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One-step anodization fabrication and morphology characterization of porous AAO with ideal nanopore arrays

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A fabrication method for one-step anodization of an anodic aluminum oxide (AAO) template with nanopore arrays using pretreated high purity aluminum foil is reported in this article. Morphology of the AAO was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Results showed that porous AAO with ideal nanopore arrays can be fabricated by one-step anodization fabrication technology on high purity aluminum foil which had been anodized at 45 V direct current (DC), in 0°C, 0.5 M $H_2C_2O_4$ solution for 48 hours. The average pore diameter and the interpore distance were 80 nm and 120 nm, respectively. Nanopores in porous AAO had very narrow size distribution and were arranged into hexagonal array. The formation mechanism of nanopore arrays in porous AAO is discussed. Porous AAO with ideal nanopore arrays provide an ideal template for preparation of many one-dimensional nanomaterials. One-step anodization of AAO is a simpler procedure and more applicable in industrial application than the previous two-step anodization technology.

Keywords: AAO; Nanopore array; One-step anodization; Characterization

1. Introduction

With the successful growth of carbon nanotube, one-dimensional nanomaterials, including nanotubes and nanowires, have attracted considerable attention, for their unique properties as well as their potentially wide applications in electronic, optical structures and devices [1–5]. To actualize most of the proposed applications, it is quite important to obtain highly ordered nanostructure arrays. There are many technological and economical limitations in lithography for large scale integrated fabrication in the forthcoming stage of sub-100 nm scale, much effort has been made on nanostructure materials fabricated by self-organizing methods.

Anodic aluminum oxide (AAO) is a kind of self-organizing material with nanopore arrays [6–11]. The ideal model of AAO can be schematically represented as figure 1.

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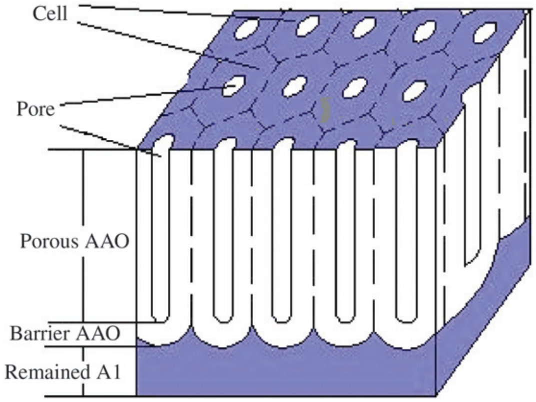

Figure 1. Ideal model of anodic aluminum oxide.

Porous AAO owns a honeycomb structure, which is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate. Therefore, the pores in porous AAO are arranged into ideal hexagon nanopore arrays, and a hexagonal structure is formed by the nearest six pores around each pore. The diameters of pores, which have narrow distribution can be controlled in nanometer scale. Due to its uniform and nearly parallel porous structure, porous AAO has become a kind of ideal template for preparation of many one-dimensional nanomaterials [12–18]. However, the geometry of porous AAO usually obtained is far from the idealized model and the irregular AAO is not an ideal template for the preparation of materials and devices in the scale of nanometer. Masuda *et al*. [6, 8–10] had fabricated AAO with ideal nanopore arrays through molding process and two-step anodization process respectively. However, the two ways are very complex in operation.

In the current study, one-step anodization preparation technology of porous AAO with ideal nanopore arrays was explored. Morphology of the obtained porous AAO was characterized by scanning electron microscope (SEM) and atom force microscope (AFM). Furthermore, formation mechanism of nanopore arrays in porous AAO was discussed.

2. Experimental

2.1. *Procedure of one-step anodization preparation technology*

Porous AAO with ideal nanopore arrays was fabricated by one-step anodization preparation technology, which includes anodization of aluminum, removal of remained aluminum, removal of barrier AAO and surface porous AAO. The procedure is shown in figure 2.

