

Fabrication of highly ordered nanoporous alumina films by stable high-field anodization

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Abstract

Stable high-field anodization (1500–4000 A m⁻²) for the fabrication of highly ordered porous anodic alumina films has been realized in a H₃PO₄–H₂O–C₂H₅OH system. By maintaining the self-ordering voltage and adjusting the anodizing current density, high-quality self-ordered alumina films with a controllable inter-pore distance over a large range are achieved. The high anodizing current densities lead to high-speed film growth (4–10 μm min⁻¹). The inter-pore distance is not solely dependent on the anodizing voltage, but is also influenced by the anodizing current density. This approach is simple and cost-effective, and is of great value for applications in diverse areas of nanotechnology.

1. Introduction

Self-ordered porous anodic alumina (PAA) films have attracted considerable attention due to their utilization as a host or template structure for the fabrication of diverse nanometre devices, such as electronic [1], magnetic [2] and photonic [3] devices. For the ordinary two-step anodization process, inter-pore distances of typical PAA films range from tens to hundreds of nanometres [4–6], whereas several hundreds of nanometres are important for applying anodic alumina in different areas, especially in the fabrication of optical devices used in the visible spectral range [7]. Masuda *et al* first reported highly ordered PAA films with an inter-pore distance of 500 nm in phosphoric acid solutions at the self-ordering voltage of 195 V [6]. Under a high anodizing voltage, it was difficult to maintain stable electrolysis without 'burning' due to serious heat dissipation problems. Thus, the applicable current density for stable anodization was very low (<100 A m⁻²), which resulted in a very low film-growth efficiency (<200 nm min⁻¹). Therefore, a long anodizing time (16 h) was required to obtain highly ordered PAA films. In recent years, a variety of pre-texturing or pre-patterning

techniques have been invented to achieve highly ordered pore arrangements over a large area [8–11]: for example, ordered depressions produced on aluminium prior to anodization with Si₃N₄ pyramids [8], optical diffraction gratings [9], silica nanospheres [10] or holographic lithography [11]. Shallow predetermined depressions can initiate the pores and guide the growth of a long channel, which leads to a highly ordered pore arrangement in the textured area. However, these pre-patterning techniques are limited because of their expense and the need for accessibility for the external treatments to achieve ordered PAA films. According to Ono *et al* [12], the condition of high current density, i.e. a high electric field, is the key factor that determines the self-ordering of the pore arrangement. Recently, Chu *et al* successfully fabricated highly ordered nanoporous alumina films in sulfuric acid solutions under a high electric field of 40–70 V and 1600–2000 A m⁻² [13]. However, high-field anodization in phosphoric acid solutions has not yet been realized due to the utilization of a much higher anodizing voltage which makes the heat dissipation problems more serious. Although it would facilitate both scientific and commercial applications, fabrication of highly ordered porous anodic alumina films with arbitrary pore intervals in the range of hundreds of nanometres

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by a low-cost, high-efficiency method has remained a major challenge.

In the present paper we report a simple and effective approach to the fabrication of large-scale self-ordered PAA films with large and controllable inter-pore distances by means of two-step high-field anodization. The main idea behind our approach is to raise current densities, i.e. anodizing fields, by using a $\text{H}_3\text{PO}_4\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ system and to maintain the anodizing potential at a self-ordering voltage of 195 V. Stable high-field anodizations ($1500\text{--}4000\text{ A m}^{-2}$), which are much higher than ordinary anodization ($<100\text{ A m}^{-2}$), have been realized in phosphoric acid solutions by adjusting the concentration of phosphoric acid, adding adequate ethanol to the electrolyte, and carefully controlling the experimental conditions. The high anodizing current density leads to high-speed film-growth ($4\text{--}10\text{ }\mu\text{m min}^{-1}$). As a result, highly ordered PAA films with controllable inter-pore distances ($320\text{--}380\text{ nm}$), pore sizes ($80\text{--}140\text{ nm}$) and barrier-layer thicknesses ($120\text{--}150\text{ nm}$) have been achieved.

