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Preparation of ideally ordered through-hole anodic porous alumina membranes by two-layer anodization

Takashi Yanagishita*, Atsushi Kato, and Hideki Masuda

Department of Applied Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

*E-mail: yanagish@tmu.ac.jp

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Ideally ordered anodic porous alumina through-hole membranes were prepared by a combination of the pretexturing of Al and subsequent two-layer anodization. In the two-layer-anodized sample, the selective dissolution of a layer formed in concentrated H_2SO_4 generated an ideally ordered through-hole membrane. The repetition of two-layer anodization and the detachment of the membrane allowed the high-throughput preparation of an ideally ordered anodic porous alumina membrane from a single pretextured Al substrate. The obtained ideally ordered through-hole membranes are expected to be used in various application fields that require ideally ordered through-hole membranes.

1. Introduction

There has been increasing interest in anodic porous alumina, which is formed by the anodization of Al in an acidic electrolyte, because of its usefulness in a wide range of application fields.[1–8] For the functional application of anodic porous alumina, the degree of ordering of its hole arrangement is important for optimizing the performance of the obtained devices.[9–11] One process for the preparation of anodic porous alumina with an ordered hole arrangement is the naturally occurring self-ordering of holes arranged under appropriate anodizing conditions.[9,12–14] Another process for controlling the hole arrangement of anodic porous alumina is the pretexturing of Al.[15] In this process, a pretextured pattern on Al formed by imprinting using a mold can control the sites for hole development at the initial stage of anodization and produce single-domain porous alumina with an ideally ordered hole arrangement without defects and dislocations over the entire sample. An additional advantage of this process is that hole array structures with an extremely high uniformity of the hole size can be obtained. On the basis of these characteristics, ideally ordered anodic porous alumina is expected to be used in various application fields, typified by precise filtration, in which uniformly sized holes are required. A problem of this process is its low throughput during fabrication because only one porous alumina membrane can be obtained from the pretextured Al. In the present work, a new process has been developed to overcome this problem. This process is based on the process for the effective preparation of through-hole membranes in naturally occurring ordered anodic porous alumina based on two-layer anodization.[16] In this process, two-layer anodization, consisting of a first anodization in an appropriate electrolyte to obtain the desired thickness and a second anodization in a concentrated H_2SO_4 electrolyte followed by the detachment of the membrane through the selective etching of the second layer, generates a through-hole membrane very easily. The selective dissolution of the second anodized layer is caused by the high solubility of the oxide layer formed in concentrated H_2SO_4. In addition to the easy formation of the through-hole membrane, the process allows the high-throughput formation of ordered anodic porous alumina owing to the possibility of the repeated use of the Al substrate with an ordered array of concaves corresponding to the structure of the barrier layer of the detached membrane. The subsequent anodization of the Al substrate with an ordered array of concaves generates the ordered anodic porous alumina because each concave acts as an initiation site for the development of a hole. The repetition of this process allows the formation of a large number of ordered porous membranes. Here, we applied the two-layer anodization process to the high-throughput fabrication of ideally ordered through-hole membranes. By adopting the two-layer anodization process, the formation of a large number of ideally ordered through-hole membranes can be achieved from a single textured Al substrate. The present process is expected to extend the range of application fields of ideally ordered anodic porous alumina membranes because it allows the easy and low-cost fabrication of ideally ordered anodic porous alumina.

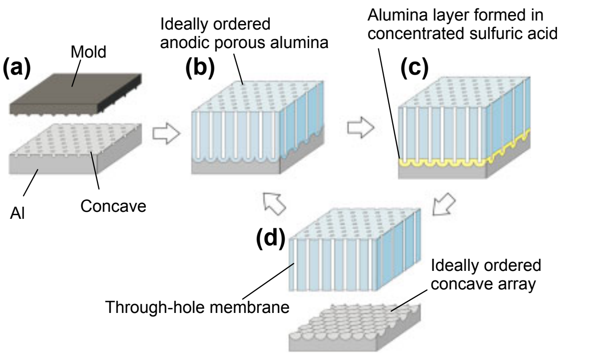

Fig. 1. (Color online) Schematic drawings of fabrication process for ideally ordered anodic porous alumina membranes: (a) pretexturing of Al; (b) preparation of ideally ordered anodic porous alumina by anodization; (c) anodization in concentrated sulfuric acid; (d) detachment of the porous alumina membrane by selective etching of bottom part of alumina layer.

