

Characterization and mesostructure control of mesoporous fluorinated organosilicate films

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Mesoporous fluorinated organosilicate films were synthesized from tetramethoxysilane and perfluoroalkylsilanes (RO)₃Si-R' [R = Me, Et; R' = (CH₂)₂CF₃, (CH₂)₂(CF₂)₅CF₃, or (CH₂)₂(CF₂)₇CF₃] under acidic conditions in the presence of cetyltrimethylammonium chloride (CTACl) by sol-gel spin-coating. Calcination at 350 °C allowed the removal of surfactants without destroying the other organic contents. X-Ray diffraction patterns of the fluorinated films with short perfluoroalkyl chains indicated that both hexagonal and cubic mesoporous fluorinated organosilicate films can be formed by varying the surfactant to silane mole ratio. On the other hand, the mesoporous fluorinated organosilicate films made from perfluoroalkylsilane with longer perfluoroalkyl chains, which acted as a surfactant, displayed a hexagonal mesostructure across a broad range of surfactant concentrations. Mesoporous fluorinated organosilicate films had higher hydrophobicity and lower refractive indices than mesoporous silica films.

Introduction

Ordered mesoporous materials using surfactant micellar structures as templates were first reported in 1992.¹ These materials have high surface areas, ordered pore structures (mostly hexagonal and cubic packed pores), and uniformly controlled pore sizes. Mesoporous silica thin films show promise in applications such as membrane separations, chemical sensors, optical devices, and electronic devices such as low-*k* dielectric films.²⁻⁴ Mesoporous thin films can be formed by spin coating or dip coating in what is called evaporation induced self-assembly (EISA).⁵⁻⁷ By changing the ratio of surfactant to silica precursor solutions, the silica films were found to acquire lamellar, hexagonal, or cubic mesostructures.^{8,9}

Organic functional groups can be incorporated into the silica inorganic network to yield specific pore surface properties such as hydrophobicity and optical and electronic activity. Co-condensation of a tetraalkoxysilane and organoalkoxysilane with Si-C bonds was used to introduce organic functionality *via* sol-gel chemistry.^{10,11} The co-condensation method allows a higher organic content and a more homogeneous organic distribution.¹² This method has been readily used for the synthesis of mesoporous organosilicate materials with varying organic functionalization. The fluoro-containing groups remained covalently bonded to the mesoporous silica network, yielding materials with potential hydrophobic, adsorbing and optical properties.¹³ In particular, the mesoporous fluorinated organosilicate films with low refractive index and hydrophobicity are applicable for optoelectronic devices and low-*k* dielectrics. The hydrophobicity of the mesoporous films is an important factor for maintaining a reasonably low dielectric constant.¹⁴ Thus, it is expected that the mesoporous fluorinated organosilicate films with high porosity and hydrophobicity might find practical applications such as in the manufacture of low-*k* dielectric material.

There have been many studies on controlling the mesostructures of lamellar, hexagonal and cubic phases in mesoporous silica materials by altering composition and process. However, studies of mesostructures for the control of organosilicate materials are rare. Recently, it was reported that

mesophase thin films with a 3-d hexagonal mesostructure were formed using fluorinated organosilanes.¹⁵ In the present study, perfluoroalkylsilanes (PFASs) with different perfluoroalkyl chain lengths were used to change the fluorine functionality. Mesoporous fluorinated organosilicate thin films using different PFASs were synthesized by rapid solvent evaporation during spin coating. After calcination at 350 °C, ordered mesoporous fluorinated organosilicate films were fabricated without loss of the fluorine moieties. Physical properties, such as refractive index and hydrophobicity, as well as mesostructure were investigated by varying the chain length of the perfluoroalkyl group. It was found that mesoporous fluorinated organosilicate films with short perfluoroalkyl chains could display both hexagonal and cubic mesoporous structures by varying the mole ratio of surfactant to silane, which is similar to results seen with mesoporous silica films. The role of PFASs with long perfluoroalkyl chains, which act as templates, was examined by changing the concentration of surfactant across a broad range.

