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Effect of anneal pre-treatment of polycrystalline aluminum sheets on synthesis of highly-ordered anodic aluminum oxide membranes

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Anodic aluminum oxide (AAO) membranes with large ordered pore domains were successfully prepared by adopting the anneal pre-treatment of polycrystalline aluminum sheets. A statistical method with Gaussian distribution was introduced to quantitatively study the size of the domain with ordered pores. The largest average area of ordered pore domains was 2.6 μm^2±0.11 μm^2. The corresponding AAO membrane was synthesized by aluminum sheets annealed at 893 K for 24 h.

anodic aluminum oxide (AAO), annealing temperature, annealing duration, Gaussian distribution

Controlled fabrication of one-dimensional (1D) materials is important in the development of nanodevices. Due to its advantages in terms of good chemical stability, highly-ordered pores and controllable pore diameter, anodic aluminum oxide (AAO) membrane is a promising template to synthesize arrayed one-dimensional materials. It has been widely used to produce polymer nanowires[1−4], metal nanowires[5−8], semiconductor nanowires[9], carbon nanotubes (CNTs)[10], heterojunction nanowires[11,12] and metal coated CNTs[13]. In most cases, the AAO templates were fabricated by a method of two-step oxidization with aluminum sheets which were annealed at 773 K or a lower temperature[5, 6]. But a serious problem we usually meet is that the traditional method cannot generally obtain highly-ordered AAO membranes with commercial polycrystalline aluminum sheets. Unlike the other parameters in the synthesis process, e.g. oxidization voltage or oxidization current density, the effect of thermal treatment of aluminum sheets has not been systemically studied. In order to obtain AAO membranes with highly-ordered pore domains, the effect of thermal treatment of polycrystalline aluminum sheets was studied in this work. The results offer an economical method to synthesize highly-ordered AAO templates.

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1 Experimental

The 99.999% polycrystalline aluminum sheets were used in our experiments. The 0.4-mm thick sheets were ultrasonically cleaned in distilled water for 20 min before being annealed at 773, 833, 873 and 893 K, respectively. Three different annealing durations, namely 6, 12, and 24 h, were studied respectively.

The annealed aluminum sheets were chemically polished in a solution of H_3PO_4-HNO_3-H_2O (8∶1∶1 by volume) for 30 s at 368 K. Subsequently, electrolytic polish of the sheets was carried out at a current density of ~0.2 A/cm^2 in a solution of $HClO_4$-CH_3CH_2OH (1∶4 by volume) for 3 min at room temperate. Finally, the facade alumina was dissolved in a solution of H_3PO_4-CrO_3-H_2O (3∶1∶41 in weight) for 12 h at the ambient temperature.

A two-step oxidization method was adopted to prepare AAO in an aqueous solution of 4wt% oxalic acid at 273 K with an experimental device specially designed for the anodic oxidization[14,15]. The first anodic oxidization was operated at 45 V. Then the facade alumina was etched in a solution of H_3PO_4-CrO_3-H_2O (3∶1∶41 in weight) for 3 h at 333 K after the first anodic oxidation. Subsequently, the second anodic oxidization was carried out with the second anodizing voltage of 60 V for 2 h. The remained aluminum at the back of AAO membrane was dissolved in a solution of $CuCl_2$-HCl. The as-prepared AAO was etched in 5 wt% phosphoric acid for 20 min to remove the barrier layer and obtain the desired pore diameter. The pores were widened at a constant velocity of ~2 nm/min. After anodic oxidization, each sample was washed with distilled water thoroughly.

The as-prepared AAO membranes were analyzed on a scanning electron microscope (SEM, JEOL 6301F) working at 5 kV accelerating voltage.

