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Preparation of a Mesoporous Silica Film with a Strictly Aligned Porous Structure through a Sol−Gel Process

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A novel strategy for the preparation of a mesoporous silica film, in which the in-plane alignment of the honeycomb packed mesochannels is strictly controlled, is developed. The highly aligned porous structure is achieved by using a substrate with a rubbing-treated polyimide coating in the evaporation induced self-assembly process. It is shown that the controlled porous structure is formed over the entire thickness of the film and that the alignment distribution is much narrower than that in the films prepared by the conventional process based on a heterogeneous nucleation and growth mechanism. In the present process, the aligned porous structure would be formed through a directional lamellar-to-hexagonal phase transition from the substrate surface toward the air/film interface. The new formation mechanism as well as the lower process temperature enables the observed strict alignment control of the mesochannels.

Introduction

Films of mesoporous silica prepared through self-assembly of surfactants are promising materials for future applications in optical and electronic molecular devices because of their optical transparency and high structural regularity.[1−10] Mesoporous silica films with hexagonally packed tubular mesochannels are of special interest because their anisotropic nanospaces can be used for anisotropic accommodation of various guest species.[11−14] Ideally, the porous structure has to be macroscopically controlled for optimal application of the anisotropic nanospaces because the properties of the films become macroscopically isotropic due to domain randomization when the alignment direction of the mesochannels is not controlled. Several methods, such as the use of a strong magnetic field or reactant flow, have been proposed for the macroscopic alignment control of mesochannels.[15−18] We have shown that substrates with surface structural anisotropy, such as a glass substrate with rubbing-treated polyimide coatings, can be effectively used for the preparation of mesoporous silica films with uniaxially aligned porous structure.[19−23] Our conventional preparation is based on heterogeneous nucleation and growth of mesostructured silica seeds on the substrates. In that process, surfactant molecules and silica oligomers are directionally deposited slowly on the anisotropic substrate surface from a dilute solution under the critical micelle concentration. This process requires harsh reaction conditions, high temperature, and high acid concentration, as well as a long preparation time for the film.

Here, we report a novel and facile strategy for the preparation of a mesoporous silica film with a highly aligned porous structure. We prepared a mesostructured silica film on a glass substrate with a rubbing-treated polyimide coating by the evaporation induced self-assembly (EISA) process, which is based on sol−gel chemistry. A simple dip-coating process leads to the formation of a mesostructured silica film in which the mesochannels are aligned perpendicularly to the rubbing direction with a very narrow directional distribution. The alignment of the pores is controlled over the entire

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thickness of the film. The alignment direction is independent of the coating direction, showing strong interactions between the surfactant molecules and the polymeric substrate surface. In this process, it is considered that aligned tubular micelles are formed on the substrate surface at the early stages of the film formation and that the total hexagonal structure is formed via a directional lamellar-to-hexagonal phase transition, from the substrate surface toward the air interface, using the aligned surface micelles as a scaffold.

The present strategy is versatile and can be extended to the alignment control of the other mesostructured materials, such as non-siliceous oxides and organosilicas. Moreover, the relatively mild condition increases the variety of usable substrate materials. The combination of various host materials with highly aligned mesoporous structures and diverse functional guest species will open the gate for new molecular devices fabricated through self-assembly.

Experimental Procedures

Preparation of the Substrate. The polyimide that undergoes rubbing treatment contains a flexible hexamethylene group, as described in our previous papers.[21−23] The polyimide film is formed on a glass substrate (Corning 7059) through spin-coating of the corresponding polyamic acid and subsequent thermal imidation (200 °C for 1 h). The thickness of the polyimide was about 10 nm as determined by ellipsometry. The polyimide film on the substrate underwent rubbing treatment using a nylon-covered cylindrical roller. The details of the rubbing treatment are described elsewhere.[21]

