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Epitaxial-like Growth of Anisotropic Mesostructure on an Anisotropic Surface of an Oblique Nanocolumnar Structure

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Abstract: Tetrahedral amorphous carbon (ta-C) films with nanoscale structural anisotropy, which are obliquely deposited on a substrate by a filtered cathodic vacuum arc deposition (FAD) technique, allow anisotropic growth of mesostructured silica films thereon. The ta-C films have a uniformly tilted nanoscale columnar structure, which is caused by the self-shadowing effect during the oblique deposition, and consequently, the surface of the film can be morphologically anisotropic when the deposition angle is large enough. When silica films with a two-dimensional hexagonal mesostructure are grown under hydrothermal conditions on these ta-C films, the cylindrical mesochannels are aligned perpendicularly to the deposition direction of ta-C. The distribution of the in-plane alignment direction of the mesochannels can be controlled by the deposition angle of ta-C; it becomes narrower with the increase of the deposition angle and the consequent increase of the surface roughness. The observed alignment of the mesochannels is caused by the anisotropic accommodation of the surfactant molecules on the structurally anisotropic surface of the ta-C films, which is consistent with the fact that the ta-C films prepared at small deposition angles with smoother surface morphology have little alignment controllability. The ta-C film can be removed with the surfactant by calcination, allowing the formation of an aligned mesoporous silica film directly on a substrate. In contrast to this, obliquely evaporated SiO_2 films with a distinct tilted columnar structure and an anisotropic surface morphology provide neither continuous film formation nor controlled alignment of mesochannels even after providing hydrophobicity by a silylation process. This suggests the specificity, in particular, intrinsic strong hydrophobicity, of the ta-C films for the aligned mesostructured silica film formation.

Introduction

The oblique deposition technique is known as a useful method to prepare inorganic films with structural anisotropy by a vacuum deposition processes on a given substrate.[1−3] In this technique, the substrate is placed obliquely with respect to the particle flux from the deposition source, and films with a nanoscale tilted hoarfrost-like structure are spontaneously formed by a self-shadowing effect, as shown in Figure 1A−D. Not only simple columnar structures but also more complex morphologies can be prepared by changing the deposition direction with respect to the substrate during the deposition process.[1−5] The anisotropic structures of the films formed by the oblique deposition technique have been used for optical elements such as filters or birefringent elements.[6−10] It has been known that obliquely evaporated SiO_2 films consisting of nanoscale tilted SiO_2 columns can control the alignment of liquid crystals (LCs) using their anisotropic surface morphology, and they are industrially used as a stable alignment layer of LCOS (liquid crystal on silicon) devices in LC projectors.[11] Such in-plane alignment of LCs is caused by anisotropic interfacial interactions, which are due to the anisotropic surface microstructure of obliquely deposited films.

Mesostructured materials prepared through self-assembly of surfactant have highly ordered mesoscale structures, which reflect the ordered lyotropic LC phases of the surfactants.[12−16] Various LC-like properties of the mesostructured materials have

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(1) Hodgkinson, I. J.; Wu, Q. H. *Birefringent Thin Films and Polarizing Elements*; World Scientific Publishing Co. Pte. Ltd.: Singapore, 1997.
(2) Robbie, K.; Sit, J. C.; Brett, M. J. *J. Vac. Sci. Technol. B* **1998**, *16*, 1115–1122.
(3) Abelmann, L.; Lodder, C. *Thin Solid Films* **1997**, *305*, 1–21.
(4) Robbie, K.; Brett, M. J.; Lakhtakia, A. *J. Vac. Sci. Technol. A* **1995**, *13*, 2991–2993.
(5) Robbie, K.; Friendrich, L. J.; Dew, S. K.; Smy, T.; Brett, M. J. *J. Vac. Sci. Technol. A* **1995**, *13*, 1032–1035.
(6) Van Popta, A. C.; Sit, J. C.; Brett, M. *J. Appl. Opt.* **2004**, *43*, 3632–3639.
(7) Hodgkinson, I. J.; Wu, Q. H. *Appl. Phys. Lett.* **1999**, *74*, 1794–1796.
(8) Hodgkinson, I. J.; Wu, Q. H.; Collett, S. *Appl. Opt.* **2001**, *40*, 452–457.
(9) Kivaisi, R. T. *Thin Solid Films* **1982**, *97*, 153–183.
(10) Smith, G. B.; Ng, M. W.; Ditchburn, R. J.; Martin, P. J.; Netterfield, R. P. *Sol. Energy Mater. Sol. Cells* **1992**, *25*, 149–167.
(11) Lu, M. *Jpn. J. Appl. Phys.* **2004**, *43*, 8156–8160.
(12) Yanagisawa, T.; Shimizu, T.; Kuroda, K.; Kato, C. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.
(13) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

