

Synthesis and optimization of porous anodic aluminum oxide nano-template for large area device applications

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Abstract—A simplified anodized aluminum oxide (AAO) nano-template fabrication process was developed in this study, which can be suited for the large area device applications. The pores of various sizes and depths were realized from the thin (less than 1 μm) aluminum film deposited on the sapphire substrate. The optimum morphological structure was obtained by adjusting the applied voltage, types of acid solution, its concentration and temperature which has evolved after two phases of anodization followed by chemical etching. The Ar plasma pre-treatment method was developed and applied to improve the surface roughness of thin aluminum film without severely sacrificing the deposited layer thickness.

Key words: Anodized Aluminum Oxide, Nano-Template, Plasma Treatment

INTRODUCTION

The anodic aluminum oxide (AAO) nano-template is a promising alternative for the fabrication of one-dimensional nano-structured materials because of its structural regularity and high pore density [1-4]. Nano-scale structures have attracted much attention in the field of fabrication of display and semiconductor devices due to their superior optical properties and unique electronic, magnetic properties suited for such novel devices [5-7].

The AAO nano-templating technology is regarded as one of the important tools in nano-technology to fabricate nano-structured templates owing to its relatively easy synthetic method and productivity, thus it can be successfully applied in many industrial fields. For example, it can be used as a template for nano-wire structure growth to realize large area LED modules and can also be used as an anode for large area thin film ordered organic bulk hetero-junction solar cells. Additionally, the AAO nano-template can be used as a nano-mask after removing resistance layer [8-11]. It is prospected that the AAO nano-templating technology will take an absolutely important role in various fields where nano-patterning is required.

The AAO nano-templating technology developed in this study has some key advantages in both process adaptability and cost effectiveness, and it is used to form bulk orderly arranged nanometer-sized pores on large area substrates. The developed technique eliminates the electro-polishing steps frequently involved in the conventional AAO process where thick (greater than 10 μm) aluminum film or foil is typically employed. Thick film or foil of aluminum makes the applicability of AAO process to large area, economic applications difficult, and process optimization and scale-up to mass production difficult.

In this study, these disadvantages were overcome by incorporat-

ing thin (less than 1 μm) aluminum film deposited uniformly on large area substrates such as sapphire or ITO-coated glass. The Ar plasma pre-treatment was used to improve the surface roughness of the thin aluminum film instead of electro-polishing prior to the AAO fabrication process.

EXPERIMENTAL

In this work, aluminum films with 600-700 nm thickness was deposited on cleaned sapphire substrate by the RF sputtering in a vacuum chamber as shown in Fig. 1. The surface roughness of sputtered aluminum was slightly higher than 20 nm, thus smoothing the surface is required to fabricate AAO nano-templates having uniform and ordered structures. The electro-polishing process utilizing perchloric acid and ethanol mixture ($\text{HClO}_4 : \text{C}_2\text{H}_5\text{OH} = 1 : 4$ in volumetric ratio) at 20 $^\circ\text{C}$ and 20 V was first attempted to reduce the surface irregularities of the aluminum film by varying polishing times and conditions, but it failed to smooth the surface morphol-

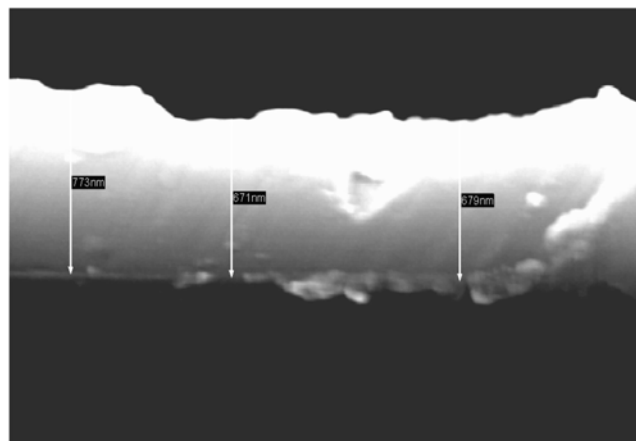


Fig. 1. SEM image of 600-700 nm thick Al film on sapphire substrate.

