纳米孔阵列阳极氧化铝膜的制备和表征

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本文通过在 0℃、0.5mol·L⁻¹ 的草酸溶液中阳极氧化高纯铝片的方法制得了阳极氧化铝(AAO)膜, 并用扫描电子显微镜(SEM)和原子力显微镜(AFM)对 AAO 膜的形貌和结构进行了表征。结果表明, 阻挡层 AAO 膜中大小一致的膜胞在铝/氧化铝界面上排成六方形阵列; 有孔层 AAO 膜中含有高度有序的纳米孔阵列和膜胞阵列, 并且孔的直径和膜胞的尺寸都具有较窄的分布。另外, 考察了阳极氧化电压对膜胞尺寸、孔径大小、孔密度和膜胞密度的影响, 表明在一定的电压范围内, 膜胞和孔径都随电压的升高而增大, 而孔密度和膜胞密度却随电压的升高而减小。

关键词: 纳米孔阵列 阳极氧化铝 制备 扫描电子显微镜 原子力显微镜
分类号: O614.3⁺1 TQ153.6

Preparation and Characterization of Anodic Aluminum Oxide Films with Nanopore Arrays

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A one-step preparation technology for the anodic aluminum oxide (AAO) films with nearly ideal nanopore arrays can be fabricated by anodizing highly pure aluminum foils in 0.5mol · L^{-1} $H_2C_2O_4$ solution at 0℃ for 48h under different voltages is reported. The morphologies and structures of the obtained AAO films were characterized by scanning electron microscope (SEM) and atom force microscope (AFM). AFM image of barrier AAO at aluminum/alumina interface was firstly observed. Results show that cells in barrier AAO are arranged in hexagonal arrays at aluminum/alumina interface. SEM and AFM analyses on porous AAO films show that cells in porous AAO films appear as columnar hexagons and each contains a pore in the center, so cells and pores in porous AAO films are also arranged in hexagonal arrays; and sizes of the cells and diameters of the pores which are on the scale of nanometer have narrow distribution. Furthermore, the mechanism on arrangement of cells and pores, the effect of experimental conditions on quality of the obtained AAO films were discussed. Results indicate that sizes of cells and diameters of pores in porous AAO films increase with the height of anodizing voltage, while densities of pores and densities of cells decrease with the height of anodizing voltage.

Keywords: **nanopore array** **anodic aluminum oxide (AAO)** **preparation** **scanning electron microscope (SEM)** **atom force microscope (AFM)**

0 Introduction

Ideal model of anodic aluminum oxide (AAO) fabricated by anodizing highly pure aluminum foil in some acid solution is shown in Fig. 1[1-3]. The geom-

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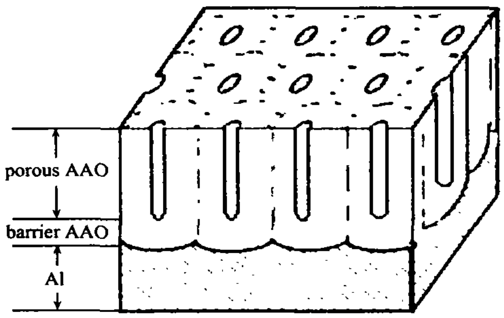


Fig. 1 Ideal model of anodic aluminum oxide

etry of porous AAO can be schematically represented as a honeycomb structure which is characterized by a close-packed array of columnar hexagonal cells, each of them contains a central pore and is normal to the substrate. Therefore, the pores in porous AAO are arranged in ideal hexagonal nanopore arrays, and a hexagonal structure is formed by the nearest six pores around each pore. The sizes of cells and the diameters of pores which have narrow distributions can be controlled on nanometer scale.

The new type of AAO film with an ideal regular structure has many applications[4~8]. For example, AAO films with nanopore arrays can be used as templates for preparation of materials on nanometer scale, such as quantum dots, nanowires and nanowire arrays of metals, semiconductors and polymers[4~6]. Furthermore, AAO films with nanopore arrays are key materials for fabrication of devices on nanometer scale, such as electronic, photoelectronic and magnetic functional devices. The long-range ordering of porous AAO is advantageous to optimize the properties of the fabricated devices. AAO films can also be applied in micro- and ultra-filtration. For these applications, well-characterized regular AAO films with ideal pore configurations are particularly useful. Owing to its structure (see Fig. 1), AAO film has recently attracted increasing attention on its fundamental studies[1~3, 7, 8], such as mechanism on arrangement of cells and pores, effect of experimental conditions on the sizes of cells, the diameters of pores, the density of pores and the density of cells, and so on.

