Effect of Supercritical Fluid Extraction Process on Self-assembled Porous Silica Film

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1. Introduction

As for the electronics applications, the mesoporous materials are expected as the most promising candidates interlayer for dielectric films in ULSI because of the low dielectric constants and low dielectric losses. In order to achieve the low dielectric constants, the surfactant templates were used and removed from the films to form pores, by calcination at high temperature. However, such high temperature processes, meso-structures is collapsed, resulting less porosity and higher dielectric constant. For low temperature process to fabricate mesoporous films, supercritical fluid extraction (SFE) technique by using supercritical CO_2 (sc-CO_2) was developed. So the substance with chemical affinity is melted by the SFE, It is investigated as extraction technique of the surfactant templates in porous silica film [1]. Carbon dioxide has the critical temperature of 31 °C and the critical pressure of 7.38 MPa. Although some techniques have been proposed to extract surfactant templates from powders of the mesoporous materials by using sc-CO_2 modified with organic solvents such as methanol [2], the extraction throughput is quite low for practical uses. In this study, we investigate the effect of the supercritical extraction process to compare the properties of silica films.

2. Experiment

Precursor solution was prepared under acidic condition in the following step. A starting mixture containing tetramethoxysilane (TEOS), acidic water (pH=3) and ethanol (C_2H_5OH) was heated at 60 °C for 1 hour. The molar ratio was TEOS : H_2O : C_2H_5OH =1:8:8. Under this condition the TEOS was partially hydrolyzed to prevent condensation. Then (ethylene oxide)-(propylene oxide)-(ethylene oxide) (EOPOEO) was dissolved into the solution and the mixture was stirred. The solution was spin-coated on Si substrates and baked at 100 °C for 5 minutes on a hotplate. In this way, transparent films were obtained. Various silica films ware prepared by different processes as shown Table 1. The films was exposed TEOS vapor at 180 degree for 5 hours, pure O_2 gas at 120 degree for 2hours, and liquid CO_2 was pumped into a mixer with a flow rate of 10 ml/min and heated to 80 °C. The pressure at 15 MPa in the chamber. The silica films ware investigated by Fourier transform infrared spectroscopy (FTIR), X-ray small angle scattering (XSAS), transmission electron microscopy (TEM) and ellipsometry, and the values were compared with various silica films prepared by different process.

3. Results

Figure 2 shows FT-IR spectra of each sample. The spectra are normalized Si-O peak (1080 cm^{-1}). The peaks of 1146 cm^{-1} (C-O-C vibration), 2974 cm^{-1} (CH_3) and 2872 cm^{-1} (CH_2) were disappeared for SFE films, which come from EOPOEO [3]. It shows that triblock surfactant is removed from SFE films. For samples 4 and 5, 1730cm^{-1} peak is observed which assigned C=O bond. It shows that EOPOEO is decomposed to low molecular weight compounds by oxidation. Figure 3 shows XSAS spectra of each sample. For samples 1, 4 and 5, these diffraction peaks shifted toward low angle. This shows the bone structures of these TEOS treated samples are stronger and the films were formed without reduction. Figure 4 shows the images of cross section TEM of these samples. The cross sections of sample 1 and 2 show formed pores clearly, while those of samples without SFE is amorphouslike, Compare to the period which calculate the diffraction peak position and bright line distances estimated from TEM, these values were almost corresponding. Table 1 shows refractive indexes of each sample. The refractive indexes of samples 1 and 2 were smaller than those of other samples. As the relation of refractive index n and dielectric constant ε,

$$n= (\varepsilon\mu/\varepsilon_0\mu_0)^{1/2}$$

the dielectric constant of the film whose refractive index are small was lower. This shows pore formed in the sample to remove triblock copolymer template by the SFE treatment. From refractive index, the porosity of the SFE films is calculated. The porosities of sample 1 and sample 2 are 26.2% and 59.3% respectively.

4. Summary

By the SFE extraction process, the super low refractive index porous silica film. By TEOS treatment, the film did not prevent from reduction and form large pores. The porosities of the SFE films are 26.2% with TEOS treatment and 59.3% without TEOS treatment respectively.

References

[1] N. Kawakami et al. Mat. Res. Soc. Symp. Proc. **788** L8.25.1 (2004)

[2] L. Simon et al. Appl. Phys. Lett. **82**,4328 (2003)

[3] J. Xi et al. Electrochemica Acta, in press

Table 1 Sample process and each experimental data of each sample.