2. Experimental details

Samples with a radius of 1 cm were cut from a rolled sheet of aluminium (99.999% purity, 0.25 mm thickness), degreased in acetone, washed in deionized water and put into a tailor-made holder with a circular area of 2 cm^2 exposed to the electrolyte. Before anodizing, the aluminium was electropolished at a constant voltage in a 1:4 volume mixture of perchloric acid and ethanol to diminish the roughness of the alumina foil surface. Highly ordered PAA films were then fabricated through a two-step high-field anodizing electrochemical procedure. A large glass beaker (2 l), a powerful low-constant-temperature bath and a vigorous stirrer (800 rpm) were employed to maintain the low temperatures required for the high-field anodization. A graphite cathode with a total surface area of 100 cm^2 was used for anodizing, through which the area ratio of anode to cathode could be easily adjusted. Anodization was performed in a $\text{H}_3\text{PO}_4\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ system at 195 V and $-10\text{--}0\text{ }^\circ\text{C}$, with the duration of each step being 5 and 10 min, respectively. After removing the remaining aluminium on the backside, pore opening was conducted in a 5 wt% H_3PO_4 solution at $45\text{ }^\circ\text{C}$ for 30 min. The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, Philips Sirion 200).

3. Results and discussion

3.1. Characterization of PAA films

Figure 1 shows typical FE-SEM images of the PAA films fabricated under different current densities. The PAA films formed in the $\text{H}_3\text{PO}_4\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ system under high current densities (figures 1(b)–(f)) exhibit an ideally hexagonal configuration, uniform cell size and highly ordered pore arrangement over a large area. The results clearly show that the extent of the order of the pore arrangement under high current density is significantly improved compared with that of PAA film formed in ordinary phosphoric acid solutions under low current density (figure 1(a)), which is consistent with the hypothesis proposed by Ono *et al* [12]. It should be

noted that a large ordered domain can be obtained in a very short anodizing time (10 min) under high current densities, while it is quite time-consuming ($>10\text{ h}$) for ordinary low-current-density anodization to achieve good results [6]. This implies that the self-ordering process of highly ordered PAA film is remarkably shortened. In addition, it was found that the growth rate of the PAA films under high-current-density anodization is rather high. For example, the thickness of PAA films formed at 4000 A m^{-2} for 10 min is approximately $100\text{ }\mu\text{m}$, so the growth rate of the film is as high as $10\text{ }\mu\text{m min}^{-1}$, which is about 100 times higher than that of ordinary low-current-density anodization. Figure 2 shows typical cross sections of PAA films formed under high-current-density anodization (195 V, 1500 A m^{-2}). The pore channels are straight throughout the film, which further indicates that the pore arrangement on the bottom is identical with that on the surface. These results show that this approach is highly efficient and reliable for fabricating high-quality self-ordered PAA films for practical applications.

3.2. The cooling effect of ethanol

Ethanol was chosen because of its extremely low freezing point ($-114.3\text{ }^\circ\text{C}$) and its very weak acidity (weaker than H_2O), so it would not react with aluminium during anodizing. By adding adequate ethanol ($\text{C}_2\text{H}_5\text{OH:H}_2\text{O} = 1:4\text{ v/v}$), the temperature of the electrolyte can be lowered to $-10\text{ }^\circ\text{C}$, which is low enough for stable high-field anodization. It has been found that the addition of ethanol not only lowered the freezing point of the electrolyte but also played an important role in cooling the films during film formation. The boiling point of ethanol is $78.4\text{ }^\circ\text{C}$, which is lower than that of water. During high-field anodization, a large amount of heat was generated at the aluminium/oxide interface. With the aid of vigorous stirring, the vaporization of ethanol at the bottom of the channels would take away the heat and keep the film at a relatively low temperature. Thus, the ethanol in the electrolyte also served as a coolant, which was especially important for maintaining the electrolysis without ‘burning’. In our experiment ‘burning’ occurred only with the ageing of solutions after they had been used for a long time, due to the volatilization loss of ethanol, although the electrolyte temperature still could be lowered to $-10\text{ }^\circ\text{C}$. Stable anodization could be regained if we added some more ethanol to the solutions. This indicates that the action of ethanol as a coolant is much more important than the low electrolyte temperature itself. It should be noted that the temperature of the electrolyte would rise by several degrees during the entire anodization due to the emission of large quantity of heat. Fortunately, the small increase in temperature would not affect the quality of PAA films as no ‘burning’ occurred. Consequently, stable high-field anodization under a self-ordering voltage of 195 V in a $\text{H}_3\text{PO}_4\text{-H}_2\text{O-C}_2\text{H}_5\text{OH}$ system has been realized without pre-anodizing of the electrolyte or using a constant current mode, both of which are usually necessary for high-field anodization in other cases [13].