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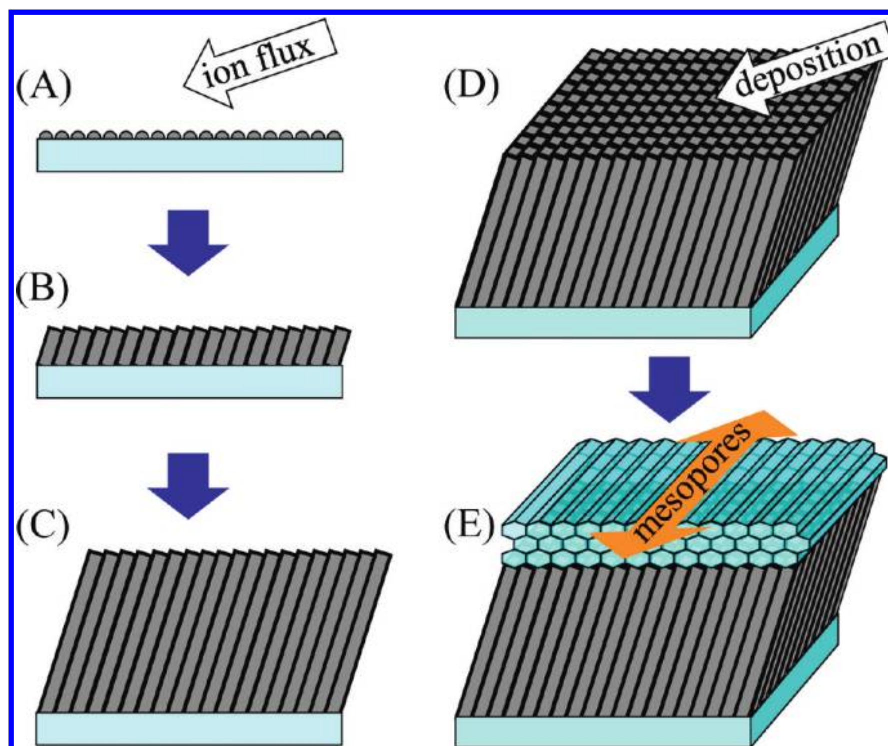

Figure 1. (A−D) Schematic drawing of the formation of a tilted columnar structure by an oblique deposition process and (E) the alignment of mesopores in the mesoporous silica film thereon.

been shown, such as birefringence[17] and alignment control by external fields.[18−22] They can be regarded as solidified lyotropic LC phases of inorganic species, and hollow mesoporous materials, which keep the structural regularity of the LC phases, are formed by surfactant removal. Mesostructured materials can be formed on a substrate as uniform films through hydrothermal and sol−gel reactions.[23−30] Because of the LC-like properties of mesostructured materials, macroscopic control of in-plane orientation of the mesostructure and the consequent formation of films with controlled in-plane mesoporous structures is expected using anisotropic substrates used for the alignment control of LCs. Such films with controlled in-plane mesostructures can be applied to optical and electronic devices with anisotropic properties, which are achieved by macroscopic control of in-plane orientation of guest species through incorporation into the controlled mesopores. Single-crystalline substrates with anisotropic surface atomic arrangement,[30−32] rubbing-treated polyimide films,[33−38] Langmuir−Blodgett films of polyimide,[39] and photo-oriented polymers[40−42] have been reported so far for the preparation of mesostructured films with controlled in-plane orientation. Control of the in-plane mesostructure can also be achieved in lithographically prepared microgrooves,[43,44] indicating the possibility of controlling the

