Structural Characteristic of Outermost Surface of Cubic Mesoporous Silica Film

Takashi Inoue,[1] Itaru Gunjishima,[1] Yoko Kumai,[1] Shinji Inagaki,[1,2] and Atsuto Okamoto*[1]
[1]*Toyota Central R&D Labs, Inc., Nagakute, Aichi-gun, Aichi 480-1192*
[2]*JST, CREST, 4-1-8 Hon-Chou, Kawaguchi 332-0012*

(Received April 9, 2007; CL-070382; E-mail: okamoto@mosk.tytlabs.co.jp)

The outermost surface structure of a calcined cubic mesoporous silica film was observed for the first time by high-resolution field emission scanning microscopy, which showed a periodic pore arrangement with inherent cage openings and one-dimensional grooves on the surface. The grooves are formed to be the interconnected A-cages associated along the ⟨100⟩ direction on the {210} crystallographic plane of SBA-1.

Since their discovery,[1,2] mesoporous silica (MPS) materials have attracted much attention for their potential applications such as molecular separation membrane,[3] catalyst supports,[4,5] and templates for the fabrication of nanomaterials.[6] On the other hand, the number of investigations into quantum wire and quantum-dot device have been increasing,[7,8] and an idea using the MPS material as a template for fabrication of nanostructures was proposed.[4,5] It is necessary for that purpose to clarify both the outermost surface and internal structure of MPS materials, especially for thin films.[9–12] A number of investigations into the internal structure of MPS materials have been reported so far.[9–14] However, structural studies on the outermost surface by scanning electron microscopy (SEM) are rather few,[11,15] for instance, Wu and co-workers revealed inherent external structures on the top surfaces of three kinds of mesoporous silica thin films through direct high resolution SEM observation.[5] On the other hand, Sakamoto and co-workers reported that powdered cubic MPS materials, so-called SBA-1 and SBA-6, have a highly ordered dual micro- and mesoscale pore structure by X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM).[13] However, to my knowledge, the outermost surface structure of cubic MPS is still unclear. In addition, when the outermost surface of the MPS is applied to nanoelectronics devices, not powder but thin film of MPS on a substrate is suitable for the actual device manufacture process. Therefore, understanding of the outermost surface structure, as in SBA-1, is the most essential and important issue. Here, we report a direct field emission SEM (FESEM) observation on the outermost surface of calcined cubic MPS thin film. The film exhibits a periodic pore arrangement with inherent cage openings and unique one-dimensional (1D) grooves on the outermost surface, and the size of some cage openings is larger than crystallographically expected one.

The cubic MPS film was fabricated by sol–gel method as follows. Octadecyltrimethylammonium chloride (C18TMACl) and tetramethoxysilane (TMOS) were used as a surfactant and a silica source, respectively. C18TMACl (1.45 g) was dissolved in a mixture of water (10 mL), ethanol (40 mL) and 2 M HCl (20 μL). The solution was then added to a hydrolyzed TMOS solution (TMOS: 3.81 g, 0.012 M HCl: 1.0 mL) to yield a sol-solution. To avoid the charge-up problem, the typical molar ratio of precursor solution was modified to a thin film specification as follows: TMOS:C18TMACl:HCl:EtOH:H_2O = 1.00:0.17:0.002:27.5:24.4. After aging of the sol solution for 40 min at room temperature, a MPS film was fabricated using a constant pull-up rate of 2 cm/min on a silicon (Si) substrate by a dip coating method from the sol solution. Details of the preparation method have been described elsewhere.[4] The film was finally calcined in air at 400 °C for 4 h. The XRD pattern of the calcined film is shown in Figure S1.[16] The pattern can be assigned to the cubic phase SBA-1, even though relative intensities between the peaks were quite different from those of powder samples.[9–11] The overwhelming intensity of the 210 and 420 reflections relative to the neighbors indicates that predominant plane parallel to the substrate is regarded as {210} crystallographic plane (inset in Figure S1).[16] The outermost surface morphology of the film without coating was investigated by FESEM (JEOL JSM-890 and Hitachi S-5500). The film exhibits a characteristic arrangement of pores with diameters of ca. 3 to 4 nm over a wide area of the outermost surface, as shown in Figure 1. Moreover, a cross-sectional SEM image of the calcined film showed a single domain structure in the direction of thickness although some defects and imperfections in the pore-arrangement structure were observed (Figure S2).[16] These mean that the domain size is at least a few hundred nanometers. It is interesting to note that there are two kinds of pore arrays on the outermost surface: one is identified as a "straight line" connecting each pore; the other is a periodic array consisting of a unit with both three and four pores perpendicular to the "straight line" (Figure 2a). In contrast, a domain with {100} plane was also detected on the outermost surface, as shown in Figure 2b. The lattice constants of before and after calcination were estimated at $a = 8.85$ and 7.68 nm by XRD, respectively. In contrast, the lattice constant estimated by FESEM image (sides of a square

