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High-Throughput Fabrication Process for Highly Ordered Through-Hole Porous Alumina Membranes Using Two-Layer Anodization

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ABSTRACT

Alumina through-hole membranes with an ordered array of holes were obtained by the wet etching of two-layered anodic porous alumina, which was formed by the first anodization of Al in an acid solution under standard conditions and the subsequent anodization in concentrated H_2SO_4. In this process, the detachment of the porous alumina membrane and through-holing could be achieved simultaneously by etching in an appropriate acid solution. This is because the oxide layers formed in concentrated H_2SO_4 were more easily dissolved than the oxide layer formed in the standard acid solution. After the detachment of the membrane, the residual Al substrate could be repeatedly used for the preparation of ordered through-hole membranes. The obtained through-hole membranes are expected to be used in various applications.

1. Introduction

Anodic porous alumina, which is formed by the anodization of Al in an acidic electrolyte, has attracted much interest owing to its applicability in a wide variety of fields [1–5]. This material has a unique geometrical structure, which is composed of a closely packed array of columnar cells with central uniformly sized pores. The recent development of anodic porous alumina with a long-range ordered hole arrangement has increased the importance of this material as a starting structure for the fabrication of various types of functional devices [6]. For the application of anodic porous alumina, the preparation of membranes with through-holes from the front surface to the back surface is important. For example, a through-hole alumina membrane is a promising candidate filter for precise filtration [7–9]. In the case of application to the synthesis of metal and semiconductor nanowires, through-hole membranes with an electrode on one side are used as templates for the electrochemical deposition of the target material [10,11]. The fabrication process for through-hole membranes has been investigated for a long time. However, a facile and reliable process that does not require special techniques has not yet been established. Usually, through-hole membranes are prepared by a process combining the detachment of a porous oxide layer from an Al substrate with the subsequent through-holing by dissolving the bottom part of the oxide called the barrier layer [12,13]. The detachment of the oxide layer is usually carried out by the selective chemical dissolution of an Al substrate using an appropriate etchant such as aqueous $HgCl_2$ or Br_2 in ethanol. The barrier layer is then removed for through-holing by chemical etching using an appropriate acid, typically H_3PO_4. A protection layer is used as necessary to prevent the dissolution of the surface of the membrane [14]. However, the inhibition of the increase in pore size is difficult owing to the dissolution of the inner walls of the pores by the infiltrating etchant. As an alternative process, the reverse-voltage detachment of the oxide layer has been reported [15]. In this process, the oxide layer is detached from the Al substrate by reversing the applied voltage from anodic to cathodic after the formation of the oxide layer. The H_2 gas that evolved at the interface between the oxide layer and the Al substrate mechanically detaches the oxide layer from the Al substrate. However, the use of this process is limited to small samples owing to the difficulty in detaching a large membrane without cracking from the Al substrate. Moreover, even in this process, the barrier layer has to be removed by chemical etching. As a process that enables detachment and through-holing in a single step, electrolysis at a high current in a mixed electrolyte of C_2H_5O and $HClO_4$ has recently been reported [16]. In this process, high-current anode electrolysis in a mixture of C_2H_5O and $HClO_4$ acid leads to the dissolution of the barrier layer and allows the detachment of the oxide layer followed by through-holing. However, the controllable formation of the through-hole membrane with the desired hole size is difficult owing to the difficulty in controlling the dissolution