Experimental

Preparation of the mesoporous fluorinated films

Mesoporous fluorinated organosilicate films were synthesized at room temperature from tetramethoxysilane (TMOS, Aldrich) and a functionalized perfluoroalkylsilane (PFAS) in the presence of a surfactant, cetyltrimethylammonium chloride (CTACl, Aldrich). The following perfluoroalkylsilanes (RO)₃Si-R' were used: 3,3,3-trifluoropropyltrimethoxysilane [3-FPTMS, R' = (CH₂)₂CF₃, Fluka], tridecafluoro-1,1,2,2-tetrahydrooctyl-triethoxysilane [13-FOTES, R' = (CH₂)₂(CF₂)₅CF₃, Avocado], and heptafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane [17-FDTMS, R' = (CH₂)₂(CF₂)₇CF₃, Toshiba]. Fig. 1 shows the molecular structures of PFASs with perfluoroalkyl chains of different lengths. In a typical preparation (10 mol% PFAS), 0.44 g of 3-FPTMS, 1.02 g of 13-FOTES, or 1.14 g of 17-FDTMS was hydrolyzed in 0.06 g of distilled water containing 0.01 M hydrochloric acid (HCl, J.T. Baker) as a catalyst for the sol-gel reaction. PFAS was reacted with weak HCl to avoid the unwanted precipitation of hydrophobic

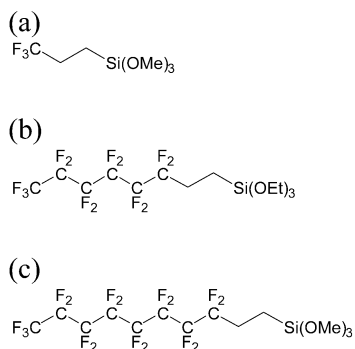


Fig. 1 Chemical structures of perfluoroalkylsilanes with different perfluoroalkyl chain lengths: (a) 3-FPTMS, (b) 13-FOTES, and (c) 17-FDTMS.

organoalkoxysilane. 2.89 g of TMOS was added to the hydrolyzed PFAS in a molar ratio of 9:1. The mixed solution was hydrolyzed in 0.65 g of 0.01 M HCl aqueous solution and then 3.96–11.86 g of methanol (CH₃OH, Merck) was added.

Finally, 0.1–4.84 g of CTACl (25 wt% solution in water) was added to achieve final reactant mole ratios of 0.9 TMOS : 0.1 PFAS : 8–16 H₂O : 0.0005–0.0006 HCl : 18–30 CH₃OH : 0.0038–0.25 CTACl. The solution was allowed to react for another 24 hours at room temperature to oligomerize. The transparent solution was filtered through a 0.22 μm-size filter to remove impurities and gas bubbles. This solution was then deposited onto p-type Si(100) wafers by spin coating at 2000 rpm for 30 s. The organosilicate–surfactant composite thin films were pre-dried at 60 °C, followed by 130 °C and then 200 °C for 1 hour at each stage, using the increasing temperature to remove the solvent, water, and organic template, respectively. The pre-dried films were calcined in flowing air at 350 °C for 12 hours, with the temperature increased at the rate of 1 °C min⁻¹ to fully remove the organic template.

Characterization

The as-synthesized and calcined films were subjected to X-ray diffraction (XRD) measurements with CuKα radiation (40 kV, 80 mA) with a 0.01° step width and 1 s step on a Rigaku

D/MAX-RC diffractometer. Infrared spectra were collected on a Bruker EQUINOX55 Fourier transform infrared spectrometer in the range of 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Quantitative analysis of the mesoporous film was performed by auger electron spectroscopy (AES, SAM 4300) at 5 kV. The contaminant on the sample surface was removed by sputtering of Ar ions before the clean surface was investigated. A JEOL JEM-2000EX electron microscope operating at 200 kV recorded the TEM micrographs of the cross-section of the calcined films. Cross-sectional film samples on Si wafers were prepared by placing films directly onto an epoxy resin substrate. Cross-sectional slices were cut using an ultramicrotome and deposited on a copper grid. An AXIC SE500 ellipsometer was used to quantify the refractive index and thickness of the films. Film thickness was also measured by scanning electron microscopy (SEM, Philips, XLSFEG). Thermal analyses using thermogravimetric analysis (TGA) were performed under a nitrogen flow using a Dupont Model 951 thermogravimetric analyzer at a heating rate of 5 °C min⁻¹ in the temperature range of 30 to 700 °C. The hydrophobicity of films was measured using a KRUSS contact angle measurement instrument.

Results and discussion

Fabrication of mesoporous fluorinated organosilicate films

Fig. 2 shows XRD patterns of the as-synthesized and the calcined mesoporous fluorinated organosilicate films with perfluoroalkyl chain groups of different length. These data indicate that mesoporous structures exist in all the films formed on the Si substrate. The XRD patterns showed a prominent peak at $2\theta = 2.0\text{--}4.0^\circ$ and some broad peaks at $2\theta = 4.0\text{--}7.0^\circ$ that are characteristic of the hexagonal structure. These were similar to the XRD of hexagonal MCM-41 materials¹ shown in Fig. 2(a) and (b). The unit cell parameter (a_0) of the hexagonal structure was calculated from $d(100)$ according to $(a_0) = 2d(100)/3^{1/2}$ where $d(100)$ was obtained from the 2θ value of the first peak in the XRD pattern, from $d(100) = \lambda/2\sin\theta$ where $\lambda = 0.15417$ nm for the Cu Kα line.¹⁶ The unit cell parameter a_0 in Table 1 is equal to the internal pore diameter and one pore wall thickness.¹⁷ According to the XRD patterns, the