Preparation of the Mesoporous Silica Film. The mesoporous silica film was prepared through the EISA process. Polyoxyethylene-10-cetyl ether ($C_{16}EO_{10}$) and tetraethoxysilane (TEOS) were sequentially dissolved in ethanol (EtOH), and then 0.1 M hydrochloric acid (HCl) and water were added to this solution. The final composition of the precursor solution is $C_{16}EO_{10}$ 0.08/TEOS 1.0/EtOH 22/H_2O 5/HCl 0.004. After 2 h of stirring, the substrate was dip-coated with this precursor solution and subsequently dried for 24 h in a 25 °C 50% RH atmosphere. Dip-coating was done with the withdrawal direction of the substrate both parallel and perpendicular to the rubbing direction. The surfactant was removed by calcination at 400 °C for 10 h in air.

Characterization. The porous structure of the films was elucidated by X-ray diffraction (XRD). Conventional $\theta-2\theta$ scanning XRD was performed with a Philips X-pert Pro using Cu Kα radiation. The in-plane XRD patterns were recorded with an X-ray diffractometer equipped with a four-axes goniometer (Rigaku ATX-G) using Cu Kα radiation. The incident angle of X-rays in the in-plane geometry was set to 0.2°. The image of cross-sectional transmission electron microscopy (TEM) was recorded on a Hitachi H-800 at an accelerating voltage of 200 kV.

Results and Discussion

Figure 1 shows the XRD patterns recorded for the film before (traces A and B) and after (traces C and D) surfactant removal. The coating direction was parallel to the rubbing direction. Traces A and C and B and D are recorded with the sample geometry in which the rubbing direction of the substrate is perpendicular and parallel to the projection of the incident X-rays at $\theta = 0°$, respectively. The patterns of the as-deposited film (traces A and B) are consistent with the two-dimensional (2-D) hexagonal mesostructure with the mesochannels parallel to the substrate surface, and the peaks were assigned to (01) and (02). A large shift in the positions and broadening were observed for the diffraction peaks through calcination, showing that the periodic structure is considerably shrinking along the vertical direction and that the order is lowered, although the porous structure is retained. An extra diffraction peak is observed in each diffraction pattern recorded in the perpendicular geometry (patterns A and C). These peaks can be assigned to $(\bar{1}1)$ and (10), which do not contribute to the XRD under the ideal $\theta-2\theta$ scanning geometry. In the present case, $(\bar{1}1)$ and (10) become observable, when the incident X-ray is directed parallel to the alignment direction of the mesochannels because of the finite X-ray divergence angle that is comparable to the small diffraction angles for these materials. It is worth noting that the positions of the diffraction peaks do not represent the actual lattice distances of $(\bar{1}1)$ and (10), although the positions of these diffraction peaks correspond to the lattice distances of twice of those of (01). With a simple geometrical reason, these lattice planes provide the diffraction peaks at such positions described previously. The observed anisotropy in the XRD patterns, which originated in the anisotropic mesoporous structure, is a proof of a uniaxially aligned channel structure, as shown in our previous paper.[23,24]

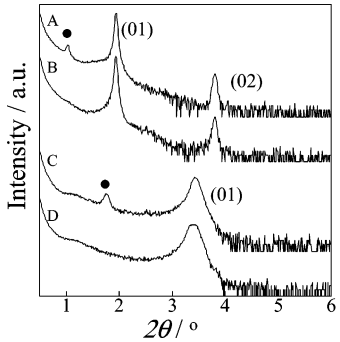

Figure 1. XRD patterns of the as-deposited film (traces A and B) and the calcined film (traces C and D). The projection of the incident X-rays is perpendicular (traces A and C) and parallel (traces B and D) to the rubbing direction. Extra peaks observed under a rubbing perpendicular to X-ray geometry are indicated by ●.