2 Results and discussion

To quantitatively study the sizes of the domain with ordered pores, a method as shown in Figure 1 was introduced. In an ideal ordered pore domain, a random pore could be chosen as the center pore to draw three beelines along the close packing directions of the hexagonal packing pores. As shown in Figure 1(a), a regular hexagon was drawn from the three lines. The area of the regular hexagon is

$$S = \frac{3\sqrt{3}}{8} D^2 (n-1)^2, \quad n=3, 5, 7, \ldots . \tag{1}$$

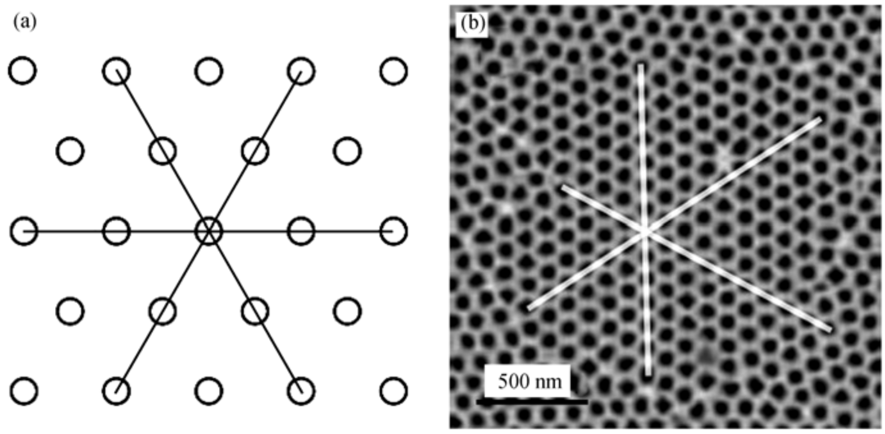

Figure 1 Schematic diagrams of the method to calculate the area of ordered pore domains of AAO samples: (a) In ideal ordered pore domain; (b) in practicable ordered pore domain.

In formula (1), S stands for the area of the regular hexagon, n is the number of pores on each line, D is the cell diameter of AAO which is always about 110 nm in our present experiments.

As shown in Figure 1(b), we could still draw different beelines along the close packing directions of local hexagonal packing pores and count the number of pores on each line in a practicable AAO sample. The most probable value of the different numbers under Gaussian distribution could be used to calculate the average area of ordered pore domains. These areas were used to characterize the size of ordered pore areas in different AAO samples.

The average area of ordered pore domains in each AAO sample was measured by the steps below. First, an image of AAO pores was taken at 8 K× magnification by SEM. Then a random pore was chosen to draw three beelines in the three close packing directions. The number of pores on each beeline was recorded separately. Twenty random pores in 20 different areas were chosen to get 20 groups of data (60 counts) to quantitatively study the size of ordered domains. The most probable value of the 60 counts under Gaussian distribution was taken as the criterion of the size of ordered area which stood for the number of periods on a common beeline. The average area of ordered pore domains was calculated with formula (1) in each AAO sample. As shown in Figure 2, the most probable values of the numbers n were obtained with Gaussian distribution in the samples which were annealed at 893 K. The numbers n for other samples were obtained with the same method. The average areas of ordered pore domains (S_g) in different samples were listed in Table 1. The curves of S_g versus the annealing times under different annealing temperatures were shown in Figure 3.

