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A new method detaching porous anodic alumina films from aluminum substrates

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Abstract Recently, a particular focus on the research of porous anodic alumina (PAA) films is taken because of the application for growth of nanostructure materials. However, during detaching the PAA films from aluminum substrate and opening the holes of PAA films, it is quite difficult to keep intact through-hole structure of PAA films using traditional chemical etching method. Furthermore, the traditional method is time-consuming and has contamination because of the use of heavy metal ion solution. Usually, the preparation time is over 20 h. In our work, a new electric- chemical method was proposed for detaching PAA films and opening the holes of PAA films in an environmental friendly solution of $HClO_4$–CH_3OH in one step. The preparation process can be finished within 5–15 s. Compared with traditional etching method in which there are two-step processes, the electric–chemical method is simple, rapid and contamination-free. A large size PAA films with intact through-hole structure can be obtained.

Keywords Porous anodic alumina (PAA) films · New electric–chemical method · Detaching PAA films · Template for growth of nanostructure materials

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1 Introduction

Porous anodic alumina (PAA) fabricated by anodization of aluminum have been studied for more than 50 years [1]. In the past decade, there has been a particular focus on the fabrication of PAA films with an ordered array of holes [2–6], for use as template of nanotubes, nanowires [7–12], nanodots, and nanopillars [13–15] as well as micro-electromechanical systems (MEMS) devices [16]. In such PAA films, the pore diameter distribution is dependant of the film preparation and is typically close to mono-disperse. PAA films with pore diameter ranging from 4 to 250 nm, density as high as 10^{11} pores/cm^2, and film thickness varying from 0.1 to 300 μm have been realized [7, 8].

During the fabrication of PAA films, it is necessary to detach the PAA films from the aluminum substrate and to remove a barrier layer covering the pore bottom of PAA films for opening of the holes. Usually, a chemical etching method is used for the detachment and pore-opening of PAA films [17]. However, it is quite difficult to keep the through-hole structure of PAA films intact using the traditional chemical etching method. Furthermore, in this process, the PAA films would be contaminated by heavy metal ions because of the use of heavy metal ion solution, such as Hg, Cu ions and so on. In order to obtain ideal PAA films with intact through-hole structure and without contamination of heavy metal ions [17], a protective coating, in general, is used to eliminate the contamination [3, 17] and prevent the pore structure from destruction or distortion during the process. It is also difficult to find an ideal protective coating. Up to now, although many efforts have been made to deal with these problems, the detaching and pore-opening processes are still beyond control and time-consuming.

In this paper, the PAA films prepared by a two-step anodic oxidization method were detached separately from the aluminum substrates by a novel electric–chemical method and a traditional chemical etching method. Through comparison of morphology of both PAA films for the different detaching processes, we are sure that the electric–chemical method is superior to the chemical etching method.

2 Experimental

2.1 Pretreatment of the aluminum foils

The aluminum foils (thickness=0.2 mm; size=3.5×4.5 cm; purity=99.999%) were used in our study. Before the anodizing experiments were performed, the aluminum foils were degreased in acetone for 30 min and cleaned for 120 s by an ultrasonic cleaner in de-ionized water. The foils were etched in 20 wt% NaOH aqueous solution until bubbles occurred over the surface of the foils. Then the foils were cleaned ultrasonically and rinsed with de-ionized water. Subsequently, the foils were electropolished in mixing H_3PO_4–H_2CrO_4–H_2SO_4 aqueous solution to obtain a cleaned surface.

2.2 Anodic oxidization of the aluminum foils by a two-step anodic oxidization

To obtain ordered, perfected through-hole structure on both sides of the aluminum foils, it is necessary to carry out the pre-oxidization treatment of the aluminum foils. The process is similar to reference [17]. First, the cleaned aluminum foils were anodized under a dc voltages of 30–60 V in a solution of 0.3 mol/l $H_2C_2O_4$ with vigorously stirring at 0–10 °C for 1 h to form a primal layer PAA films. Next, the samples were immerged in 6% H_3PO_4 and 1.8% H_2CrO_4 mixing aqueous solution at 70 °C for 1 h to remove the primal layer PAA films. The samples were then anodized again under the same solution and voltages as described above at 0–10 °C for 6–10 h, the second layer PAA films with ordered pore structure over the aluminum foils were achieved (Figs. 1 and 2).

