Critical Effect of Surfactant Concentration on the Structure of Mesoporous Silica Films Prepared on a Substrate Coated with Rubbing-Treated Polyimide

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The change of nonionic surfactant $C_{16}(EO)_{10}$ (Brij56) concentration has a critical effect on the structure of mesoporous silica films grown hydrothermally on a substrate coated with a rubbing-treated polyimide film. The uniaxially aligned two-dimensional (2D) hexagonal mesoporous structure changes into a "single-crystalline" three-dimensional (3D) hexagonal structure, which means that the in-plane arrangement of spherical pores of the 3D-hexagonal structure is fully controlled, by simply decreasing the surfactant concentration. The investigation of the early stages of the film formation suggests that the initial formation of the uniaxially aligned tubular micelles and the subsequent transformation to the spherical ones are included in the formation mechanism. It is considered that such a transformation is caused by the increase in the size of headgroups of the building units, consisting of the surfactants and silica oligomers, due to the progress of silica condensation. The small association number of surfactant molecules in the building units would allow the growth of silica oligomers in the headgroups to the level that induces the total restructuring.

Introduction

Transparent mesoporous silica films with regular porous structures and high surface areas[1−22] have widely been investigated by many research groups because of their potential applications to various optical and electronic devices.[23−26] These films can be prepared either by hydrothermal deposition, which is based on heterogeneous nucleation and growth of mesostructured silica seeds,[1−12] or by the so-called evaporation-induced self-assembly (EISA) process.[13−22] The hydrothermal deposition method is advantageous because the method is highly reproducible and the reactions are well-controlled in a closed vessel without being influenced by ambient factors such as humidity,[18] although the kind of substrates that afford continuous films is limited.

Our group has succeeded in the alignment control of mesochannels in mesoporous silica films prepared hydrothermally using the interactions between surfactants and

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substrate surfaces.[7-11] Uniaxial alignment of mesochannels is brought about by the interfacial hydrophobic interactions between alkyl chains of surfactants and the elongated polymer chains of rubbing-treated polyimide.[10,11,22] The control of the in-plane arrangement of mesochannels in films is important for several applications because films with aligned mesopores can provide anisotropic properties by incorporating various guest species.[27,28] Recently, we reported the formation of silica films with a "single-crystalline" mesoporous structure, in which the in-plane arrangement of spherical mesopores is fully controlled, by mixing surfactants with larger headgroups, under the same hydrothermal preparation conditions.[12] It is suggested that the single-crystalline mesoporous structure is formed through a phase transition from an aligned immature 2D-hexagonal structure.[12]

In general, surfactant concentration is one of the critical parameters that determines mesostructures.[29-32] It is known, in homogeneous systems, that the curvature of surfactant assemblies tends to become higher with the decrease in the surfactant concentration and that a cagelike structure is consequently formed.[29,30] Because the local concentration of surfactants on substrates may be proportional to those in reactant solutions, a similar structural change into a cagelike structure can also be expected for films by reducing the surfactant concentration. In fact, the present study clarifies that mesostructured silica films with a high structural regularity can be grown in a solution even when the concentration is very low. The local concentration of the surfactants on substrates is considered to be higher than that in a bulk solution.[31] Therefore, such a structural change of the films into a cagelike structure should take place in the conditions with much dilute surfactant concentrations than those affording a structural change in precipitated mesostructured silica particles.

Here, we report a remarkable structural change of mesostructured silica films, from a uniaxially aligned 2D-hexagonal to single-crystalline 3D-hexagonal structure, on a rubbing-treated polyimide film at an extremely dilute concentration of nonionic surfactant, $C_{16}(EO)_{10}$ (Brij56). The single-crystalline mesoporous silica film can be formed without adding a surfactant with a different size of hydrophilic part, unlike that in our previous paper,[12] and the most appropriate concentration that affords the highest structural regularity was 1/50 of that providing the uniaxially aligned 2D-hexagonal films.[11]

Under the conditions of such an extremely dilute surfactant concentration, the concomitantly precipitated mesoporous silica particles do not show structural regularity. This is the evidence that the local concentration of the surfactant on the substrate is much higher than that in the bulk solution presumably by strong adsorption.

