

## An Improved Method To Strip Aluminum from Porous Anodic Alumina Films

Terry T. Xu, Richard D. Piner, and Rodney S. Ruoff\*

Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

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### 1. Introduction

Aluminas having porous structure and fabricated by anodization of aluminum have been studied for more than 40 years.<sup>1</sup> In the past decade there has been a particular focus on the fabrication of porous anodic alumina (PAA) films with an ordered array of holes.<sup>2–7</sup> The pore diameter distribution in such films is a function of the film preparation and is typically close to monodisperse. PAA films with pore diameter ranging from 4 to 250 nm, density as high as  $10^{15}$  pores/m<sup>2</sup>, and film thickness varying from 0.1 to 300  $\mu\text{m}$  have been realized.<sup>4–7</sup> The applications of PAA films that have been explored include template growth of nanotubes and nanowires,<sup>8–12</sup> creation of nanoholes, nanodots, and nanopillars,<sup>13–16</sup> and fabrication of micro-electromechanical systems (MEMS) devices.<sup>17,18</sup>

A two-step anodization is used to fabricate the PAA film.<sup>2,3</sup> During the fabrication of through-hole PAA film (Figure 1), use of a protective coating is required.<sup>3</sup> This coating protects the pore morphology so that it will not be altered during removal of the underlying aluminum substrate and the subsequent process of opening of the nanopores. The protective coating also makes the fragile PAA film more flexible so that it is easier to handle. The requirements for an ideal protective coating are (1) it remains intact during the process of removing the aluminum substrate and during the pore-opening process, (2) there is no residue left on the PAA film following its removal, (3) it is easy to handle, and (4) it is inexpensive.

\* Corresponding author. E-mail: r-ruoff@northwestern.edu.

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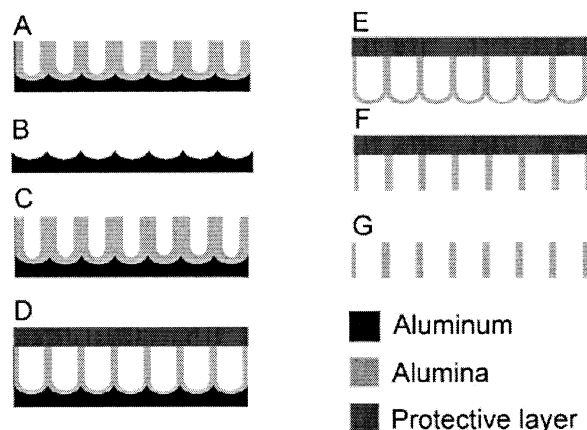
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**Figure 1.** Schematic illustration of fabrication procedures for through-hole PAA films: (A) formation of the porous alumina layer after the first anodization, (B) removal of the porous alumina layer (strip-off), (C) formation of the ordered porous alumina layer after the second anodization, (D) coating of a protective layer, (E) removal of the aluminum layer, (F) removal of the bottom layer (i.e., barrier layer), and (G) removal of the protecting layer.

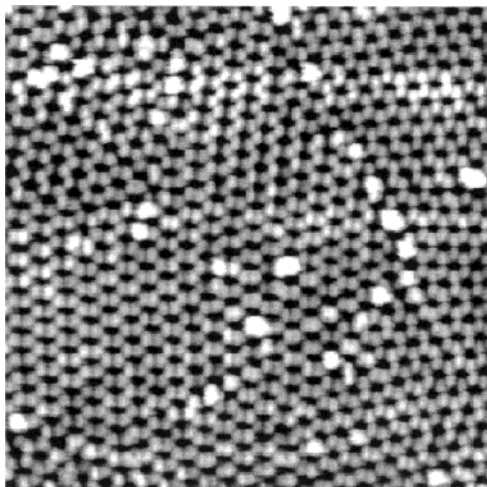
To our knowledge, little information has been provided on selection of a suitable protective coating.<sup>3–5</sup> Masuda et al. reported using a protective layer made of a mixture of nitrocellulose and polyester resin in ethyl acetate, butyl acetate, and heptane.<sup>3</sup> The preparation of this protective coating was nontrivial. Li et al. mentioned using a protective layer during fabrication. However, no detailed information was given.<sup>4,5</sup>

