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Controlled Pore Diameter in Porous Anodic Aluminium Oxide Templates for Nanotube/Nanowire Fabrication

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ABSTRACT

A porous anodic aluminium oxide (AAO) templates were fabricated on aluminium by electrodeposition method using a two-step anodization process. The AAO templates were anodized in 0.3 M oxalic acid solution by applying a constant voltage of 40V, which was afterward treated with chemical etching process in a mixed solution of 6% phosphoric acid and 1.8% chromic acid, respectively. The temperature was kept constant in 15°C during the anodization process and the anodization time were done between 20 to 60 min. All the samples were characterized using by scanning electron microscopy (SEM) to study the surface morphology of AAO templates. It was found that the pore diameters of AAO templates can be controlled by changing the anodizing time. The influence of the electropolishing were also discussed. Highly uniform self-ordered AAO template were effectively formed from these polished foils via an anodizing process.

| AAO template | electrodeposition | chemical etching | two-step anodizing | pore diameter |

1. INTRODUCTION

One-dimensional nanostructures have been recently attracted due to their potential applications, unique properties and symmetric structure in nanodevices include field emitters, hydrogen storage and molecular sieves [1-7]. Among the developed nanofabrication technique, much interests have been given to template synthesis of functional nanomaterials by chemical assembly method. The templating concept promising control on pore size and shape. In addition, the template method are simplest technique to get uniform and ordered pore structure.

Anodic aluminium oxide (AAO) templates have been extensively used as a template for the fabrication of various nanomaterials especially nanotubes and nanowires due to their thermal stability, good mechanical strength and tuneable pore dimensions [8]. The first research of AAO templates conducted by Masuda *et al*. and Fukuda *et al*. [9] in 1995 were synthesized perfect hexagonal pore structure porous alumina using the two-step anodization procedure. Moreover, many researcher were successfully developed fabrication of AAO templates on different substrates such as silicon wafers and glass [10] and using acid [11-13] and alkaline [14] electrolytes for anodizing process. Besides that, the pore dimensions of AAO templates included pore sizes, pore intervals and pore depth can be controlled easily based on anodizing condition [15-16]. AAO layers grown in acid electrolytes possess hexagonally ordered porous structures with pore diameters ranging from a few nanometers to 200 nm, pore lengths from 1μm to over 100 μm, and pores density in the range of 10^9 to 10^{12} cm^{-2}. As the original size and shape of the AAO template determine the uniformity, density and size of the sensing nanostructures, it is essential to have an accurate control over the fabrication process [17].

In this paper, we report a simple method to fabricate AAO templates by electrodeposition using oxalic acid and chemical etching with mixed solution of 6% phosphoric acid and 1.8% chromic acid, respectively. Thus, AAO templates of different pore diameters via two-step anodizations as a function of anodization time has been investigated. Moreover, we study the influence of electropolishing on the surface morphology of Al foils.

2. EXPERIMENTAL

An electrochemical cell consisted of two electrode system were employed consisted of a aluminium foil with about 0.25mm thickness as a working electrode and a graphite electrode each having dimensions 7.0 cm x 3.5 cm and spaced 4.0 cm apart. A schematic representation of the experimental setup was shown in Figure 1 described a high DC power voltage was supplied to the cell and the voltage across the electrodes was kept constant for each run at varying anodization time. Before anodization, the sample was ultrasonic in acetone, rinsed with deionized water and

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annealed at 400^0C for 3 hours in furnace to reduce mechanical stress in the aluminium substrates. . Then it was degreased in 1.5 M sodium hydroxide and put into 2.0 M nitric acid. This was followed by electropolishing in a mixtures of perchloric acid and ethanol at constant voltage of 15V for approximately 3 minutes at room temperature. The anodization process was performed in 0.3M oxalic acid as electrolyte with constant temperature of 15^0C. This anodizing process was done at 40V at temperature 15^0C for 20-60 minutes. After the complete anodization process, the AAO templates was immersed in mixture solution of 6% phosphoric acid and 1.8% chromic acid at 60^0C to chemically etching. A second anodization was performed under the same condition as the first one.

The samples characterization of alumina nanopores were performed by scanning electron microscope (Model JEOL JSM-6390 LV).