The alignment of the mesochannels was quantitatively evaluated by in-plane XRD.[19,21,23] Figure 2A shows the $\phi-2\theta\chi$ scanning profiles of the calcined film recorded with the geometry in which the rubbing direction of the substrate was perpendicular and parallel to the projection of the incident X-rays at $\phi = 0°$. The diffraction peaks, assigned as $(\bar{2}1)$ and $(\bar{1}1)$, are observed only when the rubbing direction is set perpendicularly to the projection of the incident X-rays. This clearly shows that the tubular pores are aligned perpendicularly to the rubbing direction. The observed alignment direction of the mesochannels, perpendicular to the rubbing direction, indicates that the alignment of the mesochannels has been controlled through the interfacial interactions between the polyimide chains and the surfactant molecules, as in the conventional films prepared through a heterogeneous nucleation and growth mechanism.[21,23] The parallel adsorption of the surfactant molecules

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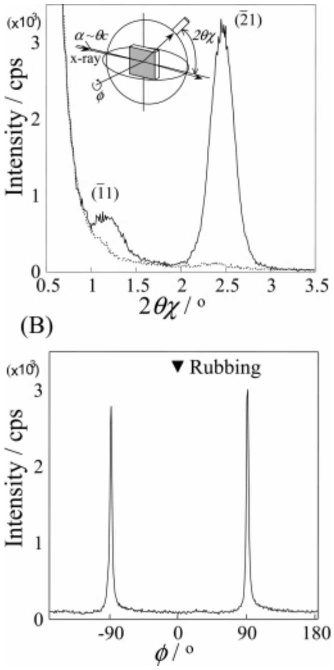

Figure 2. In-plane XRD profiles recorded for the calcined film. (A) ϕ-$2\theta\chi$ scanning profiles: the solid curve and the dotted curve are recorded under the geometry in which the incident X-ray is set perpendicularly and parallel to the rubbing direction, respectively. Inset: scanning axes of the in-plane XRD geometry. (B) ϕ scanning profile at $2\theta\chi = 2.48°$.

on the aligned polymer chains would lead to the preferred alignment of the mesochannels.

The position of the in-plane diffraction peaks was unchanged by calcination, showing that the horizontal structural period is preserved. The deviation from the ideal 2-D hexagonal structure calculated from the XRD data was 26% for as-deposited film and 58% for calcined film, respectively. The observed large vertical shrinking ratio indicates that the cross-linking level of the silica wall was quite low. Although the actual porous structure of these films thus deviates from the ideal 2-D hexagonal structure, all the XRD peaks in this paper have been assigned as using the 2-D hexagonal lattice for easier understanding.

To evaluate the degree of alignment, the in-plane rocking curve was recorded for the $(\bar{2}1)$ peak. Figure 2 (B) shows the ϕ scanning profile of the calcined film. Obviously, mesochannels are aligned perpendicular to the rubbing direction with a very narrow alignment distribution. The full width at half-maximum of the peak was estimated to be ~3°. This value is much smaller than that of our conventional aligned films prepared through heterogeneous nucleation and growth mechanism (11~12°).[23] The width of the diffraction peaks in the in-plane rocking curve has been changed very little through calcination, demonstrating that the thermal process does not disturb the in-plane alignment of the mesochannels.

The observed difference in the alignment distribution, between the present film and the conventional film,[23] comes from the differences in the formation mechanism and temperature. In the present method, condensation of silica in the pore wall predominantly proceeds slowly after the formation of the regular structure under relatively low temperature. Therefore, the surfactant micelles would be allowed to rearrange into the most stable structure. Smaller motion of the surfactant molecules on the substrate surface under lower temperature would also be favorable for the alignment of the surfactant micelles. On the other hand, in the conventional process, based on heterogeneous nucleation and growth mechanism, oligomeric silica would be deposited on the substrate followed by relatively fast condensation under higher temperature, and consequently, rearrangement into a more stable structure becomes difficult. Larger motion of the surfactant molecules on the surface at higher temperature would influence the alignment distribution.