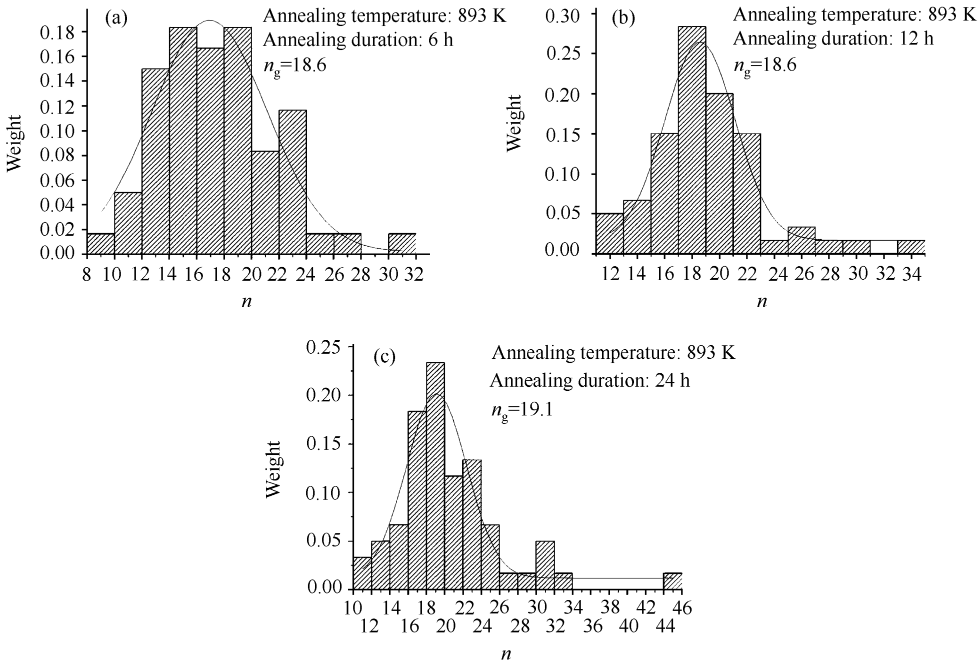

Figure 2 The most probable values of the numbers n in the samples which were annealed at 893 K for: (a) 6 h; (b) 12 h; (c) 24 h.

Table 1 The average areas of ordered pore domains in samples with different annealing temperatures and annealing durations

Annealing duration (h)	Annealing temperature (K)			
	773	823	873	893
6	1.3±0.04 μm^2	1.7±0.05 μm^2	1.8±0.1 μm^2	2.0±0.13 μm^2
12	1.4±0.04 μm^2	2.0±0.1 μm^2	2.2±0.1 μm^2	2.4±0.06 μm^2
24	1.5±0.06 μm^2	2.1±0.03 μm^2	2.5±0.08 μm^2	2.6±0.11 μm^2

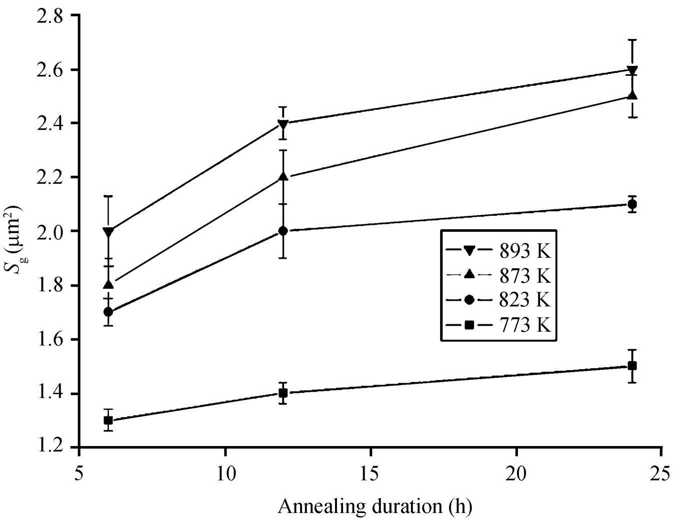

Figure 3 Curves of S_g versus annealing duration under different annealing temperatures.

It was obvious from Table 1 and Figure 3 that the average area of ordered pore domain increased with the increase of the annealing temperature and annealing duration. Müller et al.[16] presented a model which showed that the mechanical stress introduced during the anodic oxidization process played a major role in the growth of ordered pore domains. It was also reported that the mechanical stress remained in the sheets decreased with the increase of the annealing temperature and the annealing duration of polycrystalline aluminum sheets[17,18]. Furthermore, a higher annealing temperature (>773 K) and a longer annealing duration would lead to larger crystalline grains in the polycrystalline aluminum sheets, which resulted in a larger area of similar local electrochemical environment during the anodic oxidization process. But the size of crystalline grain would reach a saturation value when the annealing duration is long enough[18]. Hence, the higher annealing temperature and longer annealing time of aluminum sheets are good for the synthesis of AAO with larger ordered pore domains, while an excessive long duration would not. In our experiments, the AAO membrane that had the largest ordered pore domain was obtained at the annealing temperature and annealing time of 893 K and 24 h, respectively.

3 Conclusion

A highly-ordered AAO membrane was successfully prepared. The annealing temperature and annealing duration of polycrystalline aluminum sheets were proved to be important to obtaining highly-ordered AAO membranes. A statistical method with Gaussian distribution was introduced to quantitatively study the sizes of the domains with ordered pores. The AAO membrane with the largest pore domain in our experiments was synthesized by using polycrystalline aluminum sheets annealed at 893 K for 24 h.

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