2.2. *Fabrication and characterization of porous AAO with ideal nanopore arrays*

High purity aluminum foil (99.99%) with the thickness of 0.3 mm was cut into disc shape specimen, the diameter of which was 20 mm or so. Then the aluminum disc was

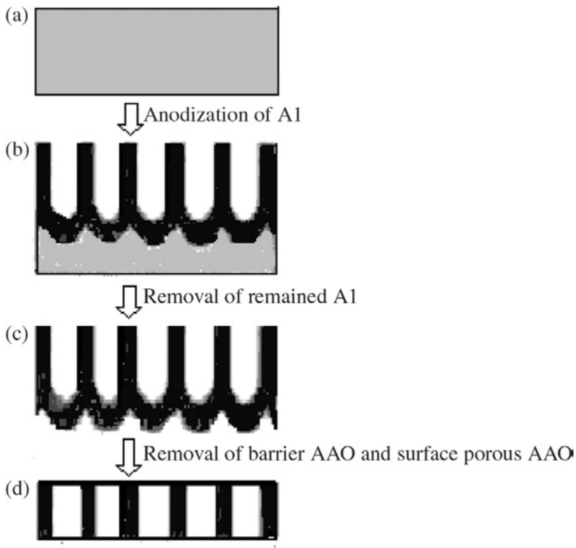

Figure 2. Procedure of one-step anodization technology: (a) high purity aluminum foil pretreated; (b) porous AAO + barrier AAO + unanodized aluminum; (c) porous AAO + barrier AAO; (d) porous AAO.

degreased in acetone, and polished in a mixed solution of 98 wt% H_2SO_4, 85 wt% H_3PO_4 and 65 wt% HNO_3 for 1.5–2 minutes, then rinsed in distilled water for 3–4 times. The pretreated aluminum disc was put into a self-made anodizing device in which a circular aluminum of 10 mm diameter was exposed to electrolyte and anodized.

The anodizing condition was as following: 0.5 M oxalic acid solution was used as electrolyte, temperature of electrolyte was kept at $0 \pm 0.2^{\circ}C$ in a thermally insulated electrochemical cell, and anodizing time was 48 hours, anodizing voltage was kept at constant 45 V direct current (DC). After anodization, remained aluminum substrate was removed from the AAO film by using saturated $HgCl_2$ solution. Subsequent etching treatment was carried out in 5% H_3PO_4 solution at 30°C for 6 hours, which makes it easy to observe morphology of porous AAO, for barrier AAO and surface part of porous AAO were removed. The morphology of AAO films was observed by scanning electron microscope (SEM, JEOL JSM-5900LV) and atom force microscope (AFM, SPA-400 SPM Unit).

3. Results and discussions

For comparison, porous AAO were respectively fabricated by one-step anodization technology shown in figure 2 and two-step anodization technology proposed by Masuda *et al.* [6] at the same condition. The morphologies of the two kinds of obtained porous AAO were characterized by SEM in figure 3. Prior to observation, the samples were treated by removal of un-reacted aluminum in saturated $HgCl_2$ solution and of barrier AAO in 5% H_3PO_4 solution. As clearly shown in figure 3, many pores, the