(14) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
(15) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.
(16) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
(17) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692–695.
(18) Tolbert, S. H.; Firouzi, A.; Stucky, G. D.; Chmelka, B. F. *Science* **1997**, *278*, 264.
(19) Yamauchi, Y.; Sawada, M.; Noma, T.; Ito, H.; Furumi, S.; Sakka, Y.; Kuroda, K. *J. Mater. Chem.* **2005**, *15*, 1137–1140.
(20) Trau, M.; Yao, N.; Kim, E.; Xia, Y.; Whitesides, G. M.; Aksay, I. A. *Nature* **1997**, *390*, 674–676.
(21) Hillhouse, H. W.; Okubo, T.; van Egmond, J. W.; Tsapatsis, M. *Chem. Mater.* **1997**, *9*, 1505–1507.
(22) Melosh, N. A.; Davidson, P.; Feng, P.; Pine, D. J.; Chmelka, B. F. *J. Am. Chem. Soc.* **2001**, *123*, 1240–1241.
(23) Ogawa, M. *J. Am. Chem. Soc.* **1994**, *116*, 7941–7942.
(24) Ogawa, M. *Chem. Commun.* **1996**, 1149–1150.
(25) Lu, Y.; Ganguli, R.; Drewien, C. A.; Anderson, M. T.; Brinker, C. J.; Gong, W.; Guo, Y.; Soyez, H.; Dunn, B.; Huang, M. H.; Zink, J. I. *Nature* **1997**, *389*, 364–368.
(26) Sanchez, C.; Boissière, C.; Grosso, D.; Laberty, C.; Nicole, L. *Chem. Mater.* **2008**, *20*, 682–737.
(27) Innocenzi, P.; Malfatti, L.; Kidchob, T.; Falcaro, P. *Chem. Mater.* **2009**, *21*, 2555–2564.
(28) Smarsly, B.; Grosso, D.; Brezesinski, T.; Pinna, N.; Boissière, C.; Antonietti, M.; Sanchez, C. *Chem. Mater.* **2004**, *16*, 2948–2952.
(29) Nishiyama, N.; Tanaka, S.; Egashira, Y.; Oku, Y.; Ueyama, K. *Chem. Mater.* **2003**, *15*, 1006–1011.
(30) Yang, H.; Kuperman, A.; Coombs, N.; Mamiche-Afara, S.; Ozin, G. A. *Nature* **1996**, *379*, 703–705.
(31) Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. M.; Gruner, S. M. *Science* **1996**, *273*, 892–897.
(32) Miyata, H.; Kuroda, K. *J. Am. Chem. Soc.* **1999**, *121*, 7618–7624.
(33) Miyata, H.; Kuroda, K. *Chem. Mater.* **1999**, *11*, 1609–1614.
(34) Miyata, H.; Kuroda, K. *Chem. Mater.* **2000**, *12*, 49–54.
(35) Miyata, H.; Noma, T.; Watanabe, M.; Kuroda, K. *Chem. Mater.* **2002**, *14*, 766–772.
(36) Miyata, H.; Kawashima, Y.; Itoh, M.; Watanabe, M. *Chem. Mater.* **2005**, *17*, 5323–5327.
(37) Miyata, H.; Suzuki, T.; Fukuoka, A.; Sawada, T.; Watanabe, M.; Noma, T.; Takada, K.; Mukaide, T.; Kuroda, K. *Nat. Mater.* **2004**, *3*, 651–656.
(38) Suzuki, T.; Miyata, H.; Watanabe, M.; Kuroda, K. *Chem. Mater.* **2006**, *18*, 4888–4893.
(39) Miyata, H.; Kuroda, K. *Adv. Mater.* **1999**, *11*, 1448–1452.
(40) Kawashima, Y.; Nakagawa, M.; Seki, T.; Ichimura, K. *Chem. Mater.* **2002**, *14*, 2842–2844.
(41) Kawashima, Y.; Nakagawa, M.; Ichimura, K.; Seki, T. *J. Mater. Chem.* **2004**, *14*, 328–335.
(42) Fukumoto, H.; Nagano, S.; Kawatsuki, N.; Seki, T. *Chem. Mater.* **2006**, *18*, 1226–1234.

total in-plane structure of mesostructured films by morphological anisotropy of the substrate surface.

Here, we report the epitaxial-like growth of mesostructured silica films on a substrate with nanoscale morphological anisotropy, which is spontaneously formed by a vacuum deposition process. We found that tetrahedral amorphous carbon (ta-C) films prepared by an oblique filtered cathodic arc deposition (FAD) can control the in-plane alignment of cylindrical micelles in mesostructured silica films prepared by the hydrothermal process. The uniformly tilted columnar structure of the ta-C film, which is spontaneously formed by the self-shadowing effect during the oblique deposition, causes uniaxial alignment of cylindrical micelles perpendicular to the deposition direction of carbon (Figure 1E). The alignment distribution becomes narrower with the increase of the deposition angle of ta-C, as a result of the increased surface roughness. The strong intrinsic hydrophobicity of the ta-C film is shown to be another indispensable factor for the alignment of cylindrical micelles, and SiO_2 films with a columnar structure, which are used for alignment control of liquid crystals, do not provide such an effect. Both, the surfactant and the ta-C film, can be removed by calcination in air, leaving hollow mesoporous silica films keeping the aligned mesostructure. In addition to the importance of the novel epitaxial-like growth behavior, the mesoporous silica films prepared by this method have improved quality with a small number of defects. Also, this method enables the aligned mesoporous silica film formation even on a substrate with a surface curvature. These advantages of the new process in this paper expand the possible application of mesostructured films especially in the field of optics.