In this paper, we report the use of nail polish as the protective layer during the fabrication of PAA films. The ingredients of nail polish are similar to those of the protective layer Masuda used.<sup>5</sup> We find nail polish fulfills the suggested requirements mentioned above: it remains intact during processing to complete the nanopore film, the film is residue-free following its removal, it is easy to handle, and it is inexpensive. The as-fabricated PAA film has a mean pore diameter of  $\sim 60$  nm, an interpore distance of  $\sim 100$  nm, and a film thickness of  $\sim 100$   $\mu\text{m}$ . The evolution of surface morphology (both top and bottom surfaces) of the PAA film was characterized by both atomic force microscopy (AFM) and scanning electron microscopy (SEM).

### 2. Experimental Section

High-purity aluminum foils (Alfa Aesar, 1.0 mm thick, Puratronic, 99.998%) were anodized. The aluminum substrates were first degreased in acetone and then mechanically polished using an oil-based diamond suspension. The roughness ( $R_a$ ) of the polished surface measured by AFM is  $\sim 6$  nm over a  $2 \times 2$   $\mu\text{m}^2$  scan area. The now standard two-step anodization<sup>2,3</sup> was used to fabricate the PAA films. Anodization was done at 40 V and 15  $^\circ\text{C}$  in oxalic acid. The first anodization lasted 12 h, the second 24 h. After the first anodization, the strip-off process was carried out in a mixture of phosphoric acid and chromic acid<sup>19</sup> at 85  $^\circ\text{C}$  for 1 h. The exposed and well-ordered concave patterns on the aluminum substrate act as self-assembled masks for the second anodization process. After the second anodization, the remaining aluminum substrate was removed in a  $\text{CuCl}_2$ -based solution (100 mL of HCl (38%) + 100 mL of  $\text{H}_2\text{O}$  + 3.4 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ )<sup>20</sup> at 15  $^\circ\text{C}$  for about 3 h. The bottoms of the pores were subsequently opened by 0.1 M phosphoric acid at 35  $^\circ\text{C}$  for 80

(19) ASTM standard B680-80.



**Figure 2.** AFM image, showing the well-ordered porous structure after the second anodization (scan area  $2 \times 2 \mu\text{m}^2$ ).

min. Before the removal of the aluminum substrate and pore-opening processes, nail polish (Maybelline Infinite Shine) was coated on the top surface of the PAA film, serving as a protective layer. At the end of processing, the nail polish layer was peeled off using tweezers. The sample was then soaked in acetone for 15 min and rinsed, resulting in a clean through-hole PAA film.

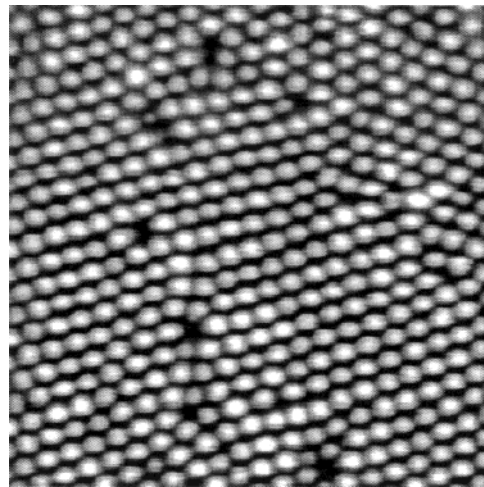
The evolution of the surface morphology was recorded by AFM (Park Instrument, model CP) and SEM (Hitachi, S-4500).

### 3. Results and Discussion

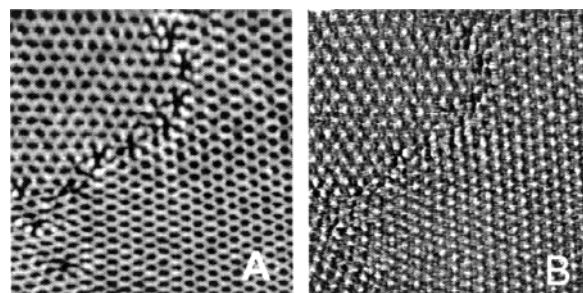
Figure 2 is an AFM image showing the top surface morphology of PAA after the second anodization. A well-ordered array of nanopores is observed. The diameter of the pores is  $\sim 60$  nm and the interpore distance is  $\sim 100$  nm. Previous researchers<sup>4,5,7</sup> reported that such well-ordered nanopore arrays could be obtained from the aluminum foils with pretreatments such as annealing and electropolishing. However, our result shows the tedious pretreatments are not necessary.

