



# Novel structure formation at the bottom surface of porous anodic alumina fabricated by single step anodization process

Ghafar Ali<sup>a,b</sup>, Maqsood Ahmad<sup>b</sup>, Javed Iqbal Akhter<sup>b</sup>, Muhammad Maqbool<sup>c</sup>, Sung Oh Cho<sup>a,\*</sup>

<sup>a</sup> Department of Nuclear and Quantum Engineering, Korea Advance Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

<sup>b</sup> Physics Division, PINSTECH, Islamabad, Pakistan

<sup>c</sup> Department of Physics and Astronomy, Ball State University, Muncie, IN 47306, USA

## ARTICLE INFO

### Article history:

Received 8 January 2010

Received in revised form 20 April 2010

Accepted 20 April 2010

### Keywords:

Anodization

Porous anodic alumina film

Nano-template

Nano-materials

## ABSTRACT

A simple approach for the growth of long-range highly ordered nanoporous anodic alumina film in  $H_2SO_4$  electrolyte through a single step anodization without any additional pre-anodizing procedure is reported. Free-standing porous anodic alumina film of 180  $\mu m$  thickness with through hole morphology was obtained. A simple and single step process was used for the detachment of alumina from aluminum substrate. The effect of anodizing conditions, such as anodizing voltage and time on the pore diameter and pore ordering is discussed. The metal/oxide and oxide/electrolyte interfaces were examined by high resolution scanning transmission electron microscope. The arrangement of pores on metal/oxide interface was well ordered with smaller diameters than that of the oxide/electrolyte interface. The inter-pore distance was larger in metal/oxide interface as compared to the oxide/electrolyte interface. The size of the ordered domain was found to depend strongly upon anodizing voltage and time.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

One of the biggest challenges in the field of nanoscience and nanotechnology is the synthesis of ordered and regular nanostructures (Almawlawi et al., 2000). Self-organized porous anodic alumina (PAA) has been the main focus of research for the last few decades due to its regularity and periodic ordered arrangements. The most commonly used procedure for the fabrication of PAA film is electrochemical anodization of pure aluminum foil in appropriate acids. Magnetic, electronic, electrical and optical properties depend mainly upon the size, shape, uniformity, regularity and ordering of nanostructures (Schmidt and Chi, 1998; Alivisatos, 1996; Brus, 1998; Lieber, 1998; Bockrath et al., 1997; Whitney et al., 1993). PAA is widely used as a nano-template for the fabrication of nanotubes, nanowires, nanorods, nanorings, nanocones and nanoparticles (Masuda et al., 1997a; Zhao et al., 2007b; Lahav et al., 2006; Masuda et al., 2000). PAA has potential applications in optoelectronics (Huang et al., 2002), magnetic recording (Nielsch et al., 2002), energy storage (Che et al., 1998), photocatalysis (Chu et al., 2003) and biosensors (Matsumoto et al., 2004). Fabrication of highly ordered and free-standing PAA films with through hole morphology are necessary and essential for nano-materials synthesis and nano-scale separation. PAA films have many advantages over

the other porous materials like, polycarbonate membranes. These include high pore density, thermal stability, and cost effectiveness (Li et al., 2005). Pore diameter, inter-pore spacing, and pore ordering are easily controlled by changing anodizing parameters, such as electrolytes and pH value, anodizing voltage, anodizing time, temperature and etching methods (Keller et al., 1953; Crouse et al., 2000; Masuda and Fukuda, 1995; Galca et al., 2003; Chu et al., 2005; Xu et al., 2002).

Pre-treatment and pre-texturing methods have been used to obtain highly ordered arrangements of pores on a large scale. A two step anodizing method was used to obtain highly ordered and perfect hexagonal alumina nanostructure over a wide range of area under proper anodizing conditions in oxalic and sulfuric acids (Masuda and Fukuda, 1995; Masuda and Satoh, 1996). Three and four step anodizing methods have also been applied for the fabrication of highly ordered nanostructure templates over a large area (Feiyue et al., 1998). Pre-texturing techniques have been applied, prior to anodizing, for obtaining a highly ordered PAA films over a wide range of area by many researchers (Masuda et al., 1997b; Sun and Kim, 2002; Krishnan et al., 2003). Pre-texturing techniques were modified, using optical diffraction grating (Mikulskas et al., 2001), scanning probe microscope (Masuda et al., 2002) and focused ion beam (Liu et al., 2003), for pre-patterning on aluminum surface. These pre-texturing techniques, used for ideal highly ordered PAA films over large area, are all external. The anodizing condition is the major internal parameter for the growth of highly ordered PAA film over a large area.

