Phase Transformation from Lamellar to Hexagonal in Mesostructured Silica Thin Films by a Water Vapor Hydrothermal Method

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The phase transformation from lamellar to 2-dimensional (2D) hexagonal structure has been observed in mesostructured silica thin films, synthesized using a self-assembly triblock copolymer ($EO_{20}PO_{70}EO_{20}$, P123) as a template, during heat treatment under water vapor hydrothermal conditions.

There have been numerous reports dealing with the synthesis of mesoporous silica materials with various mesostructures, such as lamellar,[1] hexagonal,[2] and cubic[3] ones. The desired mesostructure of the silica materials can be estimated by controlling some phase-determining factors such as charge density matching between surfactant and silica species,[4] and the surfactant packing parameters.[5] Moreover, using the same ideas has made the transformation possible from one kind of mesostructure to another since Monnier[6] (1993) found the first lamellar-to-hexagonal phase transformation. To our knowledge, however, the phase transformation in mesostructured silica materials has been mostly studied in powder form[7] by heating as-made samples in water, and the templates used are always electric surfactants (such as cethyltrimethylammonium bromide, C_nTABr), which can lead the change of charge density matching or surfactant packing parameter. In contrast, this method is not suitable for thin film samples prepared with a neutral surfactant (such as P123) because thin films will be peeled off easily from the substrate while heating in water. Most recently, the phase transformation during the cubic mesostructured silica film formation has been reported using the C_nTABr as template.[8] Although the phase transformation is very quickly (in 20 s) as reported, it may therefore hinder the further application of the phase transformation due to the fast process. Here we report a phase transformation from lamellar to 2-dimensional (2D) highly ordered hexagonal in mesostructured silica thin films, synthesized with P123 as a template, during heat treatment of the lamellar mesostructured thin films under water vapor hydrothermal conditions.

Silica/surfactant mesostructured thin films were prepared as follows: tetraethyl orthosilicate (TEOS, 98%, Wako) was partially hydrolyzed under a strong acidic condition (pH 2)[9] at 60 °C for 2 h, and then mixed with a triblock copolymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$, Aldrich) ethanol (EtOH) solution. In this study, the final precursor solution with the compositions of 1TEOS: 0.01 $EO_{20}PO_{70}EO_{20}$: 30EtOH: 0.12HCl: 11.5H_2O (in molar ratio) was prepared and spin cast coated on glass substrates to form thin films. Lamellar structured silica thin films were obtained by aging the deposited films at room temperature (R.T.) for 24 h. The water vapor hydrothermal conditions were carried out by placing the lamellar structured thin film samples in a glass container with an ample of water, and heating from R.T. to 150 °C with varied ramp rates (1 to 3 °C/min) in an electric furnace (Miwa, MT-1100). Inside the glass container, the film sample was exposed to water vapor atmosphere, which was produced as the temperature increased. Mesostructures of the synthesized silica thin films were characterized with small angle X-ray diffractometry (SA-XRD, Rigaku-Rint2000, Cu Kα), field-emission scanning electron microscopy (FE-SEM, Hitachi S5000), and transmission electron microscopy (TEM, Hitachi800, 200 kV).

Figure 1 shows the XRD patterns indicating the transition from lamellar to hexagonal phase in mesostructured silica thin films heat-treated at a ramp rate of 1 °C/min from R.T. to 150 °C under a water vapor hydrothermal condition. After aging as-made films at R.T. for 24 h (trace A), the XRD pattern showed three evenly spaced peaks corresponding to the (001), (002), and (003) reflections of a lamellar structure. The presence of strong (001) and (003) diffraction peaks and a weak (002) peak indicate the formation of highly ordered alternating silica/surfactant layers in films,[10] which can be evidenced by the TEM image shown in Figure 2a. While heating lamellar structured films under a water vapor hydrothermal condition, the (002) peak of lamellar structured films disappeared at about 80 °C (trace B) and the (200) peak of hexagonal structured films appeared at about 110 °C (trace C). After heating up to 150 °C (trace D), the XRD pattern of the transformed film showed four well-resolved peaks in the range of 0.7–6°, which can be indexed as (100), (200), (300), and (400) reflections of a highly ordered 2D hexagonal (*p*6mm) mesostructure. The appearance of only (h00) peaks in the XRD pattern

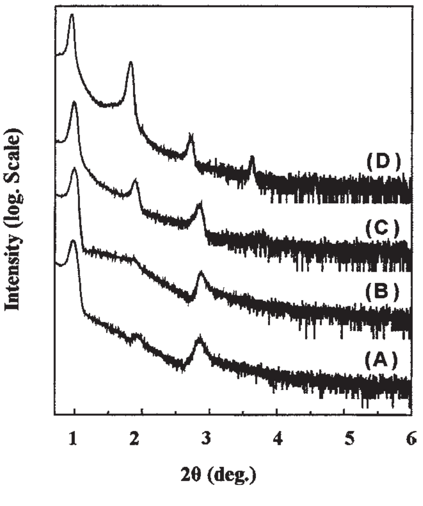

Figure 1. Small-angle XRD patterns corresponding to a lamellar-to-hexagonal phase transformation in mesostructured silica thin films synthesized using $EO_{20}PO_{70}EO_{20}$ surfactant. The sample was heated under a water vapor hydrothermal condition, where the temperature was ramped at a rate of 1 °C/min from 25 °C (trac A), to 80 °C (trace B), 110 °C (trace C), and 150 °C (trace D), respectively.