2. Experimental methods

Figure 1 shows schematic drawings of the fabrication process for an ideally ordered through-hole anodic porous alumina membrane. An Al sheet ($8 \times 1\,cm^2$, 99.99% purity) was annealed at 450 °C for 1 h to facilitate the formation of concaves on the surface of the Al sheet by a pretexturing process involving nanoimprinting. Prior to pretexturing, the Al sheet was polished electrochemically using a mixed solution of perchloric acid and ethanol. The pretexturing of Al

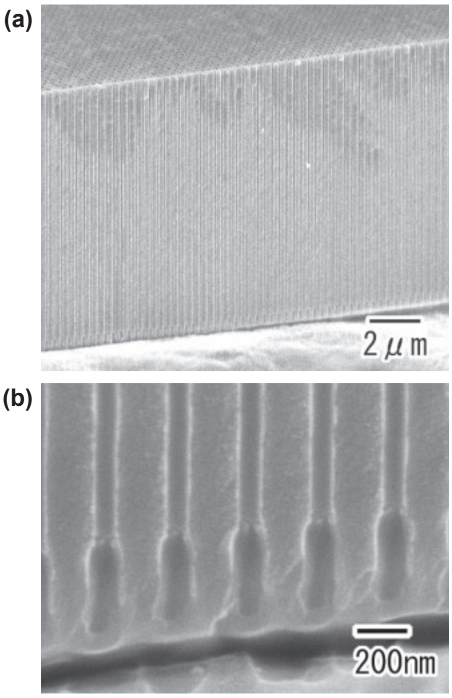

Fig. 2. Cross-sectional SEM images of ideally ordered anodic porous alumina with 300 nm period after anodization in concentrated sulfuric acid; (a) low- and (b) high-magnification views.

was carried out by nanoimprinting using a Ni mold with an ideally ordered array of convexes with a 300 nm period. For the first anodization, pretextured Al was anodized in a mixed solution of 0.3 M phosphoric acid and 0.25 M oxalic acid at a constant voltage of 120 V at 0 °C for 30 min. For the second anodization, to form a highly soluble alumina layer, the specimen was anodized in 16 M sulfuric acid at a constant voltage of 120 V at 0 °C for 25 min. After the second anodization, the ideally ordered through-hole anodic porous alumina membrane was detached from the Al substrate through the selective dissolution of the second anodization layer by etching using a mixed aqueous solution of 1.8 wt % chromic acid and 6 wt % phosphoric acid at 30 °C for 10 min. By the repeated anodization and detachment of the membrane, we can obtain a large number of ideally ordered through-hole anodic porous alumina membranes from a single pretextured Al substrate. The obtained samples were observed by scanning electron microscopy (SEM; JEOL JSM-6700F).

3. Results and discussion

Figure 2 shows cross-sectional SEM images of ideally ordered anodic porous alumina with a 300 nm hole interval after the anodization in concentrated sulfuric acid. In the low-magnification image shown in Fig. 2(a), it was observed that straight holes with a high aspect ratio were arranged at uniform hole intervals. In the case of the sample in Fig. 2, the thickness was 10 μm. From the high-magnification image shown in Fig. 2(b), it was observed that the bottom part of the oxide layer had larger holes than the upper part. The bottom part corresponds to the oxide layer formed in concentrated H_2SO_4. Owing to its relatively high solubility, the pore size increased during anodization. In the case of the sample in Fig. 2, the thickness of the alumina layer formed in the concentrated H_2SO_4 was 430 nm.

