Fabrication of Highly Ordered Anodic Porous Alumina Using Self-organized Polystyrene Particle Array

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Highly ordered anodic porous alumina was fabricated by anodization of vapor-deposited Al that had been deposited on a self-organized periodic array of polystyrene particles with a submicron-scale diameter on a glass plate. The ordered bumpy structure of the particle array surface was replicated on the deposited Al surface. Anodization was initiated at the concaves of the Al surface. Employment of the self-organized particle array to produce highly ordered anodic porous alumina with a submicron-scale channel structure was shown to be feasible.

Recently, anodic porous alumina with pores on the submicron or nanometer scale has attracted a great deal of attention as a key material in the fabrication of various submicro- and nanodevices in various fields such as electronics, optics, magnetism, biomedical science, and electrochemistry, because of its ordered arrangement and high aspect ratio of channels.[1,2] We have reported that a straight channel array structure with regular channel diameter of submicron order and an ideal hexagonal arrangement could be obtained by adding anodization of Al to the pretexturing process of Al.[3–5] In the pretexturing process, a master, which has a hexagonal array of convexes, is placed on an Al sheet and pressed to generate the array of concaves on the surface of the Al sheet. The array of concaves initiates the development of pores and guides the growth of channels. However, the master used in the pretexturing process was a SiC mold prepared using expensive electron-beam lithography and ion-etching apparatuses. In this paper, we propose a novel preparation process of anodic porous alumina with an highly ordered submicron-channel array structure, by means of a polystyrene particle array formed naturally by self-organization of the particles.[6] The structure is considered suitable for use in the formation of texture onto an Al surface for the development of highly ordered pores, because of the periodic bumpy structure of the particle array surface.

Figure 1 schematically illustrates the procedure for the fabrication of highly ordered anodic porous alumina using self-organized 2-D polystyrene particle arrays. A glass plate was immersed in ethanol and sonicated in an ultrasonic bath to clean the surface. A silicon rubber O-ring of 0.35-cm diameter was placed on the glass substrate. Polystyrene latex (20 µL, 0.2 wt%, diameter: 0.212 µm, Nissin EM) dispersed in water was dropped into the region surrounded by the silicon rubber O-ring on the glass substrate, and the droplet was uniformly spread over the inside of the silicone rubber O-ring. The substrate was dried by slowly evaporating the water solvent in an airtight box. The polystyrene particles were self-organized two-dimensionally inside the ring on the glass plate (Figure 2). An Al layer of 3-µm thickness was deposited on the 2-D particle array using a vapor deposition apparatus (ALVAC EX-201) with Al (99.99% purity, Wako) serving as the vapor deposition source, at a deposition rate of 20 nm·s^{-1} for 2.5 min. The deposited Al was mechanically cleaved from the glass plate, and then immersed in toluene to remove polystyrene particles from the Al surface. After removal of the particles, anodization was conducted at a constant voltage of 80 V at 17 °C for 3 min using a direct-current source. Pores in the porous alumina were widened by etching the sidewall of the pores in 5 wt % phosphoric acid solution at 30 °C for 80 min. The structure of the obtained porous alumina was observed using a scanning electron microscope (SEM: JEOL JSM 6100, Hitachi S-5000).

