

Enhancement of Structural Stability of Mesoporous Silica Thin Films Prepared by Spin-Coating

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A mesoporous silica film was prepared on a silicon substrate using a spin-coating process followed by a tetraethyl orthosilicate (TEOS) vapor treatment. The TEOS-treated mesostructured silica film did not contract during calcination, showing high structural stability. Thermal treatment without TEOS vapor was not effective to enhance the structural stability of mesostructured films. A flat mesoporous silica film about 250 nm thick was grown from the silicon substrate. No silica particle was deposited from TEOS vapor on the surface of the film, suggesting the penetration of TEOS vapor into the film. A periodic porous structure was observed in the FE-SEM image of the cross section of the mesostructured film. This indicates that the channels run predominantly parallel to the surface of the silicon substrate. FTIR studies suggested that the silanol groups in the film significantly decreased after the TEOS treatment. TEOS molecules penetrate into an originally deposited silicate film and react with the silanol groups. The densified silica wall has high structural stability and hardly contracts under a calcination process. The developed TEOS-treated mesoporous silica film is a promising material such as chemical sensors, low-*k* films, and other optoelectronic devices.

Introduction

Ordered mesoporous molecular sieves^{1,2} have been prepared using surfactant liquid-crystal structures which serve as an organic template for the polymerization of silicates. Recently, self-supporting thin films made of mesoporous materials with unidimensional pore structures have been prepared at air/water^{3–6} and oil/water⁷ interfaces. Supported mesoporous silica films^{8–15} have

been grown under acidic conditions at a variety of interfaces including water/mica,^{8,9} water/graphite,^{8,10} and water/silica⁸ by hydrothermal synthesis.

A simpler way to synthesize mesoporous silica films has been developed by a spin-coating^{11–13} and dip-coating^{14,15} methods. These solvent-evaporation techniques have been utilized for the coating on glass substrates^{11,12} and on silicon wafers.^{13–15}

The spin-coating technique seems to be more attractive compared to hydrothermal synthesis from the industrial point view. However, the structural contraction is observed during calcination more seriously on products prepared by spin-coating than the ones obtained by hydrothermal synthesis because the ordered mesostructure is formed at relatively low temperatures. The formation of the silicate network may be insufficient before calcination.

This problem seems to be very serious especially on supported films. When a film adhering to a substrate shrinks, the entire film is subjected to mechanical stress. This stress may lead to cracking. So far, postsynthesis methods have been attempted such as precalcination heating and HCl or ammonia vapor treatments.

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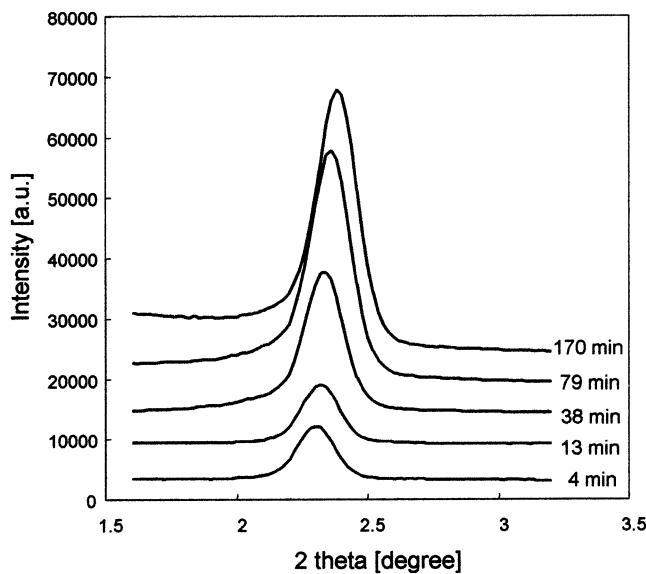


Figure 1. XRD patterns of a mesostructured silica film with time after spin-coating.

Further, Ryoo et al.^{5,16} reported that tetraethoxysilane (TEOS) treatment of as-synthesized mesoporous silica enhances the thermal stability. This treatment seems to be effective for densification of the silica wall of mesoporous silica.