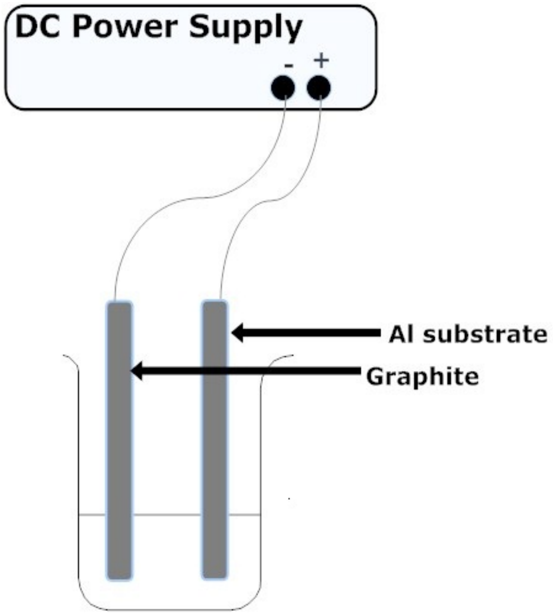

Fig. 1 Schematic diagram of experimental setup for aluminium electropolishing and anodization.

3. RESULTS & DISCUSSION

3.1 Morphology of porous film

The procedure to prepare the AAO membrane is well known and does not require sophisticated instrumentation. The AAO membrane consists of three distinct layers: aluminum metal, a thin barrier oxide layer, and a relatively thick porous oxide layer. The thickness of this layer depends upon the anodization voltage. Since it is well know that among sulphuric, phosphoric and oxalic acid, the last one is the best for the growth of aluminum oxide in terms of size and regularity of the pores, the oxalic acid has been chosen as a fixed parameter during the oxidation process.

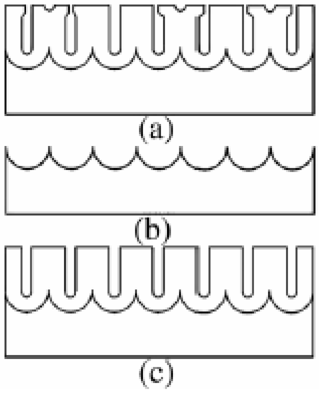

Fig. 2 Schematic view of the process flow used for the AAO templates formation: a) first anodization step b) chemical etching c) second anodization step [18].

In aluminium anodization, two main reactions at cell electrodes are:

At the anode:

$2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e^-$
(Dissolution of aluminium)

$Al_2O_3 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O$

At the cathode:

$6H^+ + 6e \longrightarrow 3H_2$

Figure 3 shows the morphology of electropolished aluminium surface in mixture ratio of perchloric acid and ethanol solution was detected by SEM in order to investigate the effects of electropolishing of aluminium on morphology of AAO templates. After electropolishing in 15V Al foil are observed an almost flat surface as smooth roughness, shinny and mirror-like [18]. According to the result, electropolishing of aluminium foils before electrochemical anodization is of paramount importance to the self-organization of AAO pores which influence the regularity, pore diameter and pore density of AAO templates. On the other hand, the low voltage using for the polishing, the longer the processing needed to obtain relatively bright surface. To improve the polishing technique, other factors like the type of electrolyte, its ratio, and the cell temperature should be considered.

The first anodization of the aluminium was performed using the electropolished aluminium foils at a constant potential of 40V in different time interval. The processing times of anodization of these samples are selected as 20, 30, 45 and 60minutes. The solution of electrolyte was stirred vigorously in order to accelerate the dispersion of the heat that evolved from the samples. Figure 4 shows the typical of SEM images of templates after initial anodization. It is known that initial anodization of nanoporous mainly act as a self-assembled mask for the following anodization process. The first 20 minutes anodization as can be seen from Figure 4(a) produces low quality and random pores. For 30 minutes anodization shown in Figure 4(b), it provides a better random pore arrangement. The average pore diameter are 23-28nm, respectively.

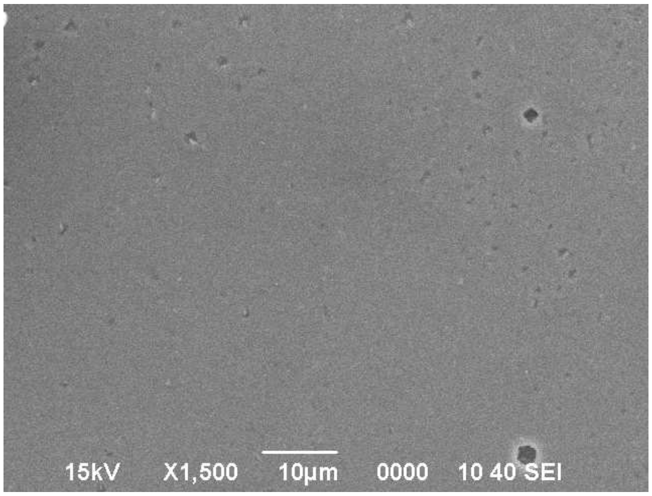

Fig. 3 Effect of electropolishing on the surface roughness of Al foil.