However, the geometry of AAO film usually obtained is far from idealized model; that is, the structures of cells in the obtained AAO film are not hexagons but irregular polygons, and the arrangements of cells and pores are irregular. The irregularity of the porous AAO causes distortion of the cross-sections of pores, broadening of the distribution of the diameters of pores and the sizes of cells. The irregular AAO films are not ideal templates for preparation of materials and devices on nanometer scale. There are many limits in the application of AAO films without ideal nanopore arrays. Therefore, preparation of AAO films with ideal or nearly ideal nanopore arrays is of importance. Masuda et al[9, 10] had fabricated AAO films with nearly ideal nanopore arrays through molding process and two-step anodization process, respectively; however, the two ways are very complicated in operation.

In this article, a one-step preparation technology of AAO films with ideal or nearly ideal nanopore arrays is reported. The morphologies and structures of the obtained AAO films are characterized by scanning electron microscope (SEM) and atom force microscope (AFM). In addition to these, the mechanism on arrangement of cells and pores, the effect of experimental conditions on the size of cells and the diameter of pores are discussed.

1 Experimental

High purity (99.99%) aluminum foils with the thickness of 0.3mm were cut into disc shape specimens whose diameters were 20mm or so. Then, the aluminum discs were degreased in acetone, and polished in a mixed solution of H_2SO_4, H_3PO_4 and HNO_3 for 1.5~2min, and rinsed in distilled water. The pretreated aluminum disc was put into a self-made anodizing device in which a circular aluminum of 10mm diameter was exposed to electrolyte and anodized.

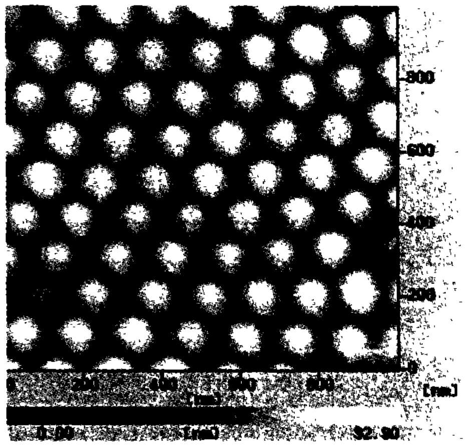
The anodizing condition was as follows: temperature of electrolyte was kept at 0 ± 0.2℃ in a thermally insulated electrochemical cell, $0.5\text{mol}\cdot\text{L}^{-1}$ oxalic acid solution was used as electrolyte, and anodizing time was 48h, anodizing voltage was kept constant at 40V, 45V and 50V direct current (*DC*), *respectively.*

After anodization, the remaining aluminum substrate was removed from the AAO film using saturated $HgCl_2$ solution. Subsequent etching treatment was carried out in a 5% H_3PO_4 solution at 30℃ for 6h, which makes it easy to observe the arrangement of pores and cells in the porous AAO by removing of the barrier AAO and broadening of the diameters of the pores. The morphologies and structures of AAO films were observed by scanning electron microscope (SEM, JEOL JSM-5900LV) and atom force microscope (AFM, SPA-400 SPM Unit).

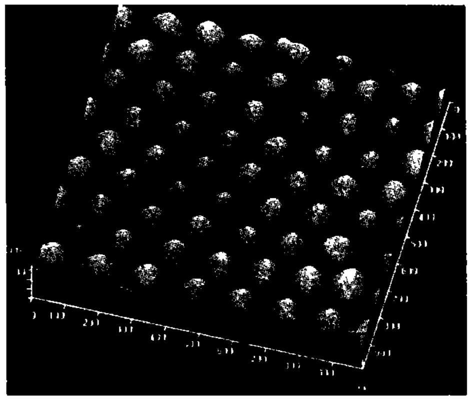
2 Results and Discussion

At the initial stage of anodization of aluminum, barrier AAO is firstly formed on the surface of aluminum. The thickness of AAO film increases with the increasing of anodization time, then AAO film is divided into barrier AAO and porous AAO. Fig. 2 shows AFM image of the barrier AAO at aluminum/alumina interface of the sample which was fabricated under 50V voltage after the un-reacted aluminum was removed by amalgamation in saturated $HgCl_2$ solution. As clearly shown in Fig. 2, there are many cells which are close-packed into a regular configuration in the barrier AAO at aluminum/alumina interface. The reason of the regular arrangement of cells is the mechanical stress which is associated with the volume expansion during the formation of AAO film[3]. The sizes of cells which are about 130nm have narrow distribution. Furthermore, a hexagonal pattern is formed by the nearest six cells around each cell, so the cells in the barrier AAO at aluminum/alumina interface are arranged in hexagonal arrays. According to the model of Masuda et al[2], the cells in barrier AAO at aluminum/alumina interface will be developed columnar hexagonal cells, each containing a central pore and is normal to the substrate in porous AAO. Therefore, the arrangement and the sizes of cells in barrier AAO at aluminum/alumina interface have a relation to those of cells and pores in porous AAO.