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Table 1. The optimized AAO fabrication steps and conditions

First anodization	Etching process	Second anodization	Hole-widening
0.2 M phosphoric acid (99%) - Sample is anode and curved aluminum plate is cathode	1.8 wt% chromic acid and 6 wt% phosphoric acid (85%) mixture - No voltage is applied during the etching process	0.2 M oxalic acid dehydrate (99%) - Sample is anode and curved alu- minum plate is cathode	0.2 M phosphoric acid (99%) - No voltage is applied during the hole-widening process

ogy due to the severe etching of aluminum during polishing. It was found that the aluminum film peeled off from the substrate for the entire range of process conditions investigated in this study, leading to the conclusion that the conventional electro-polishing process can only be successfully applied to smooth the aluminum surface when the film thickness is larger than 3 μm . Thus the sputter etching technique utilizing Ar plasma was developed in this study and applied to smooth the thin aluminum surface before going into the AAO fabrication process.

The two-step anodization process was used to prepare an ordered porous alumina nano-template using a typical anodization method, of which the details could be found elsewhere [10,11]. The thin aluminum film on the sapphire substrate was first anodized in a 0.2 M oxalic acid solution at 15 °C and 40 V, forming irregular pores. After the first anodization, the formed AAO layer was etched by immersing the specimen in a mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid at 50 °C. The second anodization was then performed under the same process conditions as used in the first anodization. Finally the pore-widening process with phosphoric acid (85%) at 30 °C was applied to enlarge the diameter and depth of the AAO nano-template structure.

The optimized process steps and conditions developed in this study are listed in Table 1. At all steps, the solution was constantly stirred at a settled speed by a magnetic bar. Anodization was carried out in a 1,000 mL jacketed-beaker designed to keep the temperature of the contained solution constant by using a thermostat.

The formed AAO structure was observed with Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4100), and the surface roughness and morphology were investigated by Atomic Force Microscopy (AFM) and FE-SEM.

RESULTS AND DISCUSSION

The surface roughness of aluminum after the Ar plasma treatment with varying plasma chamber pressures was shown in Fig. 2, which

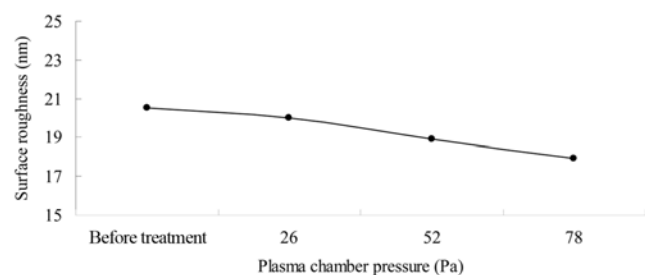


Fig. 2. Effect of Ar plasma chamber pressure on the Al surface roughness at the plasma power of 50 W for 10 min treatment time.

was measured by AFM in root mean square (RMS) average. The reduction in the surface roughness of aluminum with the increase of plasma chamber pressure was clearly observed. It is speculated that with the increase of plasma chamber pressure, the ion bombardment to the sample becomes more random thus diminishing the ion shadowing effect. The decrease in the Al thickness by the Ar plasma treatment was minimal and stayed within the measurement error boundary (less than 1 nm). Increase of plasma power and treatment time, however, was found to be ineffective in improving the surface roughness, since the roughness got worse after the treatment. The controlled use of Ar plasma pre-treatment was found to be an alternative method to replace the typical surface smoothing technique (e.g., electro-polishing). It is believed that the Ar ions in the plasma sputter off the extruded features on uneven Al surfaces and make them flatter. Increased plasma power, however, degraded the surface roughness due to the masking effect of extruded structures at the increased DC bias. The Ar plasma pre-treatment is a promising technique to remove the surface irregularities without sacrificing the deposited Al thickness.

The base AAO process conditions were developed from preliminary experiments with the oxalic acid anodizing solution: The acid concentration of 0.2 M, anodization temperature and voltage of 15 °C and 40 V were found to be optimum conditions. After the first anodization, the template was etched with the mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid under 50 °C and 0 V. The second anodization was performed under the same operating conditions as in the first (15 °C and 40 V). The pores with a diameter of approximately 40 nm were typically obtained after the second anodization. Depending on the conditions of synthetic process, pores of various sizes and depths could be reproducibly formed.