The investigation at the early stages of the film growth shows that the aligned 2D-hexagonal-like structure, which is initially formed on the substrate surface, transforms into the 3D-hexagonal-like structure with high in-plane structural regularity. This suggests that the behavior of the surfactant assembly in heterogeneous conditions is considerably different from that in homogeneous solutions, and it is expected that novel mesostructures that are allowed only in the films can be obtained by modifying the reaction conditions.

Experimental Section

Preparation of Substrates with a Rubbing-Treated Polyimide Coating. Substrates were coated with a polyimide precursor (polyamic acid) by spin coating and baked at 200 °C for 1 h in an air atmosphere for the formation of a polyimide film. Both silica glass and silicon wafers were used as the substrates. The polyimide film on the substrates underwent a rubbing treatment using a nylon-covered cylindrical roller. The details of the rubbing treatment are described previously.[10]

Preparation of Mesoporous Silica Films. Mesostructured silica films were hydrothermally deposited on the substrates. A nonionic surfactant, $C_{16}(EO)_{10}$ (Brij 56), was used as a structure-directing agent. For the formation of mesostructured silica films, the substrates with rubbing-treated polyimide films were kept in reactant solutions containing $C_{16}(EO)_{10}$, hydrochloric acid (HCl), and tetraethoxysilane (TEOS). The molar ratios of the solutions, $C_{16}(EO)_{10}$:TEOS:HCl:H_2O, were 0.1:0.05−0.2:3:100 (denoted as higher surfactant concentration) for the preparation of 2D-hexagonal films,[11] and 0.002:0.1−0.3:3:100 (lower surfactant concentration) for the 3D-hexagonal film formation, respectively. The substrates were kept in the solutions for 5 days at 80 and 60 °C for 2D-hexagonal and 3D-hexagonal films, respectively. The surfactants were removed by calcination under an air atmosphere at 400 °C for 5 h.

Characterization. The $\theta-2\theta$ scanning X-ray diffraction (XRD) was performed with a MAC Science M03XHP22 diffractometer using Mn-filtered Fe Kα radiation under the operating conditions of 40 kV and 20 mA. In-plane XRD patterns were recorded with a RIGAKU ATX-G diffractometer with a 4-axis goniometer using Cu Kα radiation under the operating conditions of 50 kV and 300 mA, and a soller slit with a vertical divergence of 0.48° was used to obtain a parallel beam. The incident angle of X-ray in the in-plane geometry was 0.2°. TEM images were taken on an Hitachi H-800 at an accelerating voltage of 200 kV.

Results

Mesoporous Silica Film Prepared with the Higher Surfactant Concentration. The continuous and optically transparent film prepared under the conditions of the higher surfactant concentration, with the TEOS/$C_{16}(EO)_{10}$ ratio of 1.0/1.0, was characterized by XRD. The profile of the $\theta-2\theta$ scanning XRD (Figure 1, trace A) is consistent with the 2D-hexagonal structure, and the anisotropy of the in-plane XRD profiles (Figure 2 A) and the profile of the in-plane rocking curve (Figure 3 A), recorded for the diffraction peak at $2\theta\chi = 1.2°$, show that the tubular mesochannels are aligned perpendicularly to the rubbing direction. Although the structural period along the direction of the film thickness was considerably shrunk, the in-plane structure was completely retained after the removal of the surfactants by

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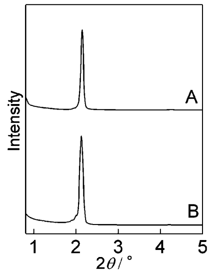

Figure 1. $\theta-2\theta$ scanning XRD patterns of mesostructured silica films. The molar ratios of the reactant solutions, $C_{16}(EO)_{10}$:TEOS:HCl:H_2O, were (A) 0.1:0.1:3:100 and (B) 0.002:0.2:3:100.

