

Fabrication of nano-scaled alumina template mask by using self-assembly anodic oxidation method

T. Y. Cheng¹, C. H. Wu^{2,3}, J. T. Sheu¹

¹Department of Electrical Engineering,
National Chi Nan University, Puli 545, Taiwan

²Institute and Department of Electrophysics,
National Chiao Tung University, Hsinchu 30050, Taiwan

³National Synchrotron Radiation Research Center,
101 Hsin-Ann Road, HsinChu Science-Based Industrial Park, Hsinchu 30077, Taiwan

Abstract

Abstract: The conditions for the self-organized formation of ordered hexagonal structures in anodic alumina were investigated with the oxalic acid as an electrolyte. Highly ordered pore arrays membranes were obtained by using self-assembly two-step anodic aluminum oxidation (AAO) process without chromic acid. The size of the ordered domains depends strongly on the anodizing voltage. This effect is correlated with a voltage dependence of the volume expansion of the aluminum during oxidation and the current efficiency for oxide formation. The ordered and close-packed hexagonally arrangement nanochannels were obtained and an average diameter of about 50~60 nm. Field emission scanning electron microscopy (FESEM, Hitachi model S-4000) and commercial atomic force microscopy (AFM) were employed to characterize the nano-scaled AAO template mask.

Key-Words: Self-organized, Two-step process, Anodic aluminum oxidation (AAO), Hexagonally nanochannels, Template mask

1 Introduction

Porous oxide growth on aluminum under anodic bias in various electrolytes has been studied for many years. It is well known that template synthesis is a simple and versatile method for preparing nano-structural materials, which entails synthesizing the desired material within the pores of a micro-porous template membrane. Anodic aluminum oxide (AAO) with naturally self-ordered porous structure has recently attracted increasing attention in decades due to their utilization as templates for nano-scaled structure applications, such as magnetic, electronic, and optoelectronic devices [6,7]. One of the important conception of self-assembly lies in its capability in forming a large area of uniform structures through inexpensive chemical processes. Nano porous AAO, which consists of vertical pore channel arrays with a hexagonal packing structure, was obtained by anodic oxidation of aluminum in

an acidic electrolyte. The porous structure is imaged as a lot of nano-channels inside the alumina. During the self-assembly anodic aluminum oxidation regulating pore growth, which leads to a densely packed hexagonal pore structure, parameters like surface roughness of aluminum, electrolyte temperature, and various electrolyte concentration are directly influence the quality of anodic process. Also, the pore diameter and the interpore distance have linearly relationship with the applied voltage or composition of electrolyte [1-5].

In order to have well-controlled spatial arrangement and highly ordered pore size distribution of AAO membrane as the x-ray mask membranes, control of anodic voltage, anodic time, electrode distance, surface roughness of an aluminum foil, electrolyte temperature, and concentration, respectively. The dependence of the structural properties on these anodization

conditions has been investigated to gain more insight into the formation conditions of ordered pore arrays. As a result, nano-scaled x-ray mask is fabricated by using self-assembly anodic oxidation method.

2 Experimental Details

In this experiment, the aluminum foils possess a highly purity (99.999%, 50mm×50mm) with a thickness of around 125 μm were chosen. Samples were cleaned by dipping in the acetone solution for 3 minutes to remove surface organic pollution particles and then blown dry using N₂ gas before performing anodic oxidation process. Prior to the anodization process, aluminum foils were annealed in atmosphere at 400°C for 6 hrs to re-crystallize and to release the foil internal mechanical stress. The surface roughness (R_q) of the highly purity aluminum foils is around 146 nm measured by atomic force microscopy (AFM). After annealing process, chemical-polish and electrolytic-polish were used for smoothing the surface of aluminum foils. The chemical-polishing process was performed in a solution of H₃PO₄ (85%)-HNO₃ (61%)-H₂O (8:1:1 by volume) for 10 minutes at 80°C. The chemical-polished surface roughness of the aluminum foil was reduced to about 60 nm in 40μm ×40μm scan region by AFM. Then, the aluminum foils were electropolished in a ratio of 4:4:2 by weight mixture of H₃PO₄, H₂SO₄, and H₂O with a constant voltage of 20V for 2min at 80°C to reduce surface roughness. The electrolytic-polished surface roughness was down to about 20 nm in 40μm ×40μm scan region by AFM. Then, AAO membranes were fabricated by using a two-step anodization process. Anodization was first carried out in a 0.3 M oxalic acid solution at 20 °C under a constant polarization voltage of 40 V for 30 min. Figure 1 illustrates the two-step anodic oxidation process for the preparation of self-ordered porous structure template membranes. The nanoporous about 2 μm in thickness as shown in Figure 1(a), was eliminated portion alumina layer by immersing the specimen in phosphoric acid (6%) at 60 °C for 15 minutes as shown Figure 1(b). The second

