

Deposition of thin mesoporous silica films on glass substrates from basic solution

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Abstract

Transparent thin (ca. 100 nm) films of silica–surfactant mesostructured materials were deposited on borosilicate glass plates and soda-lime glass tubes from aqueous solutions containing tetraethoxysilane, alkyltrimethylammonium chloride, ammonia, and methanol. By calcination in air, the films became mesoporous (BET surface area of 700–900 m² g⁻¹) with pore diameter 2.0–2.8 nm.

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1. Introduction

The preparation and the application of nanoporous silica films have been extensively investigated after the successful preparation of nanostructured and nanoporous silica films by the solvent evaporation method [1,2]. Nanoporous and nanostructured silica films on flat substrates have potential for such uses as low-dielectric-constant (low-*k*) material for semiconductor electronics [3], nanoreactors for photochemical reaction [4], matrices for laser dyes [5–7], pH sensors [8], and ionic conductors [9]. Due to the wide range of possible uses, there is a demand for films with higher quality, controlled thickness, and easier and reproducible synthesis, besides the variation of porosity, pore size, chemical composition, stability, and pore surface engineering.

For film preparation on substrates, several synthetic options have been reported [10–13] besides the solvent evaporation method. To control the macroscopic shape of the sol–gel derived products, reactions under acidic conditions are favorable, partly due to their low and controllable rate compared with those under basic conditions. Ogawa took advantage of the slow sol–gel reaction to combine surfactant template mechanisms for

the successful preparation of mesostructured silica–surfactant films by the solvent evaporation method [1,2]. The deposition of silica–surfactant films by dipping substrate in an acidic precursor solution is also used extensively. Thus, the preparation of mesoporous silica films was usually conducted from acidic precursor solutions containing alkoxy silane and surfactant. On the other hand, there are few examples of the preparation of silica–surfactant hybrid films without using acidic conditions. The formation of silica–surfactant nanostructures on substrate by the adsorption of a component or silica–surfactant from vapor phase has been reported so far [11–13]. To the best of our knowledge, there are few reports on the preparation of mesoporous silica films using basic conditions [12,14–16]. Martin et al. [14] and Nishiyama et al. [12] prepared mesoporous silica films by ammonia vapor after gel deposition. Nishiyama et al. also reported the deposition of mesoporous silica on a Stainless steel membrane by a hydrothermal treatment under a basic condition [15,16].

Very recently, we have reported a novel approach to depositing thin mesostructured silica–surfactant films from basic solutions containing tetraethoxysilane, alkyltrimethylammonium chloride, methanol, and ammonia [17]. Due to its simple operation and versatility, the method is a promising alternative to deposit thin layers on various substrates. This paper reports a detailed experimental procedure for the preparation of mesostruc-

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tured silica–surfactant films and mesoporous silica films on glass substrate from a basic solution and the characterization of the resulting films. The present film deposition from basic solution opens up new opportunities to prepare mesoporous silica film on various substrates, including those unstable in acidic solutions, organic polymers, and those with complex geometry.

2. Experimental

2.1. Materials

Methanol and 28% aqueous ammonia solution were obtained from Kanto Chemical Co., Inc. Tetraethoxysilane (abbreviated as TEOS) and alkyltrimethylammonium chlorides $[(C_nH_{2n+1})(CH_3)_3NCl]$ ($n = 12, 14, 16,$ and 18); abbreviated as C_nTAC , where n denotes the carbon number in the alkyl chain] were obtained from Tokyo Kasei Kogyo Co., Ltd. All chemicals were used without further purification.

2.2. Sample preparation

Following is a typical synthetic procedure: C16TAC (0.211 g), deionized water (17.7 g), methanol (100 ml), and 28% aqueous ammonia solution (7.2 g) were mixed in a poly(propylene) bottle (250 ml, As One Corporation) and the solution was shaken for 15 s at room temperature. To this solution was added TEOS (0.368 ml) and then the mixture was shaken for another 3 s. The molar ratio of TEOS:C16TAC:deionized water:methanol:ammonia was 1:0.4:774:1501:72. A plate (borosilicate glass, $30 \times 30 \times 0.2$ mm, Matsunami Glass Ind., Ltd.) or a capillary tube (soda-lime glass, Hilgenberg GmbH) was soaked into the solution perpendicularly as shown in Fig. 1 and aged at room temperature for 20 h. The products were washed with methanol and were dried at room temperature for 1 day. To remove surfactant, the products were calcined in air at 350°C for 10 h at a heating rate of $2.5^\circ\text{C min}^{-1}$.