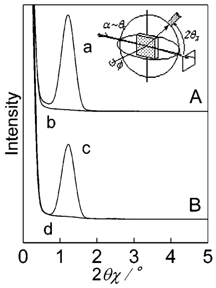

Figure 2. In-plane $\phi-2\theta\chi$ scanning XRD profiles of the mesostructured silica films. The molar ratios of the reactant solutions, $C_{16}(EO)_{10}$:TEOS:HCl:H_2O, were (A) 0.1:0.1:3:100 and (B) 0.002:0.2:3:100. (a, c) Rubbing direction ⊥ X-rays and (b, d) rubbing direction // X-rays at $\phi = 0°$. Inset: scanning axes of the in-plane XRD geometry.

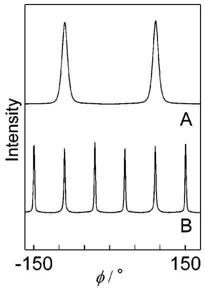

Figure 3. In-plane ϕ scanning profiles of mesostructured silica films. The molar ratios of the reactant solutions, $C_{16}(EO)_{10}$:TEOS:HCl:H_2O, were (A) 0.1:0.1:3:100 and (B) 0.002:0.2:3:100.

calcination (Supporting Information, Figure S1A). These data are all consistent with our previous report.[11]

Mesoporous Silica Film Prepared with the Lower Surfactant Concentration. The mesostructured film prepared under the conditions of the lower surfactant concentration, with the TEOS/$C_{16}(EO)_{10}$ ratio of 100/1.0, was continuous and optically transparent, similar to the uniaxially aligned 2D-hexagonal film described above. However, the optical micrographs of the films (Figure S2) indicate the structural difference between the two films. The characteristic texture, which is observed for aligned 2D-hexagonal films,[10,11] was not observed in the film prepared under the conditions of lower surfactant concentration.

Trace B in Figure 1 shows the $\theta-2\theta$ scanning XRD profile of the film prepared under the lower surfactant concentration. One strong peak was observed at a position of $d = 5.2$ nm. This shows that a highly ordered mesostructured film was prepared even under the very low concentration of the surfactant.

The in-plane $2\theta\chi-\phi$ scanning profiles of the film prepared under the lower surfactant concentration are shown in Figure 2B. Traces c and d were recorded with the sample geometries in which the rubbing direction was set perpendicular and parallel to the projection of the incident X-rays at $\phi = 0°$, respectively. A strong diffraction peak was observed at a position of $d = 7.2$ nm in trace c, but no substantial diffraction peaks were observed in trace d, showing the strong in-plane structural anisotropy of the film. Although the profiles shown in Figures 1 and 2 do not suggest remarkable structural differences between the two film samples, the in-plane rocking curve of the film prepared under the lower surfactant concentration unveiled the structural difference very clearly. Figure 3B is the in-plane ϕ scanning profile recorded at a position of $2\theta\chi = 1.2°$ by fixing the detector. Substantially, identical six sharp diffraction peaks were observed with an interval of 60°, showing the formation of the mesostructure with 6-fold symmetry. Because of the very small incident angle of X-rays, this profile shows that the in-plane arrangement of spherical surfactant assemblies is controlled over the entire surface of the substrate; that is, the film has a “single-crystalline” mesoporous structure.[12] The in-plane ϕ scanning profile of the film did not change by calcination (Figure S1 B) although the large shrinkage along the thickness direction took place, showing that the in-plane structural regularity is completely retained.