\* Corresponding author. Tel.: +82 42 350 3823; fax: +82 42 350 3810.  
E-mail address: [socho@kaist.ac.kr](mailto:socho@kaist.ac.kr) (S.O. Cho).

A simple approach is adopted in this paper for the growth of highly ordered PAA films over a large area in  $\text{H}_2\text{SO}_4$  solution through single step anodization, without the use of additional pre-patterning procedures. Thick and free-standing PAA films with through holes are obtained by chemical detachment of the remaining aluminum substrate from the back side without pore widening and heavy metal detections, using a single step method. Pores are found for the first time to be highly ordered with a perfect hexagonal pattern with smaller diameters on the back side (metal/oxide interface) of PAA films. The effects of anodizing voltage on the pore diameter, pore arrangement and thickness of PAA films are investigated.

## 2. Experimental procedure

Highly pure (99.999%) aluminum foils of 0.1 mm thickness were used as a starting material. The foils were annealed at  $500^\circ\text{C}$  for 5 h before anodization, to remove mechanical stresses, increase grain size, and re-crystallize texture along (1 0 0) direction. This procedure provided good quality PAA films from aluminum foils (Ali et al., 2010). The foils were etched in 1.0M NaOH at room temperature until bubbles were observed over the surface and then washed several times with distilled water. Anodization was carried out in a specially designed two electrodes cell in 0.4M sulfuric acid under a constant DC voltage of 10V, 15V and 26V for 24 h using aluminum foil as a counter electrode. The temperature was kept at  $-3 \pm 1^\circ\text{C}$  with a refrigerator during the anodization process. Very thick (180  $\mu\text{m}$ ) and stable PAA films were obtained. The remaining aluminum substrates along with barrier layers were chemically etched out in a saturated  $\text{CuCl}_2$  solution in a single step. The free-standing PAA films were sonicated in distilled water to remove debris. The morphology of the PAA films was examined by high resolution scanning transmission electron microscope (HRSTEM) and the chemical composition of these films was determined using an energy dispersive X-ray (EDX) analyzer.

## 3. Results and discussion

Fig. 1 shows HRSTEM images of the sample anodized in  $\text{H}_2\text{SO}_4$  at 26V for 24 h at  $-3 \pm 1^\circ\text{C}$ . Fig. 1(a) shows a low magnification cross-sectional image of mechanically broken PAA film with an average thickness of about 180  $\mu\text{m}$ , detached chemically from aluminum substrate. This shows that the growth rate of PAA film corresponds to about 125 nm/min. Similarly free-standing PAA films with an average thickness of 85  $\mu\text{m}$  and 115  $\mu\text{m}$  (results not shown) were obtained for samples anodized at 10V and 15V, respectively. The growth of these PAA films versus anodizing voltage plot is shown in Fig. 1(b), which indicates that the growth rate increased with the increase in anodizing voltage. Thus, the growth rate of PAA films depends upon the anodizing voltage. This result is consistent with the literature (Chu et al., 2005; Zhao et al., 2007a). The HRSTEM image (top view) at a low magnification of PAA film is shown in Fig. 1(c). The resulting pores are uniform in shape and diameter, and are arranged in perfect hexagonal order in a very small domain; that is short range order is present but long-range order is missing. Surface debris at some regions were clearly seen.