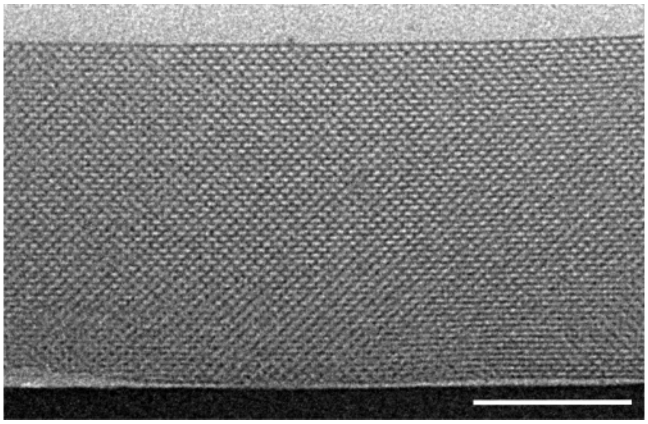

Figure 3. Cross-sectional TEM image of the as-deposited film sliced parallel to the rubbing direction. Scale bar: 100 nm.

Some reports show that the regular structure is formed only in the vicinities of the air/film and the substrate/film interfaces in a dip-coated film and that the middle of the film has a disordered structure.[1,25] This indicates the possibility that only a part of the present film, in the vicinity of the substrate, has the uniaxially aligned porous structure. However, the existence of the randomly aligned hexagonal structure at the air/film interface region is excluded by the in-plane ϕ-scanning profile. If such a region with random in-plane orientation would exist, undulation in the bottom of the in-plane ϕ-scanning profile should be seen because the diffraction intensity becomes maximum when the projection of the incident X-rays is parallel to the diagonals of the sample under the grazing incidence geometry for the in-plane XRD. Complete alignment of the mesoporous structure is undoubtedly proven by transmission electron microscopy. Figure 3 is the cross-sectional TEM image of the film sliced parallel to the rubbing direction. The formation of the aligned hexagonal porous structure over the entire thickness is confirmed.

The withdrawal direction of the substrate in the dip-coating process may affect the alignment direction of the mesochannels.[26] To check this, the film was prepared with a coating direction perpendicular to the rubbing direction. However, substantially no difference was observed in the ϕ scanning XRD profile. This shows that the alignment effect through the coating process is negligible as compared to the strong alignment effect by the rubbed polymer.

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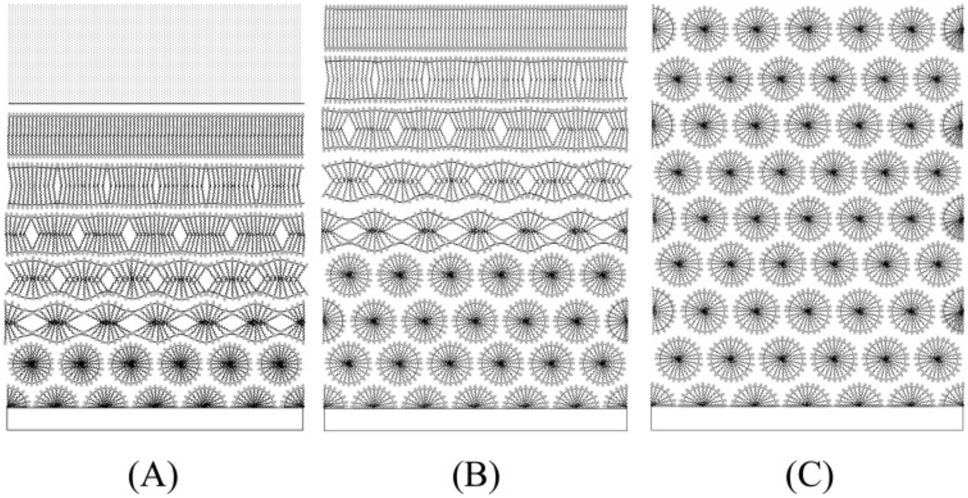

Figure 4. Schematic illustration of the formation mechanism of the uniaxially aligned mesoporous structure.