Experimental Section

Preparation of Substrates. The ta-C films are deposited on silica glass and silicon substrates by FAD. The experimental system has been described in detail previously.[45] The cathode is high purity carbon with a 60 mm diameter, and the arc plasma was filtered with a 90° magnetic duct. The arc source is operated at a DC current of 80 A, and the positive ion flux is measured to be 200 mA at the position of the substrate. The substrate is mounted on an earthed isolated substrate holder that can be set at a fixed angle to the incident carbon ion flux. The angle of incidence with respect to the substrate normal is adjusted in the range between 60 and 85°. The deposition angle is measured with a precision digital protractor to the desired deposition angle within ±0.5°. The deposition rate is set to be 1−2 nm s^{-1}, which depends on the deposition angle. The thickness of the ta-C films is controlled to be 8−20 nm by the deposition time.

Preparation of Mesoporous Silica Films. Mesoporous silica films are prepared on the substrates with the ta-C coatings through a hydrothermal reaction.[35] A nonionic surfactant Brij56 ($C_{16}EO_{10}$) and tetraethoxysilane (TEOS) are used as structure-directing agent and silica source, respectively. The molar ratio of the solution is 0.10 TEOS:0.11 Brij56:100 H_2O:3.0 HCl. The substrates are kept in the solution at 80 °C for 5 days for the preparation of mesostructured silica films. The mesostructured films are washed with deionized water and are calcined at 400 °C for 10 h to remove the surfactant and the ta-C film.

Characterization of the Films. The morphology of the ta-C films were characterized using a Hitachi S-5500 high-resolution scanning electron microscope (HR-SEM) and a Nano-Navi scanning probe microscope operated in a noncontact atomic force microscope (AFM) mode. The porous structure of the mesostructured films was analyzed by X-ray diffraction (XRD) in Bragg−Brentano and in-plane geometries using a Philips X'pert Pro X-ray diffractometer and a RIGAKU ATX-G diffractometer with a 4-axis goniometer, respectively, using Cu Kα radiation. The two-dimensional (2D) XRD patterns were recorded under a reflection geometry with an incidence angle of 0.2° using synchrotron radiation at the Photon Factory (KEK Japan) on beamline 4A using a 3 μm × 3 μm X-ray microbeam with 8 keV. Cross-sectional images of scanning transmission electron microscopy (STEM) were recorded on a Tecnai F30 at an accelerating voltage of 300 kV in a high angle annular dark field (HAADF) mode.

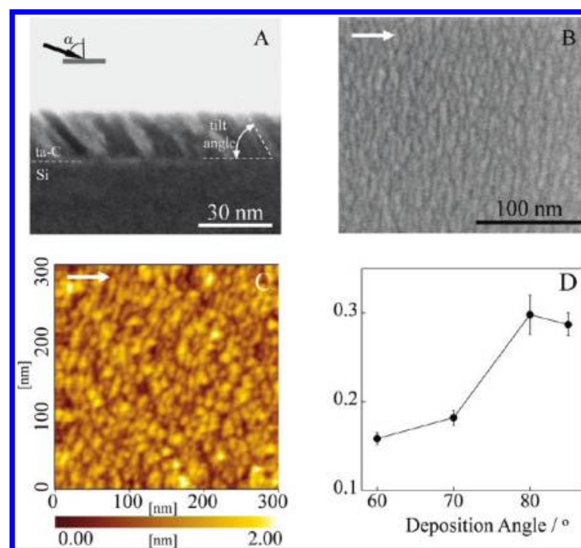

Figure 2. Characterizations of the ta-C films prepared by oblique FAD. (A) Cross-sectional and (B) surface HR-SEM images (deposition angle α = 80°; the deposition angle is defined in the inset of A), (C) AFM image (deposition angle α = 80°), and (D) dependence of surface roughness on the deposition angle. Arrows in (B) and (C) show the projected direction of FAD.

Results and Discussion

Characterization of the ta-C Film. The FAD process is based on the formation of ionized energetic flux of a cathode material through the vacuum arc process. Undesirable particles in the ion flux are removed by deflecting the plasma from the source around a curved vacuum duct fitted with magnetic coils. The carbon films prepared by this FAD process consist of pure carbon predominantly in a tetrahedral coordination state, which is called tetrahedral amorphous carbon (ta-C).[46] Though high energy of the ion flux in the FAD process usually results in a dense film formation, we found that nanoscale structural anisotropy is provided in the ta-C film by the self-shadowing effect when the substrate is placed obliquely with respect to the carbon ion flux during the deposition. The cross-sectional HR-SEM image of the ta-C film prepared at a deposition angle (α) of 80°, shown in Figures 2A, clearly shows the formation of an oblique columnar structure. The direction and the tilt angle of the columnar structure with respect to the substrate are determined by the direction and the energy of the ion flux during the deposition process, and in general, the tilt angle decreases with the deposition angle. As shown in Figure 2B, single-nanoscale wrinkles oriented normal to the deposition direction