In order to investigate the effect of voltage on diameters of pores and sizes of cells in porous AAO, pretreated aluminum foils were anodized under different anodizing voltages. SEM micrographs of three porous AAO films obtained in 0.5mol · L^{-1} $H_2C_2O_4$ solution at 0℃ for 48h under 40V, 45V and 50V voltage respectively are shown in Fig. 3. Prior to observation, the three 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 Fig. 3, porous AAO films with nearly ideal pore arrays and cell arrays can be obtained under 40V, 45V and 50V in 0.5mol · L^{-1} $H_2C_2O_4$ solution, which is different from the fabrication conditions employed by Masuda et al[10] and Jessensky et al[3] who had obtained porous AAO films with nearly ideal pore arrays in 0.3mol · L^{-1} $H_2C_2O_4$ solution under 40V voltage. The cells which appear as columnar hexagons are

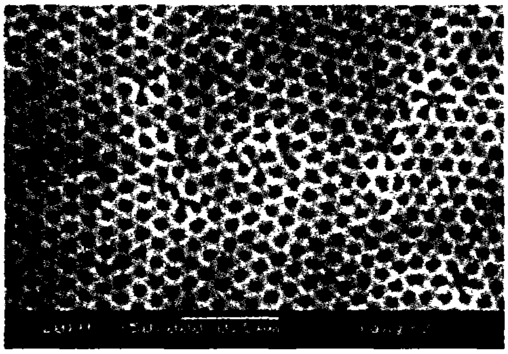


(a)



(b)

Fig. 2 AFM image of barrier AAO at aluminum/alumina interface
(a): plane-image, (b): 3d-image



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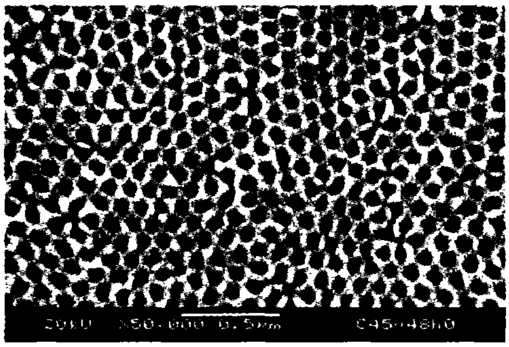

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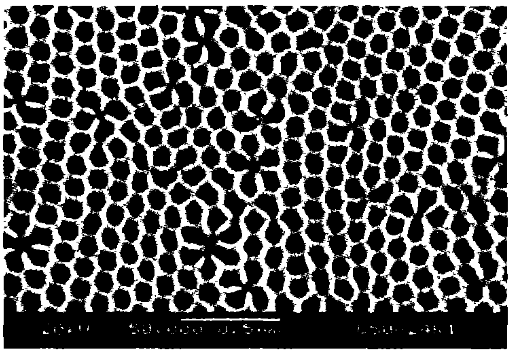


(c)

Fig. 3　SEM micrographs of porous AAO films obtained under voltages
(a): 40V, (b): 45V, (c): 50V

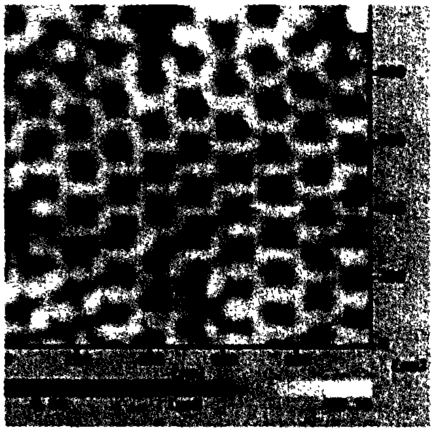
close-packed in porous AAO. Every cell contains a pore in the center, so the density of cells is the same as the density of pores for a sample. The average size of cells, the average diameter of pores and the density of cells, the density of pores in the three porous AAO films are indicated in Table 1. As clearly indicated in Table 1, the average size of cells and the average diameter of pores increase with the height of anodizing voltage, while the density of cells and the density of pores decrease with the height of anodizing voltage,