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of the barrier layer in high current anode electrolysis. In addition, in both the above methods, the repeated use of the Al substrate for the preparation of an ordered anodic porous alumina membrane is difficult owing to the roughening of the Al surface by the extremely high current density used to detach the oxide layer. In the present work, we describe a new high-throughput process for fabricating through-hole alumina membranes with a controlled pore size. This process is based on the new finding that through-hole membranes can be easily obtained by dissolving a two-layered sample in an appropriate etchant, which was formed by a first anodization under standard anodizing conditions and a subsequent anodization in concentrated H_2SO_4 [17]. This is because the oxide layer formed in the concentrated H_2SO_4 can be easily dissolved in an appropriate etchant. Accordingly, both the detachment of the oxide and through-holing can be achieved simultaneously by etching. This process has several advantages over existing processes. It enables the high-throughput fabrication of large through-hole membranes without using any special technique. In addition, this process has precise controllability of the pore size of the obtained through-hole membrane owing to the unnecessity of prolonged etching, which increases the pore sizes. Another advantage is that the process allows the repeated use of the Al substrate for the preparation of an anodic porous alumina membrane with an ordered hole arrangement, because the detachment of the membrane under mild conditions does not roughen the Al surface. In this process, the ordered array of concaves, corresponding to the structure of the detached oxide barrier layer, can be maintained on the Al surface even after the detachment of the oxide layer by wet etching. Accordingly, the subsequent anodization of the Al substrate at the same anodizing voltage as the first anodization generates the ordered porous alumina from the surface, because the formation of ordered concaves by the first anodization leads to the highly ordered hole arrangement [6,14]. By the repetition of this process, we can repeatedly obtain highly ordered through-hole membranes. This high-throughput fabrication process for ordered through-hole membranes is expected to be used for the fabrication of various types of functional device requiring an ordered hole arrangement with a specific pore size.

2. Experimental

Fig. 1 shows a schematic for the fabrication of through-hole porous alumina membranes. An Al plate ($90 \times 40\,mm^2$, 99.99% purity) was electrochemically polished using a mixed solution of perchloric acid and ethanol. In the present study, for the preparation of anodic porous alumina with an ordered arrangement from the front surface to the bottom on the Al substrate, a two-step anodization process was adopted [14]. In this process, an oxide layer, the bottom of which has an ordered hole arrangement induced by a first anodization step, was removed in an etchant, and the subsequent anodization step was conducted at the same anodization voltage as the first anodization. The ordered array of concaves formed on Al after the removal of the oxide layer acts as an initiation site for hole development and generates a highly ordered hole arrangement from the surface. The Al was anodized at a constant voltage of 40 V in 0.3 M $H_2C_2O_4$ at 17 °C for 12 h. The obtained oxide layer was removed in a mixed solution of CrO_3 (1.8 wt%) and H_3PO_4 (6 wt%) at 50 °C. The Al with an ordered array of concaves on the surface was anodized under the same conditions as the first anodization for 90 min. After rinsing the sample in distilled water, the sample was anodized again in 12 M H_2SO_4 at a constant voltage of 40 V at 0 °C for 20 min. The detachment and through-hole formation were carried out in the mixed solution of CrO_3 and H_3PO_4 at 30 °C for 15 min. The anodization in 12 M H_2SO_4 generated the oxide layer, which readily dissolved in the mixed solution of CrO_3 and H_3PO_4. The through-hole membrane was obtained by detaching the membrane from the Al substrate. The repetition of this process generated a through-hole membrane with a highly ordered hole arrangement, because highly ordered concaves on the Al were maintained even after detaching the alumina membrane from the Al. For the formation of through-hole membranes with smaller intervals and holes, the first anodization was carried out in 0.3 M H_2SO_4 at 25 V. Even in this case, two-step anodization was adopted as necessary. The second anodization was carried out in concentrated H_2SO_4 at the same voltage. The etching of the sample in a mixed solution of CrO_3 and H_3PO_4 generated the through-hole membrane. The obtained samples were observed by SEM (JEOL JSM-6700).

