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A facile approach to formation of through-hole porous anodic aluminum oxide film

Yanchun Zhao, Miao Chen*, Yanan Zhang, Tao Xu, Weimin Liu

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

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Abstract

Highly ordered through-hole anodic porous alumina film was fabricated using a facile single side and two-step anodization approach without any special pretreatment. The as-fabricated anodic aluminum oxide (AAO) film has a mean pore diameter of 80 nm and the interpore distance is ~150 nm. The pore density can be high as 1.0×10^{10} cm^{-2}. During the processes of removal of aluminum substrate and pore opening, a simple setup was used. The evolution of surface morphology of the AAO film was characterized by scanning electron microscopy (SEM). The fabricated pore-through AAO film can then be used as templates for growth of well aligned nanowire, nanotube and nanodevice.

Keywords: Template synthesis; Porous anodic alumina; Anodization

1. Introduction

Anodic aluminum oxide (AAO) films in the form of self-ordered honeycomb array of uniformly sized parallel channels are attractive for many technical applications in the rapidly growing nanotechnology field due to their high pore density [1–4]. The pore diameter distribution in such films is a function of the film preparation and is typically close to monodisperse. AAO films grown in acid electrolytes possess hexagonally ordered porous structures with pore diameters ranging from below 10 to 200 nm, pore lengths from 1 to over 100 μm, and pore density in the range of 10^9 to 10^{12} cm^{-2}. These unique structure properties and their thermal and chemical stability make AAO films ideal templates for the fabrication of uniform nanoscale structures and masking. Thus, by filling the pores of the AAO template, arrays of aligned nanowires or nanotubes uniform in diameter and length, are obtained reproducibly and economically [5–7].

In the past decade, there has been a particular focus on the fabrication of AAO film with ordered array of holes [8–10]. Masuda et al. advocated a two-step oxidation technology [11] and molding [12] process to prepare highly ordered pore arrays. Recently, pore nucleation and growth of AAO with square cells were fabricated using imprinting process [13]. However, two main factors should be born in mind for successful fabrication of perfect AAO. The first factor involves the pretreatment including annealing and polishing of the aluminum sheet, which is considered to be essential for the preparation of ordered pores [13,14], these two processes make the fabrication process tedious and boring. The second factor is the removal of an oxide barrier layer between the porous alumina and the aluminum base to ensure the pores open-through. Up to now although many efforts have been made to deal with these problems [15–17], the detaching and pore-opening processes are still a challenge and are difficult to do.

In this paper, we reported a facile procedure to fabricate through-hole AAO template. The pretreatment processes including annealing and electrochemical polishing of the aluminum base were not necessary. Simple degreasing and oxide removal pretreatment was enough for obtaining clean and flat Al species that were essential for symmetrical

* Corresponding author. Tel.: +86 931 4968189; fax: +86 931 8277088.
E-mail address: miaochen@lsl.ac.cn (M. Chen).

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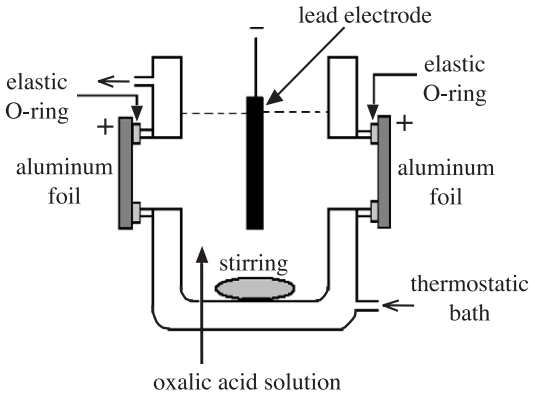

Fig. 1. Setup for anodic oxidation of aluminum sheet.

distribution of applied electric field on the aluminum surface in the followed anodizing process for achieving ordered pores. A schematic representation of the setup for the anodization and the whole procedure was shown in Figs. 1 and 2. The as-fabricated AAO film has a mean pore diameter of 80 nm. The evolution of surface morphology of the AAO film was characterized by scanning electron microscopy (SEM).