2.3 Detaching porous alumina films from the aluminum substrate and opening the holes of PAA films

For comparison, PAA films were prepared both by a traditional chemical etching method and a new electric–chemical method.

In the traditional chemical etching process, after the second anodization was carried out as described, the samples were etched in a $CuCl_2$ solution (5 g $CuCl_2{\cdot}2H_2O$+100ml H_2O) at 15 °C for about 24 h for detaching the PAA films. The detached PAA films were cleaned carefully to remove residues of metal ions (Fig. 3). Then the cleaned PAA films were immerged in 3 wt% phosphoric acid at 35 °C for 40–80 min, and the pore bottom of the PAA films were subsequently opened (Fig. 4). The samples were soaked in acetone for 15 min, and rinsed in de-ionized water to complete the preparation of through-hole PAA films.

For the same purpose, a new novel method, an electric–chemical process was adopted. The samples anodized after second oxidization process were immerged in a mixing solution of $HClO_4$–CH_3OH (v/v=1:1) with some polyglycol. A dc voltage of 25–45 V was applied for 5–15 s to separate the PAA films from the aluminum substrate. They were subsequently cleaned in de-ionized water. The cleaned PAA films were immersed in 3 wt% phosphoric acid by ultrasonic cleaning for 10 min, and finally the samples were