Systematic variation of process parameters (chemical concentration, voltage, temperature, time, etc.) and characterization of the results were implemented at each step to realize regular pores with as high aspect ratio as possible. Determination of the process conditions for optimum morphological structure was made based on the criteria of 1) smoothness of the Al surface prior to the anodization and etching process and 2) maximum possible aspect ratio of the holes developing from the AAO process. Reaching to the bottom of the Al layer was accomplished by the pore-widening process. Careful control of pore-widening process parameters was necessary to keep the pore structures from collapsing.

Fig. 3 and 4 show the morphological evolutions and pore-size variations of AAO nano-template structures with varying process conditions. As the anodization voltage increases from 40 V to 60 V, the size of the pores was increased from 30 nm to 130 nm, and with the temperature increase from 0 °C to 15 °C, the size of the pores was also increased from 20 nm to 50 nm. The voltage is another factor in determining the regularity and size of the nanopore arrays. Virk [12] studied the effect of voltage by using three different anod-

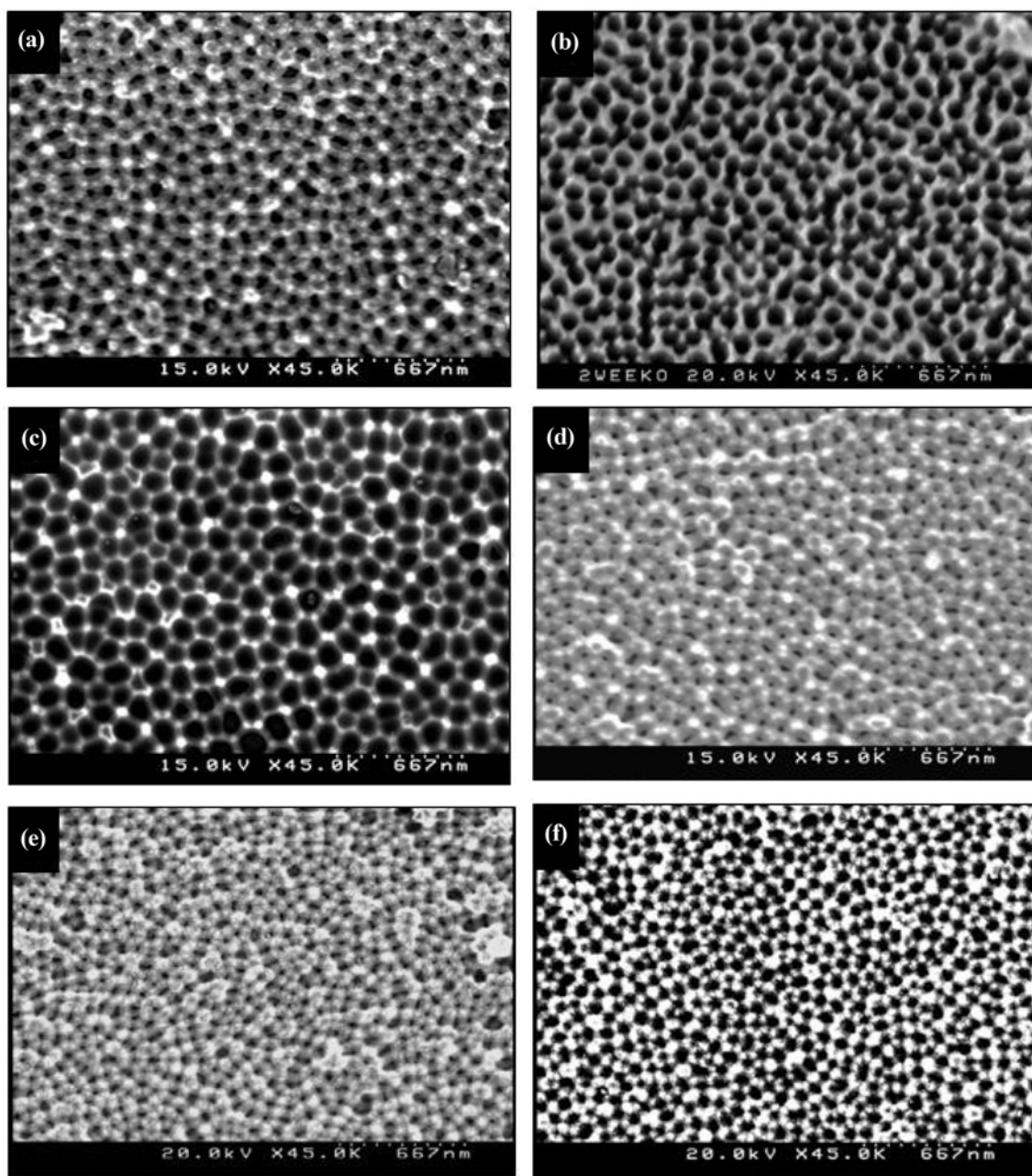


Fig. 3. AAO nano-template formed with different anodization voltages on an Al/sapphire: (a) 40 V, (b) 50 V, (c) 60 V; and AAO nano-template formed with different anodization temperature on an Al/sapphire: (d) 0 °C, (e) 10 °C, (f) 15 °C.

ization voltage values at 30, 40 and 50 V and observed the increase of pore diameter as voltage increases. Since, the anodization is performed under an applied electric field; pores grow in the direction perpendicular to the aluminium surface, while equilibrium is established between