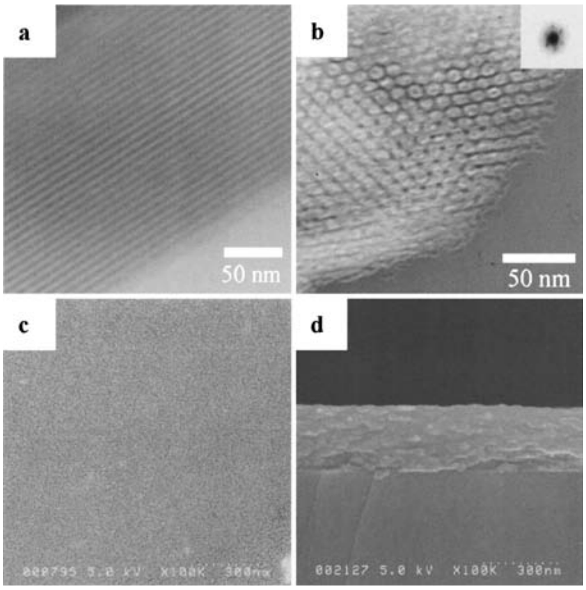

Figure 2. a,b) TEM images of a) lamellar structured films before phase transformation along [100] zone axes and b) hexagonal structured films after phase transformation along [1001] zone axes. c,d) SEM micrographs of c) surface and d) cross section of phase transformed hexagonal silica films after calcination.

for hexagonal mesostructured films has been interpreted that pore channels in the film are highly oriented and parallel to the substrate surface,[11] which can obviously be seen from a cross-section TEM image (Figure 2b). The transformed films are transparent and continuous with smooth surfaces and mesostructures (see Figure 2c, d).

After calcination at 450 °C for 4 hours to remove the surfactant template, the five diffraction peaks in the XRD pattern for the transformed hexagonal films are still observed (Figure 3a); however, the XRD peaks for the lamellar structured films (Figure 3b) became broad and shifted to larger angles due to the collapse of the structure.[12] This can also prove the phase transformation of the mesostructures in silica films.

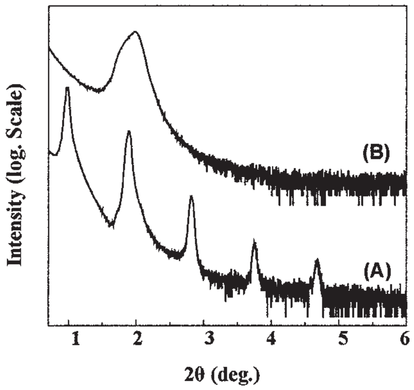

Figure 3. XRD patterns of mesoporous silica thin films with (A) hexagonal structure and (B) lamellar structure after calcination in air at 450 °C for 4 h.

We have tried to calculate the activation energy of the lamellar-to-hexagonal phase transformation in films by measuring the transition temperatures at varied ramp rates according to Ozawa equation[13] ($\ln(\text{ramp rate}) = -E_{\text{activation energy}}/RT_{\text{transition temp}} + c$). However, the film samples heated under water vapor hydrothermal conditions were hard to be characterized by in situ XRD measurement. Therefore, the data of transition temperatures in this study were collected by *ex-situ* studies, where many samples were used to determine the transformation temperature at a fixed ramp rate. The ramp rates were varied from 1 to 3 °C/min. From the results, the transition was observed to occur at higher temperature at faster ramp rate. The estimated value of the activation energy was about 22 kJ/mol from the Ozawa equation,[13] which is much smaller than that in the powder cases as reported[14] (145 kJ/mol). The possible reasons may be due to the differences of sample forms (film versus powder), surfactant electricity (neutral versus electric), and the synthesis conditions. The exact mechanism and the reasons of such low activation energy for the phase transformation in the block copolymer templated films are now in progress to investigate.

In summary, we have observed the phase transformation from lamellar to 2D highly ordered hexagonal in mesostructured silica thin films by heating as-made film samples under water vapor hydrothermal conditions. XRD patterns show the gradual transition process, and the SEM and TEM images prove that the transformed films are transparent with smooth surface and highly ordered mesostructures. This phase transformation process not only benefits us to understand the mesophase formation mechanism during the synthesis of mesoporous silica thin films with block copolymer as template, but also is expected to supply a novel pathway to prepare highly ordered mesoporous thin films via precise control of the phase transformation process.

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