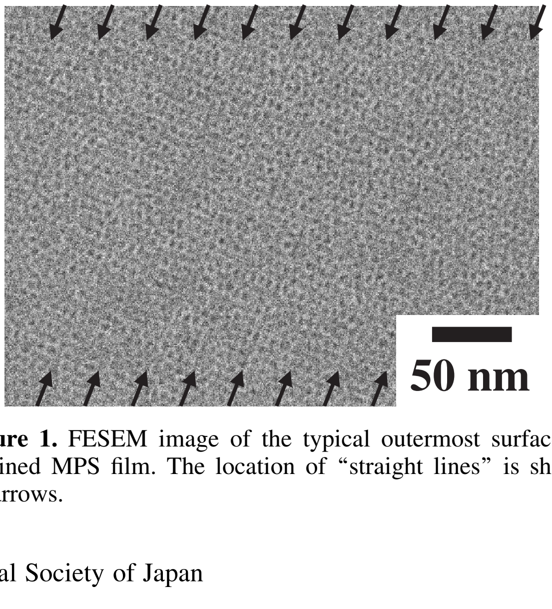

Figure 1. FESEM image of the typical outermost surface of calcined MPS film. The location of "straight lines" is shown by arrows.

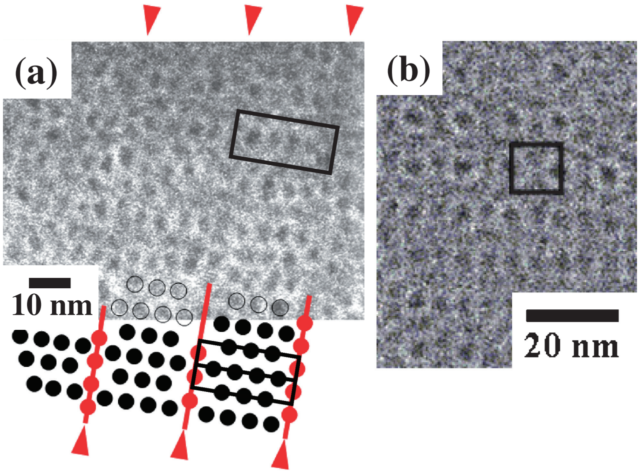

Figure 2. (a) FESEM image of the typical outermost surface of calcined MPS film prepared by a precursor solution with the molar ratio of TMOS:C18TMACl:HCl:EtOH:H_2O = 1.00:0.17:0.0025:5.15:13.4. The location of "straight lines" is shown by both red line and arrow. (b) FESEM image of the outermost surface with an incidentally detected {100} domain.

in Figure 2b) is ca. 11–12 nm. The difference in the lattice constant may be due to a constrained 1D shrinkage along the direction vertical to the substrate during calcination.[10]

For further understanding of the size and arrangement of pores on the outermost surface of the film, we examine the pore arrangement on a {210} plane of SBA-1 using a schematic pore arrangement on the plane as presented in Figure 3a. As is clear from the figures, there are five nonequivalent cage openings in a rectangular cell which is also illustrated in Figure 3b. The cage openings of Nos. 1–3 and No. 4 are the cross sections of A-cage and B-cage, respectively, as expected from Ref 13. The "straight lines" on the outermost surface are associated with the interconnected A-cages along the ⟨001⟩ direction on the {210} plane of SBA-1 (red lines in the Figures 2 and 3). On the other hand, the cage opening of No. 5 is attributed to the micropore window between the A- and B-cages. The size of cage opening of No. 5 observed on the outermost surface is larger than that from the {210} cross sections. Since the actual outermost surface is a grown surface in nonequilibrium state containing a liquid–vapor interface during a simple evaporation-induced self-assembly process and the existence of the adsorbed hydration layer surrounding the micelle is strongly suggested,[14] the expansion of the cage opening may result from the structural rearrangement of outermost surface during solvent evaporation. It is surprising that the outermost surface of the film exhibits not a disordered pore arrangement but the periodic one with interconnected cages, which reflects that of the {210} cross section for SBA-1 except for the size of specific pores. In the future, these periodic interconnected cages on the outermost surface will be useful as a template for fabricating the 1D nanostructure such as nanocarbons and metal nanowires.