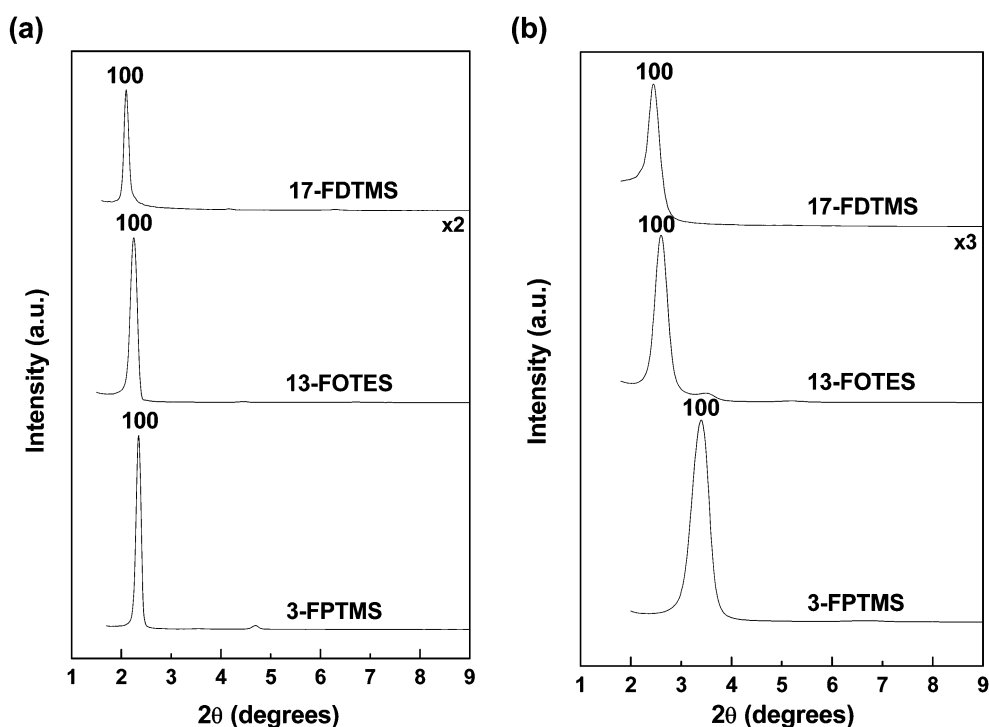


Fig. 2 XRD patterns of (a) as-synthesized and (b) calcined mesoporous fluorinated organosilicate films with different perfluoroalkyl chain lengths.

Table 1 Unit cell parameters and mesoporous structures deduced from XRD and contact angles and refractive indices (obtained by ellipsometry at 632.8 nm) of mesoporous fluorinated organosilicate films

Perfluoroalkylsilanes	Unit cell parameter/nm		Contact angle/ $^{\circ}$	Mesoporous structure	Refractive index
	As-synthesized	Calcined			
3-FPTMS	4.34	3.00	67.7	Hexagonal Cubic	1.268 1.135
13-FOTES	4.53	3.92	99.1	Hexagonal	1.256
17-FDTMS	4.86	4.17	108.4	Hexagonal	1.240

mesoporous structure is retained even after decomposition of CTACl by calcination at 350 °C in flowing air for 12 hours. The XRD of the calcined mesoporous organosilicate film was qualitatively similar to that prior to calcination except for a substantial decrease in $d(100)$ spacing. The reduction of $d(100)$ spacing for the 350 °C heated sample, compared to an as-deposited one, clearly suggests the corresponding shrinkage of the pores.¹⁸ The shrinkage of the pores results from the evaporation of alcohols and water, the gradual removal of surfactants and the condensation of the silanol groups during the thermal treatment of the gel films. The $d(100)$ spacing decreased by about 0.5–1.3 nm for calcined *versus* the as-synthesized samples. The broadening of the $d(100)$ peak on calcination suggests less structural ordering in the film after surfactant decomposition.

