Asian Journal of Chemistry Vol. 17, No. 1 (2005), 73–78

Study on Preparation of Highly Ordered Nanochannel Array Aluminium Oxide Template

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A kind of big anodic aluminium oxide (AAO) templates with highly ordered nanochannel array has been prepared by two-step anodizing approach. Numerous conditions, *e.g.*, anodic voltage, temperature, concentration of electrolyte and time have confirmed that 99.999% aluminium was anodized in 1.0 mol/L sulfuric acid electrolyte with 20 V steady potential at 0–5°C would produce the best microporous Al_2O_3. After removing the Al substrate and corrupting the barrier layer, the closely packed hexagonal monodisperse cylindrical nanochannel array was obtained with average porous diameter at 30 nm, channel length at about 30–40 μm and porous density at 4.8×10^{10} pores cm^{-2}. The formation process and mechanism of the self-organizing nanochannel array have been discussed in detail.

Key Words: Anodic Aluminium oxide template, Two-step anodizing method, Ordered nanochannel array.

INTRODUCTION

Nanostructural materials have attracted great interest of material scientists because of their numerous potential applications in various areas such as materials and biomedical sciences, electronics, optics, magnetism, energy storage and electrochemistry. So, many methods have been developed to prepare many kinds of nanomaterials. However, up to date, the controllable and adjustable synthesis is still very difficult. The application of template-based synthesis technology has greatly enhanced the preparation of nanomaterials[1]. The method involves fabrication of the desired material within the pores or channels of a nanoporous template. Consequently, the fabrication of nanoporous template will affect the formation of the tailored nanomaterials to a large extent. There are many kinds of nanoporous templates, such as track-etch nano-polycarbonate or polyester[2], anodic aluminium oxide (AAO)[3], nanochannel glass[4], mesoporous zeolites[5], nanoporous protein[6] and array of polypeptide tubules[7]. But the AAO template possesses many merits, *e.g.*, low cost, easy preparation, very uniform nanochannel array and high porous density and have been extensively utilized for fabrication of various functional nanomaterials.

In the present work, the influence of voltage, temperature, concentration of

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electrolyte and time on the porous diameter, depth of pores, ordered degree and porous density in H_2SO_4 electrolyte has been investigated. Scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscope (AFM) were applied to observe the surface and interior microstructure of AAO template. The formation of highly ordered closely packed hexagonal nanochannel array was considered by a self-organizing process under effect electric field force.

EXPERIMENTAL

All the common chemicals were of analytical grade and were commercially available. The water used in all experiments was twice distilled with quartz heating tube.

A model Hitachi S-5200 scanning electron microscope (SEM) was used to observe the surface of template. A model JEM-100SX transmission electron microscope (TEM) was used to take photos of the template fragments. A model DI-D3000 atomic force microscope (AFM) was used.

Preparation of AAO template: 0.2 mm thickness of 99.999% Al slice was polished with electrochemical method, in which the Al slice anode and equivalent area stainless steel slice cathode were placed in 70% perchloric acid-ethanol solution and electrolyzed with 20 V potential for 10 min between 0 and 5°C. After washing with water, the Al slice was anodized with the same stainless steel slice cathode and 20 V steady potential in 1.0 mol/L H_2SO_4 electrolyte between 0 and 5°C with stirring for 1.5 h. Then the Al slice was corrupted in a mixed solution containing 6% phosphoric acid and 1.8% chromic acid at 60°C for 30 min. After finishing of the anodization, the Al slice was washed with a great deal of water and dried in air. Then the back side (the side facing the cathode was called the front side) was covered with vaseline. The Al slice was anodized again under the same condition as above for 5 h with stirring. After the second anodization, the vaseline was removed carefully and the Al slice was washed thoroughly. After drying in air, the back side of the Al slice was coated in NaOH saturated aqueous solution for decomposing the thin Al_2O_3 layer. Then the back side was swilled out and aluminium at the back side was uncovered, which was removed in $SnCl_2$ saturated aqueous solution. The transparent Al_2O_3 film was washed carefully and dried in air. Then the Al_2O_3 film was floated on 5% H_3PO_4 solution with only the back side touching the acid solution. After about 30 min, a layer of uniform beads appeared on the upside of the film. The template was washed with water and soaked in water.