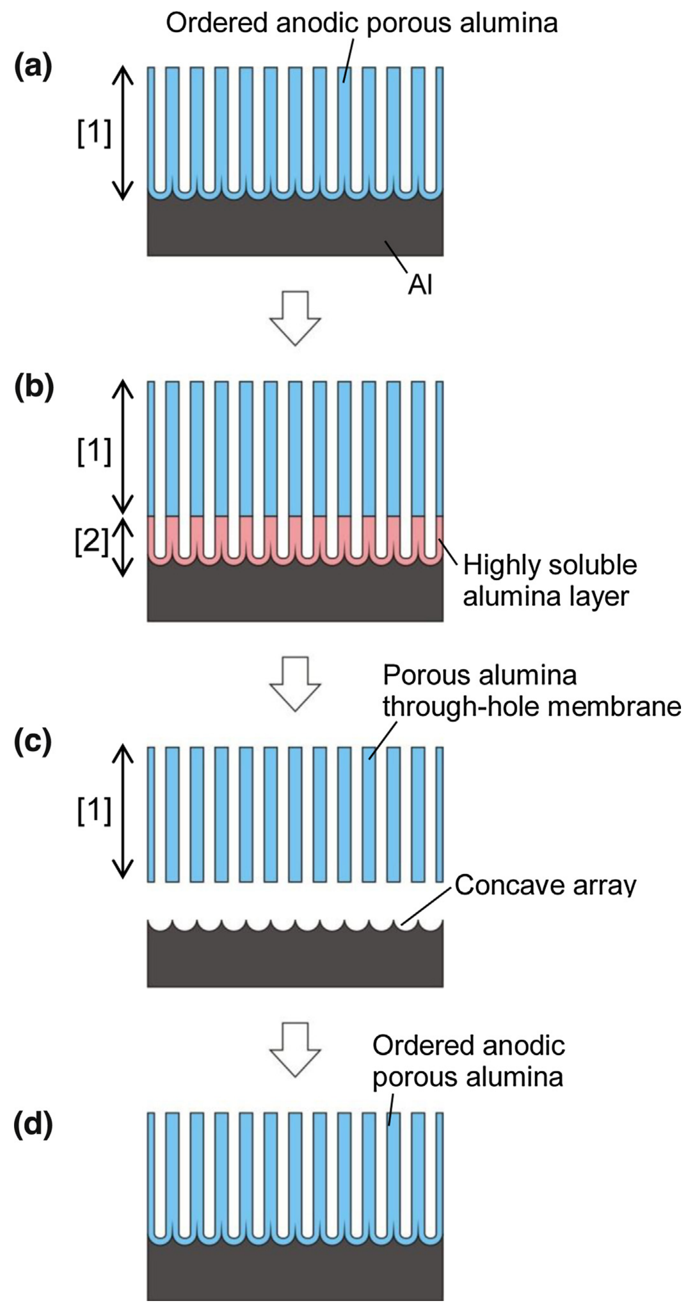

Fig. 1. Schematic drawing of fabrication process for anodic porous alumina through-hole membranes: (a) anodization of Al substrate in $H_2C_2O_4$; (b) anodization in concentrated H_2SO_4; (c) selective dissolution of bottom part of alumina layer by wet etching; (d) anodization in $H_2C_2O_4$.

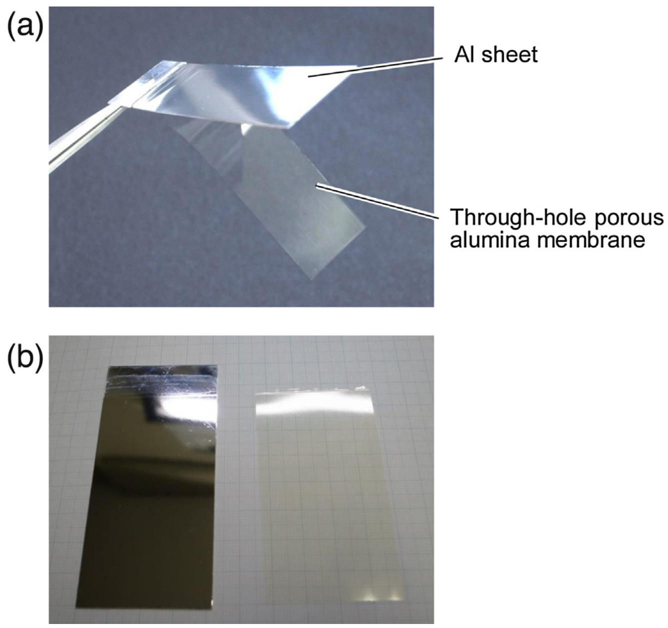

Fig. 2. Photographs of (a) anodic porous alumina detached from Al substrate by etching; (b) anodic porous alumina through-hole membrane after separation.