Table 1 shows that the 17-FDTMS fluorinated films with long perfluoroalkyl chain have a large unit cell parameter and that the unit cell parameter of 3-FPTMS fluorinated films with shorter perfluoroalkyl chain is similar to that of mesoporous silica films using the same surfactant. The unit cell parameter increased with increasing perfluoroalkyl chain length. Therefore, this result implies that long perfluoroalkyl chains play an important role in the formation of mesostructure. From the XRD results, it was expected that the mesoporous fluorinated films made with long perfluoroalkyl chain PFASs would have larger pores or thicker walls than mesoporous silica films. The apparent wall thickness increased because hydrophobic organic groups extended into the channels.¹¹ 13-FOTES and 17-FDTMS organosilicate films prepared using low surfactant concentration show smaller d -spacing changes between the as-synthesized and the calcined films. However, the 3-FPTMS fluorinated films showed a larger d -spacing change because of the decomposition of excess surfactants compared to the other fluorinated films. The ordered structures of the calcined mesoporous fluorinated organosilicate films containing 3-FPTMS and 17-FDTMS demonstrated the presence of channels. The existence of highly oriented hexagonal mesoporous 17-FDTMS organosilicate films with thicker walls than 3-FPTMS films was confirmed by TEM, as shown in Fig. 3.

After mesophase organosilicate/surfactant films are formed, solvent extraction is the usual method to remove surfactants but avoid degrading the covalently bonded organic groups. In order to increase the thermal and structural stability of mesoporous fluorinated organosilicate films, a calcination method was used in this study. TGA of the as-synthesized fluorinated samples showed weight losses near 60 °C, 260 °C and 500 °C. These loss peaks indicate the desorption of solvent and decomposition of CTACl and perfluoroalkyl chains. For the purpose of full decomposition of surfactant and prevention of decomposition of the perfluoroalkyl chains, the calcination temperature was set at around 350 °C, with this temperature taken from the TGA results. Fig. 4 shows the FT-IR spectra of the as-synthesized mesoporous 17-FDTMS organosilicate film and samples heated at 350 °C and 450 °C. The band appearing at around 1072 cm^{-1} (α) was associated with Si–O–Si asymmetric bond stretching.¹⁹ The bands at 1146 and 1206 cm^{-1} were assigned to C–H bending and C–F stretching modes in the perfluoroalkyl chains (β and γ).²⁰ Perfluoroalkyl groups

appeared to be degraded in the spectra after calcination at 450 °C. Finally, the films calcined at 350 °C showed perfluoroalkyl groups covalently bonded to Si atoms and formation of mesoporous fluorinated organosilicate films. Fig. 5 shows the variation of the relative F/Si ratio analyzed by AES. The relative F/Si ratio decreases after 550 °C calcination