In the present study, we have developed TEOS treatment for mesoporous silica thin films prepared by a spin-coating method. The effect of TEOS treatment on the structural stability, density, and existence of silanol groups in the mesoporous films has been studied.

Experimental Section

The precursor solution was prepared under acidic conditions using TEOS, cetyltrimethylammonium bromide (CTAB), HCl, ethanol, and deionized water. The aqueous acid–surfactant mixture was prepared first, and TEOS was then added. A clear solution with the molar ratio of 3.0 TEOS: 0.25–1.2 CTAB: 2.5 HCl: 100 H₂O was obtained after stirring for 5–15 min. The solution was dropped onto a silicon substrate spinning 50 rpm, and then the substrate was spun at 2000–4000 rpm for 1 min.

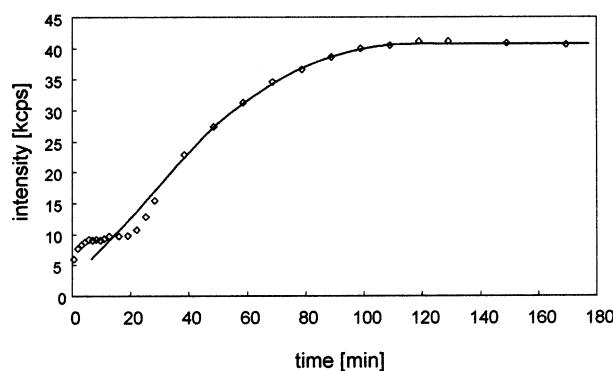
The film was exposed to TEOS vapor in the closed vessel at 135 °C for 3 h. The calcination was conducted at 400 °C for 5 h with a heating rate of 1 °C/min.

The product was identified by X-ray diffraction (XRD). The patterns were recorded on a Rigaku Mini-flex using Cu K α radiation with $\lambda = 1.5418 \text{ \AA}$ in θ – 2θ scan mode. The surface and the cross-section of the film were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S8000). Fourier transform infrared (FTIR) spectra of the films were recorded on a FTIR-8200PC spectrometer (Shimadzu Co.) at 4 cm⁻¹ resolutions. The amount of methanol adsorbed on untreated and treated silica powders was measured at 20 °C using a saturated methanol vapor in He.

Results and Discussion

Figure 1 shows XRD patterns of a mesostructured silica film on a silicon substrate with time after the spin-coating using a solution with a TEOS/CTAB molar ratio of 6. The time-course of peak intensity and *d*(100) spacing of the mesostructured silica films after spin-coating was shown in Figure 2. The peak for (100)

(a) Peak intensity



(b) *d*-spacing

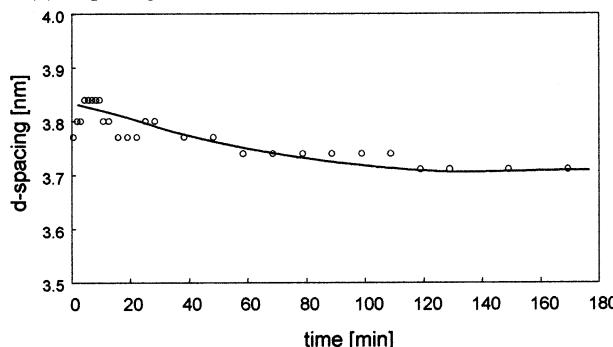


Figure 2. Time-course of (a) peak intensity and (b) *d* spacing of a mesostructured silica coated on a silicon substrate after spin-coating.

reflection appeared within 1 min after coating, indicating that the periodic ordered structure of the silica–surfactant composite already formed in the first 1 min. The peak width did not change significantly after coating. However, the peak intensity increased with time and reached plateau after 120 min. The formation of the ordered structure seemed to be completed 120 min after coating. The *d*(100) spacing decreased with time and needed 120 min to reach plateau. This structural contract is attributed to the evaporation of solvent and ethanol produced from TEOS among silicate. Slow condensation of silicate also is thought to contribute to the decrease in the *d* spacing. The length of the unsteady period depended on the composition of the precursor solution and coating conditions because rapid evaporation of solvent and rapid reaction of TEOS cause the films to reach steady state in a short time. In this study, the mesostructured films with the steady-state XRD patterns were used for TEOS treatment, thermal treatment, and calcination.

