA/SiO_2 mesostructure film.

We find that this Fe-TMA/SiO_2 mesostructure film shows electronic conductivity properties in Fig. 3. The results can be divided to two regimes. In the high temperature regime ($60°C < T < 180°C$), the linear relationship between logarithmic conductivity and temperature [1000/T (in Kelvin)] displays very good electronic conductivity properties in $\exp(-\Delta E/kT)$ of Fe-TMA/SiO_2 mesostructure film. Here, ΔE is the active energy of conductivity of Fe-TMA/SiO_2 mesostructure film with about 1·0 eV according to the results. The mechanism can be explained as: the ferrocenyl (I^0) ligand is oxidized to form the I^+ state and leaves one free electron there, this electron can be transported along the ferrocenyl chain (including I and I^+) from I^0 into I^+ to form $I^+\text{–}I^0$ by redox reaction in the ferrocenyl chain. This conductivity is benefited by high orientation of ferrocenyl in lamellae phase.

4 Conclusion

Meso-structure silica films with amorphous, 1d-hexagonal, cubic and lamellar phases are directly formed by controlled the C_{16}TMACl surfactant concentration, and mesoporous 1d-hexagonal and cubic phases film are produced by calcination. In lamellar phase of Fe-TMA/SiO_2 meso-structure, electronic conductivity is found possibly due to the electrons transporting in ferrocenyl chain. The simple spin casting technique has been successfully used for producing thin functional mesoporous films on a silica substrate. The films are fairly homogeneous and relatively easy to produce.

References

1. Kresge, C. T., Leonowiez, M. E, Vartuli, J. C. and Beck, J. S., *Nature*, 1992, **359**, 710.

2. Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T.-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B. and Schlenker, J. L., *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3. Honma, I. and Zhou, H. S., *Chem. Mater.*, 1998, **10**, 103.
4. Zhou, H. S., Sasabe, H. and Honma, L., *J. Mater. Chem.*, 1998, **8**(3), 515.
5. Chun-Guey Wu and Bein, T., *Science*, 1994, **264**, 1757.
6. Ogawa, M., *J. Amer. Chem. Soc.*, 1994, **116**, 7941.
7. Yang, H., Kuperman, A., Coombs, N., Mamiche-Afra, S. and Ozin, A., *Nature*, 1996, **379**, 703.
8. Kundu, D., Zhou, H. S. and Honma, I., *J. Mater. Sci. Lett.*, in press.
9. Aksay, I. A., Trau, M., Manne, S., Honma, I., Yao, N., Zhou, L., Fenter, P., Eisenberger, P. M. and Gruner, S. M., *Science*, 1996, **273**, 892.
10. Trau, M., Yao, N., Kim, E., Xia, Y., Whitesides, G. M. and Aksay, I. A., *Nature*, 1997, **390**, 674.
11. Borisch, K., Diele, S., Goring, P., Kresse, H. and Tschierske, C., *J. Mat. Chem.*, 1998, **8**, 529.
12. Seddon, J. M. and Templer, R. H., *Phil. Trans. R. Soc. Lond. A*, 1993, **377**.
13. Fontell, K., *Colloid and Polymer Science*, 1990, **268**, 264.