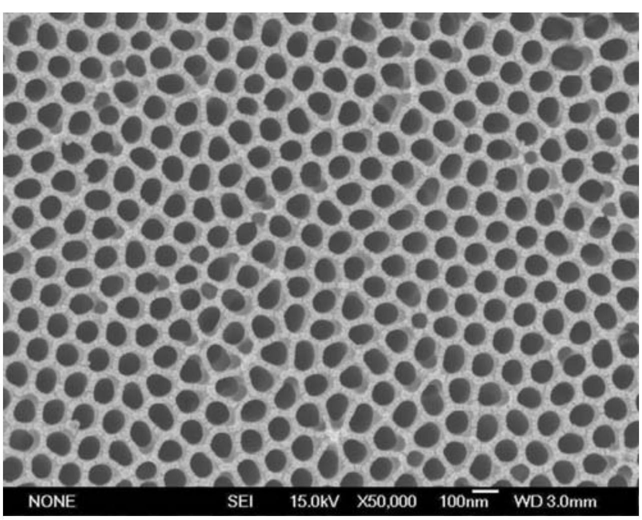

Fig. 1 SEM images of the top surface of the PAA films

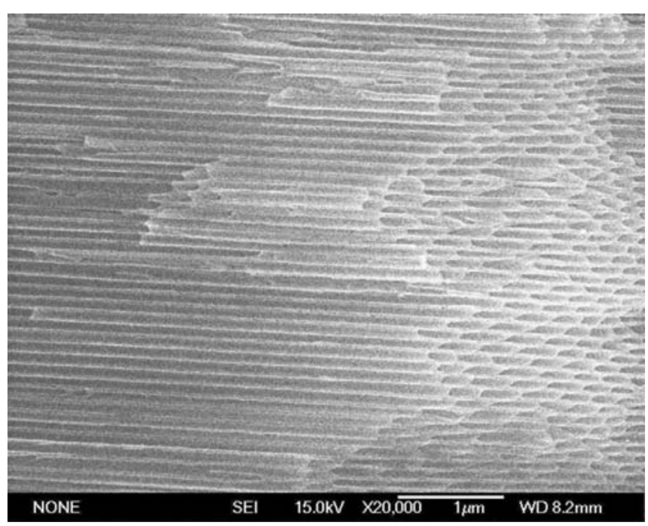

Fig. 2 SEM images of the cross section of the PAA films

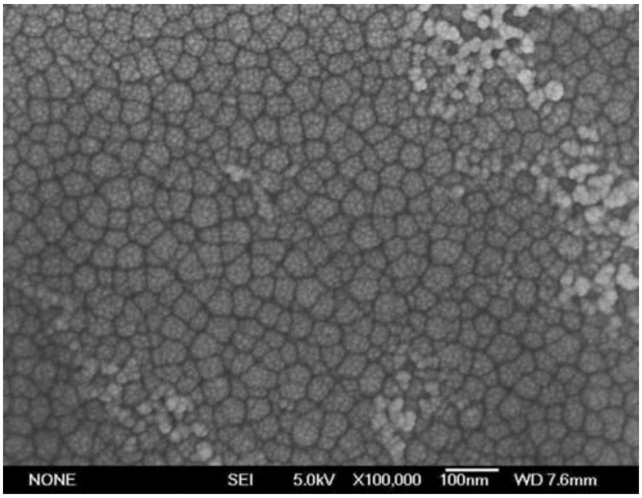

Fig. 3 SEM images of the bottom surface of the PAA films before the removal of the barrier layer detached by traditional chemical etching method

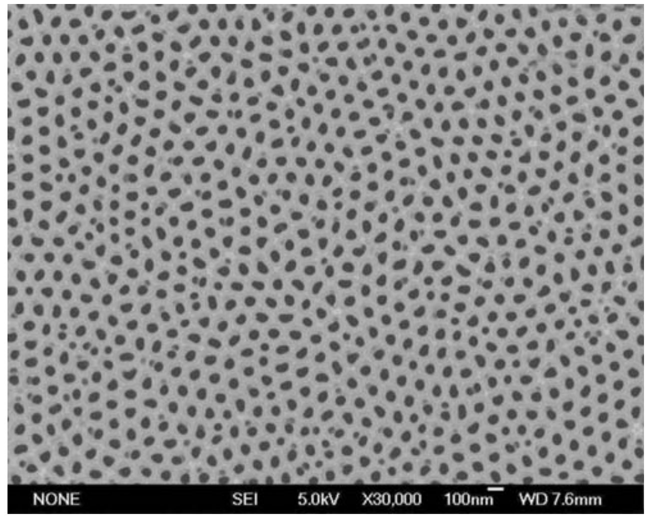

Fig. 5 SEM images of the bottom surface of the PAA films detached by electric chemical method

rinsed in de-ionized water. The PAA films were obtained (Figs. 5 and 6).

3 Results and discussion

Figures 1 and 2 exhibit typical SEM images of top surface and cross section of PAA film which was anodized in a 0.3 M $H_2C_2O_4$ solution with a dc voltage of 40 V applied for 6 h at 4 °C. It can be seen from the top surface of the PAA film in Fig. 1, the pores are arranged in a hexagonal configuration within the range of several micrometers. Figure 2 shows the cross section of PAA films, it is seen clearly that the holes were tightly arranged and well-aligned with one another. The average diameter of the pores and distance between pores are 85 and 120 nm respectively. The pore density is estimated about 10^{10} pores/cm^2.

Figure 3 shows the bottom surface photograph of the PAA film detached by traditional chemical etching method in $CuCl_2$ solution. It is very obvious that the pore bottom of PAA films was covered completely by a barrier layer. Figure 4 shows the bottom surface morphology of the PAA film after the barrier layer was removed in a 3% H_3PO_4 aqueous solution. Compared with the morphology of the PAA film before the detaching process (see Fig. 1), it can be seen that the morphologies are very different. The pores were partially damaged, and there was some residual barrier layer at the edge of holes.