the field-enhanced dissolution of oxide layer at oxide/electrolyte interface and the growth of oxide layer at the metal/oxide interface [13]. The porous alumina layer was formed by the electrochemical oxidation of aluminium, which is dependent on the diffusion of both O^{2-} ions and the Al ions. The volume expansion at the metal/oxide interface generates a mechanical compressive stress, which leads to the repulsive forces among the growing pores and pushes the pore walls upwards. Therefore, it can be hypothesized that reorientation of the O^{2-} and Al^{3+} ions at the interface coupled

with compressive stresses favors the formation of ordered pores on the surface of anodic alumina. During oxidation of Al, huge amount of heat is liberated and this heat generated during anodization may cause thermal stress in and formation of bigger holes. But the method of varying voltage and temperature required extremely accurate and stable control in handling the experiments, because the results could vary with even a small change in the voltage or temperature due to the remarkably thin aluminum film. The sensitivity of the results on the change in the process conditions was too high. Thus a better way to increase the pore-size with controllable sensitivity is to use the phosphoric acid pore-widening step under 30 °C temperature and 0 V, and the results are shown in Fig. 5. This method could provide better AAO morphology by preserving the walls be-

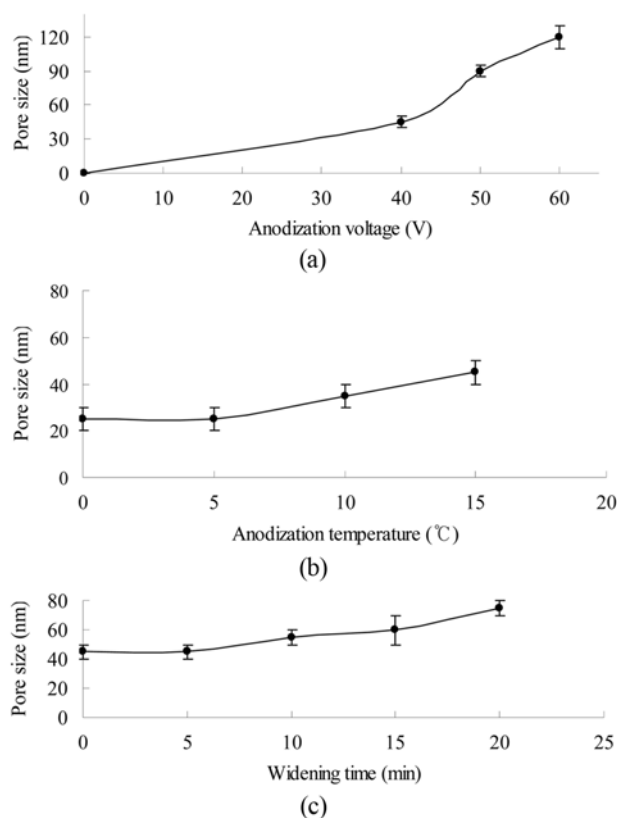


Fig. 4. Variation of AAO nano-template pore size on the conditions of synthetic process: (a) anodization voltage; (b) anodization temperature; (c) pore-widening time.

tween pores relatively intact compared to the morphology obtained with changing the anodization temperature and voltage.