The HRSTEM images (top view) of as-anodized PAA films at different voltages are shown in Fig. 2. The pores tend to arrange in hexagonal pattern with increase in anodizing voltage. The pores appeared at random locations with non-uniform diameter and ordered hexagonal domains no longer exist, in case of sample anodized at 10V as shown in Fig. 2(a). However the sample prepared at 15V shows a hexagonal ordered pattern with smaller domain size as shown in Fig. 2(b). Pore ordering is better in the sample anodized at 26V, as indicated by the parallel arrange-

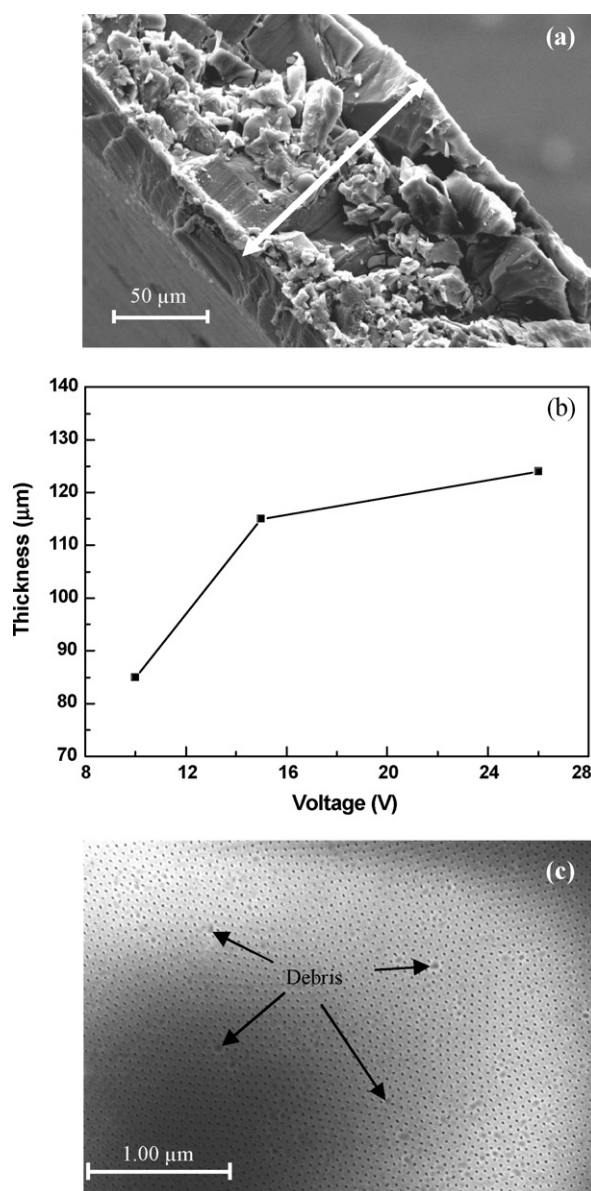


Fig. 1. HRSTEM images of PAA fabricated in 0.4M  $\text{H}_2\text{SO}_4$  at 26V and  $-3 \pm 1^\circ\text{C}$ . (a) Cross-sectional view of mechanically broken PAA film, (b) graph between film thickness and anodizing voltage and (c) top view of PAA film at low magnification.

ment of hexagonal cells with larger domain size (Fig. 2(c)). The ordered domain covers approximately 85% area of the surface of aluminum substrate exposed to electrolyte. These results show that a linear relationship exists between pore diameter and the anodizing voltage in a given electrolyte. The average pore diameter was about 22 nm, 30 nm and 44 nm for the samples anodized at 10V, 15V and 26V, respectively. Smaller pores have smaller inter-pore spacing (center-to-center distance between neighboring pores) in case of 10V and 15V as compared to the larger pores in the 26V anodized sample. Pore diameter and the inter-pore spacing depend linearly on anodizing voltage of electrolyte without altering the thickness of barrier layer (Zhao et al., 2007a). In order to investigate the back side (metal/oxide interface) morphology of PAA films, the remaining aluminum substrate and the barrier layer was chemically etched out from back side in a saturated  $\text{CuCl}_2$ . The subsequent morphology of the bottom surface was examined using HRSTEM and compared with the top surface. No additional electrolyte was used for the removal of barrier layer

Download English Version:

<https://daneshyari.com/en/article/1589239>

Download Persian Version:

<https://daneshyari.com/article/1589239>

[Daneshyari.com](https://daneshyari.com)