Table 1　Results from Fig. 3

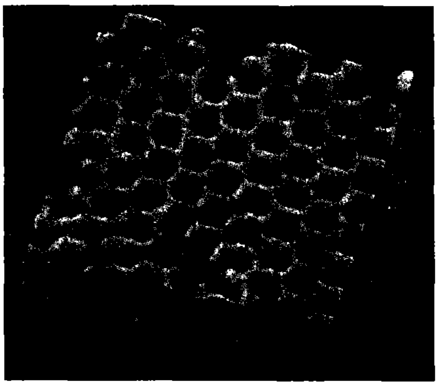
	40V	45V	50V
the average size of cells/nm	100	120	130
the average diameter of pores/nm	50	70	90
the density of cells/($\times 10^{10} cm^{-2}$)	1.25	0.97	0.78
the density of pores/($\times 10^{10} cm^{-2}$)	1.25	0.97	0.78

which coincides with the result of O' Sullivan et al[11]. The sizes of cells and the diameters of pores in every porous AAO film have narrow distribution. When the anodizing voltage is below 35V or above 60V, AAO films with nearly ideal nanopore arrays can not be easily obtained. Moreover, the voltage required for self-organized formation of AAO films with ideal or nearly ideal nanopore arrays has a relation to the kind of electrolyte. And only between 18V and 27V DC, the AAO films with nearly ideal pore arrays and cell arrays can be obtained in H_2SO_4 solution[3].

AFM image of porous AAO film obtained in 0.5



(a)

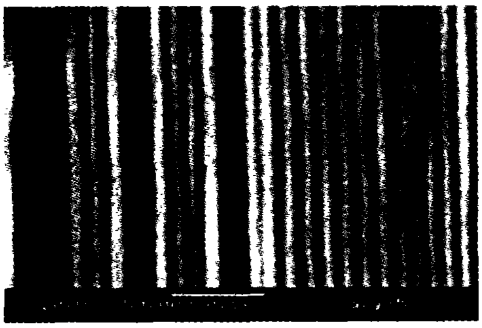


(b)

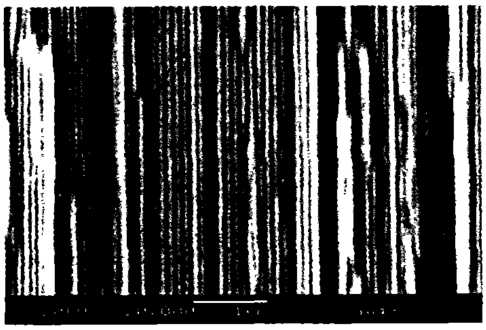
Fig. 4　AFM image of porous AAO film obtained under 40V
(a): plane-image, (b): 3d-image

mol · L^{-1} $H_2C_2O_4$ solution at 0℃ for 48h under 40V voltage is shown in Fig. 4. As clearly indicated in Fig. 4, every cell containing a central pore is a hexagonal configuration, and the cells are close-packed in porous AAO film. The nearest six pores around each pore form a hexagonal structure, so the pores are arranged in hexagon array. There are some distorted pores in the porous AAO film, and the patterns of the distorted pores are not absolute circles but irregular polygons. The sizes of pores and cells coincide with those shown in Fig. 3(a).

SEM micrographs of cross-section of the porous AAO film obtained under 40V voltage is shown in Fig. 5. From these photographs, the growth of straightly parallel pores perpendicular to the substrate can be confirmed. The average diameter of pores and the average size of cells are 50nm and 100nm respectively, which coincides with the results shown in Fig. 3 (a) and Fig. 4. Fig. 5(b) shows that a large area of AAO film with nearly ideal nanopore arrays can be obtained under the experimental conditions.



(a)



(b)

Fig. 5 SEM micrographs of cross-section of the porous AAO film obtained under 40V
(a): ×50000, (b): ×20000

3 Conclusion

AAO films with nearly ideal nanopore arrays are fabricated by a simple one-step preparation technology in which highly pure aluminum foils were anodized in 0.5mol · L^{-1} $H_2C_2O_4$ solution at 0℃ for 48h under 40V, 45V and 50V voltage respectively. Morphologies and structures of barrier AAO at aluminum/alumina interface, surfaces and cross-sections of the obtained AAO films are characterized by scanning electron microscope (SEM) and atom force microscope (AFM). Results show that cells in the barrier AAO at aluminum/alumina interface, cells and pores in porous AAO films are all arranged in hexagonal arrays; the sizes of cells and the diameters of pores which are on nanometer scale have narrow distribution. AAO films with nearly ideal nanopore arrays have many applications in preparations of nano-materials, nano-devices and in fundamental studies. Therefore, the one-step preparation technology for AAO films with nearly ideal nanopore arrays is a promising technology.

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