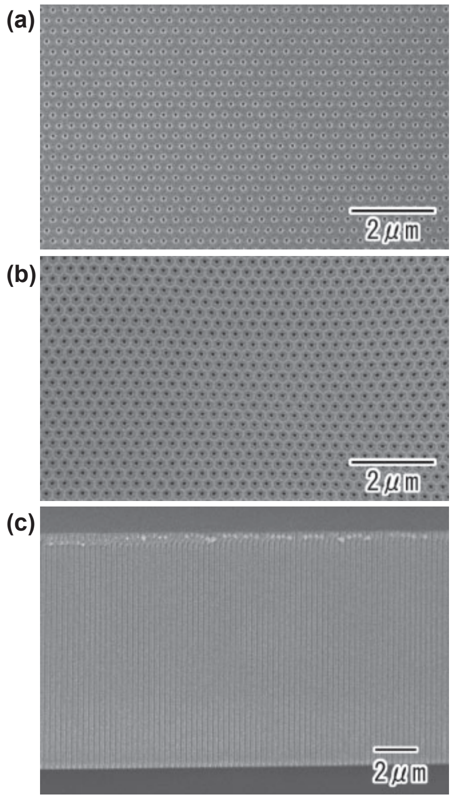

Fig. 3. SEM images of ideally ordered anodic porous alumina through-hole membrane after detaching the Al substrate: (a) top-surface, (b) back-surface, and (c) cross-sectional views.

Figure 3 shows SEM images of an ideally ordered through-hole anodic porous alumina membrane with a 300 nm hole period obtained by detaching it from the Al substrate. The detachment of the through-hole membrane was carried out through the selective dissolution of the second anodization layer formed in concentrated H_2SO_4 using a mixed solution of chromic acid and phosphoric acid for 10 min. From the top-surface and back-surface SEM images shown in Figs. 3(a) and 3(b), respectively, it was confirmed that uniformly sized holes were arranged ideally with a 300 nm period. The cross-sectional SEM image shown in Fig. 3(c) reveals that the alumina layer formed in concentrated H_2SO_4 was dissolved selectively by the wet-etching treatment.

In the present process, the ideally ordered hole arrangement must be maintained in the depth direction of the oxide layer to fabricate a large number of ideally ordered membranes from a single textured Al substrate. The degree of hole ordering during the growth of the oxide layer in the pretextured Al substrate depends on the anodizing conditions;[17] thus, the selection of appropriate anodizing conditions is important for the growth of ideally ordered anodic oxide membranes. Through an investigation of the appropriate conditions for maintaining the ordering of the hole arrangement in the depth direction of the oxide, it was found that an ideally ordered hole arrangement could be maintained for a thickness of over 100 μm for the first anodization layer by using the mixed electrolyte of oxalic acid and phosphoric acid. In contrast, in the second anodization layer formed in the concentrated H_2SO_4, the degree of ordering decreased with the growth of the oxide, and the maintainance of the ideally ordered hole arrangement was difficult in the case of