	Design thickness (nm)	TEOS treatment	Oxidation treatment	SFE treatment	Thickness (nm)	refractive index	Period (FWHM) (XSAS) (nm)	Period (TEM) (nm)
Sample 1	600	○	○	○	559.8	1.32	11.4 (3.2)	12
Sample 2		×	○	○	532.2	1.17	9.8 (5.1)	7.6
Sample 3		×	○	×	505.9	1.49	9.8 (2.7)	9.6
Sample 4		○	○	×	545.9	1.52	15.3 (7.5)	11.1
Sample 5		○	×	×	595.5	1.46	14.6 (8.9)	13.4
Sample 6		×	×	×	548.7	1.49	10.2 (3.0)	10.5

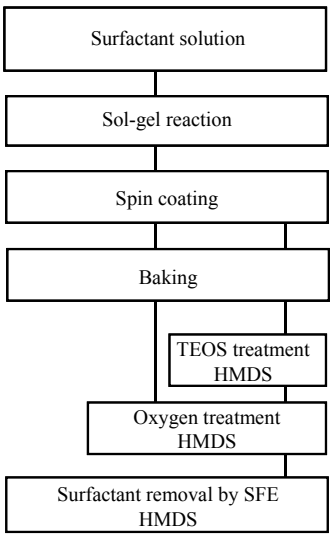

Fig. 1 Fabrication of self-assembled porous silica with supercritical fluid extraction process.

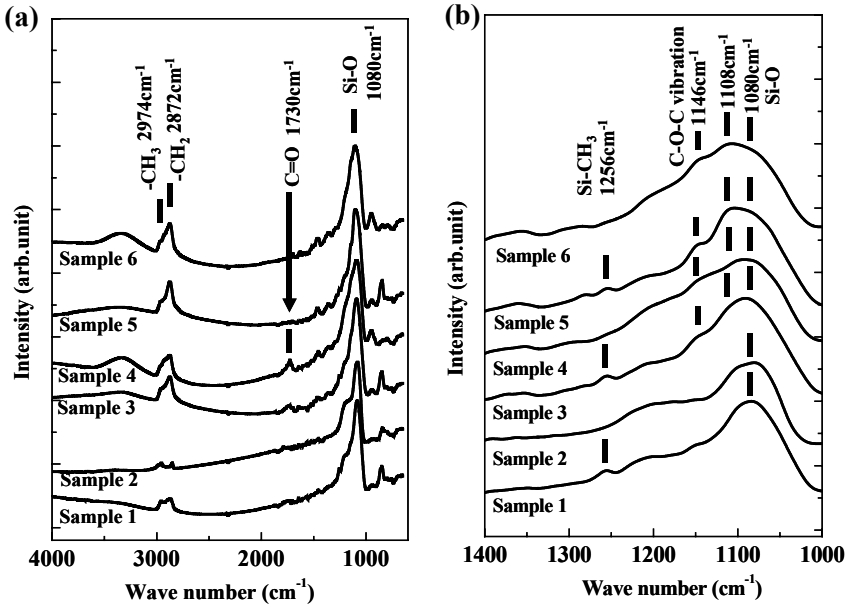

Fig. 2 FT-IR spectra of self-assembled porous silica films. (a) spectra of 650-4000 cm^{-1} (b) magnification 1000-1400 cm^{-1} of (a).

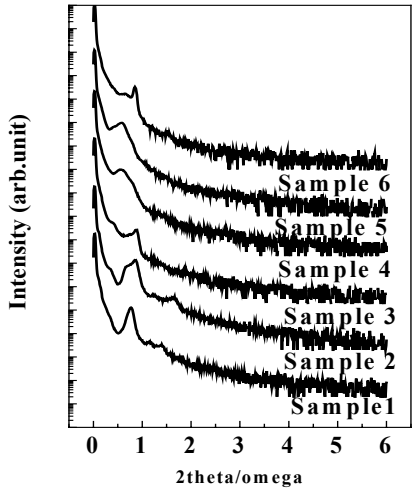

Fig. 3 X-ray small angle scattering spectra of self-assembled porous silica films.

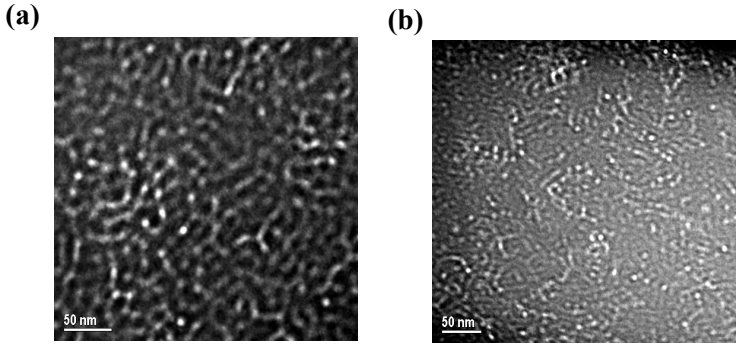

Fig. 4 Cross section TEM images of (a) sample 1 and (b) sample 3.