anodization of the prestructured aluminum foil was then performed for 2 hours under the same chemical condition as the first one. After the second anodization step, highly uniform and periodic nanopores were formed, as shown in Figure 1(c), which will then be used as the x-ray template mask membrane. The diameter of the as-grown pores is about 60~70 nm and can be enlarged by immersing AAO membranes in phosphoric acid (5%) for 30min at room temperature. The surface morphology and porous depth structures images of the nano-scaled AAO template membranes were examined by means of a JEOL field-emission scanning electron microscope and commercial atomic force microscopy.

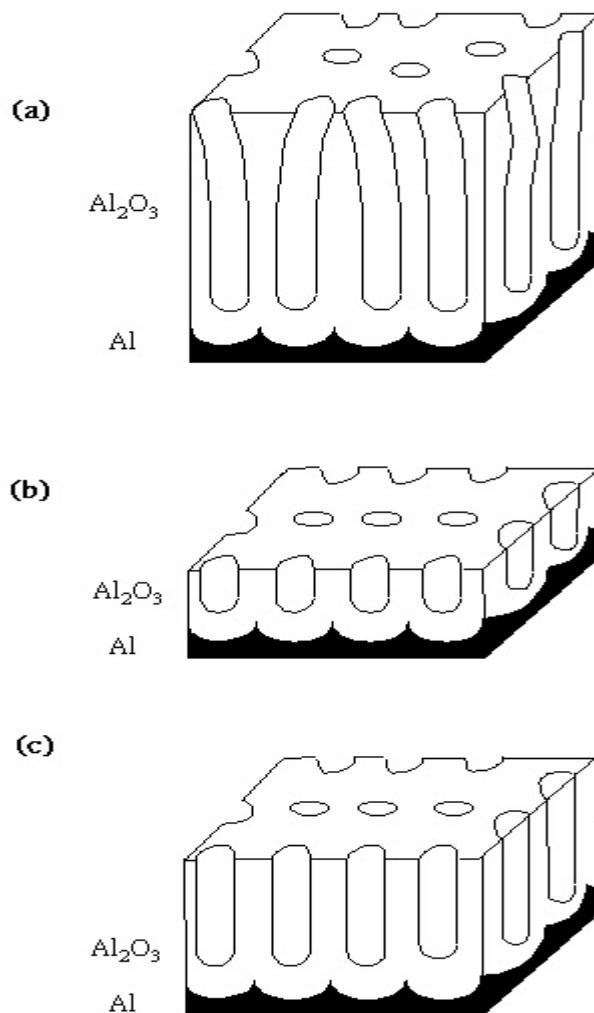


Figure.1 Schematic diagram describing the

fabrication of highly ordered porous alumina matrix. (a) nanostructures after first anodic oxidation step; (b) the pre-structured aluminum film after elimination of portion aluminum oxide; (c) nanostructures after second anodic oxidation step.

3 Results and Discussion

The scheme of the experiment process is shown in Figure 1. The alumina film and surface organic pollution particle are removed from the aluminum foil surface by chemical etching first. Before polishing, there are a lot of defects and line scratches on the aluminum foil surface. The surface root mean square roughness of the highly purity aluminum foils is about 146 nm measured by AFM. After polishing process, the line scratches and defects are removed and the surface root mean square roughness is reduced down to ~1 nm in $5 \times 5 \mu\text{m}^2$ scan region by AFM. A porous anodic alumina film is created on an aluminum foil sample surface by the first-step anodic oxidation process. Then, portion of alumina in upper layer of the surface was eliminated by immersing the specimen in H_3PO_4 (6 wt %) at 60 °C for 15min. In this process, CrO_3 was not chosen to remove alumina after first-step anodic oxidation. In stead, we used only the H_3PO_4 to remove the upper portion of alumina layer. Since the toxicity of chromic acid is very strong and environmental pollution is concerned if not properly handled. Subsequently, anodizing the sample again, the texture of the aluminum surface after alumina removal helps the growth of nanoporous channels into a better order.

During the anodic oxidation of the aluminum foil layer, the anodic current density was rather steady at around $26\text{mA}/\text{cm}^2$ except at the initial stage. As the oxidation of the aluminum foil layer transferred to AAO layer, the anodic current density also dropped. This process can get an ordered structure on the alumina film, but the ordered domain size is still similar about 25~30 nm. Figure 2 shows surface morphology of the AAO layer after first-step anodic oxidation. The nanopores is not arranged orderly. Figure 3 shows

the top-view atomic force microscopy (AFM) image of the nanoporous AAO film after pore widening in a 5% H_3PO_4 solution at room temperature for 15 min. The self-organized nanopores with a uniform size distribution have a pore diameter about 50~60 nm and an inter-pore distance about 160 nm.