The absence of the (110) reflection indicates that the (100) family of planes of the hexagonal unit cell is oriented parallel to the surface of the silicon substrate, which is consistent with the literature results.^{11–13}

Figure 3 shows XRD patterns of untreated mesostructured silica films on the silicon substrate before and after calcination. The molar ratio of TEOS/CTAB in the starting solution was ranged from 2.5 to 12. When the molar ratio of TEOS/CTAB was 12, a broad peak for the (100) reflection with small intensity was observed before calcination. However, the ordered structure was maintained even after calcination. The films prepared at the TEOS/CTAB ratio of 6 maintained ordered

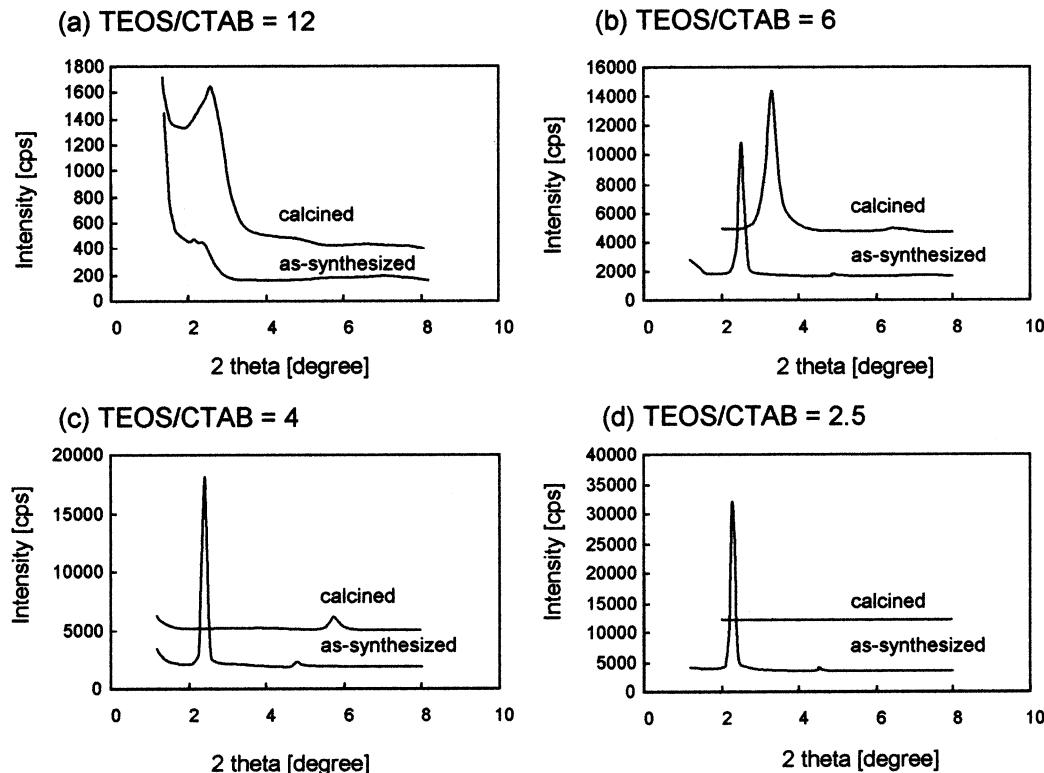


Figure 3. XRD patterns of as-synthesized and calcined mesostructured silica films on a silicon substrate.

structure after calcination, while the peak for the (100) reflection was shifted to higher angle. The (100) *d* spacing reduced from 3.50 to 2.64 nm after calcination, which corresponds to 25% contraction.

