

A Simple Method for Fabrication of Mesoporous Films Using a Rapid Heating Process

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(Received November 29, 2004; CL-041450)

Mesoporous silica SBA-15 and SBA-16 films can be successfully prepared on a substrate by a simple method involving a rapid heating process, which is controlled by a voltage applied to a heating electrode on the substrate. This advantageous method has considerable potential for electronic device fabrication processes.

Mesoporous materials, which are synthesized using self-assembled surfactants as templates,^{1,2} have attracted considerable interest because of their self-assembled porous structure and high surface area. These mesoporous materials have a uniform pore size and a periodic porous assembled structure that has potential application in molecular sieves, adsorbents, low dielectric constant (low-*k*) dielectric coatings, gas sensors, and catalysts.³⁻⁵ To enable them to be applied in electronic and optical devices, they need to be made in the shape of a thin film.⁶⁻⁹ The evaporation speed of the sol solution during the synthesis process is the main determining factor in constructing mesoporous films. Until now, almost all thin films of these materials have been prepared by dip coating or spin coating.⁶⁻⁹ However, it is very difficult to control the coating area using these methods¹⁰ because the whole area of one side of a substrate is coated by the spin coating and whole area of both sides by the dip coating. Although some results have been achieved by using patterned masks, removal of the mask tends to damage the mesoporous film. If photolithographic or reactor etching engineering was used for such coating patterning, however, it would make the process more complex.

Here, we report, for the first time, a simple rapid heating process for fabricating mesoporous films that uses an applied voltage method. In traditional fabrication processes, the evaporation speed is controlled by the substrate rotation speed in spin coating and by the pull-up speed in dip coating. In our simple rapid heating process, the applied voltage is used to control the evaporation speed. Moreover, the coating area can be readily controlled by limiting the drop area. Using this method, we have succeeded in constructing a self-ordered hexagonal SBA-15 type and a cubic SBA-16 type mesostructure film restricted to the drop area of the sol solution.

A 1 mm-thick glass substrate is sputtered to create a Pt electrode film on one side. This Pt film is used as the heating resistor. Mesoporous silica films are prepared on the glass substrate on the obverse side to the Pt film. Figure 1 shows the relationship between the voltage applied to the Pt film and the temperature property of the film fabrication area. The temperature of the substrate surface is measured using a remote infrared irradiation thermometer, which can record the profile of temperature. These results demonstrate that Pt film heating by applying voltage can achieve rapid heating in the film fabrication area.

The precursor sol solutions for coating are prepared from two solutions.⁹ One is a polymer solution, containing a template EO_{*n*}PO_{*m*}EO_{*n*} type triblock copolymer dissolved in ethanol (EtOH). The other is a solution of tetraethylorthosilicate (TEOS), EtOH, ultrapure water, and hydrochloric acid. These polymer and silica solutions are mixed and used as the coating sol solution. The mole ratio of chemicals in the coating sol solution is TEOS:EO₂₀PO₇₀EO₂₀(P123):H₂O:HCl:EtOH = 1:0.014:15:0.16:39 for the hexagonal structured SBA-15 silica film; and TEOS:EO₁₀₀PO₆₅EO₁₀₀(F127):H₂O:HCl:EtOH = 1:0.041:15:0.16:40 for the cubic structured SBA-16 silica film. The coating sol solution is dropped onto the film fabrication area on the substrate and rapidly heated to a predetermined temperature following one of the profiles in Figure 1. Finally, calcination is carried out at 723 K for 12 h to remove the triblock copolymer.

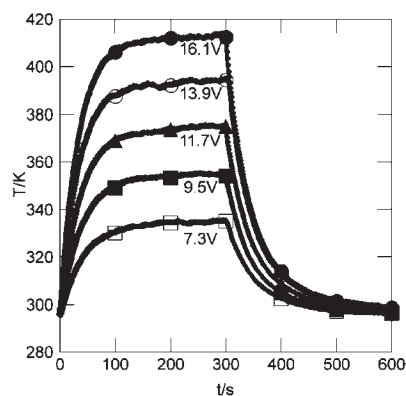


Figure 1. The relationship between temperature profile at the fabrication area and voltage applied to the Pt film. The applied voltage is switched off at 300 s. The open squares, closed squares, closed triangles, open circles, and closed circles respectively indicate the 7.3, 9.5, 11.7, 13.9, and 16.1 V profiles.

