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Formation and thermal-induced changes of mesostructures in fluorinated organosilicate films

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Abstract

Mesoporous fluorinated organosilicate films were synthesized from tetramethoxysilane and perfluoroalkylsilanes $(RO)_3Si\text{-}R'$ under acidic conditions in the presence of cationic surfactant or triblock copolymer by sol–gel spin-coating. The mesoporous fluorinated organosilicate films made from perfluoroalkylsilanes (PFASs) with long perfluoroalkyl chains, which acted as a template, displayed a hexagonal mesostructure with very low concentration of surfactants, regardless of the kind of surfactants. Although most of the surfactants and organic moieties were decomposed above 550 °C, the mesostructure of mesoporous fluorinated organosilicate films was maintained up to 650 °C. After calcination at 550 °C, their composition was similar to that of mesoporous silica films, and the cylindrical mesostructure was changed to less ordered and broken mesostructure when PFASs with long perfluoroalkyl chains were used. However, the cylindrical mesostructure was maintained when PFASs with short perfluoroalkyl chains were used. Therefore, PFASs with long perfluoroalkyl chains acted as a structure directing agent, and the chain length of PFASs affected the formation of mesostructure and thermal-induced mesostructural change. Also, the increase of calcination temperature caused the change of the composition, mesostructure, and optical property in the mesoporous fluorinated organosilicate films.
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1. Introduction

The mesoporous materials having uniformly controlled pore sizes are promising materials in such applications as catalyst supports, sensors, filtration membranes and in a variety of optoelectronic applications [1–3]. Especially, mesoporous silica thin films show application potentials in membrane separations, chemical sensors, optical devices, and electronic devices such as low-*k* dielectric films. Such mesoporous silica thin films can be formed by spin coating or dip coating in what is called evaporation induced self-assembly (EISA) [4–6]. By changing the ratio of surfactant to silica precursor solutions, the silica films were found to acquire lamellar, hexagonal, or cubic mesostructures [7,8]. Furthermore, organic functional groups can be incorporated in the inorganic network by co-condensation method, yielding specific pore surface properties such as hydrophobicity, optical or electronic activity. Co-condensation of a tetraalkoxysilane and organoalkoxysilane with Si–C bonds was used to introduce organic functionality via sol–gel chemistry [9,10]. The co-condensation method allows a higher organic content and a more homogeneous organic distribution [11]. This method has been readily used for the synthesis of mesoporous organosilicate materials with varying organic functionalization.

Especially, the fluoro-containing groups remained covalently bonded to the mesoporous silica network, yielding materials with potential hydrophobic, adsorbing and optical properties [12]. In particular, the mesoporous fluorinated organosilicate films with low refractive index and high hydrophobicity are applicable for optoelectronic

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devices and low-*k* dielectrics. The hydrophobicity of the mesoporous films is an important factor in maintaining a reasonably low dielectric constant [13]. Thus, it is expected that the mesoporous fluorinated organosilicate films with high porosity and hydrophobicity might find practical applications in the manufacture of low-*k* dielectric material. In our previous study, using cationic surfactant (CTACl) 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 the results seen with mesoporous silica films [14]. However, the films with long perfluoroalkyl chains could display only hexagonal mesoporous structures. Furthermore, the role of PFASs with long perfluoroalkyl chains, which act as templates, was examined by changing the concentrations of surfactant across a broad range.

The mesoporous fluorinated organosilicate films with long perfluoroalkyl chain were also formed with triblock copolymer (Pluronic F68). This study examined the possibility of using PFASs with long chain as co-surfactants to form mesoporous organosilicate films, regardless of the kind of surfactant. However, the difference in used templates caused the changes in the range of mesostructure formation. It was found that these changes could result from the different interactions among hydrophilic silica groups, hydrophobic perfluoroalkyl groups and amphiphilic surfactant. Also, the mesostructural change in the films with increasing calcination temperature was studied with XRD and TEM. Moreover, the chain length of perfluoroalkyl group changed the mesostructure with increasing calcination temperature. The composition and optical property as well as the mesostructure of the films was changed with calcination temperature.