Calcination of the as-synthesized films at the TEOS/CTAB less than 4 resulted in the collapse of ordered structure. The decrease in the peak intensity (Figure 3 parts c and d) and the increase in the peak width (Figure 3b) after calcination indicate poor thermal stability. The formation of a silicate network of as-synthesized films seems to be insufficient because the coating process is conducted at room temperature. The structural stability strongly depends on the composition of the solution. The mesostructured silica films prepared with TEOS-rich solution have high structural stability. The structural stability might be improved by optimizing the TEOS/CTAB ratio and the amount of acid. However, to obtain diverse films with different physical and chemical properties for widespread applications, the enhancement of the structural stability of mesostructured silica films prepared with a different solution is important.

Treatment with TEOS vapor at 135 °C was performed before calcination using mesostructured films prepared at a TEOS/CTAB molar ratio of 2.5–12. The XRD patterns of TEOS-treated silica films were shown in Figure 4. The peak shift of the (100) reflection was hardly observed after TEOS vapor treatment for the samples prepared at a TEOS/CTAB molar ratio of 4–12. The increase in the peak intensity after calcination may result from the increase in the scattering density constant and condensation of silicate. No peak shift of the (100) reflection indicates that calcination caused the condensation of the silicate network preserving the ordered hexagonal structure without contraction. The width of the (100) reflection did not change significantly

with calcinations, indicating the high thermal stability of the mesoporous structure. The sample prepared at a TEOS/CTAB molar ratio of 2.5 increased in the peak intensity after calcination like the other samples although the peak shift was observed. Compared with the results for the untreated films, we found that the TEOS treatment was very effective to enhance structural stability of all of the samples prepared at different TEOS/CTAB molar ratios. The *d* value of the (100) reflection of the calcined TEOS-treated film ranged from 3.4 to 4.1 nm depending on the synthetic conditions.

The heating effect might have been important to enhance the stability of the silica films because TEOS treatment was carried out at 135 °C. Thus, a thermal treatment without TEOS vapor was attempted before calcination. The XRD patterns of the silica films with heating processes are shown in Figure 5. The results of the thermal treatment are very similar to those for the untreated films. When Figure 5b is compared with Figure 3b, it is found that the peak shift was somewhat depressed by the thermal treatment. However, the peak shift for the sample prepared at the TEOS/CTAB molar ratio of 2.5 appeared even before calcination, suggesting that thermal treatment is not a sufficient technique for various samples prepared with different solutions. We concluded that the treatment with TEOS vapor is more effective for stabilizing the mesostructure compared to a conventional thermal treatment.

The obtained mesoporous silica film is transparent even after the TEOS vapor treatment. There existed no silica particles on the original film on the optical microscope observation. Figure 6a shows the FE-SEM image of the cross section of the TEOS-treated mesoporous silica film. A flat silica film about 250 nm thick was grown from the silicon substrate. This film was prepared with a spinning rate of 2000 rpm in the spin-