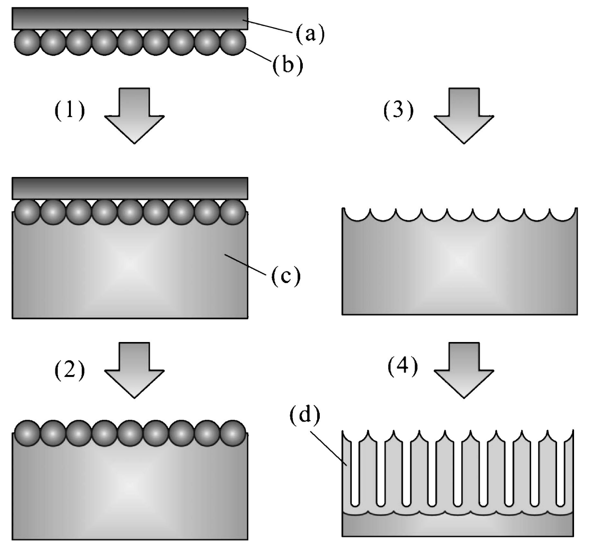

Figure 1. Schematic diagram of fabrication of highly ordered porous alumina using self-organized 2-D polystyrene particle array. (1) deposition of Al on the polystyrene particles array, (2) cleavage of the glass plate from the deposited Al, (3) removal of polystyrene particles by immersing the Al substrate into toluene, (4) anodization for formation of porous alumina. (a) glass plate, (b) self-organized polystyrene particle array, (c) Al, (d) porous alumina.

Figure 3 shows a surface SEM image of Al fabricated by depositing Al onto the polystyrene two-dimensional array. This SEM image demonstrates that highly ordered concaves can be replicated from the polystyrene particle array onto the surface of the deposited Al. The concaves fabricated on the deposited Al have a pore diameter of 200 nm and pore period (center-to-center distance between adjacent pores) of 200 nm.

Figure 4 shows surface and cross-sectional SEM images of the porous alumina after anodization in 0.5 to 2.8 wt % oxalic acid solutions and pore widening in a 5 wt % phosphoric acid solution for 80 min. The images reveal an almost ideally arranged

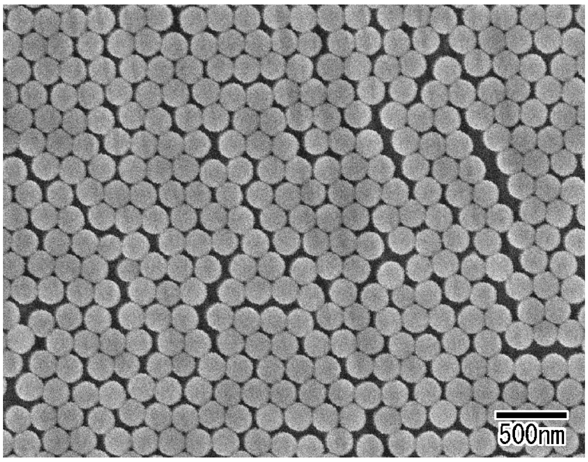

Figure 2. SEM image of self-organized two-dimensional array of polystyrene particles on a glass plate. Average diameter of the particles is 200 nm.

hexagonal cell configuration having a cell size of approximately 200 nm which corresponds to that of the pretextured concaves on the surface of deposited Al, straight parallel channels which are perpendicular to the substrate. Moreover, observation confirmed that concaves fabricated using the self-organized particle array served as a starting point for the formation of pores and the growth of channels. Thus, the results demonstrate the feasibility of employing a self-organized particle array as a master for the introduction of an appropriate texture on an Al surface in the fabrication of long-range-ordered channel array architecture.

We have demonstrated the feasibility of fabricating highly ordered anodic porous alumina with a channel of high aspect ratio, using a self-organized array of polystyrene particles. Ordered concaves formed by replicating the surface structure of the self-organized array of polystyrene particles to the Al surface initiate the development of pores and guide the growth of channels. Furthermore, this process advances to the fabrication of highly ordered anodic porous alumina with a nanometer-scale periodicity. Monodispersed metal colloids[7] and biomolecules[8] with ten or less than ten nm in diameter have been reported to be arranged in a 2-D hexagonal closed pack structure over large

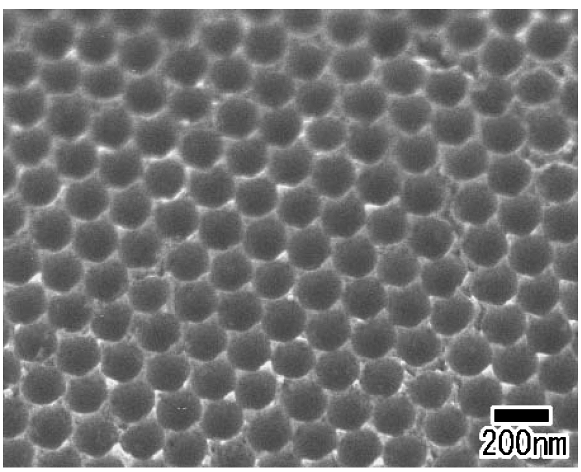

Figure 3. SEM image of Al surface after removal of ordered polystyrene particle array from the deposited Al.