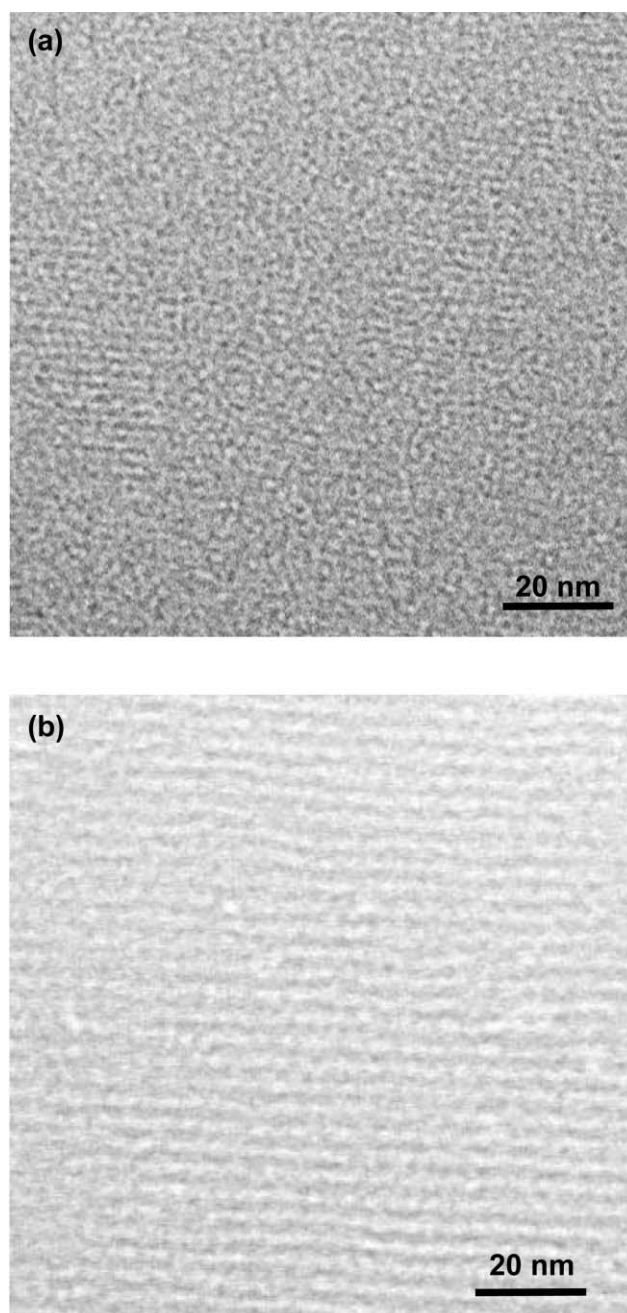


Fig. 3 TEM cross-sectional images perpendicular to the pores of hexagonal mesoporous (a) 3-FPTMS and (b) 17-FDTMS organosilicate films, showing the presence of channels.

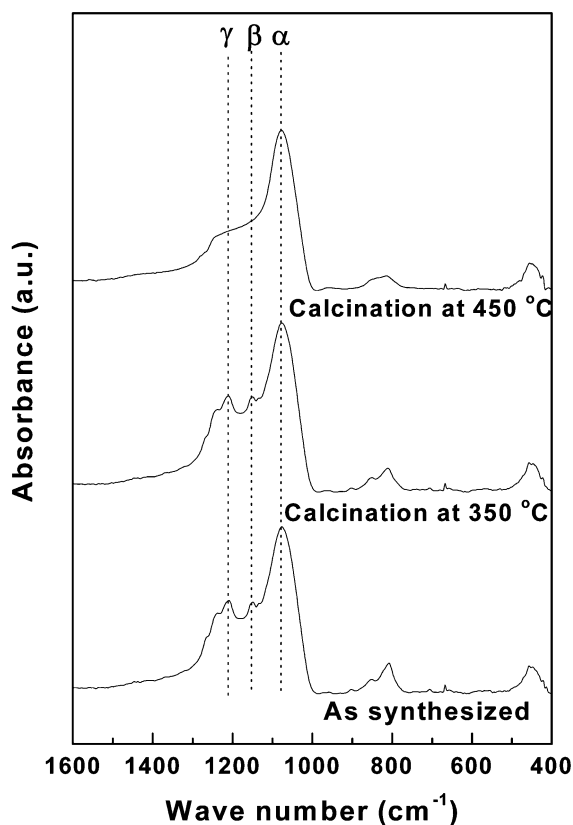


Fig. 4 FT-IR absorption spectra of mesoporous 17-FDTMS fluorinated organosilicate films. The y-axis shows the relative intensities of the absorption coefficient.

temperature. However, the ratio was maintained in the samples after 350 °C calcination. This compositional variation with increasing calcination temperature agrees well with the result of FT-IR spectra. From the above results, the fluorinated mesoporous organosilicate films can be formed through a thermal calcination process without the decomposition of perfluoroalkyl groups.

Physical properties of mesoporous fluorinated organosilicate films

The hydrophobicity of the calcined mesoporous fluorinated films was affected by their fluorine content. The contact angles

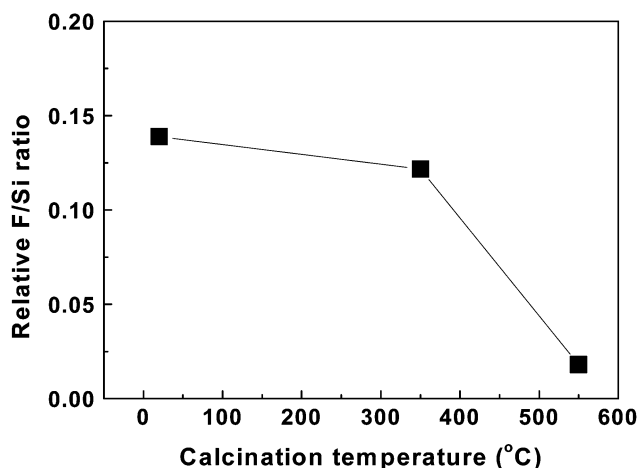


Fig. 5 AES relative F/Si ratio of mesoporous 17-FDTMS organosilicate films with increasing calcination temperature.

of self-assembled $\text{RSiO}_{3/2}$ monolayers containing 17-FDTMS and 13-FOTES were 112° and 105°, respectively.²¹ Table 1 indicates that the static water contact angle of mesoporous fluorinated films containing 10 mol% of 17-FDTMS and 13-FOTES was very similar to that of the $\text{RSiO}_{3/2}$ monolayers using the same precursors. These results indicate that the hydrophobicity of the mesoporous films was influenced by the fluorine content of the PFAS. The hydrophobicity could be controlled by the perfluoroalkyl chain length of PFASs.