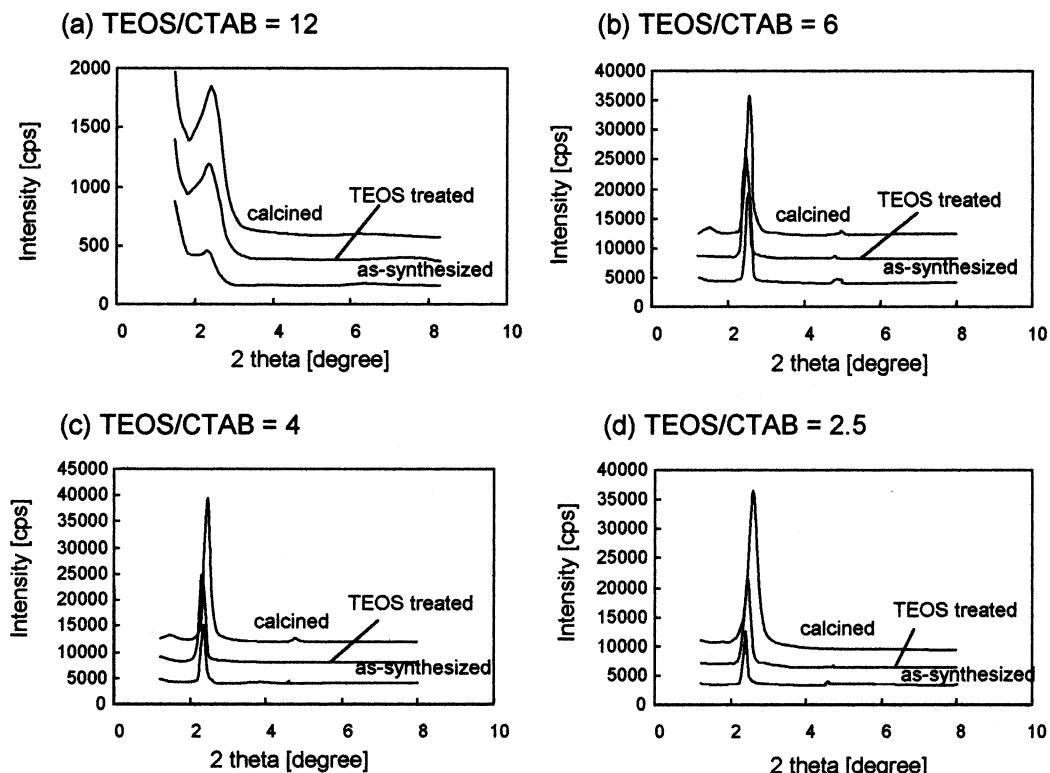


Figure 4. XRD patterns of as-synthesized, TEOS-treated, and calcined mesostructured silica films on a silicon substrate.