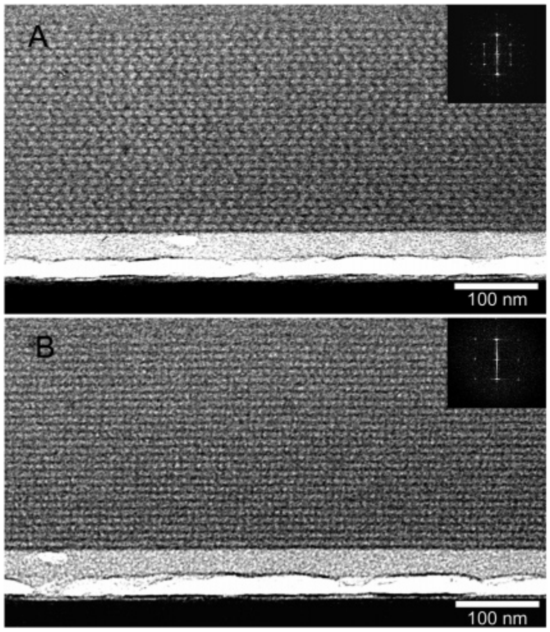

Figure 4. Cross-sectional TEM images of mesostructured silica films prepared with the lower surfactant concentration. The tilt angles are (A) $\phi = 30°$ and (B) $\phi = 0°$. Inset: corresponding two-dimensional fast Fourier transformation patterns.

Figures 4A and 4B show the cross-sectional TEM images of the as-grown film prepared under the lower surfactant concentration. The tilt angles are (A) $\phi = 30°$ and (B) $\phi = 0°$, respectively. These images, as well as the two-dimensional fast Fourier transformation patterns of the images (insets), are substantially the same as those observed for the single-crystalline 3D-hexagonal structure prepared by adding another surfactant with a large headgroup,[12] and consistent with the 3D-hexagonal structure consisting of spherical micelles.

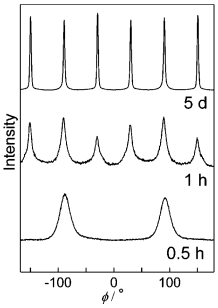

Figure 5. In-plane ϕ scanning profiles at the early stages of the mesostructured silica films prepared.

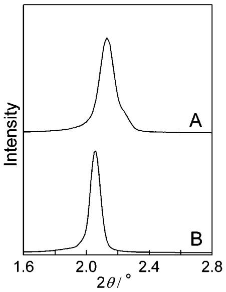

Figure 6. $\theta-2\theta$ XRD patterns of the mesostructured silica films prepared under the different TEOS/surfactant ratios; TEOS/surfactant = (A) 100/2.0 and (B) 100/4.0.

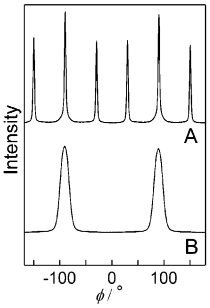

Figure 7. In-plane ϕ scanning profiles of the mesostructured silica films prepared under the different TEOS/surfactant ratios; TEOS/surfactant = (A) 100/2.0 and (B) 100/4.0.

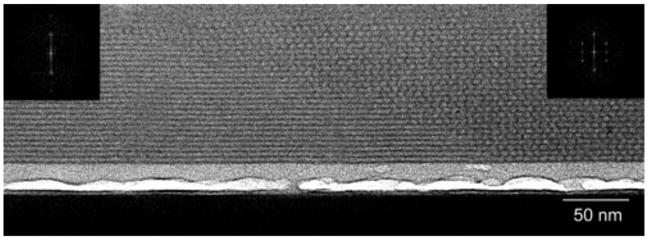

Figure 8. Cross-sectional (sliced parallel to the rubbing direction) TEM image of a mesostructured silica film prepared under the TEOS/surfactant = 100/2.0. Inset: corresponding two-dimensional fast Fourier transformation patterns.

These results show that the single-crystalline 3D-hexagonal mesoporous structure can be formed by simply decreasing the surfactant concentration, without mixing any surfactants with different packing parameters,[33] and suggest the critical effect of the surfactant concentration on the mesostructure.