(43) Wu, C.-W.; Ohsuna, T.; Edura, T.; Kuroda, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5364–5368.
(44) Bolger, C. T.; Farrell, R. A.; Hughes, G. M.; Morris, M. A.; Petkov, N.; Holmes, J. D. *ACS Nano* **2009**, *3*, 2311–2319.
(45) Martin, P. J.; Bendavid, A.; Kinder, T. J.; Wielunski, L. *Surf. Catal. Technol.* **1996**, *86*−*87*, 271–279.
(46) Martin, P. J.; Bendavid, A. *Thin Solid Films* **2001**, *394*, 1–15.

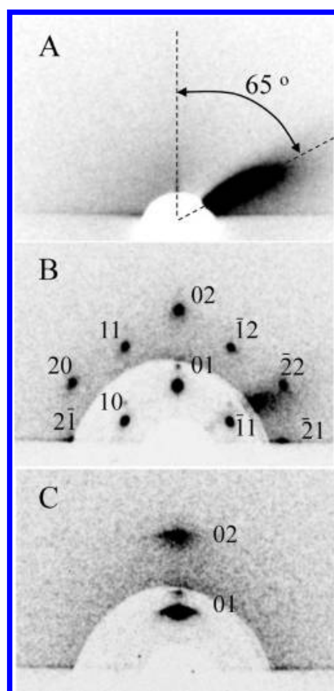

Figure 3. (A) 2D-XRD patterns of the ta-C film deposited at 80° and (B and C) the as-grown mesostructured silica film formed thereon. The deposition direction is set (B) perpendicular and (C) parallel to the projection of the incident X-rays.

are observed on the surface of the ta-C film deposited at 80°. This surface anisotropy is definitely due to the columnar structure, and such anisotropic morphology can be confirmed by HR-SEM only for the films deposited at angles over 80°. The ta-C film deposited at 60° is relatively smooth without morphological anisotropy, and the columnar structure is not evident in the cross-section. It should be noted that this SEM image is taken at high magnification, and therefore, the surface of the film is actually very flat. The AFM image shown in Figure 2C is in good agreement with the SEM image (Figure 2B) proving the anisotropic surface morphology. For the films deposited at lower angles, the surface anisotropy is difficult to observe even by AFM. The surface roughness of the films can be quantitatively estimated by AFM, and the rms values of the roughness are plotted against the deposition angle. As shown in Figure 2D, the surface roughness increases with the deposition angle, while those for the 80 and 85° films are comparable. The anisotropic oblique columnar structure can also be proven by 2D-XRD. Figure 3A is the 2D-XRD pattern of the ta-C film deposited at 80° recorded under the geometry in which the projection of the incident X-rays is perpendicular to the deposition direction. The oval-shaped diffused diffraction was observed as shown in the figure, and this shows that the columnar structure is oriented along a preferred direction. The tilt angle is estimated to be 65°, which is in good agreement with that obtained from the cross-sectional HR-SEM image shown in Figure 2A. Regardless of the controlled orientation of the columnar structure, the broad pattern indicates that the spacing of the columns has some distribution. When the 2D-XRD pattern is recorded with X-rays parallel to the deposition direction, no spots are observed (data not shown), which proves that the columnar structure is inclined in the same direction reflecting the direction of the carbon ion flux during the deposition process.

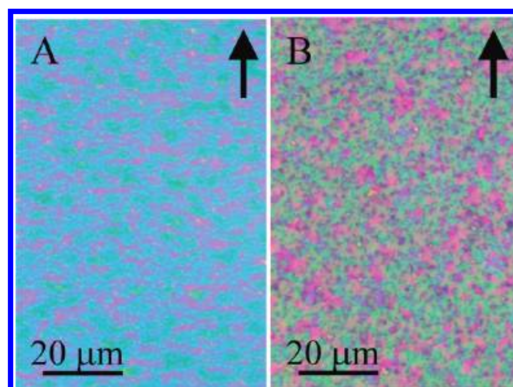

Figure 4. Optical micrographs of the as-grown mesopostructured silica films formed on the ta-C films deposited at (A) 80° and (B) 60°. Arrows show the deposition direction.