After coating the nail polish layer on the top surface of the PAA film, the remaining aluminum substrate was removed in the  $\text{CuCl}_2$ -based solution mentioned above. Compared with the commonly used  $\text{HgCl}_2$  solution, we believe our use of the  $\text{CuCl}_2$ -based solution has certain advantages. First, the etching rate of the  $\text{CuCl}_2$ -based solution is much faster. Second, the solution is environmentally friendly, since no hazardous products (that is, Hg) will be produced. Figure 3 shows the bottom surface of the PAA film after the aluminum substrate was removed. The pore bottom is covered by an oxide layer, the so-called "barrier layer".

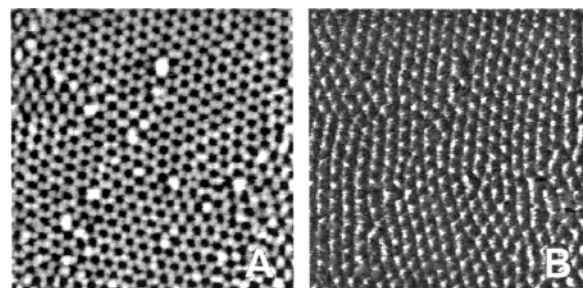
The PAA film was then dipped into  $0.1 \text{ M H}_3\text{PO}_4$  solution to remove the barrier layer, followed by removal of the protective nail polish layer. Figure 4a shows the bottom surface of the PAA film and the opened pores. The pore diameter is  $\sim 60$  nm and the interpore distance is  $\sim 100$  nm, consistent with the pore diameter and interpore distance measured at the top surface. Both AFM and SEM measurements of pore diameter are in good agreement. Figure 5a shows the top surface of the PAA film. Upon comparing Figure 5a with Figure 2, no significant morphology change can be observed. In other words, the top surface was well-protected by the nail polish layer during the processes of removing the aluminum substrate



**Figure 3.** AFM image, showing the pore bottom after removal of the aluminum substrate (scan area  $2 \times 2 \mu\text{m}^2$ ).



**Figure 4.** (A) AFM image, showing the bottom surface of the PAA film after the removal of the nail polish layer. (B) Corresponding lateral force microscope (LFM) image, showing the surface has low friction.



**Figure 5.** (A) AFM image, showing the top surface of the PAA film after the removal of the nail polish layer. (B) Corresponding LFM image, showing the surface has low friction.

and opening the pore bottom. The friction data (Figures 4b and 5b) for the top and bottom surfaces demonstrate low friction, indicating that both surfaces are residue-free.

The thickness of the as-fabricated PAA film was measured under an optical microscope and was  $\sim 100 \mu\text{m}$ . This PAA film was then used as a template for growth of carbon nanotubes by thermal deposition from ethylene. The carbon nanotubes could be released from the PAA film by dissolving the film in hot  $6 \text{ M NaOH}$ .

### 4. Conclusions

A new process step involving the use of nail polish as a protecting layer was implemented to improve the fabrication of anodic alumina having an array of nanopores. The pore diameter was  $\sim 60$  nm, the interpore distance  $\sim 100$  nm, and the film thickness  $\sim 100 \mu\text{m}$ . The PAA film was fabricated from aluminum foil without any special pretreatment (e.g., annealing, electropolishing).

(20) Private discussion, K. Nielsch from Max-Planck-Institute of Microstructures Physics.

An environmentally friendly  $\text{CuCl}_2$ -based solution was used to etch away the aluminum substrate. During the processes of removal of aluminum substrate and pore opening, nail polish was used. The nature of nail polish (e.g., robust in most acids, easy to handle, residue-free after removal, inexpensive) suggests its use as an excellent protective and handling coating layer when fabricating PAA films.

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