Formation Process of the Silica Film with a Single-Crystalline Mesoporous Structure. To investigate the formation process of the film with a single-crystalline mesoporous structure prepared under the lower surfactant concentration, the structures of the films were investigated after the short reaction periods. Figure 5 shows the in-plane ϕ scanning profiles of the films grown for 0.5 and 1 h. For comparison, the profile after the growth for 5 days is also shown. The film grown for 0.5 h provides only two diffraction peaks, but six diffraction peaks are observed after 1 h. These results show that the preferentially aligned 2D-hexagonal-like structure, presumably consisting of tubular micelles, is formed in the beginning of the film formation, and that it transforms to the 3D-hexagonal-like structure with spherical micelles, keeping the macroscopic arrangement.

Dependence of the TEOS/Surfactant Ratio on the Mesostructure. The mesostructure of the film prepared under the conditions of the lower surfactant concentration also depends on the TEOS/surfactant ratio. The $\theta-2\theta$ scanning XRD profile of the as-grown film prepared with the molar ratio of TEOS/surfactant 100/2.0 is shown as trace A in Figure 6. A strong peak ($d = 5.2$ nm) accompanied by a shoulder in the higher angles was observed. The existence of the shoulder suggests that the formed structure is not uniform. The in-plane ϕ scanning profile of this film is shown as trace A in Figure 7. The six sharp diffraction peaks were also observed in this case, but two out of the six peaks at ±90° were selectively large. This profile is consistent with the structure of the single-crystalline 3D-hexagonal structure containing a small part of uniaxially aligned 2D-hexagonal structure. This is confirmed by the TEM image shown in Figure 8, which clearly shows the coexistence of both structures in the film. The TEM image and the two-dimensional fast Fourier transformation patterns in the insets show that the structural period of the 2D-hexagonal domain in the thickness direction is smaller than that in the 3D-hexagonal domain, which is consistent with the observed profile of the $\theta-2\theta$ scanning XRD showing the nonuniformity (Figure 6 A). This can be geometrically explained; that is, the different structural periods come from the difference in the packings between the tubular and the spherical micelles.

When the TEOS/surfactant is 100/4.0, the structure of the film drastically changed though the concentration of the surfactant is kept very low. The $\theta-2\theta$ scanning XRD profile of the as-grown film prepared under this molar ratio is shown as trace B in Figure 6. A diffraction peak was observed at a position of $d = 5.3$ nm. The diffraction profile without a shoulder indicates that the film has a uniform structure. The structure of this film is unveiled by the in-plane XRD. The in-plane rocking curve recorded for this film (trace B, Figure 7) shows that the six peaks were not observed anymore and two relatively broad peaks were observed at the positions of ±90°. This profile proves that the uniaxially aligned mesoporous structure was formed again by decreasing the TEOS/surfactant molar ratio. As explained above, the TEOS concentration with respect to surfactant is a very important parameter that determines the mesostructure grown on the substrate.

Dependence of the Temperature on the Mesostructure. The mesostructure of the film grown on the substrate is related to the micelle conformations in the reactant solution. Here we examined the influence of the synthetic temperature

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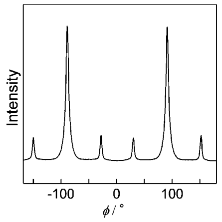

Figure 9. In-plane ϕ scanning profile of the mesostructured silica film prepared at 80 °C.

on the structure of the film prepared under the conditions of the lower surfactant concentration. We prepared a film by raising the synthetic temperature from 60 to 80 °C using the same reactant solution that was used for the preparation of the film with the uniform single-crystalline 3D-hexagonal structure (TEOS/surfactant = 100/1.0). The in-plane ϕ scanning profile of the film prepared under the synthetic temperature of 80 °C is shown in Figure 9. Six sharp diffraction peaks were observed, but the two peaks at ±90° were selectively strong as in trace A in Figure 7. This indicates the coexistence of the two structures dominated by the 2D-hexagonal domains. These results show that the preparation temperature can change the controlled mesostructure of the film without changing the composition of the solution.

Discussion

Formation Mechanism of the 3D-Hexagonal Structure. In the present study, we could obtain a single-crystalline 3D-hexagonal mesoporous silica film under the conditions of extremely low surfactant concentration with an optimized TEOS/surfactant molar ratio. The small association number of the surfactant molecules in the dilute solution, coupled with the increased headgroup size resulting from the large TEOS/surfactant molar ratio, causes the change of the effective packing parameter of the silica-surfactant building units, and consequently, the curvature of the surfactant micelles wrapped by silica is increased.