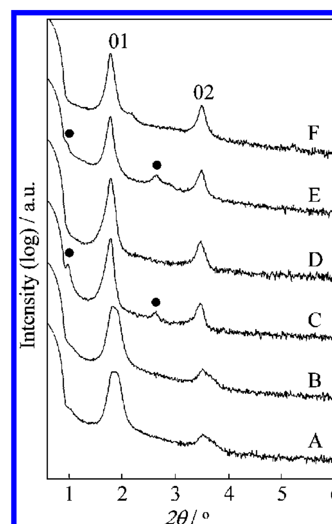

Figure 5. XRD profiles of the mesostructured films recorded under the Bragg–Brentano geometry. Traces (A), (B): as-grown film on the ta-C film deposited at 60°, (C), (D) and (E), (F): as-grown and calcined film on the ta-C film deposited at 85°. The deposition direction is set perpendicular (A, C, E) and parallel (B, D, F) to the projection of the incident X-rays.

Mesoporous Silica Films on Obliquely Deposited ta-C Films. The optical micrographs of the as-deposited mesostructured silica film formed on the ta-C film deposited at 80 and 60° are shown in Figure 4A and B, respectively. While no anisotropy is observed in the film prepared on the ta-C deposited at 60°, a characteristic texture aligned normal to the deposition direction is observed in the film formed on the ta-C deposited at 80°. The observed texture indicates the structural anisotropy of the mesostructured silica film. As shown in Figure 4A, the film on the 80° ta-C is highly homogeneous with few discontinuous parts such as particle-like defects, which are hard to avoid when a rubbing-treated polyimide is used as an alignment-controlling layer.[34,35]

The structure of the films is characterized by XRD. The XRD profiles of the as-deposited films recorded in Bragg–Brentano geometry are shown in Figure 5. The diffraction intensity is shown on a log scale to display all the diffraction peaks with different intensities simultaneously. Both of the films, formed on the ta-C films prepared at 60° (traces A, B) and 85° (traces C, D) deposition angles, give strong diffraction peaks, showing the formation of an ordered mesostructured film. The XRD profiles of the two samples are consistent with the 2D-hexagonal structure and are substantially the same although the peak

positions are slightly shifted. The profiles of the 85° sample show obvious structural anisotropy: two additional peaks, indicated by (●) in the figure, are observed when the projection of the incident X-rays is perpendicular to the deposition direction of the ta-C film. It has been shown in our previous study that this anisotropy in the θ-2θ scanning XRD profile is evidence of the formation of a film with a controlled in-plane mesostructure.[35,47] On the other hand, the XRD profile of the 60° sample has little dependence on the direction of the ta-C film, showing a macroscopically isotropic mesostructure.

The removal of the surfactant by calcination causes little change in the XRD patterns (Figure 5 traces E, F), suggesting the retention of the mesostructure. The *d*-spacing of the mesostructured films is almost unchanged by calcination, which is caused by improved silica condensation state of the pore walls of the hydrothermally prepared mesostructured silica film. The dark color caused by the absorption by a ta-C film disappears completely by the calcination process at 400 °C, suggesting the removal of the ta-C undercoat by oxidation (Figure S1, Supporting Information). When the ta-C films are about 10 nm thin, the calcination process does not cause cracks in the silica film, allowing the formation of a continuous aligned mesoporous silica film directly on the substrate, as confirmed by the optical micrographs shown in Figure S2 (Supporting Information). However, the thicker ta-C films cause cracks and partial peeling of the mesoporous silica film from the substrate. When the calcination temperature is reduced to 350 °C, which is insufficient to remove the ta-C film, only the surfactant is removed, leaving the mesoporous silica film on the ta-C film.

The structural anisotropy of the mesostructured silica films is obvious when looking at the 2D-XRD patterns. Figure 3B and C are the patterns of the as-grown film formed on the ta-C film deposited at 80°, recorded with the incident X-rays perpendicular and parallel to the deposition direction of ta-C, respectively. The observed anisotropy of the diffraction patterns clearly shows that the cylindrical micelles of a 2D-hexgonal structure are aligned perpendicularly to the deposition direction of ta-C. In Figure 3B, the oval-shaped diffuse diffraction spot caused by the ta-C film is overlapped with the XRD spots of the mesostructured silica film, whereas it is not found in Figure 3C. These two images show the relationship between the in-plane orientation of the mesochannels and the inclination direction of the underlying columnar structure.

To estimate the degree of the in-plane structural anisotropy of the mesostructured silica films, a detailed in-plane XRD study[34] is performed. The in-plane XRD profiles ($\phi - 2\theta\chi$ scanning) are recorded at two sample directions with respect to the deposition direction of the ta-C films. For the films on the ta-C films deposited at 70, 80, and 85°, the strong in-plane XRD peaks are observed only under the geometry that the deposition direction of ta-C is perpendicular to the projection of incident X-rays, whereas the 60° sample gives the in-plane XRD peaks independent of the sample rotation (Figure S3, Supporting Information). These results suggest that the structural anisotropy of the mesostructured silica film is small in the case of the 60° sample, which is consistent with the results of $\theta - 2\theta$ scanning XRD shown in Figure 5.