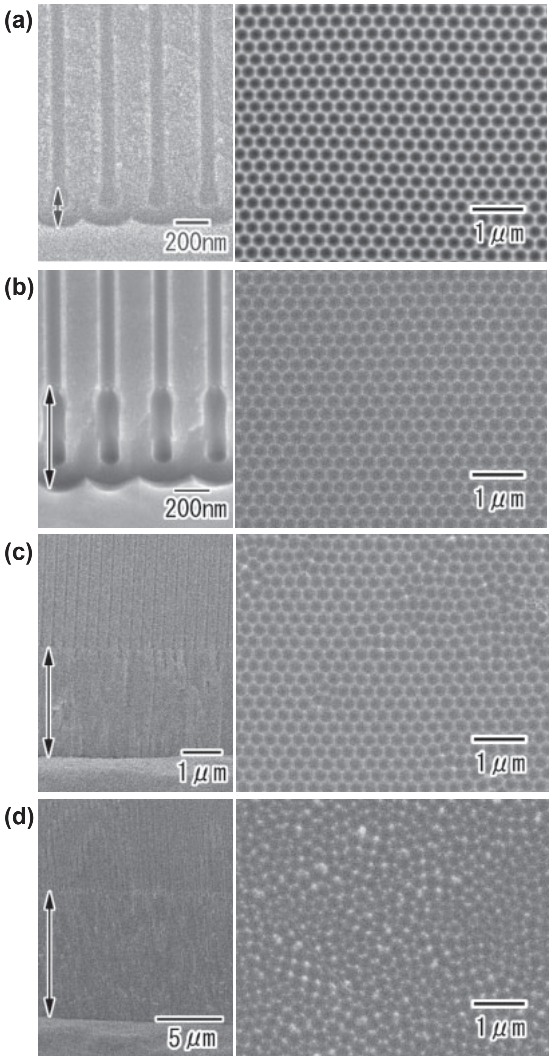

Fig. 4. Dependence of degree of ordering of hole arrangement on the thickness of the alumina layer formed in concentrated sulfuric acid. Layers are shown with thicknesses of (a) 0.2, (b) 0.5, (c) 3, and (d) 10 μm. The anodization in concentrated sulfuric acid was conducted in 16 M sulfuric acid at 160 V and at 0 °C for (a) 10, (b) 30, (c) 50, and (d) 150 min.

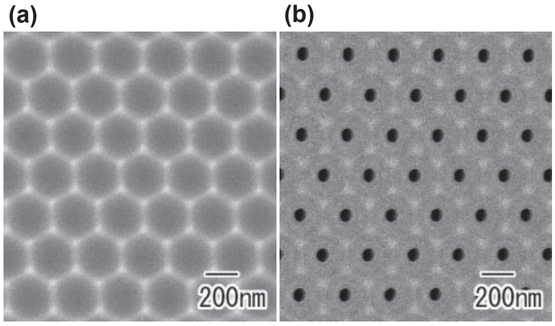

Fig. 5. (a) SEM image of Al substrate after detachment of ideally ordered anodic porous alumina membrane; (b) SEM image of ideally ordered anodic porous alumina formed by subsequent anodization of Al substrate.

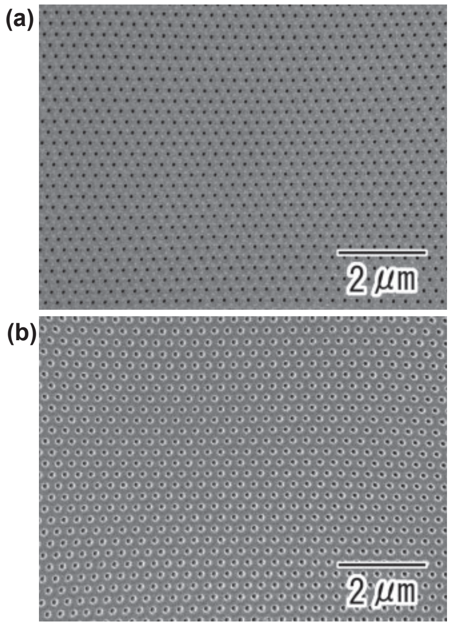

Fig. 6. SEM images of ideally ordered anodic porous alumina membranes obtained by (a) three and (b) five repetitions of the process.