Figures 2 and 3 show X-ray diffraction patterns (XRD), transmission electron micrograph (TEM) images of the hexagonal SBA-15 film and cubic SBA-16 film after calcination, respectively. In Figure 2, the SBA-15 film has been prepared using the 11.7 V profile curve in Figure 1 (closed triangles). The XRD patterns exhibit two well-resolved peaks of (100) and (200) of a 2-dimensional (2D) hexagonal structure; the TEM images also indicate that the film has a highly oriented hexagonal structure and the pore channels are parallel to the substrate surface. Therefore, the self-ordered hexagonally structured SBA-15 film is concluded to be a 2D hexagonal structure. Compared to the XRD pattern of powder hexagonal mesoporous silicate,^{2,4,8,9} the (110) and (210) reflections have disappeared, which also suggests that the films have a highly oriented hexagonal structure and the pore channels are parallel to the substrate surface.^{8,9}

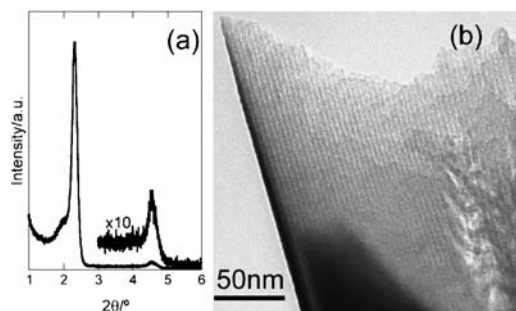


Figure 2. The XRD pattern of a self-ordered SBA-15 film made using the rapid heating process (a) and TEM images of it (b).

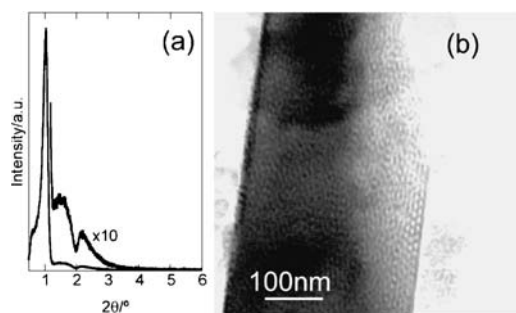


Figure 3. The XRD pattern of a self-ordered SBA-16 film created by the rapid heating process (a) and TEM images of it (b).

These patterns and images clearly exhibit the same properties as conventional spin-coated hexagonal SBA-15 films.

In Figure 3, SBA-16 film is prepared using the 16.1 V profile curve in Figure 1 (closed circles). The XRD patterns exhibit two strong peaks with d spacings of 8.41 and 4.12 nm and two weak peaks with d spacings of 5.96 and 4.85 nm. These peaks have a d spacing ratio of $1/\sqrt{2}:1/2:1/\sqrt{6}:1/\sqrt{8}$ and can be indexed as the (110), (200), (211), and (220) reflections associated with a cubic structure.^{2,4,5,8} It can be also observed in the TEM image that the pores in this film state have a 3D structure.

These results demonstrate that mesoporous films can be fabricated by this rapid heating process using an applied voltage. They also indicate that the applied voltage on the substrate can be used to control the evaporation speed of the source sol solutions in an equivalent way to that used in the spin- and dip-coating methods. Therefore, this method is capable of constructing mesoporous film by means of a sol solution drop process. It has strong potential for controlling the film fabrication area by the heating process or the heat distribution in the substrate, which is affected by electrode property, electrode shape, or thickness of substrate. Furthermore, this method demonstrates the potential for making mesoporous film easily anywhere in the heating area of the heater electrode. It therefore offers an advanced and elegant technique for assembling mesoporous films for device applications.

On the other hand, according to previous mesoporous film formation reports on the dip-coating method, the mesostructured film must form within 30 s of drying.^{7,11,12} Therefore, in our substrate heating method, enough heat must be applied to the sol solution to evaporate the solvent within 30 s. Hence, SBA-15 and SBA-16 films need to be subjected to the 11.7 and 16.1 V temperature profiles in Figure 1, respectively. In particular, their in-

itial properties are significantly affected by evaporation of the main solvent, EtOH. It is very difficult to control these kinds of evolution of heat in a conventional furnace. In our method, however, the direction of heat conduction is from the substrate to the solvent, which makes it ideal for controlled evaporation of solvent.

Our substrate heating method can be used to prepare SBA-15 and SBA-16 type mesoporous films which are equivalent to those prepared using the spin- and dip-coating methods. Furthermore, this method has potential for controlling the coating area, since it forms the mesoporous film by simply heating the surface of the substrate. This method can be used to construct film not over the whole area of one side of the substrate as in the spin-coating method, or on both sides of the substrate, as in the dip-coating method, but on just the heated area of the substrate.

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