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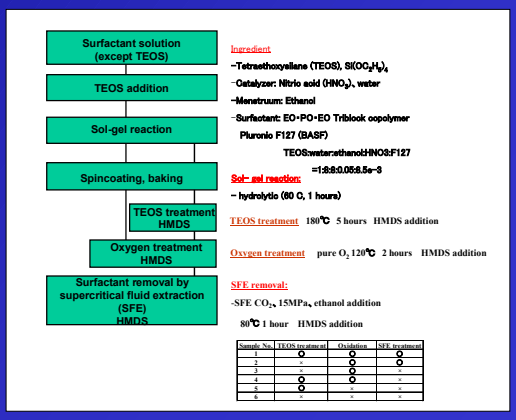
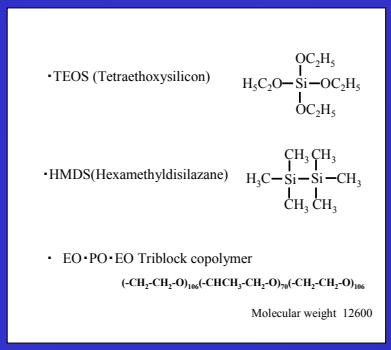
[Introduction]

For low temperature process to fabricate mesoporous films, supercritical fluid extraction (SFE) technique by using supercritical CO_2 (sc-CO_2) was developed. In this study, we investigate the effect of the supercritical extraction process to compare the properties of silica films.

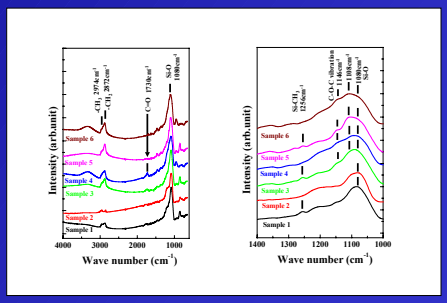
[Process]



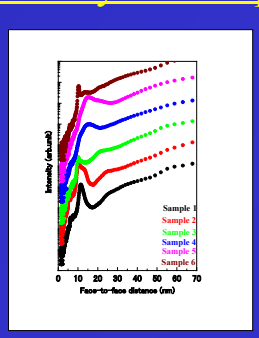


[Result]

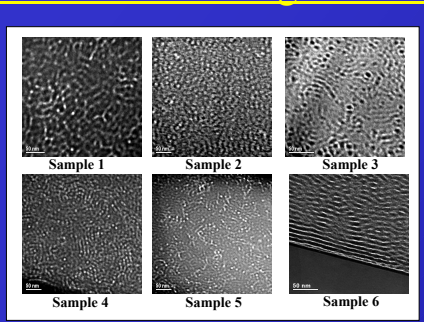
FT-IR spectra



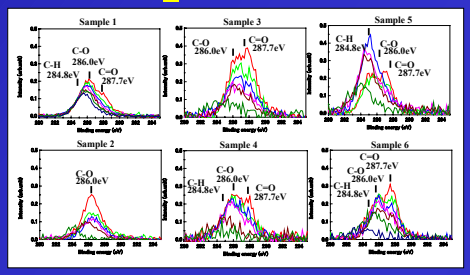
The periodic distance estimated by SXAS spectra



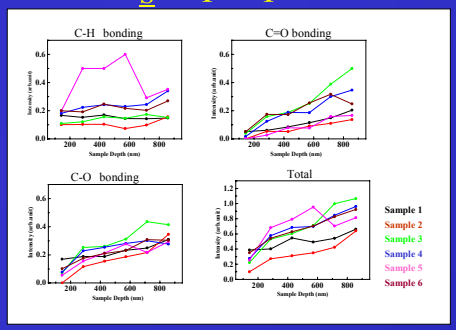
Cross section image of TEM



C 1$_S$ XPS spectra



C 1$_S$ depth profile



Porosity

Lorentz-Lorenz equation

$B_p = \Sigma N_i \alpha_i = 3/4\pi[P(n_1^2-1)/(n_1^2+2) + (1-P)(n_2^2-1)/(n_2^2+2)]$

B_p:Polarizability for each unit volume

P: porosity

It is assumed that only the silica film remains after SFE.
(inner pore filled air perfectly)

$P = 1-[(n_p^2-1)/(n_p^2+2)]/[(n_1^2-1)/(n_1^2+2)]$

Refractive indexes

SiO_2	1.45
Poly(ethylene oxide)	1.4539
Poly(propylene oxide)	1.4570

Sample No.	Thickness (μm)	TEOS treatment	Oxidation	SFE treatment	Thickness (nm)	Refractive	Porosity
1	0.6	○	○	○	559.8	1.32	26.2%
2		×	○	○	532.2	1.17	59.3%
3		×	○	×	505.9	1.49	-7.58%
4		○	○	×	545.9	1.52	-13.1%
5		○	×	×	595.5	1.46	-1.91%
6		×	×	×	548.7	1.49	-7.58%

Comparison table

		TEOS treatment	Oxidation treatment	SFE treatment	thickness (nm)	refractive index	period (XSAS) (nm)	FWHM (XSAS period) (nm)	period (TEM) (nm)
Sample 1	0.6	○	○	○	559.8	1.32	11.4	3.2	12
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[Summary]

- By the SFE extraction process, the super low refractive index porous silica film .
- By TEOS treatment, the film did not prevent from reduction and form large pores.
- The porosities of the SFE films are 26.2% with TEOS treatment and 59.3% without TEOS treatment respectively.

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