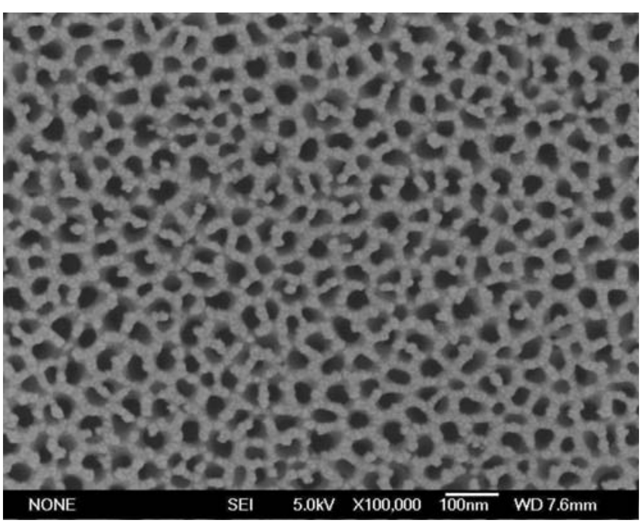

Fig. 4 SEM images of the bottom surface of the PAA films after the removal of the barrier layer detached by traditional chemical etching method

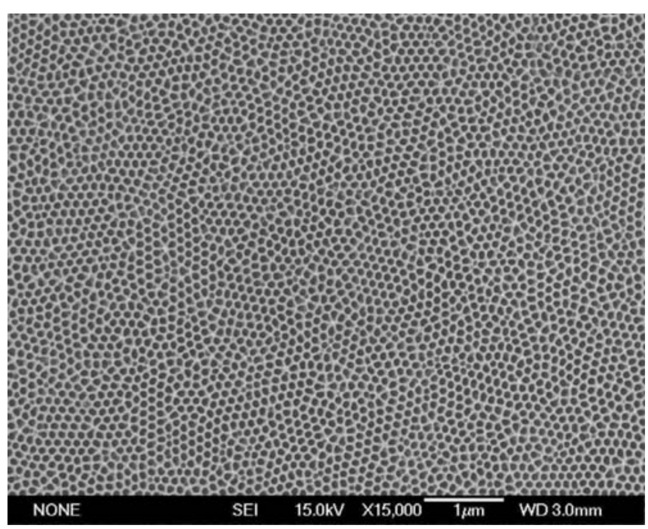

Fig. 6 SEM images of the top surface of the PAA films detached by electric chemical method

Figures 5 and 6 show the bottom and top surface photographs of the PAA film detached by the electric–chemical method. It can be seen, the morphologies of bottom and surface of PAA films are almost similar, and the pores have been completely opened during the detaching step. It demonstrates that both detachment and pore-opening steps can be carried out at the same time. The morphologies are also the same as that shown in Fig. 1 with no barrier layer remains at the holes bottom. The pores and the hexagonal configuration are still perfect. The results prove that the electric–chemical process is a good method that does not destroy the pore structure of the PAA films.

There is obvious difference between the two films preparation processes. In the traditional etching method, the preparation of through-hole PAA films needs about 25 h, but using the new method, that of the PAA films can be ready within 15 s.

Moreover, there are three advantages for the new electric–chemical process. Firstly, the pore size can be retained at its original size, while the chemical etching method usually results in pore being enlarged due to partial dissolution of pore walls in the base etching solution. Secondly, $HClO_4$ and CH_3OH solution are environmental friendly and free of heavy metallic ions. The problems caused by residues of metal ions do not exist. Thirdly, for separating the PAA films and opening the holes, a long processing time is not necessary; the new way is simple and rapid.

As a result, a larger size PAA films of 2 cm and width of 2 cm, the thickness of 30–100 μm with perfect through-hole structure can be obtained. It can be a better template for growth of nanostructure materials.

Further understanding of the detaching mechanism is being carried out.

4 Conclusions

A new electric–chemical process has been proposed, which is simple, rapid and contamination-free, without the need for chemical etching solution that contains heavy metal ions. The two-step process of detachment and opening holes of PAA films can be accomplished in a short time (<15 s). In particular, the new process does not destroy the pore structure. A large size PAA films of 2×2 cm and thickness of 30–100 μm with perfect through-hole structure can be obtained. The average diameter of pores and distance between pores are 85 and 120 nm respectively, and the pore density is about 10^{10} pores/cm^2. The PAA films can be used as templates for growth of nanowires and nanotubes.

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