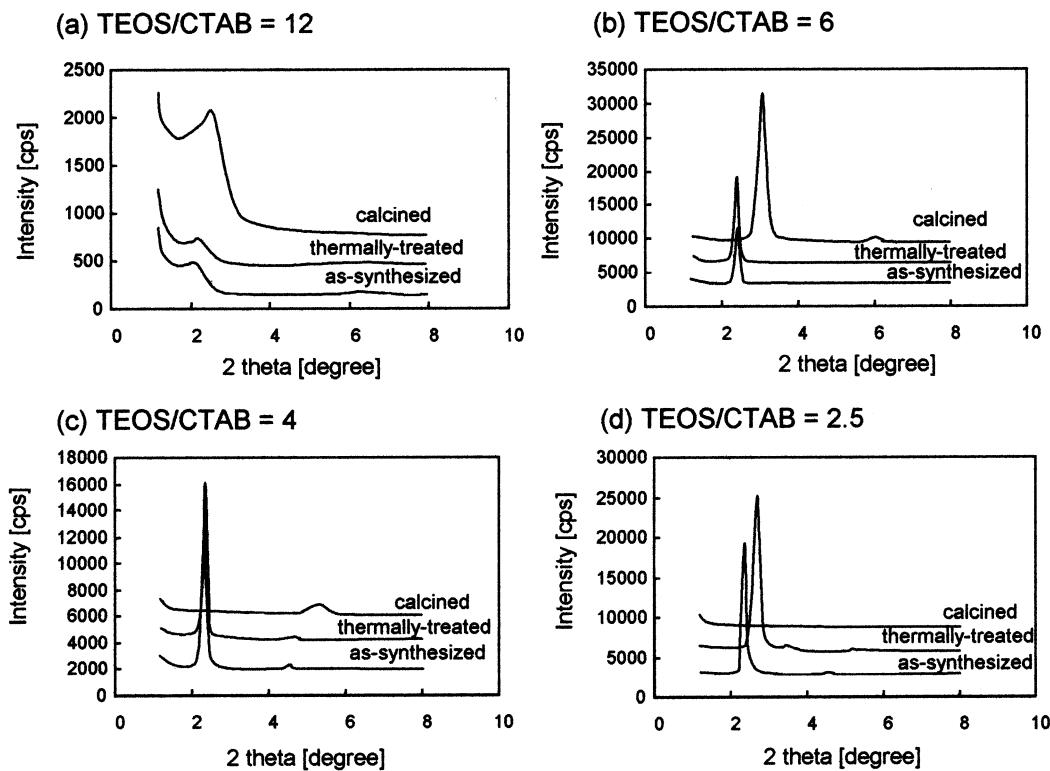


Figure 5. XRD patterns of as-synthesized, thermally treated, and calcined mesostructured silica films on a silicon substrate.

coating process. The film thickness can be controlled by changing a spinning rate and a viscosity of precursor solution. No silica particle was deposited from TEOS vapor on the surface of the film, suggesting the penetration of TEOS vapor into the film. A periodic porous structure can be observed in the cross section of the film shown in Figure 6b. This indicates that the channels run predominantly parallel to the surface of the silicon

substrate, which is consistent with the results of the XRD patterns.

Figures 7 and 8 show FTIR spectra for the untreated and the TEOS-treated mesostructured films on the silicon substrate, respectively. The sharp adsorption bands at 1100 cm^{-1} observed in all of the spectra are ascribed to the Si—O—Si framework. The broad band observed at about 3300 cm^{-1} in Figures 7 and

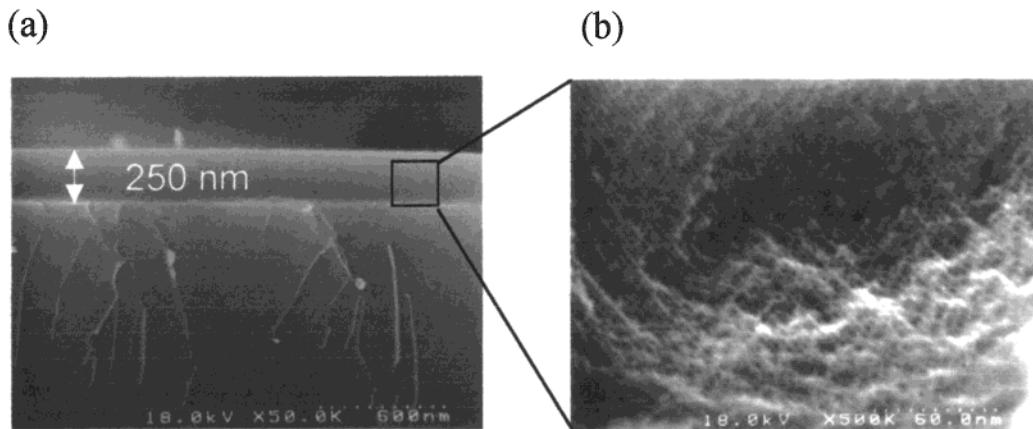


Figure 6. FE-SEM images for the cross-section of a calcined mesoporous silica film.

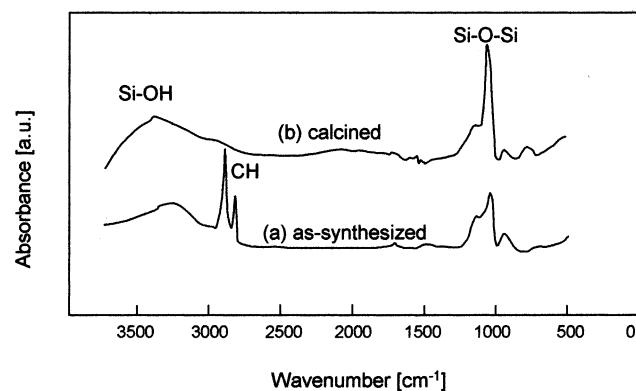


Figure 7. FTIR spectra of as-synthesized, thermally treated, and calcined mesostructured silica films.