As shown in Table 1, the refractive index of the films decreased with fluorine content. The refractive index of mesoporous silica films prepared without addition of organoalkoxysilanes in this system was 1.271, which is lower than that of nonporous silica because of higher porosity. The films with longer perfluoroalkyl chain lengths had a lower refractive index. The refractive indices of the calcined hexagonal and cubic mesoporous 3-FPTMS organosilicate films were approximately 1.268 and 1.135, respectively. The difference in the refractive indices between hexagonal and cubic mesoporous films arose because the cubic mesostructure was more porous than the hexagonal mesostructure, as was reported in a previous study.²² The reduction in refractive index was a function of the fluorine content and mesostructure of the films.

Mesoporous materials with high porosity and low refractive index have been recognized as candidates for low-dielectric-constant (low- k) inter-level dielectrics in microchip integration. The hydrophobicity of mesoporous fluorinated organosilicate films is a desirable property for low- k applications. Thus, mesoporous fluorinated organosilicate films with lower refractive index are expected to have a lower dielectric constant than the mesoporous silica films.

After the surfactant was removed, the thickness of the mesoporous fluorinated organosilicate films was about 500 nm and the average film roughness was estimated to be less than 2 nm over an area of 10 μm^2 . The calcined mesoporous fluorinated organosilicate films had over 90% optical transmission through quartz.

Control of mesostructure on mesoporous fluorinated organosilicate films

The hexagonal and cubic mesostructures of mesoporous silica films were controlled with surfactant concentration. The control of mesostructure provided opportunities for changing the pore accessibility and through-film pore connectivity. Mesoporous 3-FPTMS organosilicate films with short perfluoroalkyl chains have a hexagonal mesostructure, and films with a cubic phase were also synthesized by changing the surfactant to silane mole ratio, as shown in Fig. 6(a) and (b). At a surfactant to silane mole ratio of around 0.17, the predominant phase was a hexagonal mesostructure. However, at a surfactant to silanes mole ratio of approximately 0.13, a cubic phase was produced, as shown in Fig. 6. These changes in mesostructure with surfactant concentration were similar to that of mesoporous silica films.²³ PFAS with short perfluoroalkyl chains in the mesoporous fluorinated film did not affect mesostructure formation, so the predominant phase (hexagonal or cubic) could be controlled with the surfactant/silanes ratio.

In Fig. 7, the mesoporous 17-FDTMS organosilicate films show a hexagonal mesostructure independent of decreasing surfactant concentration. The mesostructures thus formed were maintained after calcination. To avoid decimal numbers and easily compare the surfactant/silanes mole ratios, R was set to $[\text{CTACl}]/[\text{Silanes}] \times 263$. The mesoporous fluorinated organosilicate films have a hexagonal structure at around $R = 50$, which was the same value necessary for the formation of the hexagonal mesoporous silica films. However, hexagonal mesoporous fluorinated organosilicate films were formed at $R = 1$. It was reported that MCM-41 and MCM-48 were