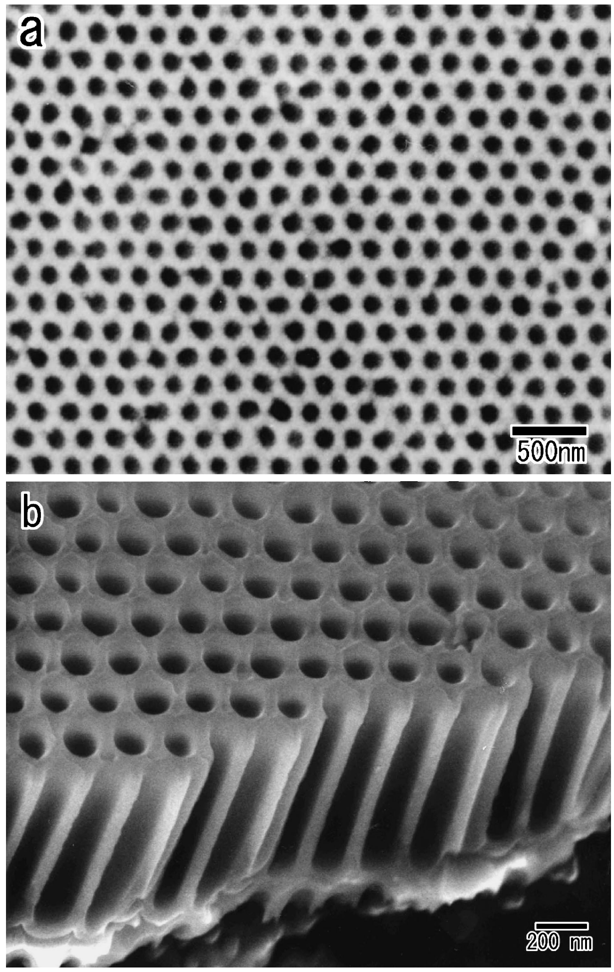

Figure 4. SEM images of highly ordered anodic porous alumina fabricated using self-organized two-dimensional polystyrene particle array from (a) surface and (b) cross-sectional views.

area. The so-called top down process, such as conventional electron-beam lithography systems are hard to fabricate the structure of few tens nm, so that the smallest interval of texturing mold for the fabrication of porous alumina is reported 63 nm in periodicity.[9] Employment of these 2-D crystals leads to the fabrication of highly ordered anodic porous alumina with a smaller period than that of the porous alumina fabricated using conventional electron-beam lithography.

References

1 C. A. Huber, T. E. Huber, M. Sadoqi, J. A. Lubin, S. Manalis, and C. B. Prater, *Science*, **263**, 800 (1994).
2 H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
3 H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, and T. Tamamura, *Appl. Phys. Lett.*, **71**, 2770 (1997).
4 H. Asoh, K. Nishio, M. Nakao, T. Tamamura, and H. Masuda, *J. Electerochem. Soc.*, **148**, B152 (2001).
5 H. Masuda, M. Yotsuya, M. Asano, K. Nishio, M. Nakao, A. Yokoo, and T. Tamamura, *Appl. Phys. Lett.*, **78**, 826 (2001).
6 N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, *Langmuir*, **8**, 3183 (1992).
7 X. M. Lin, H. M. Jaeger, C. M. Sorensen, and K. J. Klabunde, *J. Phys. Chem. B*, **105**, 3353 (2001).
8 I. Yamashita, *Thin Solid Films*, **393**, 12 (2001).
9 H. Asho, K. Nishio, M. Nakao, A. Yokoo, T. Tamamura, and H. Masuda, *J. Vac. Sci. Technol., B*, **19**, 569 (2001).

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