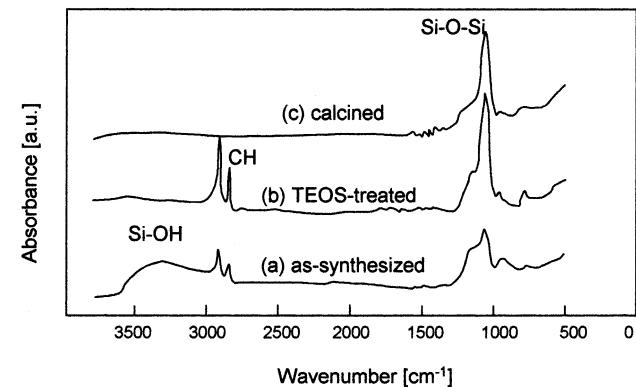


Figure 8. FTIR spectra of as-synthesized, TEOS-treated, and calcined mesostructured silica films.

8a is assigned to the silanol groups.

The absence of this broad band in the spectra of the TEOS-treated samples shows that the concentration of the residual silanol group is extremely low even before calcination. This is the reason the TEOS-treated films hardly contract during calcination. The densified silica wall by successive penetration of TEOS molecules has high structural stability and hardly contracts under calcination process. The surface of TEOS-treated silica films is thought to be more hydrophobic than the untreated ones because of low concentration of the silanol groups. If the films are used as low- k films, a low adsorption capacity of water is an attractive feature because the dielectric constant of water is very large ($k = 81$). We confirmed from FTIR spectra that the surfactant molecules still remain in the TEOS-treated

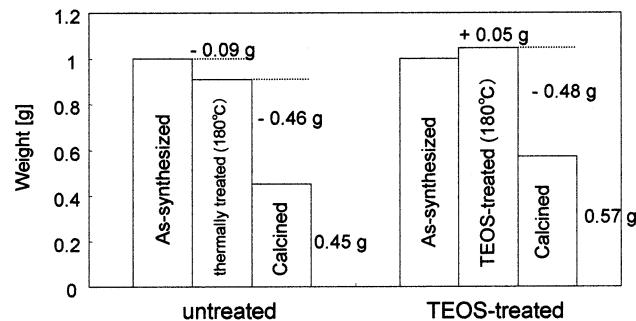


Figure 9. Change in weight of mesostructured silica powders.

film. We believe that TEOS molecules cannot enter the pores and be deposited inside the pores. Complete removal of surfactant molecules after calcination at 400 °C was confirmed on FTIR spectra.

Mesostructured silica powders were treated using TEOS vapor to quantitatively verify the densification of silica during the TEOS treatment. Figure 9 shows the change in weight of the untreated and the TEOS treated mesostructured silica powders. The untreated silica powders decreased in weight by 9% after the thermal treatment at 180 °C. The decrease in weight is due to dehydration and evaporation of ethanol produced from TEOS. On the contrary, the mesostructured silica powder treated with TEOS vapor at 180 °C increased in weight by 5%, showing the penetration of TEOS into the silica powder. The weight loss in the calcination process, which is mainly attributed to decomposition of surfactant molecules, is 46–48% of the original silica powders for both of the samples. These results clearly showed that surfactant molecules still remain densely inside the pores during the TEOS treatment. Namely, TEOS molecules cannot enter the pores to push the surfactant molecules away from there. Therefore, it is considered that penetrating TEOS molecules was not deposited in the pores but react in the silica wall.

Figure 10 shows the XRD patterns of the untreated and the TEOS-treated mesostructured silica powders before and after calcination. The TEOS-treated mesostructured silica powder did not contact after calcination, indicating that TEOS treatment is useful in improving the structural stability of powder samples as well as thin films.