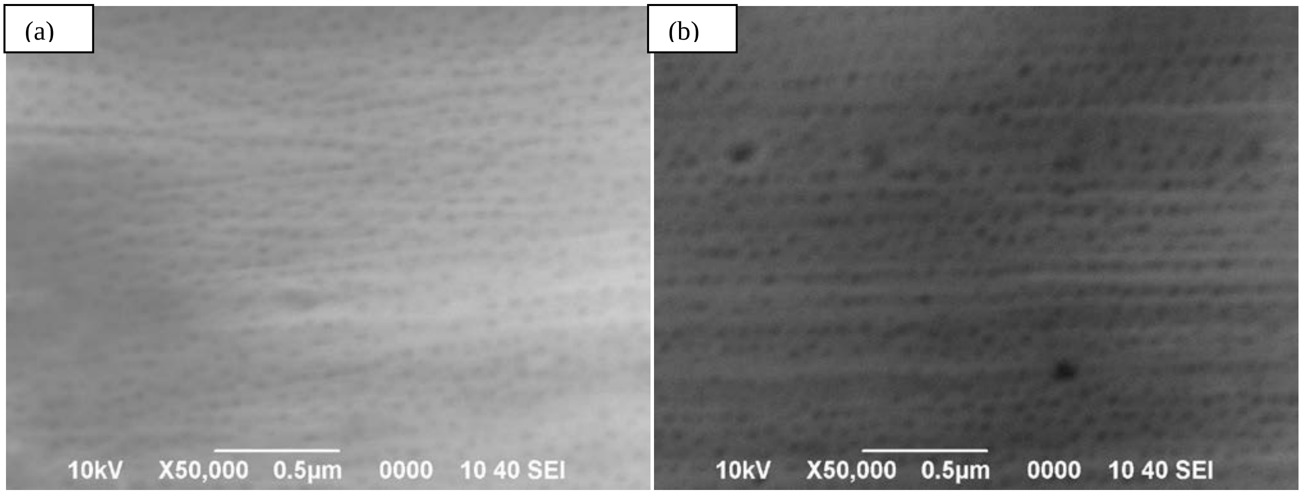

Fig. 4 SEM images of AAO templates after first anodization for (a) 20 mins, (b) 30 mins

Samples are chemically etching for 30 minutes to remove oxide layer in mixture solution of H_3PO_4 (6wt%) and H_2CrO_4 (1.8%), respectively. That was followed by second anodization in the same condition as mentioned above. Figures 5(a), (b), (c) and (d) give the SEM images with high magnification resolution of the templates after the second anodization, respectively. The processing times of two-step anodization of these samples are selected as 20, 30, 45 and 60 minutes Samples are chemically etching for 30 minutes to remove ozide layer in mixture solution of H_3PO_4 (6wt%) and H_2CrO_4 (1.8%), respectively. The first and second anodization steps were conducted in the same condition as mentioned above.

The observation through SEM micrographs shows that the AAO templates with uniformly pores but irregular shape for all different anodization time, which can be easily used as templates in fabrication of nanotube/nanowire arrays due to their small pore dimensions. The average pore diameter is in the range of 40-55 nm. However, the pore diameter of AAO templates is is not clear in SEM measurement images. This problem can be solved before characterization. The samples were coated with a thin gold film by sputtering using low deposition rate. A well organized pore hexagonal AAO pores array could be achieved if the samples were deposited with gold particle.