The mesoporous silica films in this study, prepared under strong acidic conditions, are considered to be formed through the $(S^0H^+)(X^-I^+)$ pathway.[29] Under these strongly acidic conditions, the ethylene oxide moieties of $C_{16}(EO)_{10}$ charges positively by protonation,[29] and these moieties electrostatically interact with positively charged silica oligomers intermediated by negative halide ions. The progress of silica condensation decreases the density of the positive charge on the siliceous species located at the hydrophilic part of surfactants, and consequently, the size of silica, which electrostatically interacts with the surfactant hydrophilic group, is increased. This leads to the change of the packing parameter of the silica-surfactant building units, which results in the increase of the curvature of the assemblies. The curvature becomes too large to keep the cylindrical morphology, and then the shape of the building units changes to the spherical one that allows such a large curvature.

In this formation mechanism, the possibility of the formation of a cubic phase under the presence of nonionic surfactants cannot completely be excluded. However, all the cross-sectional TEM images indicate the formation of only the 3D-hexagonal structure in this study. It is considered that the 3D-hexagonal structure is most stable thermodynamically, and the mesostructure in the initial film with immaturely condensed silica walls gradually transforms to the most stable structure.

When the concentration of the surfactants is high enough, the increased intermolecular interactions in the micelles, caused by the large association number, would not allow the total morphological change of the building units, and consequently a 2D-hexagonal structure would be preferentially formed.

Even under the preparation conditions with such a low surfactant concentration, the structural change becomes incomplete when the parameters, affecting the packing parameter of the building units, are not optimized. When the molar ratio of TEOS/$C_{16}(EO)_{10}$ was decreased, the headgroup size of the silica-surfactant building units becomes smaller, and the consequent incomplete change from the tubular to the spherical morphologies lead to the observed intermediate structure consisting of the 2D-hexagonal and 3D-hexagonal structures. This is consistent with the fact that the further decrease of the TEOS/$C_{16}(EO)_{10}$ ratio provides the uniform structure consisting of uniaxially aligned mesochannels.

The synthetic temperature also causes the change of the packing parameter. When the temperature was increased, the hydrophilicity of the PEO moieties is reduced by the increased motion of water molecules.[34−36] This leads to the decrease of the effective headgroup size of the silica-surfactant building units. Condensation of silanol groups increases with the temperature, which may increase the effective headgroup size of the silica-surfactant building units. However, the result shows that the 2D-hexagonal mesostructure was predominant with the rise of the temperature. This means that the decrease of the hydrophilicity and the related conformation change of the surfactant assembly dominate the final structure.

We tried to prepare similar single-crystalline mesoporous silica films using a cationic surfactant (hexadecyltrimethylammonium chloride (C_{16}TAC)) under the low concentration because a mesoporous silica film with a uniaxially aligned 2D-hexagonal structure can be prepared under relatively higher concentrations of C_{16}TAC.[10] The reactant solution with the similar molar ratio of the components under the low concentration resulted in the formation of a film that provides no diffraction peaks, indicating the lack of mesostructure. Because the critical micelle concentration of C_{16}-TAC is about 10 times higher than that of Brij56,[37,38] the spherical micelle formation does not take place for C_{16}TAC. The optimum selection of surfactants is important to obtain a mesoporous silica film with single-crystalline porous structure through the hydrothermal reaction.

