Synthesis of Mesoporous Silica Thin Film with Three-dimensional Accessible Pore Structure

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Continuous mesoporous silica thin films with three-dimensional (3-D) accessible pore structures have been prepared by a dip-coating technique using F127 triblock copolymer as the structure-directing agent under acidic conditions.

Since their discovery[1,2] mesoporous materials prepared in various forms have generated a lot of interests. For example, mesoporous metal oxide films offer great promises for applications including sensor, separations, optoelectronics, and microelectronics. To fully realize the potential applications of these materials, it is essential that the order and the orientation of the nanoscopic domains are controlled. Recent efforts have led to many major advances in pore orientation and film patterning using electric[3] and magnetic field alignments[4] as well as substrate surface modifications.[5] Silica nanostructured materials produced with block copolymer surfactants have already been studied in the various forms of bulks, films, and fibers. Zhao et al.[6] have reported the formation of 2-D hexagonal and 3-D cubic films with copolymers, Pluronic P123 (PEO20-PPO70-PEO20) and F127 (PEO106-PPO70-PEO106), respectively. It is known that mesoporous silica film formation proceeds via evaporation-induced self-assembly (EISA).[7] During this process the structure evolution and precursor condensation occurs simultaneously, hindering the control of film orientation and morphology. However, as far as pore accessibility is concerned, 3-D pore structures, as in SBA-16,[8] appear to be promising because of their unique pore structure and connectivity.

Here we report formation of continuous mesoporous thin films with 3-D accessible pore structure using F127 surfactant. The films exhibit mesostructures with 3-D pore connectivity and the accessible pores in the films have been clearly observed under a field-emission scanning electron microscope (FE-SEM). It is revealed that orientation of the nanoscopic domains and the film structure are dependent on the sol preparation as well as coating conditions. To find out the best conditions for pore accessibility and their orientation, we prepared a number of films under different preparative conditions. The results obtained on the best sample with the highest density of the accessible pores are discussed here. The mesoporous silica film was prepared from the coating sol with the molar composition 1TEOS: 40ETOH: 0.0072F127: 9.2H_2O: 0.21 HCl, by dip-coating on a thin Pyrex® glass slide at a dip rate of 6 cm/min. Coating solution was typically prepared by the addition of 1.6 g F127 dissolved in 15.3 g of ethanol into polymeric silica sol, that was prepared by heating a mixture of 3.5 g of TEOS, 15.3 g of ethanol, 2.45 g of distilled water, and 0.35 g of 1 M HCl, at 65 °C for 1 h. To increase the degree of polymerization of the silica framework and to further improve its thermal stability, the as-deposited film was heated at 80 °C overnight, in air. The film was then calcined in air at 500 °C. The temperature was raised at a heating rate of 1 °C/min, and the furnace was maintained at 500 °C for 4 h. It is known that, during mesoporous silica film formation, solvent evaporation simultaneously induces formation of micelles leading to the self-assembly of micelles and inorganic species resulting in the polycondensation of the mesoporous film network.[7] The firstly formed micelles were self-organized in the liquid film to form randomly oriented domains. Then the domains that are close to the film/substrate interface tend to align in the directions parallel to the surfaces. In aqueous F127 silica sols only spherical micelles are formed; however, in alcoholic F127 silica sols spherical as well as cylindrical micelles are formed.[9] The domains that are close to the interfaces (air/film and substrate/film) align in the direction of the surfaces with the alignment progressing towards the film centre. The extent of alignment is known to depend on the degree of silica condensation, concentration of surfactant and dip rate. Transmission electron microscopy (TEM) studies on mesoporous silica films, during their formation from F127, ethanol and water, have revealed the presence of two phases; one with randomly oriented domains of organized pore channels near the film center, and the other at the interfaces with channels well-aligned to the substrate.[9] The external surface morphology of the film was studied by FE-SEM and the images taken at different magnifications are shown in Figure 1. The film shows the presence of a large number of uniformly sized, accessible pores on its top surface. Although arranged in a less-ordered fashion, the accessible pores have uniform diameter of ≈10 nm, and the porous structure extends over a wide area of the film as can be seen from the FE-SEM images. The X-ray diffraction (XRD) pattern of the film is shown in Figure 2, the film shows two peaks corresponding to $d = 10$ nm and 5 nm, indicating periodically arranged pores in 3-D structure. The cross-sectional TEM image of the sample depicted in Figure 3 shows that the film is consisting of layers that are arranged horizontally on the substrate with the periodic arrangement of the pores found along with the layers. Broadly, the film could be divided into two regions, A and B. Region A is a well-aligned phase at the film/substrate interface. This phase has presumably been resulted from the 1-D shrinkage of the film along substrate axis on calcination.[7] The second region B is disordered and is located at the top film/air interface. Note that 3-D accessible pores are developed in region B. An interlayer (between the region A and substrate), possibly formed owing to strong substrate–film interaction, is also seen in the image. The observation of different types of phases resulting from the formation of more than one type of domains is well-known.[7,9] From the FE-SEM and TEM images, two types of pores are observed in the films; the accessible pores on the top surface and