the thick oxide layers. For the reproducible detachment of the membrane, the growth of a sufficiently thick second anodization layer to allow its detachment is required. Therefore, the establishment of an appropriate thickness for the second anodization layer is essential. Figure 4 shows the dependence of the thickness of the second anodization layer and the degree of ordering of the hole arrangement on the anodization time. The degree of ordering of the hole arrangement was evaluated by observing the arrangement of the concaves on the Al substrate obtained after the detachment of the membrane. From Fig. 4, it was observed that the thickness of the second anodization layer increased as the second anodization proceeded. The thicknesses of the second anodization layer were 0.2 μm [Fig. 4(a)], 0.5 μm [Fig. 4(b)], 3 μm [Fig. 4(c)], and 10 μm [Fig. 4(d)] for the anodization times of 10, 30, 50, and 150 min, respectively. Concerning the dependence of the degree of ordering of the hole arrangement, the ideally ordered hole arrangement was maintained at the thicknesses of 0.2 and 0.5 μm. However, a certain amount of disorder was observed at the thickness of 3 μm, and no ordering was observed at the thickness of 10 μm. From these results, we concluded that a thickness of 0.5 μm was most appropriate for the second anodization layer. In the remainder of this study, a second anodization layer of this thickness was adopted.

Figure 5 shows the results of the subsequent repeated anodization of the Al substrate obtained after the detachment of the porous alumina membrane. In the surface SEM image of the unanodized Al shown in Fig. 5(a), an ideally ordered concave array with a 300 nm period was observed over the sample. This array was formed through the transcription of the structure of the barrier layer in the previously fabricated anodic oxide layer. The subsequent anodization of the Al substrate was carried out under the same anodizing conditions as the first anodization. In this sample, the thickness of the alumina layer formed in concentrated H_2SO_4 was 0.5 μm. From the surface image of the anodic porous alumina after the subsequent anodization shown in Fig. 5(b), an ideally ordered hole arrangement was confirmed. This indicates that the ordered concaves formed by the first anodization can act as initiation sites for hole development during the second anodization.

Figure 6 shows SEM images of through-hole porous alumina membranes obtained by three and five repetitions of the process. The thickness of both membranes shown in

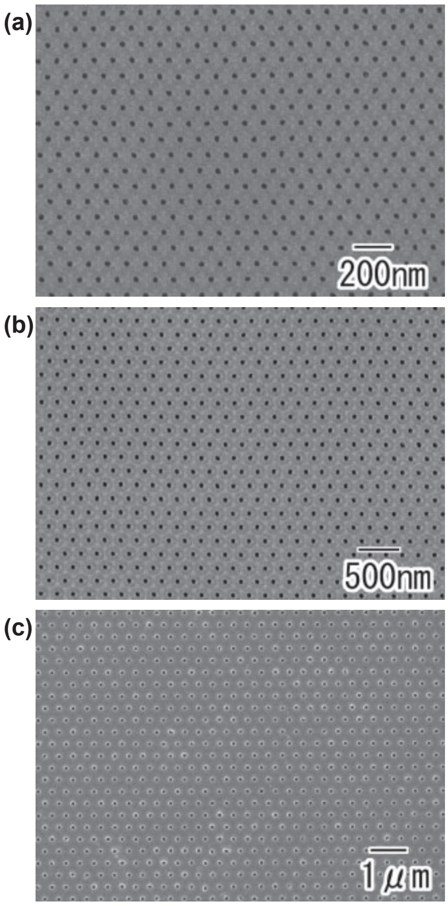

Fig. 7. SEM images of ideally ordered anodic porous alumina with different hole periods obtained by two repetitions of the process. The hole intervals in the porous alumina membranes were (a) 100, (b) 200, and (c) 400 nm.

Fig. 6 was 10 μm. The surface SEM images shown in Fig. 6 reveal that the ideally ordered porous alumina was maintained even after multiple repetitions of the process. This means that this process allows the fabrication of a large number of ideally ordered through-hole anodic porous alumina membranes from a single pretextured Al substrate.