RESULTS AND DISCUSSION

The Optimal Results: Under the experimental conditions described in the preparation section, a highly ordered nanochannel array AAO template has been obtained. SEM photographs as shown in Fig. 1 revealed that all nanopores in the whole area were closely hexagonal packed. Porous diameter was very uniform and every pore was nearly circular with about 30 nm diameter. TEM photographs (Fig. 2) display clearly the microstructure of the AAO template transverse section. The picture indicates that the nanochannels are cylindrical and the inner diameter of every channel is also uniform. The microcosmic morphology of the AAO template was further characterized by AFM (Fig. 3), which revealed that the front side of the template was relatively smooth. The monodispersed pores distribution and uniform porous diameters were observed at the same time.

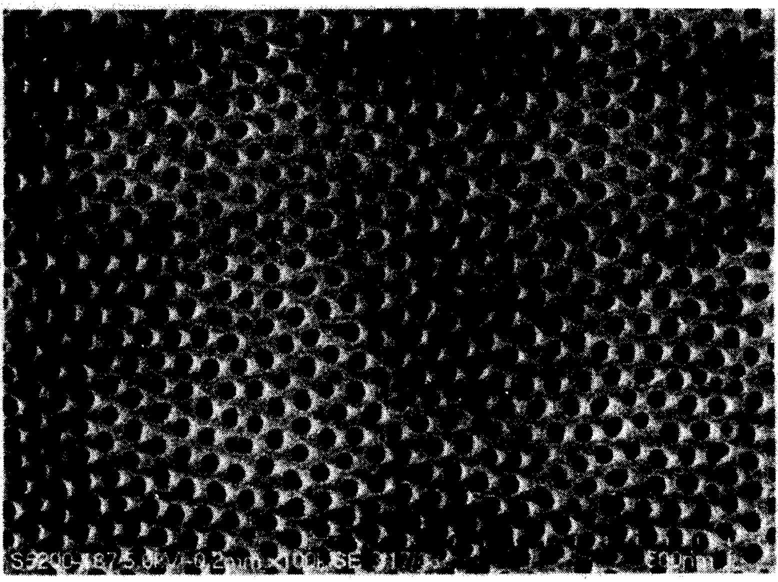


Fig. 1. SEM photograph of AAO template

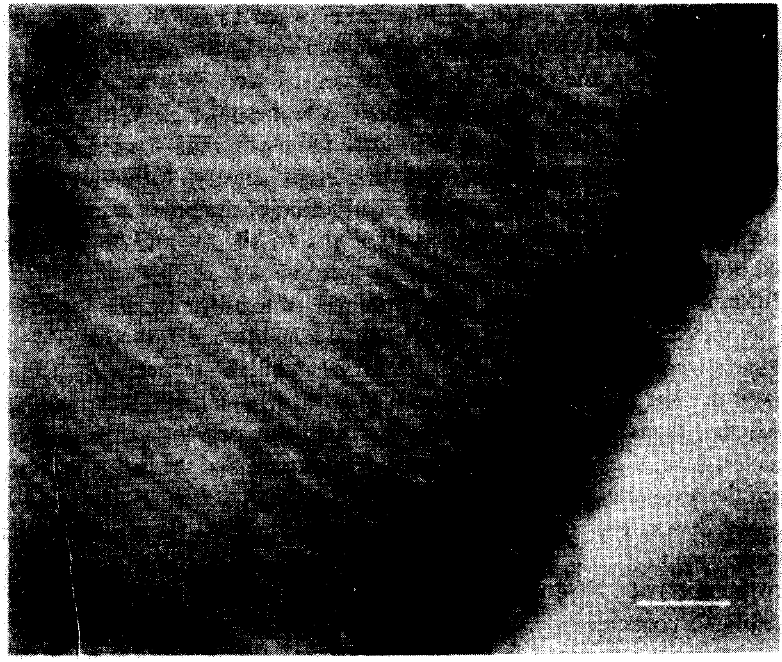


Fig. 2. TEM photograph of AAO template fragment. The bar is 200 nm.