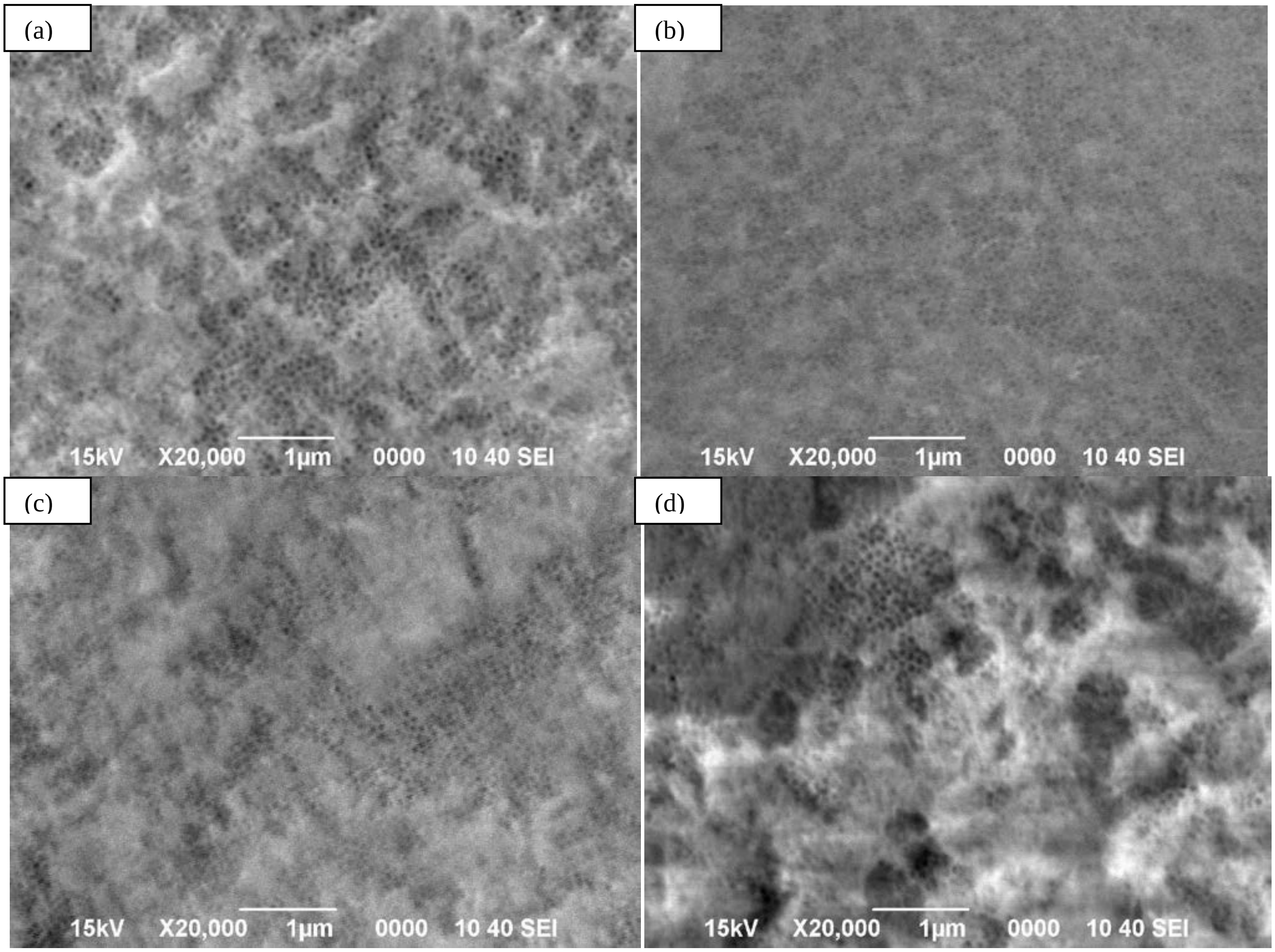

Fig. 5 SEM images of AAO templates after two-stepanodization for (a) 20 mins, (b) 30 mins, (c) 45mins and (d) 60mins

3.2 AAO pore diameter

In this study, the aluminium foils were anodized in different anodizing time from 20 to 60 minutes. The result shows that the average pore diameter was gradually increased by increasing the anodizing time as shown in Figure 5. At 20 minutes, the average pore diameter of AAO template was about 40 nm. The pores were irregular and smaller. The pore diameter was increased to 41 nm when anodizing time was increased to 30 minutes. The pore diameter was continually increased to 43 nm as the anodizing time was set to 45 minutes. The largest pore diameter was shown in the longest anodization time which at 60 minutes. The formation of AAO porous structure on the surface of AAO templates is due to the dissolution of oxide layer. Reference [19] have reported that the rate of dissolution of oxide layer increases with anodizing time.

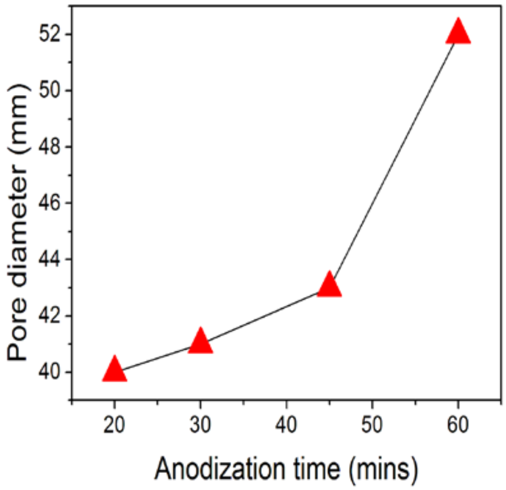

Figure 4 : The average pore diameters of the AAO emplates as a function of anodization time.

4. CONCLUSION

In summary, a porous AAO templates with high aspect ratio were fabricated by two-step anodization and etching process. From the results, the pore sizes were affected by anodization times. Accordingly, the average pore diameter increased with increasing anodization time. The electropolishing effect of Al films will also produce uniform and high order of nanopores. It was noticed that these results could be used for making AAO templates with various pore dimensions. These alumina nanostructures may be expected to have potential applications in the fabrication nanotubes and nanowires.

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