2. Experimental

Single side of high-purity aluminum sheet was anodized by a regulated DC power supply in a 0.3 M oxalic acid solution. The aluminum substrate were first degreased in acetone for 6 h and followed by 180 s of ultrasonic cleaning. Then the samples were rinsed with distilled water and etched in 3.0 M NaOH until bubbles over the surface occurred and finally the samples were rinsed with distilled water. Anodization was performed in 0.3 M $H_2C_2O_4$ at either 0 or 15 °C, in a constant-temperature bath. For obtaining pores on a single side, experiments were carried out using a two-electrode setup (Fig. 1) from a vigorously stirred solution of 0.3 M oxalic acid. The cleaned aluminum sheet was used as the anode and Pb foil as the cathode. The first anodization lasted 3 h and the second 8 h. After the first anodization, the strip-off process was carried out in a mixture solution (0.4 M H_3PO_4+0.2 M H_2CrO_4) at 80 °C for 1 h. The exposed and well-ordered concave patterns on the aluminum substrate acted as self-assembled mask for the second anodization process. After the second anodization, the remaining aluminum substrate was removed in a $CuCl_2$-based solution (100 ml of HCl (38%)+100 ml H_2O+3.4 g of $CuCl_2 \cdot H_2O$) at room temperature for about 10 min. The bottom of the pores was subsequently opened by 5% H_3PO_4 at room temperature for 2 h. Both detaching and pore-opening processes were carried out in a setup described in Fig. 2F.

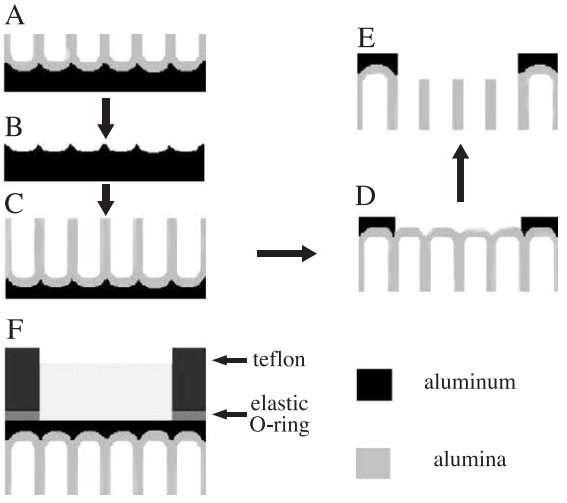

Fig. 2. Schematic diagram of the preparation procedure for the formation of through-hole AAO film. (A) Formation of the porous alumina layer after the first anodization; (B) removal of the porous alumina layer; (C) formation of ordered porous alumina layer after the second anodization; (D) removal of the aluminum layer; (E) removal of the bottom layer; (F) setup for the detaching and pore-opening processes.

3. Results and discussion

Alumina film was fabricated by anodizing aluminum metal in oxalic acid solution at the voltage of 60 V and 0 °C. The current densities (using geometric area of aluminum exposed to solution) distribution curves as a function of the anodic oxidation time were reported in Fig. 3. The solid and dashed curves were for the first and second oxidation process, respectively. The current densities for the first and second anodization were divided into three regions: formation of the barrier oxide layer, initiation of pore formation and steady state pore growth (formation of the porous oxide layer) [18]. Although the same current behaviors for the first and second anodic process were similar, there were several important differences between the results observed in the first and second anodic oxidation. First, for the second anodic oxidation, the time for reaching

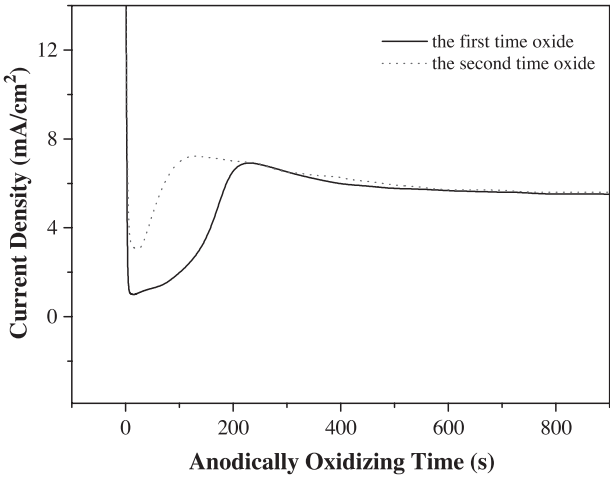

Fig. 3. Current–time anodization curve for anodization in 0.3 M $H_2C_2O_4$ at 60 V and 0 °C (constant-voltage mode).