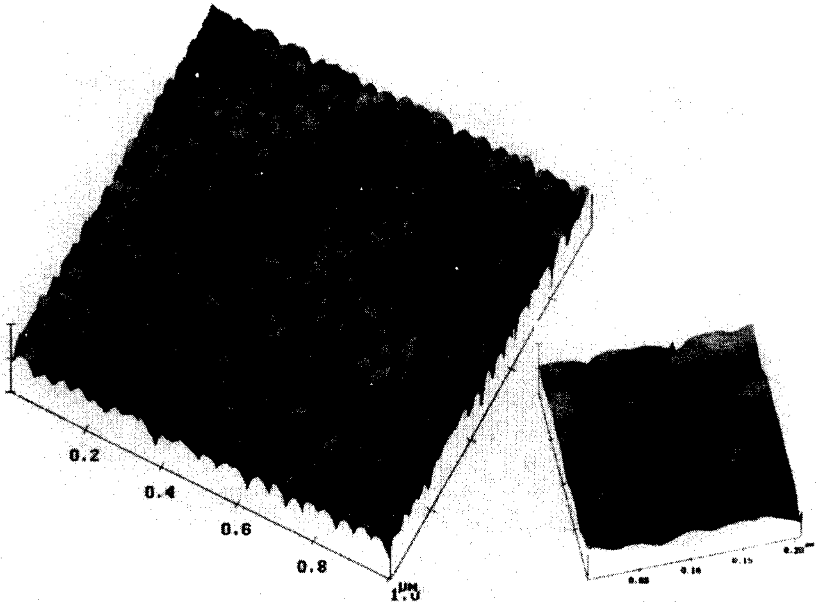


Fig. 3. AFM photograph of AAO template surface.

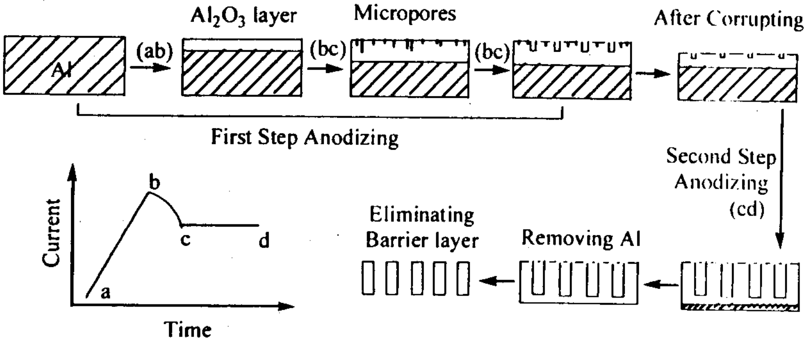
Influence of Potential: The influence of anodizing potential was investigated under the same experimental conditions as the preparation section, but the anodizing voltage changed from 5 to 40 V with step interval 5 V. Experimental results indicate that the anodizing potential between 15 and 30 V would produce a relatively good AAO template. If the potential was lower than 15 V, the template would be very thin and brittle. The porous density went little and ordered degree becomes poor. However, when the voltage is higher than 30 V, the thickness of the template had not increased. It is attributed to the fact that the outer layer Al_2O_3 was dissolved quickly with increase in current density. Although the porous diameter increased, the shape and the distribution of the pores became irregular. When the potential was higher than 40 V, the Al slice would be damaged and could not be fabricated further.