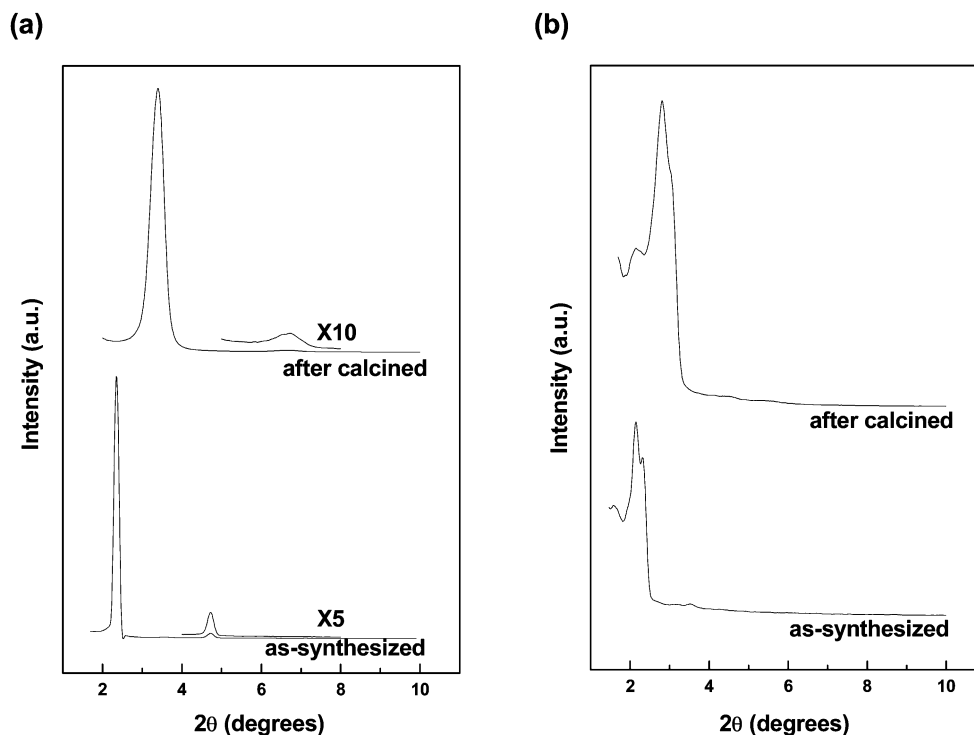


Fig. 6 XRD patterns of as-synthesized and calcined mesoporous 3-FPTMS fluorinated organosilicate films with (a) hexagonal ($[CTACI]/[Silanes] = 0.17$) and (b) cubic ($[CTACI]/[Silanes] = 0.13$) mesostructures.

synthesized using a covalently bonded surfactant-silica source.²⁴ Also, PFASs with a hydrophilic silanol head group and long hydrophobic perfluoroalkyl chains were amphiphilic in nature, as were other templates.¹⁵ Thus, it was reported that PFASs acted as co-surfactants. Although the surfactant to silanes mole ratios decreased, an ordered hexagonal mesoporous structure was formed, but not without the addition of surfactant. This result suggested that PFASs also act as

a structure directing agent when the reactant was mixed with small amount of surfactant (CTACI). The 17-FDTMS fluorinated organosilicate films with long perfluoroalkyl chains assumed a hexagonal mesostructure regardless of surfactant concentration. This result can be explained by the local effective surfactant packing parameter providing a criterion for the surfactant organization in amphiphilic liquid-crystal arrays. The packing parameter g is given by $g = V/a_0l$ where V is the

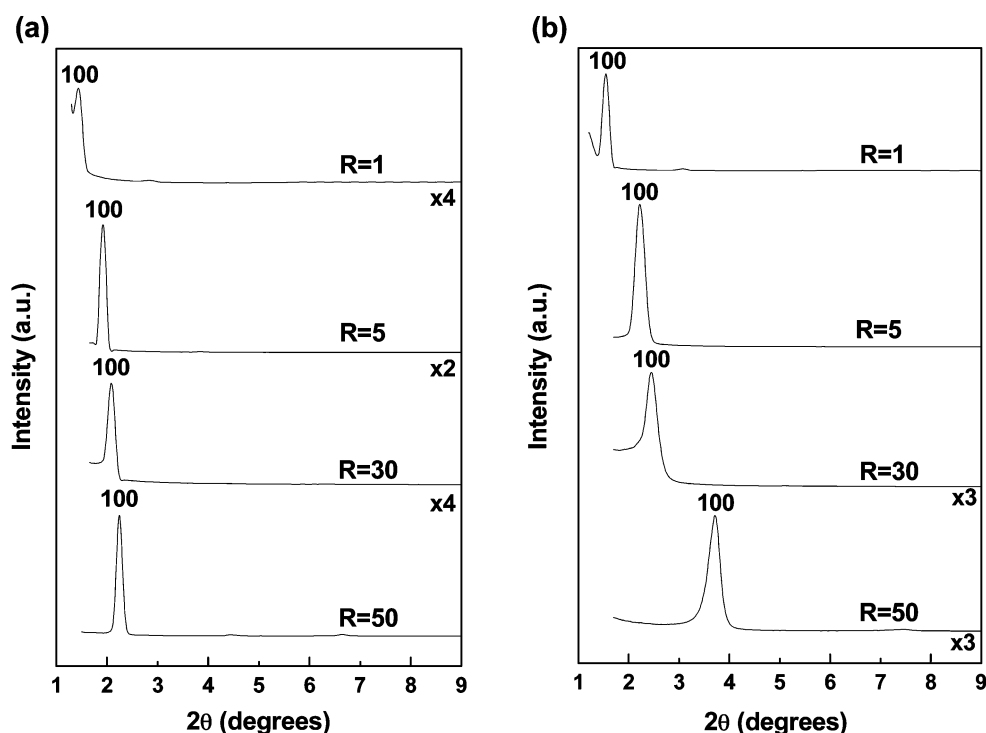


Fig. 7 XRD patterns of (a) as-synthesized and (b) calcined mesoporous 17-FDTMS fluorinated organosilicate films with different R values ($R = [CTACI]/[Silanes] \times 263$).