Control of the In-Plane Arrangement of the Spherical Pores. Figure 10 shows the schematic formation mechanism

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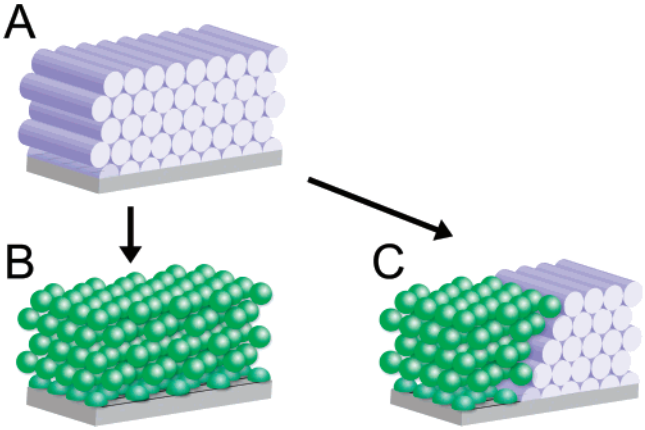

Figure 10. Illustration of the formation processes of silica thin films with single-crystalline mesoporous structure. (A) Early stage of the film formation indicating a uniaxially aligned mesoporous structure. (B) Single-crystalline mesoporous structure formed by the transformation from a uniaxially aligned mesoporous structure. (C) Single-crystalline mesoporous structure with 2D-hexagonal domains formed by the transformation from a uniaxially aligned 2D-hexagonal mesoporous structure.

of the film with a single-crystalline mesoporous structure prepared under the conditions of low surfactant concentration. As shown in Figure 5, the uniaxially aligned mesoporous structure, likely to be 2D-hexagonal, is formed at the early stages of the film formation. When the substrates were contacted with a reactant solution, surfactant molecules would be adsorbed on the rubbing-treated polyimide surface, and an adsorption layer would be formed. The hydrophobic interactions between the alkyl chains of the surfactant molecules and the polyimide chains have the surfactant molecules adsorbed parallel to the polymer chains. The preferred adsorption of the surfactant molecules on the anisotropic polymer surface leads to the formation of a mesostructure in which the tubular pores are aligned perpendicularly to the rubbing treatment, just like the formation of aligned 2D-hexagonal mesostructured silica films (Figure 10A).[11]

With the progress of the condensation of silanol groups, the charge density of the siliceous species at the hydrophilic region decreases, and consequently, the size of headgroups of the silica-surfactant building units increases. This leads to the increase of the curvature of the silica-surfactant assemblies, and eventually the tubular assemblies transform into spherical ones. The phase transformation would take place thermodynamically to make the total energy of the system minimum, and this would suppress the formation of the stacking faults and prompt the formation of the single-crystalline mesostructure (Figure 10B). If the TEOS/$C_{16}(EO)_{10}$ ratio becomes smaller or the synthetic temperature becomes higher, the size of the headgroup would be insufficient to cause the total structural transformation to spherical assembly, resulting in the formation of the mixed phase (Figure 10C). The observed nonuniformity suggests the uneven adsorption of the surfactants at the early stages of the film formation. Although the total structure was thus changed, the first layer might still have a tubular structure because of the higher concentration of the surfactants on the surfaces.

Conclusion

Mesoporous silica films with the uniaxially aligned 2D-hexagonal and the single-crystalline 3D-hexagonal structures were prepared on a substrate coated with rubbing-treated polyimide film by simply changing the concentration of nonionic surfactant, $C_{16}(EO)_{10}$. It is considered that the small association number of the surfactant molecules in a micelle, coupled with the large TEOS/surfactant molar ratio, allows the increase of the headgroup of the silica-surfactant building units to a level that afford the morphological transformation of the silica-surfactant assembly. The decrease of the TEOS/surfactant molar ratio as well as the rise of the synthetic temperature led to the formation of a nonuniform film consisting of 2D-hexagonal and 3D-hexagonal structures. The use of an appropriate surfactant with optimized synthetic conditions is very important for the strict control of the mesostructure in mesoporous silica films grown hydrothermally. The preparation of silica films with novel mesoporous structures controlled macroscopically is expected through the fine control of preparation conditions on a substrate with structural anisotropy.

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Supporting Information Available: Figure of in-plane ϕ scanning profiles of the calcined mesoporous silica films and optical microscopic images of the as-grown mesostructured silica films (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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