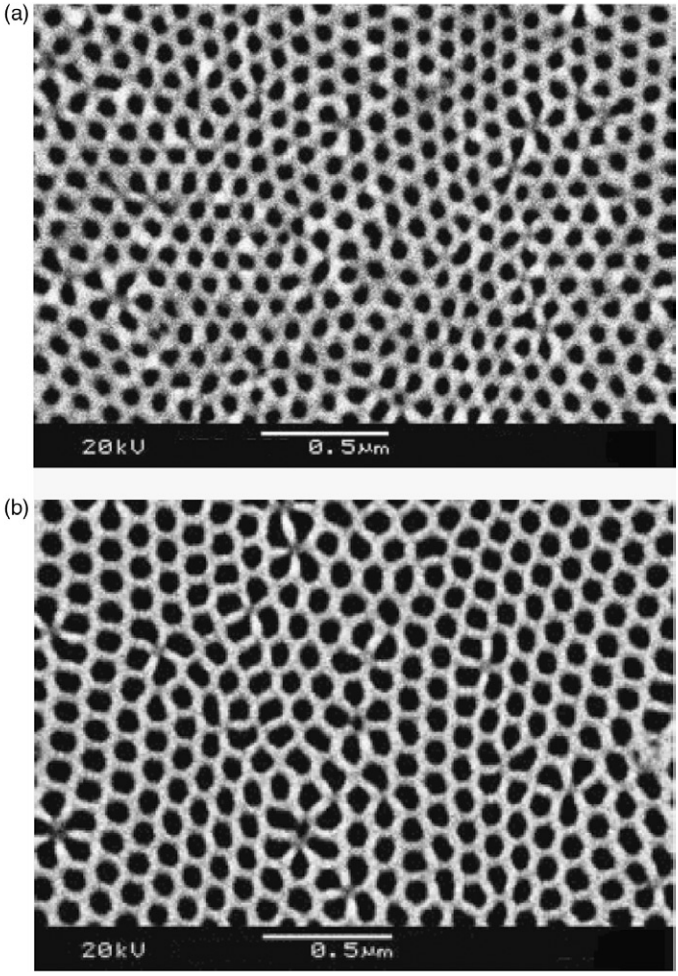

Figure 3. SEM micrographs of porous AAO obtained by, (a) one-step anodization technology; (b) two-step anodization technology.

sizes of which were on nanometer scale were obtained in the two kinds of porous AAO templates. The mean pore diameter was about 80 nm and the interpore distance was 120 nm or so. The size distribution of nanopores was very narrow and pores in two kinds of porous AAO templates were arranged in hexagonal arrays. Furthermore, some distorted pores could be seen in the two SEM images of porous AAO. Therefore, porous AAO with ideal pore arrays can be obtained by the two kinds of preparation technology. The size, the size distribution and the arrangement of pores in porous AAO fabricated by one-step anodization technology are nearly the same as those of pores in AAO fabricated by two-step anodization technology.

According to the growth model of AAO proposed by Masuda *et al.* [9, 10], morphology and arrangement of pores in the initial part of porous AAO are irregular. Following the formation of AAO, the morphology and the arrangement of pores in porous AAO are changed more and more regular because of the mechanical stress,

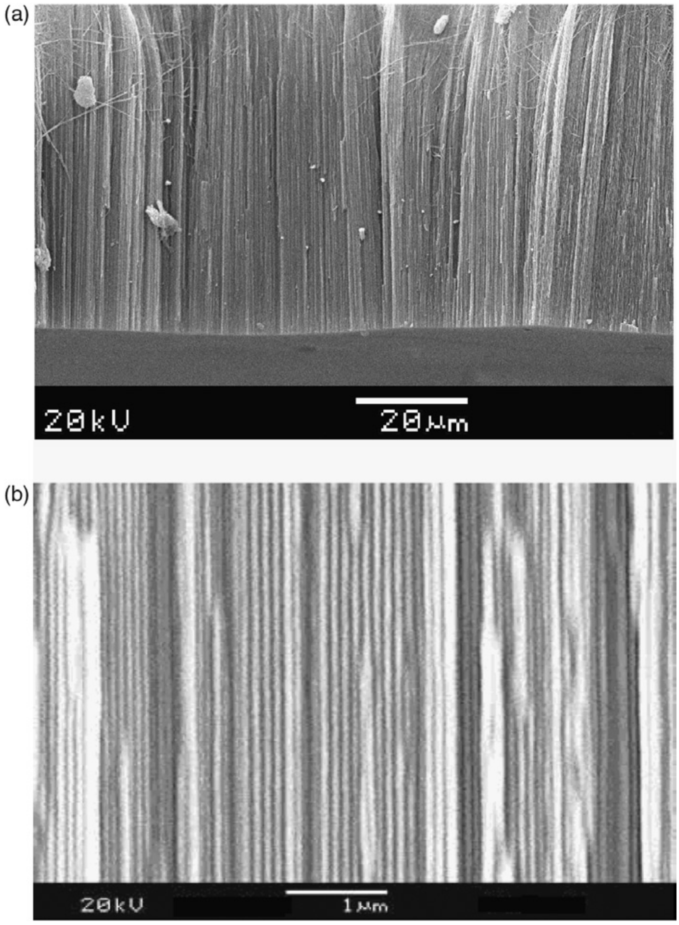

Figure 4. SEM micrographs of cross-section of porous AAO obtained by one-step anodization; (a)×800; (b) ×20,000.

which is associated with the volume expansion during the formation of AAO. In one-step anodization technology shown in figure 2, barrier AAO, as well as the surface part of porous AAO in which the morphology and the arrangement of pores are irregular, can be removed by etching treatment of AAO in 5% H_3PO_4 solution, because their compositions are alumina. Porous AAO with ideal pore arrays can be obtained by one-step anodization technology, which is easier in operation than two-step anodization technology. Because the barrier AAO and the surface irregular porous AAO are etched by 5% H_3PO_4 solution at the same time, and the preparation procedure of through-hole porous AAO with ideal nanopore arrays in one-step anodization technology is easier than the facile approach proposed by Zhao *et al.* [19].