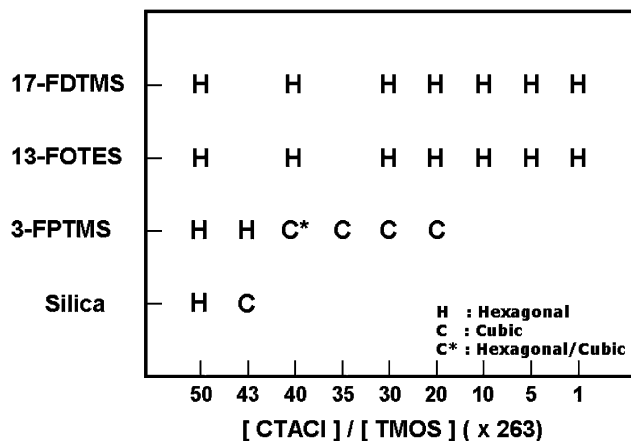


Fig. 8 The mesostructures of products prepared at various [CTACl]/[Silanes] ratios. Letters denote the observed mesophases; H: hexagonal, C: cubic, and C*: cubic or hexagonal.

total volume of the surfactant chains plus any co-solvent organic molecules between the chains, a_0 is the effective head group area at the micelle surface, and l is the kinetic surfactant tail length or the curvature elastic energy.^{24–26} The increase of g value reflects a decrease in surface curvature from cubic through hexagonal and lamellar. Thus, the hexagonal mesostructure of 17-FDTMS organosilicate film is a result of the reduction of micellar curvature on the incorporation of PFASs with long perfluoroalkyl chain into the hydrophobic interior of micelle with small amount of surfactants.

When the surfactant concentration was decreased, the $d(100)$ spacing of the films increased. Previously, it was reported that as the concentration of organoalkoxysilane increased, both the $d(100)$ spacings and the pore sizes of the channels were significantly reduced. One possible explanation for the shrinkage in cell dimensions may be a stronger interaction between the nonpolar organic groups and the tails of the surfactant molecules, which then draw the organic precursors further into the micelles.¹¹ From these research results, the increase in surfactant concentration caused a decrease of d -spacing. This is in line with the results of a similar previous investigation¹¹ showing that the increase of organoalkoxysilane concentration leads to a decrease in d -spacing.

Conditions of formation of fluorinated organosilicate films and those of mesoporous silica films with the corresponding surfactant to silane molar ratios are summarized in Fig. 8. Mesoporous silica films had a hexagonal structure at around $R = 50$ and a cubic structure at around $R = 43$ when the same surfactant, CTACl, was used. Mesoporous 3-FPTMS organosilicate films had both hexagonal and cubic structures across a broad range of surfactant to silane ratios, in comparison with mesoporous silica films when CTACl was used. PFASs with short perfluoroalkyl chains cannot act effectively as structure-directing agents and do not interfere with the formation of hexagonal and cubic mesoporous structures. When PFASs with long perfluoroalkyl chains were used in the formation of mesoporous fluorinated organosilicate films, a final ordered hexagonal mesostructure was formed with very low surfactant concentrations. Hexagonal mesoporous 17-FDTMS and 13-FOTES organosilicate films were formed using 1/50 of the surfactant concentrations necessary for the formation of hexagonal mesoporous silica films. When the surfactant concentration decreased, the hexagonal mesostructure was maintained, in comparison with mesoporous silica films and organosilicate films with short perfluoroalkyl chains. Thus, these results showed that PFASs with long perfluoroalkyl chains acted as surfactants and formed only hexagonal mesostructures by the incorporation of hydrophobic groups.

Conclusion

Ordered mesoporous fluorinated organosilicate films were formed with co-condensation of TMOS and different PFASs as a function of concentration of the surfactant. Mesoporous fluorinated organosilicate films were formed through a heat treatment process up to 350 °C without decomposition of the fluorinated groups. Mesoporous fluorinated organosilicate films have lower refractive indices and higher hydrophobicities than mesoporous silica films. Transparent mesoporous fluorinated organosilicate films have applications as optical devices and as low- k dielectrics. PFASs with different perfluoroalkyl chain lengths affect mesostructure formation and act as surfactants. Mesoporous 3-FPTMS fluorinated organosilicate films with short perfluoroalkyl chains have both hexagonal and cubic mesostructures, similar to silica films. Mesoporous 13-FOTES or 17-FDTMS fluorinated films with long perfluoroalkyl chains have an ordered hexagonal mesostructure even when 1/50 of the surfactant necessary for the formation of silica films with hexagonal mesostructure was used. PFASs of amphiphilic nature can act as templates, while the length of perfluoroalkyl chains affects the controllability of hexagonal and cubic mesoporous structure.

Acknowledgements

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