3. Preparation of Porous Alumina Through-Hole Membrane

Fig. 2 shows the sample after the etching of the two-layered oxide film in a mixed solution of CrO_3 and H_3PO_4. As shown in Fig. 2a, the second layer formed in the concentrated H_2SO_4 was selectively dissolved and the porous alumina membrane was detached from the Al substrate. This detachment was caused by the extremely high solubility of the oxide layer in the concentrated H_2SO_4. It is thought that the high solubility of the alumina formed by the anodization in concentrated H_2SO_4 originates from the containment of sulfate anions in the alumina layer. Form the inductively-coupled plasma analysis, it is confirmed that the alumina layer formed in the concentrated H_2SO_4 contains lots of S derived from sulfate anions of the electrolyte. During the etching, the barrier layer dissolved at the same time to generate the through-hole membrane. After separating the membrane from the substrate, the through-hole membrane was obtained (Fig. 2b). In the present process, the minimum thickness of the alumina layer formed in concentrated H_2SO_4 required for the easy detachment of the membrane was ca. 300 nm. The size of the obtained membrane in Fig. 2b was $75 \times 40\,mm^2$.

Fig. 3 shows scanning electron microscope (SEM) images of the detached through-hole membrane. Note that, a conventional one-step anodization can also be used for the fabrication of through-hole membranes. In this study, a two-step anodization process reported previously was adopted to form through-hole membranes with a highly ordered hole arrangement on both sides of the membranes [14]. In the SEM image of the front surface (Fig. 3a), the highly ordered hole arrangement originating from the two-step anodization process can be observed. The SEM image of the back surface on the side of the barrier layer shows opened holes with an identical arrangement to those on the front surface. This indicates that the etching in the mixed solution of CrO_3 and H_3PO_4 selectively dissolved the second oxide layer formed by the anodization in concentrated H_2SO_4 and enabled both detachment and through-holing in a single step. The pore sizes on the front and back surfaces were 40 and 35 nm, respectively, which are similar to those of the as-anodized anodic oxide layer. This means that the pores were not enlarged by the dissolution in the etchant. The cross-sectional SEM image in Fig. 3c shows that uniformly sized straight holes were formed from the front surface to the back surface. For the sample in Fig. 3, the aspect ratio, given by the hole length divided by the diameter, was 530.

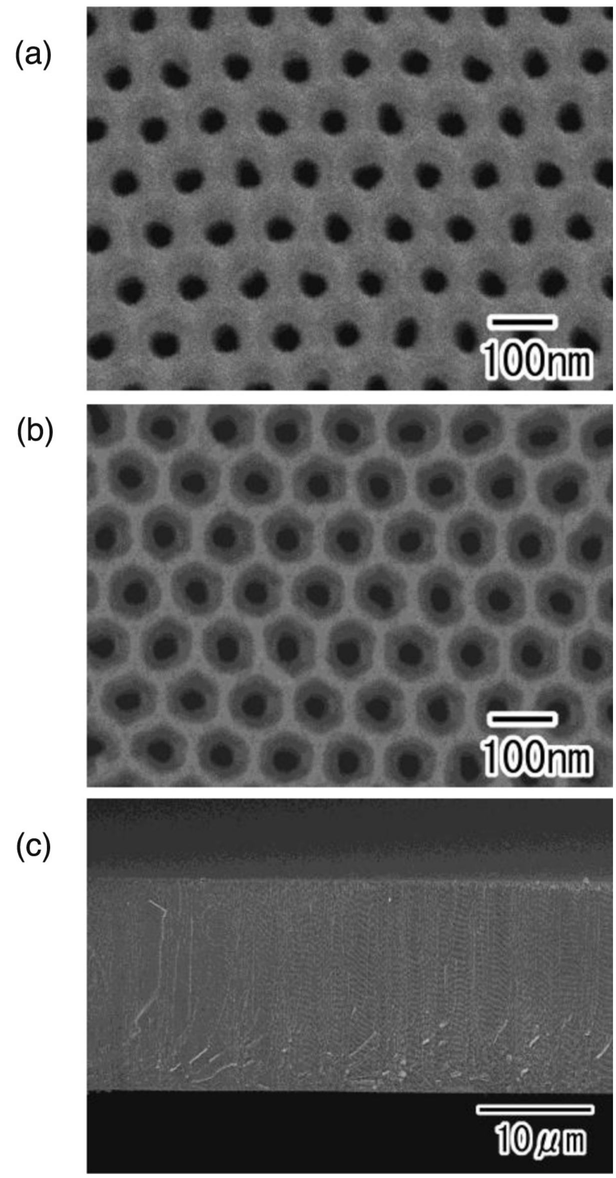

Fig. 3. SEM images of detached through-hole membrane: (a) front surface, (b) back surface, and (c) cross section.