The as-synthesized products were allowed to react with ammonia by placing them in a desiccator (ca. 1 L), where a bottle containing 28% aqueous ammonia solution (100 ml) was placed, and were aged at room temperature for 10 or 24 h. The products were dried in air at 60°C for 1 day and calcined in air at 350°C for 10 h ($2.5^\circ\text{C min}^{-1}$).

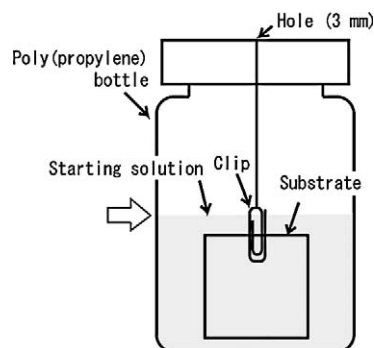


Fig. 1. Schematic drawing of the experimental setup used for film deposition.

2.3. Characterization

Scanning electron micrographs (SEM) were obtained on a Hitachi S-2380N scanning electron microscope. The nitrogen adsorption isotherms were measured at -196°C on a Belsorp TCV (BEL Japan, Inc.). Prior to the measurements, the samples were dried at 120°C under vacuum for 3 h. The film thickness was evaluated using a surface profilometer, Surfcomer SE 1700 (Kosaka Laboratory, Ltd.). X-ray diffraction (XRD) was performed on a RAD IB diffractometer (Rigaku) using monochromatic $\text{CuK}\alpha$ radiation, operated at 40 kV and 20 mA. Transmission electron micrographs (TEM) were obtained on a JEOL JEM-100CX transmission electron microscope. Prior to the measurement, the sample was peeled off from the substrate before the calcination.

3. Results and discussion

When the reaction was conducted in the absence of the substrate, the solution became turbid after aging for ca. 10 min due to the generation of surfactant–silica spherical particles and the reaction proceeded until the TEOS was completely consumed [18]. In the present experiment, the solution became turbid after aging for ca. 10 min due to the generation of surfactant–silica spherical particles, which grew to be ca. $1.2\ \mu\text{m}$ in diameter until the silica source was completely consumed (20 h in the present condition). The substrates were placed in the solution perpendicularly as shown in Fig. 1, so that the formed spherical particles were sedimented at the bottom of the bottle and only a small amount of spherical particles was deposited on the substrate. The spherical particle on the substrates was removed by washing with methanol, as evidenced by SEM observation of the substrate surface. In the present experiment, the major part of TEOS was used for the spherical particles, the particles were also collected, and the yield and composition were evaluated as reported in our separate paper [18].

The weight of the plate (30×30 mm) increased by 0.2 mg after the reaction and the subsequent washing and drying, indicating the deposition of silica on the substrate. These values are thought to include surfactant and silica. During the coating and drying, volatile species are thought to be vaporized and the amount of the volatile species in the films should be very small. The film was transparent, as shown in Fig. 2a. SEM observations indicated that the surfaces of the films were macroscopically smooth and there were no cracks. The thickness of the film deposited on the glass plate was 100 nm, which was determined by the surface profilometer, and the thickness was homogeneous in the films. The thickness was controlled by repeating the reaction using fresh precursor solution; the thickness of the film became 300 nm after deposition for three times. Coating was not achieved when the reaction was conducted in the absence of C16TAC, indicating the important role of the interactions, which is probably as an electrostatic interaction between the cationic group of CTA^+ and the silanol group of the substrate surface.

The photograph and the SEM image of the calcined film are shown in Figs. 2b and 3. During the calcination, Si–O–Si

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