Table 1 lists the amount of methanol adsorbed on the calcined mesoporous silica powders using a saturated

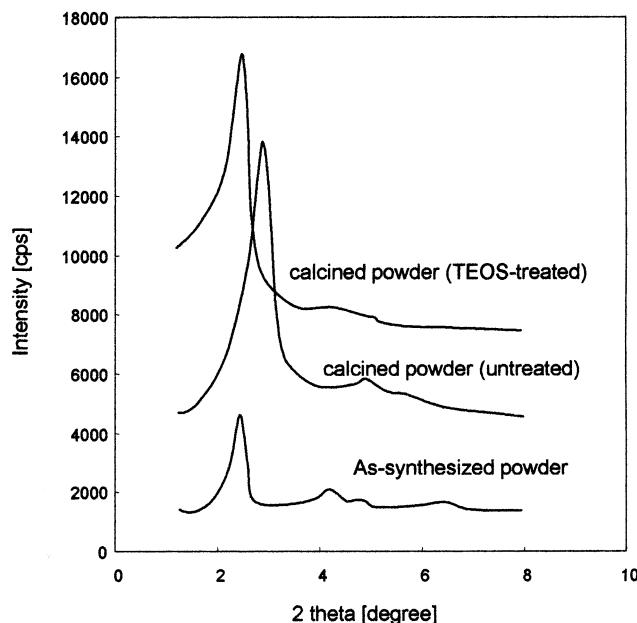


Figure 10. XRD patterns of untreated and TEOS-treated mesostructured silica powders before and after calcination.

Table 1. Amount of Methanol Adsorbed on Calcined Mesoporous Silica Powders (20 °C)

samples	amount adsorbed [wt %]
untreated silica	48
thermally treated silica (180 °C)	55
TEOS-treated silica (180 °C)	53

methanol vapor in He. The mesopores of silica are fully filled with methanol molecules at the relative pressure of methanol vapor ≈ 1 . The amount of methanol adsorbed on the TEOS-treated sample is similar to that on the untreated and thermally treated samples, indicating that they have similar pore volume. This result strongly suggests that TEOS molecules can hardly be deposited inside the pores. The pore volume of the untreated and thermally treated samples was not as large as was expected, considering that the density of the untreated silica wall might be low. The untreated mesoporous structure seemed to partly collapse under the calcination process.

The mechanism of the improvement of thermal stability by TEOS treatment can be summarized as follows: The structural stability of a formed silica network in the as-synthesized film is thought to be insufficient because the reaction rate of the condensation of silanol groups is not high at temperatures below 135 °C. A temperature elevation makes surfactant molecules start to diffuse out of the pores before the condensation of

silanol groups is complete. The imperfect silica network during the removal of surfactant molecules causes structure collapse. Furthermore, the density of the silica wall surrounding the surfactant molecules could be low, resulting in the structural contraction in the condensation process of silanol groups. On the other hand, in the TEOS treatment, TEOS molecules penetrate into an originally deposited silicate and react with silanol groups. Surfactant molecules are densely present during the TEOS treatment. The pores are blocked by the surfactant molecules and prevent TEOS molecules from diffusing inside the pores. The densified silica wall of TEOS-treated films has high structural stability and hardly contracts under a calcination process. Therefore, the TEOS treatment is more effective than conventional precalcination heating and HCl or ammonia vapor treatments for the production of thermally stable films.

The TEOS vapor treatment contains two competitive processes: (1) the penetration of TEOS and (2) the reaction of the silanol groups. For successive penetration of TEOS, both the penetration and the reaction rates should be optimized. For example, when the reaction rate of the silanol groups is very high, the silica network loses its flexibility immediately before the complete penetration of TEOS. On the other hand, when the reaction rate of the silanol groups is very low, it takes a long time to complete the condensation of silicate. It is considered that the rates of the two competitive processes can be controlled by optimizing HCl concentration, reaction temperature, film thickness, and vapor pressure.

Conclusions

We developed a TEOS treatment for the mesoporous silica films prepared by spin-coating. The densified silica wall by successive penetration of TEOS molecules has high structural stability and hardly contracts under the calcination process. The concentration of the residual silanol group is extremely low even before calcination. The TEOS-treated mesoporous silica is a promising material such as low- k films and other optoelectronic devices.

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