Figure 7 shows SEM images of ideally ordered anodic porous alumina with different hole intervals obtained by two repetitions of the present process. The ideally ordered anodic porous alumina with different hole intervals was prepared by changing the interval between the convexes of the mold used for the pretexturing of Al. The hole intervals in the obtained through-hole membranes were 100 nm [Fig. 7(a)], 200 nm [Fig. 7(b)], and 400 nm [Fig. 7(c)]. The thickness of the alumina layer formed in concentrated sulfuric acid was 500 nm in all samples. The concentration of H_2SO_4 was adjusted for the formation of membranes with various hole intervals, which were determined by the anodizing voltage. For the membranes with small hole intervals formed at low voltages, a relatively low concentration of H_2SO_4 was adopted because a very high concentration of H_2SO_4 would have reduced the growth rate of the oxide. In contrast, for the membranes with large hole intervals formed at high anodizing voltages, a high concentration of H_2SO_4 was adopted to eliminate the excess current, which would destroy the membrane by burning. As a result of optimizing the concentrations, we used electrolytes with concentrations of 12, 14, and 17 M for the hole intervals of 100, 200, and 400 nm, respectively. In all cases, an ideally ordered hole arrangement was observed in the SEM images shown in Figs. 7(a)–7(c). From these results, we can conclude that the present process allows the high-throughput preparation of ideally ordered anodic porous alumina membranes with various hole intervals.

4. Conclusions

Ideally ordered anodic porous alumina membranes with through-holes were prepared by a combination of the pretexturing of Al and two-layer anodization using concentrated sulfuric acid. The repetition of the anodization and detachment of the membranes allowed the fabrication of ideally ordered through-hole membranes from a single textured Al substrate. The hole interval of the obtained ideally ordered through-hole membranes could be controlled by changing the interval in the pattern on the mold and by adjusting the anodizing conditions. The obtained through-hole membranes are expected to be used in various functional application fields requiring an ideally ordered hole arrangement.

1) S. H. Jeong, H. Y. Hwang, K. H. Lee, and Y. Jeong, Appl. Phys. Lett. **78**, 2052 (2001).
2) G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R. B. Wehrspohn, J. Choi, H. Hofmeister, and U. Gösele, J. Appl. Phys. **91**, 3243 (2002).
3) A. Kolmakov, Y. Zhang, G. Cheng, and M. Moskovits, Adv. Mater. **15**, 997 (2003).
4) P. L. Taberna, S. Mitra, P. Poizot, P. Simon, and J.-M. Tarascon, Nat. Mater. **5**, 567 (2006).
5) S. A. Needham, G. X. Wang, and H. K. Lin, J. Power Sources **159**, 254 (2006).
6) E. M. I. M. Ekanayake, D. M. G. Preethichandra, and K. Kaneto, Biosens. Bioelectron. **23**, 107 (2007).
7) Y. Cao and T. T. E. Mallouk, Chem. Mater. **20**, 5260 (2008).
8) A. Thormann, N. Teuscher, M. Pfannmöller, U. Rothe, and A. Heilmann, Small **3**, 1032 (2007).
9) H. Masuda and K. Fukuda, Science **268**, 1466 (1995).
10) H. J. Fan, W. Lee, R. Scholz, A. Dadgar, A. Krost, K. Nielsch, and M. Zacharias, Nanotechnology **16**, 913 (2005).
11) Y. Piao, H. Lim, J. Y. Chang, W. Lee, and H. Kim, Electrochim. Acta **50**, 2997 (2005).
12) H. Masuda, F. Hasegawa, and S. Ono, J. Electrochem. Soc. **144**, L127 (1997).
13) H. Masuda, K. Yada, and A. Osaka, Jpn. J. Appl. Phys. **37**, L1340 (1998).
14) H. Masuda, M. Nagae, T. Morikawa, and K. Nishio, Jpn. J. Appl. Phys. **45**, L406 (2006).
15) H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, and T. Tamamura, Appl. Phys. Lett. **71**, 2770 (1997).
16) T. Yanagishita and H. Masuda, Electrochim. Acta **184**, 80 (2015).
17) H. Asoh, K. Nishio, M. Nakao, T. Tamamura, and H. Masuda, J. Electrochem. Soc. **148**, B152 (2001).