3.3. The effect of current density on PAA film structure

Figure 3 (the left axis) gives the relationship between the ratios of inter-pore distance (D_{int}) to anodizing voltage (E_{a}) and the

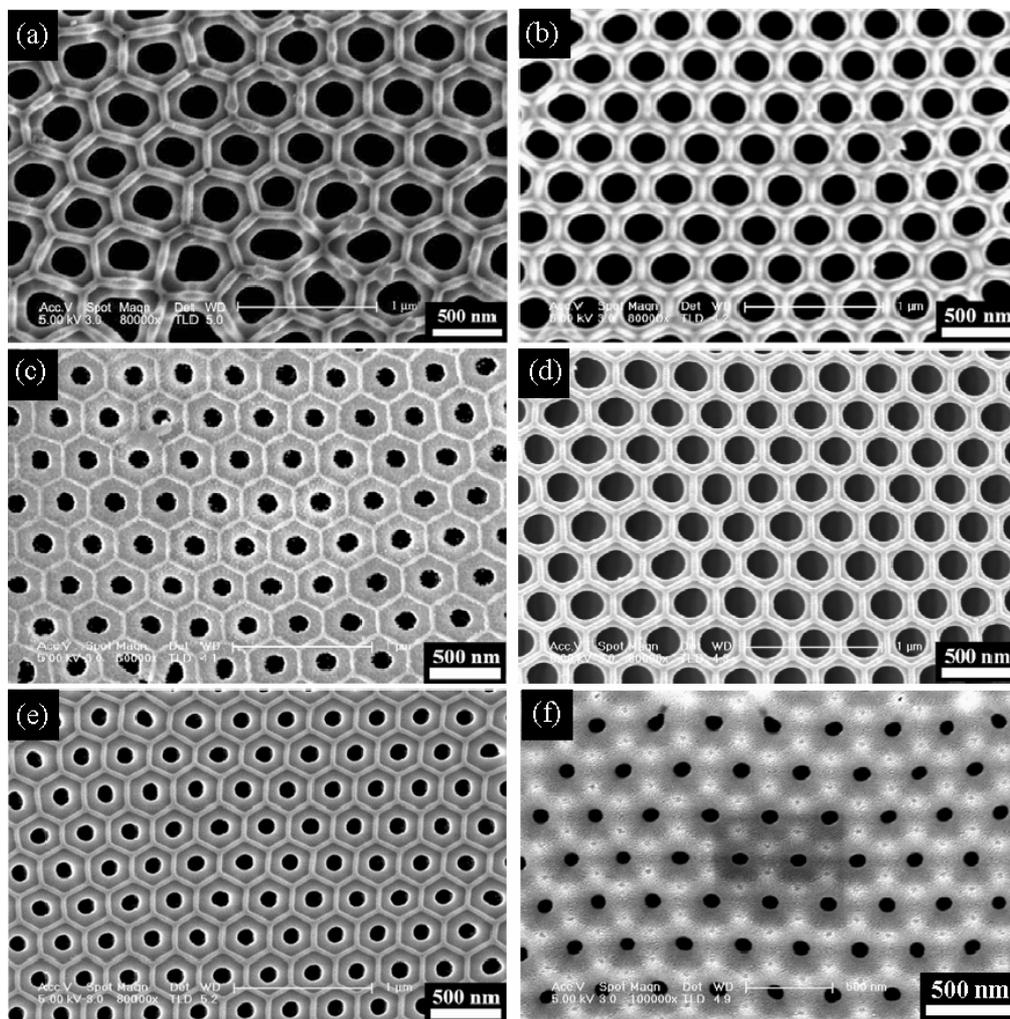


Figure 1. FE-SEM images of the PAA films formed under different current densities at 195 V: (a) 0.1 M H_3PO_4 , 30 A m^{-2} , 0.1°C , 6 h; (b) 0.25 M H_3PO_4 , 1500 A m^{-2} , -5°C , 10 min; (c) 0.3 M H_3PO_4 , 2000 A m^{-2} , -5°C , 10 min; (d) 0.5 M H_3PO_4 , 3000 A m^{-2} , -10°C , 10 min; ((e), (f)) 0.4 M H_3PO_4 , 4000 A m^{-2} , -10°C , 10 min. (a)–(e) Bottom view; (f) top view. The area ratios of anode to cathode were: (a), (d) 1:10, and (b), (c), (e), (f) 1:50.