2. Experimental section

2.1. 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 cationic surfactant, cetyltrimethylammonium chloride (CTACl, 25% in water, Aldrich) or PEO-PPO-PEO triblock copolymer, Pluronic F68 ($PEO_{77}PPO_{29}PEO_{77}$, 10% in water, Sigma). The following PFASs $(RO)_3Si\text{-}R'$ were used: 3,3,3-trifluoropropyltrimethoxysilane [3-FPTMS, $R' = (CH_2)_2CF_3$, Fluka], tridecafluoro-1,1,2,2-tetrahydrooctyltriethoxysilane [13-FOTES, $R' = (CH_2)_2(CF_2)_5CF_3$, Avocado], and heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane [17-FDTMS, $R' = (CH_2)_2(CF_2)_7CF_3$, Toshiba]. PFAS was hydrolyzed in distilled water containing 0.01 N hydrochloric acid (HCl, J.T. Baker) as a catalyst for the sol–gel reaction. To avoid unwanted precipitation of hydrophobic organoalkoxysilane, PFAS was reacted with weak HCl. TMOS was added to the hydrolyzed PFAS solution in a molar ratio of 9:1. The mixed solution was hydrolyzed under acidic conditions and then methanol (CH_3OH, Merck) was added. Finally, CTACl was added to achieve the final reactant mole ratios of 0.9 TMOS:0.1 PFAS:8–16H_2O:0.0005–0.0006HCl:18–30CH_3OH:0.0038–0.25CTACl [14]. When triblock copolymer Pluronic F68 was used as templates, mesoporous silica films were formed over a range of reaction compositions, for example, 1 TMOS:30–50H_2O:0.09–0.11HCl:6–20CH_3OH:0.006–0.01 Pluronic F68 in the molar ratio [15]. However, 17-FDTMS organosilicate mesoporous films with long perfluoroalkyl chains could be grown at room temperature with small contents of templates on substrates when the composition of final gel was 0.9TMOS: 0.117-FDTMS:8–16H_2O:0.0005–0.0006HCl:18–30CH_3OH: 0.0006–0.0024 Pluronic F68. After the addition of templates, the solution was allowed to react for another 24 h at room temperature to oligomerize. To remove impurities and gas bubbles, the transparent solution was filtered through a 0.22 μm-size Teflon filter. This solution was then deposited onto p-type Si(1 0 0) wafers and quartz substrates 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 h at each stage, using the increasing temperature to remove the solvent, water, and organic template, respec-

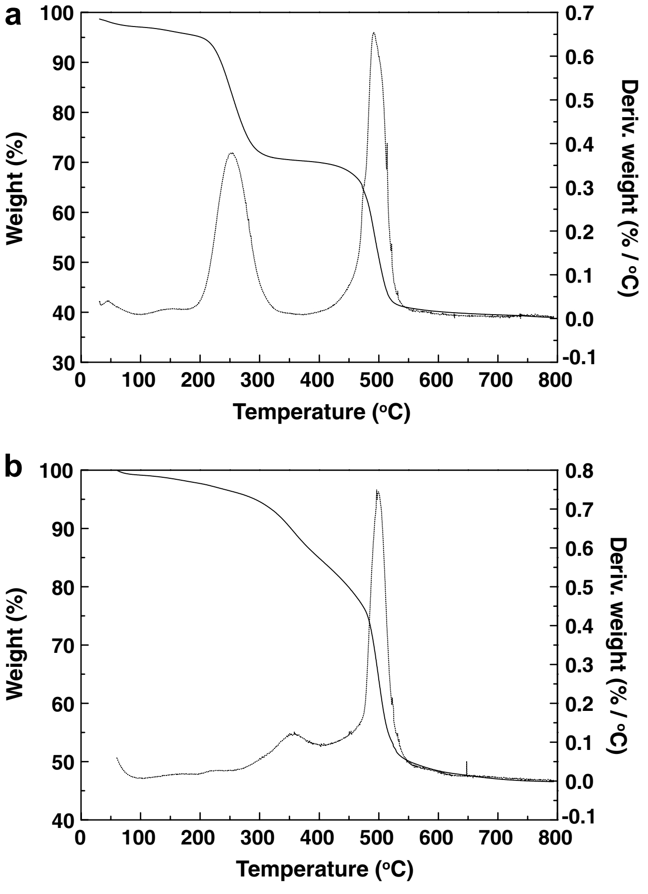

Fig. 1. TGA curves of 17-FDTMS organosilicate materials made from (a) CTACl and (b) Pluronic F68.

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