The increase of anodization time did not affect the size of pores significantly but caused the increase of pore depth. However since the starting aluminum thickness was very thin, over-time anodization resulted in the decrease of aluminum thickness drastically, resulting in the collapse of the pores.

The electro-polishing steps frequently involved in the conventional AAO technique was eliminated due to its severe etching characteristics of aluminum, and the Ar plasma pre-treatment was involved instead to prepare smoothed surface for the subsequent anodization and etching processes. The diameter, length and density of the nano-template pores could be reproducibly controlled simply by changing the conditions of AAO process (anodization voltage, types of acid solution and its concentration).

The technique developed in this study is applicable to other large area substrates such as ITO-coated glass or Si wafer, opening its usefulness to basically any large area substrates for nano-structure formation and device applications.

CONCLUSIONS

A two-step anodization process has been developed in this study to realize highly regular AAO nano-template. The anodization voltages and temperatures affect the pore size, pore depth, which further increases by the second anodization time. In addition, reduced surface roughness of aluminum was observed by Ar plasma treatment. To obtain hexagonally ordered pore arrays in anodic oxide film, Ar plasma is used to remove the surface irregularities for the

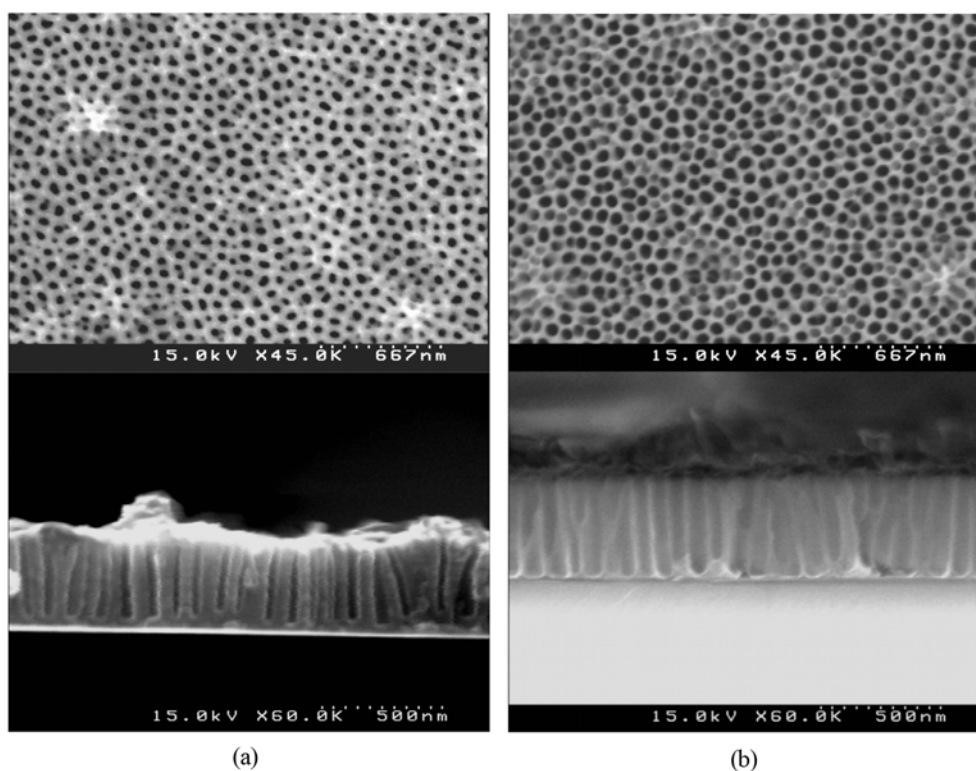


Fig. 5. (a) AAO nano-template formed with an optimum process conditions developed in this study with anodization voltage of 40 V; (b) AAO nano-template after the pore-widening process by phosphoric acid at 30 °C.

remarkably thin aluminum film. The synthesized AAO template could be successfully used to obtain orderly arranged nanometer-sized wires for large area device applications.

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