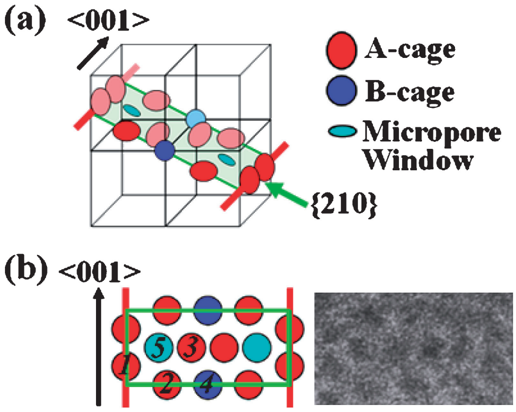

Figure 3. (a) The schematic pore arrangement on the {210} plane of SBA-1 expected from Ref 13. (b) The actual pore arrangement of the {210} plane and FESEM image of the outermost surface. The pore arrangement of the outermost surface is represented by five nonequivalent pores (Nos. 1–5).

The authors acknowledge Mr. J. Seki and Mr. H. Kadoura (Toyota Central R&D Labs., Inc.) for their help to SEM observation.

References and Notes

1 a) T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988. b) S. Inagaki, Y. Fukushima, K. Kuroda, *J. Chem. Soc., Chem. Commun.* **1993**, 680.

2 a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710. b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

3 A. Yamaguchi, F. Uejo, T. Yoda, T. Uchida, Y. Tanamura, T. Yamashita, N. Teramae, *Nat. Mater.* **2004**, *3*, 337.

4 a) A. Fukuoka, H. Araki, Y. Sakamoto, N. Sugimoto, H. Tsukada, Y. Kumai, Y. Akimoto, M. Ichikawa, *Nano Lett.* **2002**, *2*, 793. b) Y. Kumai, H. Tsukada, Y. Akimoto, N. Sugimoto, Y. Seno, A. Fukuoka, M. Ichikawa, S. Inagaki, *Adv. Mater.* **2006**, *18*, 760.

5 C.-W. Wu, Y. Yamauchi, T. Ohsuna, K. Kuroda, *J. Mater. Chem.* **2006**, *16*, 3091.

6 Y.-J. Han, J. M. Kim, G. D. Stucky, *Chem. Mater.* **2000**, *12*, 2068.

7 S. J. Tans, A. R. M. Verschueren, C. Dekker, *Nature* **1998**, *393*, 49.

8 Y. Cui, C. M. Lieber, *Science* **2001**, *291*, 851.

9 M. Ogawa, *Chem. Commun.* **1996**, 1149.

10 Y. Lu, R. Ganguli, C. A Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang, J. I. Zink, *Nature* **1997**, *389*, 364.

11 a) N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, K. Ueyama, *Chem. Mater.* **2002**, *14*, 4229. b) N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, K. Ueyama, *Chem. Mater.* **2003**, *15*, 1006.

12 D. Grosso, F. Cagnol, G. J. de A. A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, C. Sanchez, *Adv. Funct. Mater.* **2004**, *14*, 309.

13 Y. Sakamoto, M. Kaneda, O. Terasaki, D. Y. Zhao, J. M. Kim, G. Stucky, H. J. Shin, R. Ryoo, *Nature* **2000**, *408*, 449.

14 M. W. Anderson, C. C. Egger, G. J. T. Tiddy, J. L. Casci, K. A. Brakke, *Angew. Chem., Int. Ed.* **2005**, *44*, 3243.

15 a) H. W. Hillhouse, T. Okubo, J. W. van Egmond, M. Tsapatsis, *Chem. Mater.* **1997**, *9*, 1505. b) H. Miyata, K. Kuroda, *Adv. Mater.* **1999**, *11*, 857. c) S. P. Naik, S. Yamakita, Y. Sasaki, M. Ogura, T. Okubo, *Chem. Lett.* **2004**, *33*, 1078.

16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

Published on the web (Advance View) June 9, 2007; doi:10.1246/cl.2007.862