The anisotropic in-plane mesostructure can quantitatively be characterized by recording the in-plane rocking curve by rotating the sample around the ϕ axis fixing the detector at the peak position determined by the $\phi - 2\theta\chi$ scanning. The ϕ scanning

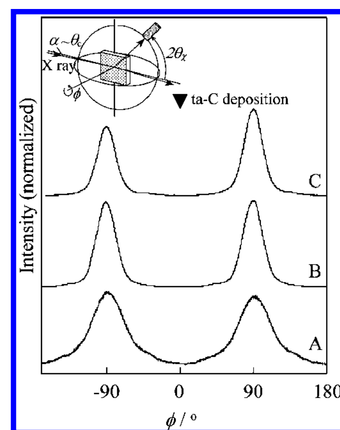

Figure 6. In-plane ϕ scanning profiles of the as-grown mesostructured silica films prepared on the ta-C films deposited at (A) 70°, (B) 80°, and (C) 85°. (Inset) Scanning axes of the in-plane XRD geometry.

profiles in Figure 6 clearly show that the alignment distribution of the mesochannels becomes narrower with the increase of the deposition angle of ta-C. The fwhm values of the in-plane rocking curves are estimated to be 26.8, 28.8, and 44.0° for 85, 80, and 70° samples, respectively by averaging the values of the two peaks. Although the ta-C film deposited at 70° retains the preferred alignment of the mesochannels, the 60° film shows little alignment effect: only the variation of the diffraction intensity originating from the rectangular shape of the specimen is observed (data not shown). The observed dependences of the in-plane alignment distribution of the mesochannels on the surface roughness of the ta-C films are quite consistent. The ta-C films deposited at 80° and 85°, which have comparable surface roughness, give mesostructured silica films with comparably narrow alignment distribution. The ta-C film deposited at 70° has a smoother surface, for which anisotropy of the surface morphology is not evidently shown by HR-SEM and AFM, results in the inferior alignment of mesochannels. When the surface roughness falls below a threshold value, the preferred alignment of the mesopores is eventually lost (on the 60° film). These results mean that the distribution of the in-plane alignment of mesochannels can be controlled to some extent by the deposition angle of ta-C. The fact that the alignment distribution tends to be saturated above 80° is advantageous when a uniformly aligned mesoporous silica film is formed on a substrate with a surface curvature. Because the ion flux is collimated in the FAD process, if we use an appropriate substrate, which guarantees the deposition angle of 80−85° over the whole substrate, we can prepare a uniformly aligned mesoporous silica film on it. The use of a substrate with a curvature is difficult in the conventional rubbing process because the curved surface makes the strength of rubbing nonuniform.

Figure 7 is the cross sectional STEM image of the mesostructured silica film formed on the ta-C film deposited at 80°. Both the aligned mesostructured silica and the uniformly tilted nanoscale columns of ta-C are clearly observed. It is also shown in this image that the mesochannels of the mesostructured silica film are aligned normal to the tilt direction, that is, the deposition direction of ta-C. The alignment is achieved over whole the film thickness of ∼200 nm (Figure S4, Supporting Information).

Mesoporous Silica Films on Silica Films with an Oblique Columnar Structure. Films with an oblique columnar structure can be formed by an oblique deposition technique using various materials. SiOx films prepared by oblique evaporation have a tilted columnar structure accompanied by surface anisotropy, and have

(47) Noma, T.; Miyata, H.; Takada, K.; Iida, A. *Adv. X-ray Anal.* **2001**, *45*, 359–364.

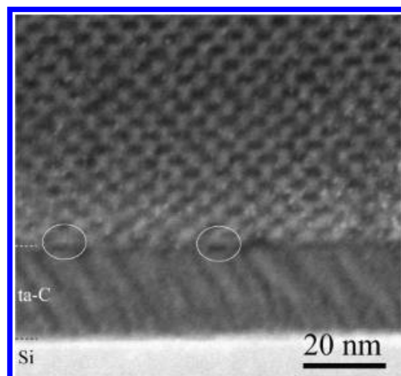

Figure 7. Cross-sectional STEM image of the mesostructured silica film formed on the ta-C film deposited at 80°.