4. Repeated Preparation of Ordered Through-hole Membranes

Fig. 4a shows a SEM image of the Al substrate used to form the through-hole membrane in Fig. 3 after the detachment of the oxide layer. From the SEM image, the formation of an ordered array of shallow concaves was confirmed. The interval between the concaves was 100 nm, corresponding to the structure of the detached oxide barrier layer. This indicates that the shallow ordered concaves are maintained without any roughening even after the detachment of the oxide layer. Fig. 4b shows a SEM image of the anodic porous alumina membrane obtained by the subsequent anodization of the Al substrate with the ordered concaves. From the SEM image, the formation of an anodic porous alumina membrane with a highly ordered hole arrangement was confirmed. This indicates that each shallow concave acts as an

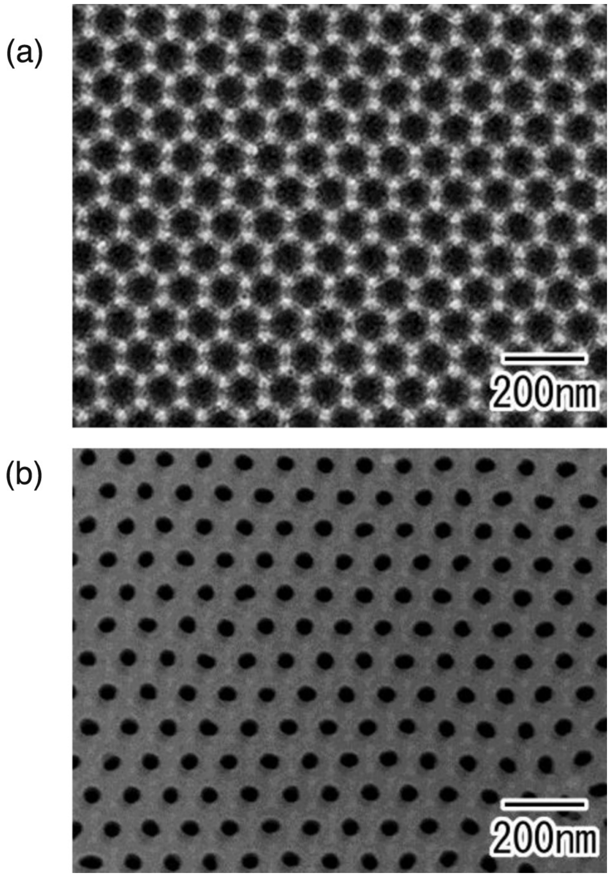

Fig. 4. (a) SEM image of Al substrate after detachment of porous alumina membrane; (b) SEM image of anodic porous alumina after anodization of Al substrate.

initiation site for hole development during the anodization and generates a highly ordered hole arrangement.

Fig. 5 shows SEM images of the through-hole membranes obtained after five and ten repetitions of the process. In both cases, the formation of through-hole membranes with a highly ordered hole arrangement was confirmed. This demonstrates that the process allows the fabrication of a large number of membranes with high throughput.