anodizing current densities (i_a). The inter-pore distance or cell size decreases with increasing current density under the same anodizing potential, which is consistent with the results obtained in other cases [12, 13]. As shown in figure 1, D_{int} decreases from 380 to 320 nm when i_a increases from 1500 to 4000 A m^{-2} and E_a is maintained at 195 V. The relationship between the ratio of D_{int} (in nm) to E_a (in V) and i_a (in A m^{-2}) can be obtained by fitting the experimental data:

$$\frac{D_{\text{int}}}{E_a} = 1.57 + e^{-\frac{i_a}{1000}}. \quad (1)$$

This clearly shows that the inter-pore distance is not solely dependent on the anodizing voltage but is also influenced by the anodizing current density, which is different from the empirical relationship $D_{\text{int}} = 2.5E_a$ first reported by Keller *et al* for ordinary anodization [14]. The result implies that pore initiation and the steady growth of alumina cells are strongly influenced by the high current density, i.e. high electric field strength. During the initial stages of film growth, the penetration paths that develop [15] (which are the precursors

of the regular pores) are more densely distributed due to the high anodizing current densities. Accordingly, more pores are initiated from the concentration of the field and the hence current. Thereafter, steady film growth is attained with the development of the major pores and the repulsive interaction between the alumina cells. The repulsive interaction force, which is associated with expansion during film formation at the aluminium/oxide interface [16], increases with electric field. The strong repulsive or expansion force under high current density limited the transverse growth of alumina cells and forced them to form close-packed hexagonal arrays, thus producing highly ordered PAA films over a large area [13].

The effects of current density on the barrier-layer thickness (D_{bar}) are summarized in figure 3 (the right axis). The barrier-layer thickness of the PAA films formed under high current density (195 V, 1500 A m^{-2}) is about 150 nm, while the D_{bar} of PAA film formed under ordinary anodization in phosphoric acid solutions at 195 V is about 200 nm. This indicates that the barrier-layer thickness of the PAA films under high current density significantly decreases compared with that

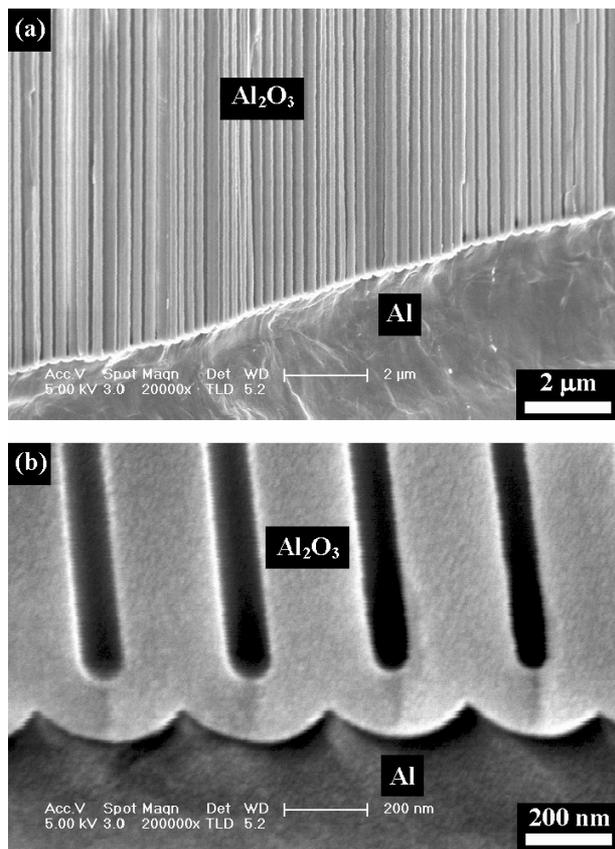


Figure 2. FE-SEM images of the cross sections of PAA films formed under high-current-density anodization.