Because the alignment of the mesochannels is controlled over the whole film, there is no doubt that the hexagonal structure is formed from the substrate/film interface toward the film surface. The formation of a surface layer with unaligned hexagonal structure is prevented, obviously, by controlling the solvent evaporation process.

In the previous study using the same surfactant, the formation of an incipient lamellar structure via correlated micelle intermediate was reported.[25] It is reasonable to consider that the present hexagonal structure is also formed via such a lamellar structure. However, we have to take into account the hydrophobic nature of the polyimide surface. In the previous report, silicon wafers, whose surface is covered by a hydrophilic native oxide layer, were used. On hydrophilic silicon substrates, a fully lamellar structure can be formed because surfactant molecules can be accommodated perpendicularly on the surface with the hydrophobic tail groups outward. On the other hand, surfactant molecules would be adsorbed on the hydrophobic polyimide film parallel to the surface through strong hydrophobic interaction. Furthermore, the uniaxial alignment of the mesochannels perpendicular to the rubbing direction is only explainable by the anisotropic adsorption of the surfactant molecules along the rubbing direction.[21,23] Because the formation of a lamellar structure perpendicular to the surface, like a bookshelf, is highly unusual, it is probable to consider that hemicylindrical surface micelles are formed on the surface at the early stages in the film formation. Even when the surfactant concentration is lower than the critical micelle concentration, micelles can be formed on the surface because of the restriction of the motion. The formation of micelle multilayers on a graphite surface has been confirmed in a dilute surfactant solution using atomic force microscopy.[27] As the solvent evaporates, the isotropic solution on the surface micelle layer turns into the lamellar structure, possibly via the correlated micelle intermediate,[25] as schematically shown in Figure 4A. Further evaporation of the solvents induces a gradual phase transition from the lamellar structure into the hexagonal structure as well as the completion of the lamellar structure (Figure 4B). The phase transition would take place from the substrate side toward the air/film interface using the aligned cylindrical micelles at the substrate surface as a scaffold, just like in epitaxial growth. The lamellar-to-hexagonal phase transition would preferentially take place at the lamellar/hexagonal interface rather than at the free surface. The phase transition of thermotropic liquid crystals shows a similar behavior, that is, it favorably takes place at an interface of two continuous phases. Finally, a totally aligned hexagonal structure is formed after the completion of the phase transition over the whole thickness of the film (Figure 4C). The rearrangement of the micelles would be allowed because of the immature condensation of the silica walls before solidification, otherwise such narrow alignment distribution over the whole of the film cannot be explained. It is thus considered that the formation mechanism of the aligned mesoporous film is based on a different mechanism from that in the previous method based on heterogeneous nucleation and growth, although the driving force for the alignment control is identical.

In addition to the advantage of simplicity of the process of the present method, this method would provide a diversity of mesoporous material films with uniaxially aligned mesochannels. By using different inorganic sources, we will be able to change the pore wall materials. Again, if we use blockcopolymers, such as pluronic P123, as a structure-directing agent, it would be possible to enlarge the size of the aligned mesopores. Such diversity in the composition and structure of the mesoporous materials films will allow us to develop various nanoscaled devices in which materials are controlled on the molecular scale.

Conclusion

We have succeeded in the preparation of a mesoporous silica film with highly aligned mesochannels by a simple dip-coating process using a rubbing-treated polyimide coating on a substrate. The alignment direction was perpendicular to the rubbing direction and was independent of the coating

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direction. The advantage of this method is not only the facility of the process but also the narrower directional distribution of the mesochannels in the resultant film. The present method, based on sol−gel chemistry, can also be applied to non-siliceous materials and allows the use of various substrates. The presented method will extend possible applications of films of mesostructured materials.

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