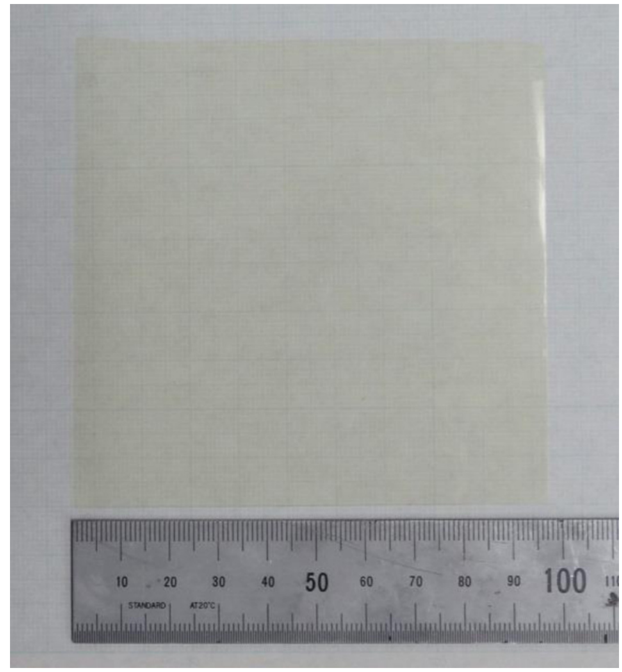

Fig. 6. Photograph of large porous alumina through-hole membrane.

Fig. 6 shows a large through-hole membrane of $100 \times 100\,mm^2$ size. This result indicates that the present process is effective for the fabrication of large through-hole membranes.

5. Through-Hole Membrane with Reduced Hole Interval

Fig. 7 shows the result of applying this process to the fabrication of a through-hole membrane with a shorter hole interval and a smaller hole size. For this sample, the anodization to form the first

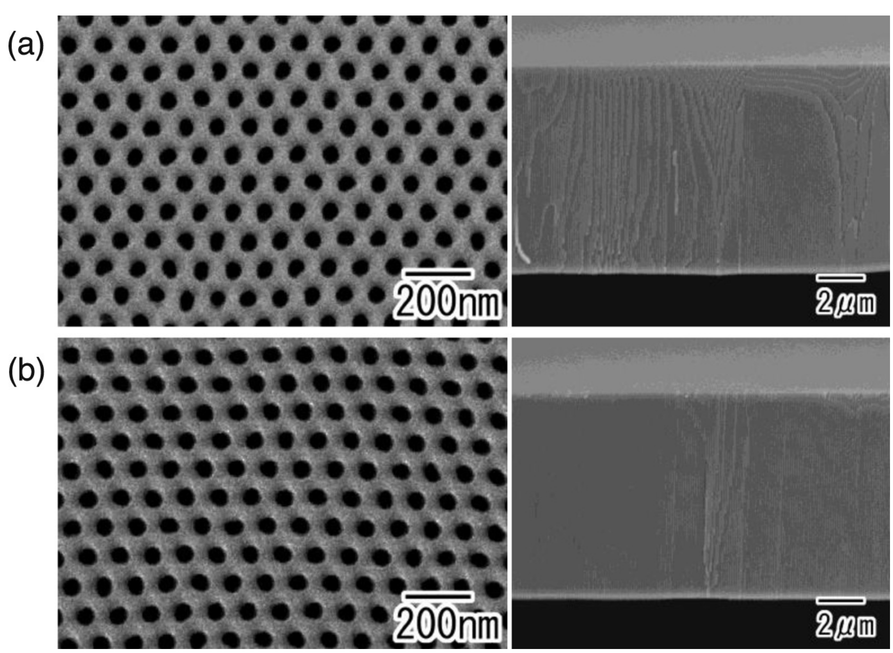

Fig. 5. Surface and cross-sectional SEM images of through-hole membranes obtained after five (a) and ten (b) repetitions of process.