been industrially applied as an alignment-controlling layer in liquid crystal (LC) devices. We performed the preparation of a mesoporous silica film on a SiO_2 film deposited by electron-beam evaporation with a deposition angle of 80°. However, not only the in-plane alignment control of mesochannels fails but also a continuous film formation is not observed on the SiO_2 layer (Figure S5, Supporting Information). This is despite the formation of a more strongly pronounced inclined columnar structure with larger surface roughness than the oblique ta-C films deposited at the same angle by FAD (HR-SEM images are shown in Figure S6, Supporting Information). In our previous study, it has been suggested that the continuity of the hydrothermally prepared mesostructured silica films tends to be improved by increasing the surface hydrophobicity. Consequently, we tried to form the mesostructured silica film after silylating the oblique SiO_2 layer in an attempt to increase the surface hydrophobicity. However, the morphologies of the formed mesostructured silica films are quite similar as that on the unsilylated one. These results indicate the specific properties of the oblique ta-C film for the preparation of the continuous aligned film of mesostructured silica, in particular, the intrinsic strong hydrophobicity.

We made LC cells using the two kinds of substrates with an oblique ta-C film and an oblique SiO_2 film, and injected MLC6608, which is a commercial liquid crystal material that prefers homeotropic alignment (principal axis of LC is perpendicular to a substrate) on a solid surface. The LC cell with the oblique SiO_2 film shows homeotropic alignment with a pretilt angle (deviation angle from the normal of a substrate) of ~5°, but that with the oblique ta-C film shows complete homogeneous alignment (principal axes of LC molecules are parallel to the substrate). The observed homogeneous alignment is caused by exceptionally strong anchoring of the LC molecules at the ta-C surface, and this is consistent with the formation of the uniaxially aligned mesostructured silica film. Because of the strong hydrophobicity of the surface, the surfactant molecules are anchored parallel to the morphologically anisotropic surface resulting in the formation of aligned surface micelle structure, which is responsible for the total alignment of cylindrical micelles. The possible model for the controlled alignment on the obliquely deposited ta-C film is schematically shown in Figure 8. In the cross-sectional STEM image shown in Figure 7, hemicylindrical shapes are partially observed in the first layer of the mesostructured silica film (in white circles). Although the image is not sufficiently clear because of the finite thickness of the specimen (~100 nm), this image supports the proposed alignment mechanism. It has been shown that SiO_2 films prepared by oblique FAD, which have much smoother surface morphology than the obliquely evaporated SiO_2 film, provide

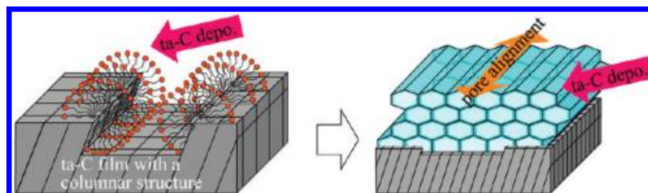

Figure 8. Schematic drawing of the alignment mechanism of the cylindrical micelles on the ta-C film with an inclined columnar structure.

common homeotropic alignment of the same LC,[48] suggesting that the homogeneous alignment on the oblique ta-C film is achieved by the specific chemical property, that is, intrinsic hydrophobicity of the ta-C film.

Conclusion

Mesoporous silica films with a uniaxially aligned 2D-hexagonal porous structure are prepared on ta-C films prepared by an oblique FAD technique. The alignment distribution can be controlled by the deposition angle of the ta-C film, and it becomes narrower with the increase of the deposition angle. The alignment is perpendicular to the deposition direction, and the anisotropic surface morphology of the ta-C films, which originates from the self-shadowing effect during oblique deposition, causes the alignment of the mesopores. The formation of a film without a preferred in-plane alignment of the mesochannels on the ta-C film deposited at 60° suggests the existence of a threshold value of the surface roughness for the alignment control of the mesopores. Neither alignment control nor continuous film formation is achieved on an obliquely evaporated SiO_2 film with a definite columnar structure, suggesting the strong contribution of the hydrophobic properties of the ta-C films. The ta-C films can be removed with the surfactant by calcination, allowing the direct formation of an aligned mesoporous silica film on a substrate. The alignment control of mesopores by an anisotropic under-layer with a high surface flatness improves the quality of the film by reducing the defect formation originating from surface roughness of a substrate, which is important for the application of these mesoporous films to molecular-scale devices in the field of electronics and optics.

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Supporting Information Available: Change of the visible spectrum of the sample film by calcination, optical micrographs of the sample film before and after the removal of the ta-C film, in-plane ϕ-$2\theta\chi$ scanning profiles of the mesostructured silica films on the ta-C films, wide-area cross-sectional STEM image, optical micrograph of the mesostructured silica formed on a silica film with an oblique columnar structure, cross-sectional SEM image of a silica film with an oblique columnar structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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