Influence of Temperature: The influence of temperature was made according to the same approach as the potential condition experiment. The AAO templates were prepared under 0, 5, 10, 15, 20 and 30°C, respectively. The results showed that the temperature between 0 and 5°C was suitable. If the temperature was higher than 10°C, the template went very thin and the shape of the pores irregular. Also, the porous diameter was not uniform and the order became poor. When the temperature was higher than 30°C, the AAO template would not be obtained. It was possible that the dissolving speed of Al_2O_3 was more than the forming speed.

Influence of Electrolyte Concentration: The influence of H_2SO_4 electrolyte's concentration was investigated in the same way as above. The AAO templates were fabricated in 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol/L H_2SO_4, respectively. The experimental results showed that the relative ideal AAO template could be fabricated between 0.5 and 1.5 mol/L H_2SO_4. If the concentration was less than 0.1 mol/L or more than 3.0 mol/L, the AAO template was not formed. Because a low concentration of electrolyte would decrease the current density, it is possible for the Al_2O_3 layer not to be formed. On the other hand, the high concentration H_2SO_4 possesses strong dissolution ability, which would hinder the growth of the Al_2O_3 layer.

Influence of Anodization Time: The purpose of the first anodization step is to produce a regular mask for the second one. So, it was suitable for the first anodization step to spend about 1 h. During the second process, the experimental results at 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 h were observed and they indicated that the relatively good AAO templates were produced between 4 and 10 h. The shorter and longer time both made the thickness of the template decreased. When the time was less than 3 h, the porous ordered degree and diameter uniform degree both became poor. After considering the fabrication efficiency and the template quality, 5 h was selected as the optimal time for the second anodization step.

Analysis of Mechanisms: The formation mechanism of nanochannel array AAO template is described **(Scheme-1).** After polishing, the Al slice was first anodized. During the beginning period, a layer of Al_2O_3 was formed rapidly and the oxide current increased continuously (ab segment, the whole current change's curve shown in **Scheme-1**). When the whole surface was covered by Al_2O_3 layer, the oxide current started to decrease (bc segment). Meanwhile, numerous micropores formed on the surface of Al_2O_3 layer at random because of H_2SO_4 and affect the electric field. When the dissolution of outer layer Al_2O_3 comes to equilibrium with the forming of inner layer Al_2O_3, the current approached a constant (cd segment). Due to the electric field the micropores constantly grew, reorganized and merged with the dissolution and formation of Al_2O_3. During ceasing competition process, the big pores were formed gradually. Although many micropores were still formed, they were either combined or dissolved. These big pores became deeper and deeper, bigger and bigger. The corrupting process dissolved all these micropores and the very low pores. The remainder pores showed a relatively ordered form and became a good mask for the second



Scheme 1
The chart of AAO template forming mechanisms.

anodization step. In the successive oxidization process, the effect of electric field became very important. Porous walls among many neighboring pores have turned fully into Al_2O_3 and they were parallel to the electric field. So the dissolution speed became very slow. However, at the bottom of the pores, the formation and dissolution of Al_2O_3 were still active, where Al^{3+} was dissolved into the electrolyte solution and O^{2-} was constantly diffused into the Al_2O_3 inner layer. During the whole anodization process, the formation and dissolution of Al_2O_3 in every pore produced some stress under the electric field's assistance[8], which repulsed and confronted ceaselessly each other. Therefore, the formation and growth of all the pores in the whole Al slice complied with the stress minimum rule. In other words, the formation and growth of all the pores is a self-organizing process under the electric field stress.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (20375008), the Natural Science Foundation of Guangdong Province (No. 32167), Technologies R&D Programs of Guangdong Province (No. C31902) and the Natural Science Research Programs of High School (No. Z03091).

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(*Received*: 31 October 2003; *Accepted*: 6 July 2004) AJC-3495