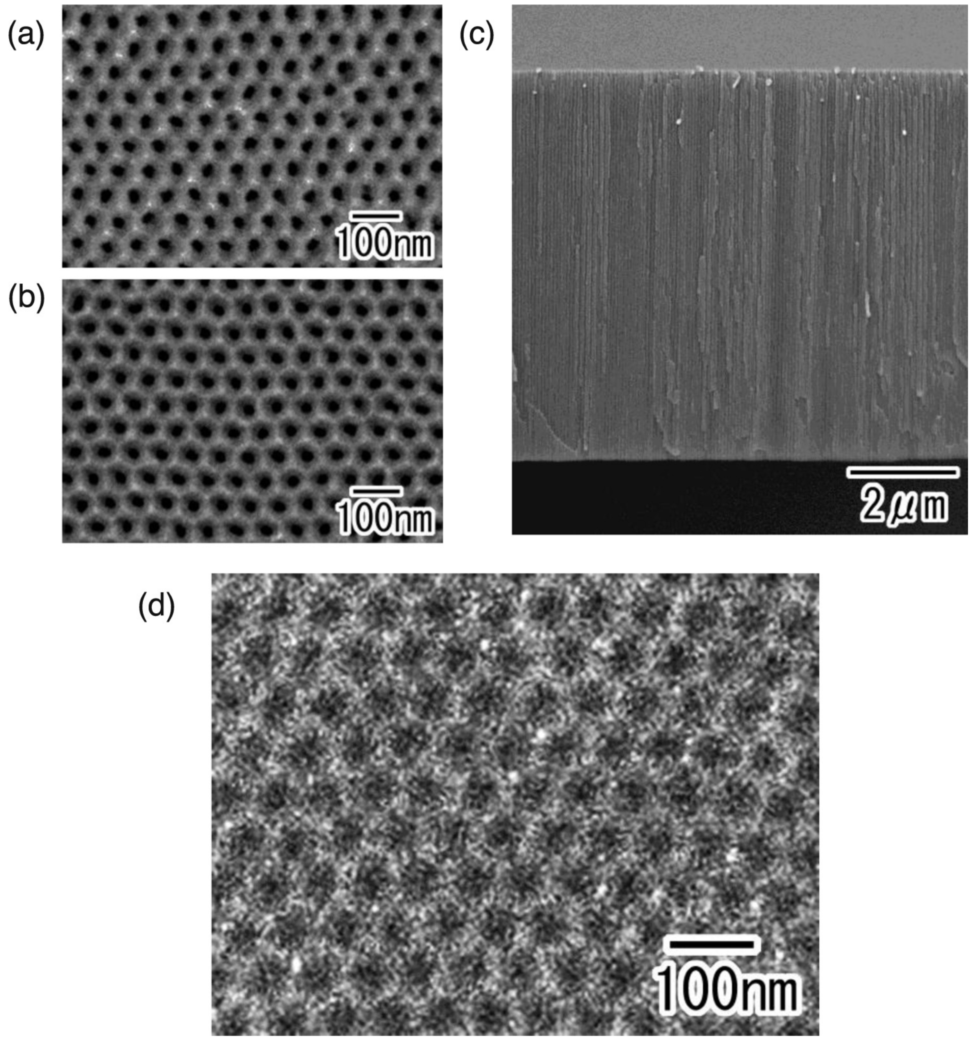

Fig. 7. SEM images of through-hole membrane with shorter hole interval; (a) front surface, (b) back surface, (c) cross-sectional image of through-hole membrane; (d) SEM image of surface of Al substrate after detachment of membrane.

oxide layer was carried out in 0.3 M H_2SO_4 at 25 V and the anodization to form the second oxide layer was carried out in concentrated H_2SO_4 at 25 V [18]. For the sample shown in Fig. 7, a two-step anodization process was adopted [14]. In the SEM image of the front surface, an ordered arrangement of holes formed by two-step anodization can be observed. The SEM image of the back surface shows an identical arrangement of open holes. This indicates that the etching enables the simultaneous detachment and through-holing even in the case of a membrane with a shorter hole interval. The cross-sectional SEM image in Fig. 7c confirmed the growth of straight holes at uniform intervals through the entire thickness of the membrane. The ordered shallow concaves on the Al substrate were maintained without roughening even after the detachment of the oxide layer as shown in Fig. 7d. As a result, a through-hole membrane with an ordered hole arrangement can be obtained repeatedly.

6. Conclusions

Two-layered anodic porous alumina was obtained by a first anodization under standard anodizing conditions and a subsequent anodization in concentrated H_2SO_4. Because the anodic porous alumina formed in the concentrated H_2SO_4 was easily dissolved by wet etching treatment, a through-hole membrane was obtained by dissolving the two-layered anodic porous alumina. After the detachment of the porous alumina membrane, the Al substrate can be repeatedly used for the preparation of through-hole membranes. This process allows the high-throughput preparation of ordered anodic porous alumina through-hole membranes because the ordered array of concaves on the surface of the Al substrate is maintained even after the detachment of the through-hole membrane. The obtained through-hole membranes with an ordered hole arrangement can be applied to various functional devices.

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