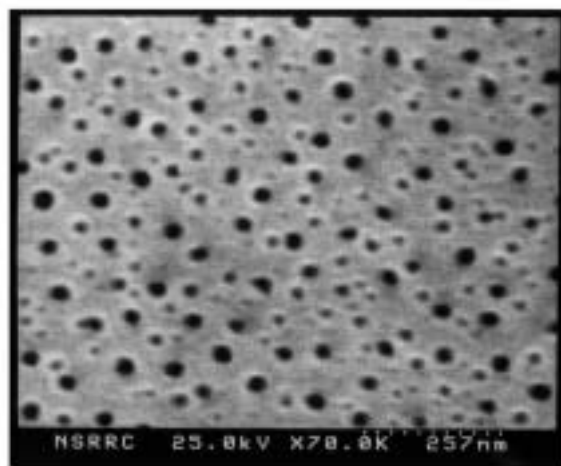


Figure 2. Top-view SEM image of the first-step anodic oxidation nanoporous AAO film.

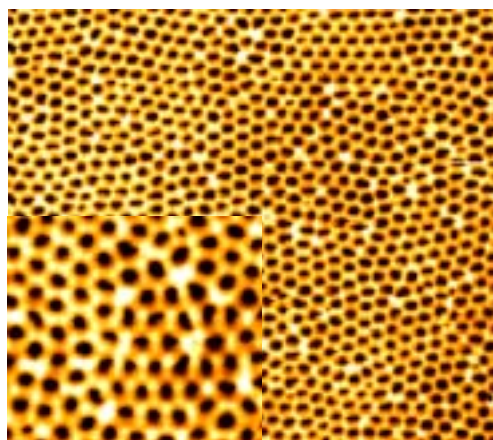


Figure 3. The atomic force microscopy (AFM) image of the nanoporous AAO film after pore widening in a 5% H_3PO_4 solution at room temperature for 15 min. The inset shows a close-up view of the hexagonal arrangement of the nanopores.

The self-assembly alumina layer thickness about 6 μm and pore diameter 60nm. The AAO nano-pores do not show a long range ordering, but within a pore array domain, ordered nanopore with a hexagonal arrangement clearly observed. The highly density of the ordered hexagonal nanopore template have an average diameter about 60 nm as shown in Figure 4. The size of the locally anodized nano-porous can be varied over a wide range because the diameter of the self-ordered nano-pores is dependent upon anodization parameters, such as polarization voltage, bath temperature, electrolyte species, and electrolyte concentration. The pore diameters are tunable in the range of ten to several hundred nanometers, making AAO an ideal x-ray template mask membranes for fabricating ordered arrays of nano-structured materials.

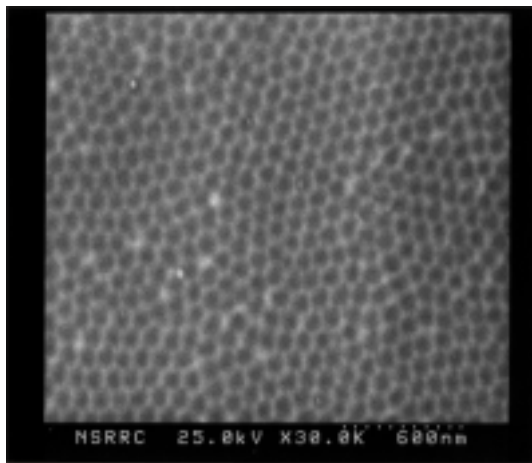


Figure 4. SEM image of AAO nanopores after two-step process.

4 Conclusion

We have demonstrated the highly ordered pore arrays membranes by using self-assembly two-step anodic aluminum oxidation (AAO) process. The ordered and close-packed hexagonally arrangement nano-channels were obtained and an average diameter of about 50~60 nm. This effect is correlated with a voltage dependence of the volume expansion of the aluminum during oxidation and the efficiency for oxide formation. With properly control of the thickness, the AAO membranes not only can be

applied in the x-ray lithography for pattern transfer, it also can be used as the mask templates for deposition of nanopatterns in biomedical, electronic, and magnetic applications.

Acknowledgement

This work was supported by the Nation Science Council of Taiwan under the contract number: NSC-91-2215-E-260-004.

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