of PAA film formed under ordinary anodization. It can be further decreased as the anodizing current density increases. The thinnest barrier layer of about 120 nm was obtained under 195 V, 4000 A m^{-2} , giving the smallest anodizing ratio, 0.62 nm V^{-1} . The thinning of the barrier layer is ascribed to the local increase in temperature at the pore tips under the high electric field and increasing acid concentration. The local temperature increase enhanced chemical dissolution of the anion-containing outer layer of the barrier layer. However, the anodizing current density can be considered as the total result of the local temperature and the acid concentration. Through fitting the experimental data, the relationship between the D_{bar}/E_a ratio and i_a is obtained as:

$$\frac{D_{\text{bar}}}{E_a} = 0.58 + 0.45e^{-\frac{i_a}{1700}} \quad (2)$$

where D_{bar} is in nm, E_a is in V and i_a in A m^{-2} .

Moreover, the pore size of PAA films can also be controlled by adjusting the anodizing current density under the same anodizing voltage. In our case, pore sizes between 80 and 140 nm are obtained under different current densities.

The results obtained above indicate that the inter-pore distance, pore size and barrier-layer thickness are dependent on both the anodizing voltage and the current density. Based on this rule, it is possible to fabricate highly ordered PAA films with arbitrary inter-pore distances, pore sizes and barrier-layer thicknesses by adjusting the anodizing current density. It has

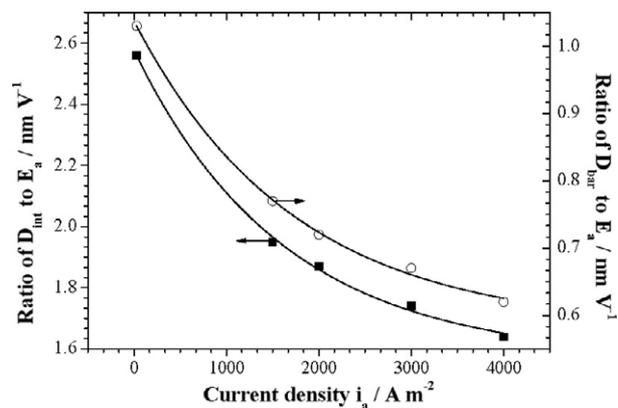


Figure 3. Variation of the ratio of inter-pore distance or barrier-layer thickness to anodizing potential with current density.

been found that many factors influence the current density. For instance, the concentration of phosphoric acid and the amount of ethanol in the electrolyte; the temperature of the electrolyte, which is determined by the efficiency of the cooling system, the size of the electrolysis cell and the speed of stirring; and the area ratio of anode to cathode. It should be noted that the area effect, i.e. the area ratio of anode to cathode, becomes more evident under high-current-density conditions. When the area ratio of anode to cathode varies from 1:10 (figure 1(d)) to 1:50 (figure 1(e)), the current density increases from 3000 to 4000 A m^{-2} , although the concentration of phosphoric acid is decreased. Therefore, different current densities can be attained at the same anodizing voltage by carefully controlling those factors mentioned above. It provides a new low-cost and high-efficiency way to fabricate highly ordered PAA films with arbitrary pore intervals in the range of hundreds of nanometres.

4. Conclusions

In conclusion, we have successfully fabricated highly ordered PAA films with large and arbitrary inter-pore distances through stable high-field anodization ($1500\text{--}4000 \text{ A m}^{-2}$) in a $\text{H}_3\text{PO}_4\text{--H}_2\text{O--C}_2\text{H}_5\text{OH}$ system without raising the anodizing voltage. The high anodizing current densities lead to high-speed film-growth ($4\text{--}10 \mu\text{m min}^{-1}$). The acid–water–ethanol system is an ideal electrolyte for realizing stable high-field anodization. Ethanol not only lowers the freezing point of the electrolyte but also serves as a coolant. In contrast to the conventional methods, the strategy employed in this work for the fabrication of PAA film not only eliminates ‘burning’ of alumina film under high electric fields, but also is highly efficient and improves the self-ordering of the PAA films. This approach can also be used in other acid systems to fabricate highly ordered PAA films with inter-pore distances in a large continuous range for practical applications.

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