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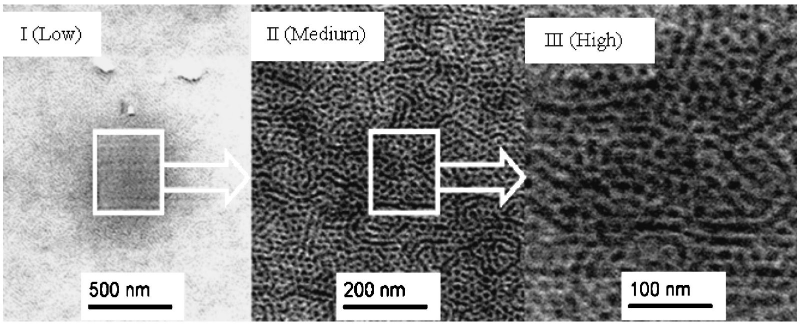

Figure 1. FE-SEM images under different magnifications on the top surface of mesoporous silica film.

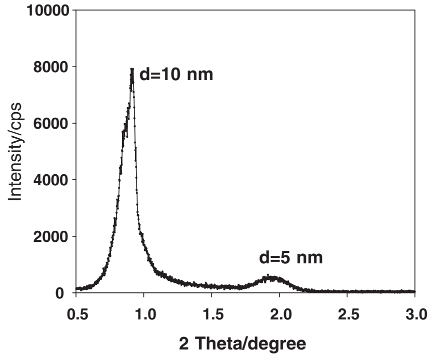

Figure 2. The XRD pattern of the calcined mesoporous silica film.

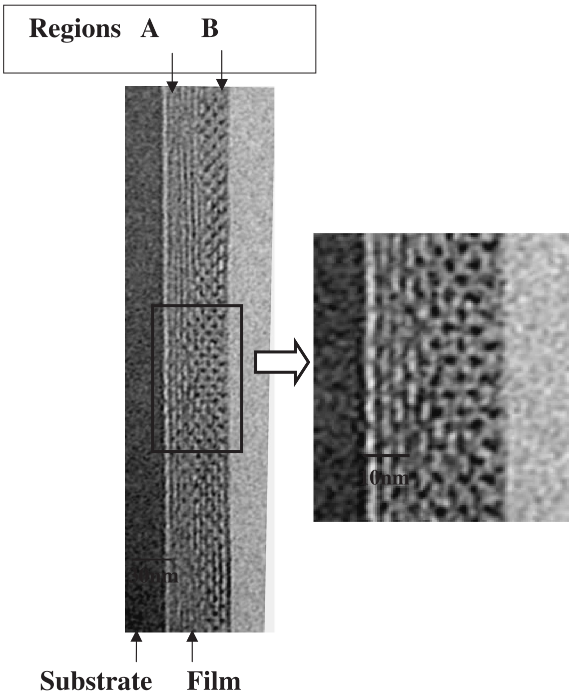

Figure 3. A cross-sectional TEM image of the mesoporous silica film.

the pores present in each of the horizontal layers on the cross-sectional surface of the film. The thickness of the film is $\approx$50 nm and it comprises ten layers each of thickness 5 nm. N_2 ads/des studies on the film yielded a sharp mesopore centered on 7 nm and a less remarkable peak at 3 nm. The BET surface area of the film was found to be 330 m^2/g. Although further studies are required to understand the details of the film formation and orientation of domains, we have shown through this study that films with high density of accessible pores could be produced via control of preparative and coating conditions. The films have already been used in the synthesis of single-walled carbon nanotubes by a low-temperature CVD process[10]

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