Figure 4 indicates SEM micrographs of cross-section of porous AAO obtained by one-step anodization. As shown in figure 4(a), the thickness of porous AAO with ideal nanopore arrays fabricated by one-step anodization technology was 80 μm or so, that is,

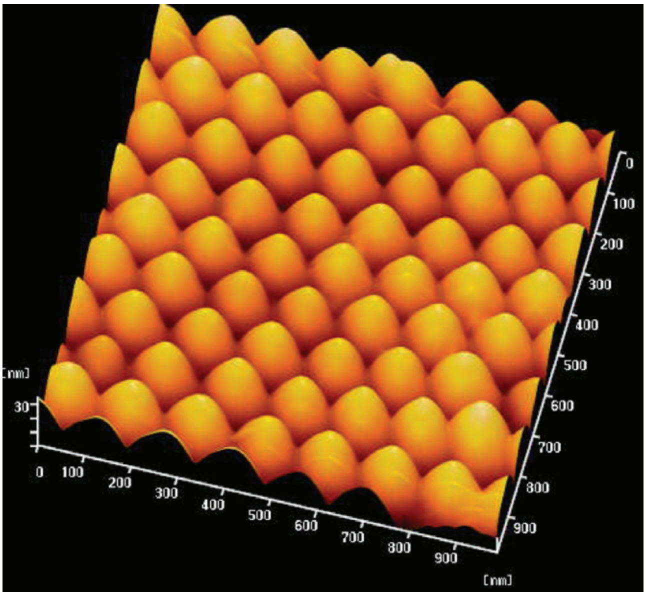

Figure 5. 3-D AFM image of barrier AAO at aluminum/alumina interface.

the depth of nanopores in porous AAO could be 80 μm or so. The porous AAO is a kind of ideal template for the preparation of nanowires and nanotubes. Furthermore, as shown in figure 4(b), nanopores, the size distribution of which was very narrow were parallelly arranged into array in porous AAO. The average pore diameter and the interpore distance were respectively about 80 nm and 120 nm or so, which were consistent with those shown in figure 3(a).

According to the growth model of AAO, barrier AAO is firstly formed on the surface of aluminum at the initial stage of anodization of aluminum. The thickness of AAO increases with the increasing of anodization time, then AAO is divided into barrier AAO and porous AAO as shown in figure 1. With the increasing of anodization time, thickness of porous AAO increases constantly because barrier AAO is constantly changed into porous AAO. During the progress of anodization, the position of porous AAO changes constantly, the thickness of which remains the same. The regularity of morphology and arrangement of cells in barrier AAO increases with the change of its position and this is due to the mechanical stress, which is associated with the volume expansion. Figure 5 shows 3-D AFM image of barrier AAO at aluminum/alumina interface of the sample fabricated by one-step anodization technology. As clearly shown in figure 5, there were many cells which were close-packed into regular configuration in the barrier AAO at aluminum/alumina interface. The sizes of cells, which were about 100 nm, had narrow distribution. Furthermore, hexagonal pattern was formed by the nearest six cells around each cell, so the cells in the barrier AAO at aluminum/alumina interface were arranged into hexagonal arrays. Cells in barrier AAO at aluminum/alumina interface will be developed into columnar hexagonal cells, each containing a central pore in porous AAO. Therefore, the size, the size distribution and the array arrangement of cells in barrier AAO at aluminum/alumina interface must have direct relation with those of nanopores in porous AAO.

4. Conclusions

The procedure of one-step anodization preparation technology of porous AAO with ideal nanopore arrays was reported in this article. One-step anodization technology is simpler in operation and easier in industrial application than two-step anodization technology. Porous AAO with ideal nanopore arrays was fabricated by one-step anodization fabrication technology on high purity aluminum foil which had been anodized at 45 V DC, in 0°C, 0.5 M $H_2C_2O_4$ solution for 48 hours. The average pore diameter and the interpore distance were respectively about 80 nm and 120 nm. Nanopores in porous AAO were arranged into hexagonal array and had very narrow distribution, the size of which was on nanometer scale. Porous AAO with ideal nanopore arrays is a kind of ideal template for preparation of one-dimensional nanomaterials, nanodevices and nanoarrays.

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