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Various Modifications of Electrochemical Barrier Layer Thinning of Anodic Aluminum Oxide

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***Abstract*—**In this paper, two options of anodic alumina barrier layer thinning have been demonstrated. The approaches varied with the duration of the voltage step. It was found that too long step of the barrier layer thinning process leads to chemical etching of the nanopores on their top. At the bottoms pores are not fully opened what is disadvantageous for further applications in nanofabrication. On the other hand, while the duration of the voltage step is controlled by the current density (value of the current density cannot exceed 75% of the value recorded during previous voltage step) the pores are fully opened. However, pores at the bottom obtained with this procedure have smaller diameter, nevertheless this procedure provides electric contact between the bare aluminum (substrate) and electrolyte, what is suitable for template assisted electrodeposition, one of the most cost-efficient synthesis method in nanotechnology.

***Keywords*—**Anodic aluminum oxide, anodization, barrier layer thinning, nanopores.

I. Introduction

ANODIC aluminum oxide (AAO) is commonly known as a template for nanofabrication. With the use of AAO template, variety of nanowires, nanotubes and nanodots are being formed by the researchers to enhance or change materials properties accordingly to the size. Popularity of the AAO templates in nanofabrication is acknowledged to the ease of pore diameter, interpore distance and oxide layer thickness precise control by operating conditions, including type of electrolyte, its temperature, applied voltage and duration of the anodizing process [1]-[4]. Pore diameter and interpore distance increase linearly with applied voltage. The anodizing voltage range is determined by type of applied electrolyte. For example at voltage range 15-25 V sulfuric acid is used and for wider voltage range 5-100 V oxalic acid is used. Pore diameter increases also with electrolyte's temperatures. Moreover, voltage increase causes exponential current density increase what increases in the same manner oxide layer thickness (anodizing is a typical faradic process). Moreover, electrolyte's temperature increases results also in current density increase, due to the enhanced ionic mobility, what also causes oxide layer thickening [1]-[4]. All these facts are significant stimulus for further research on new experimental conditions, routes of anodic alumina formation and new applications of this material.

Recently, new anodizing procedures including anodization in new electrolytes [5], [6], mixtures of electrolytes, anodization in non-aqueous solutions [7], or in water solutions with various additives are being researched. All these procedures allow forming AAO with wider range of geometrical features. However, to make an AAO template, suitable for nanofabrication i.e. electrodeposition, from AAO sample formed after second step of the anodization, various post treatment methods have to be applied. To make AAO template suitable for nanofabrication, various methods have been applied. For example, remaining, unoxidized aluminum can be selectively, chemically removed by $HgCl_2$ [8], or $CuCl_2$ dissolved in HCl [9] due to the simple redox reaction. Next, closed pores at the bottoms are opened by immersing the alumina from bottom side in diluted ortophosphoric acid. Here much optimization experiments have been performed by researchers, because too short immersing does not open the pores and too long causes significant porosity increase or even destruction of the hexagonally arranged nanoporous array. Further, to make AAO template suitable for electrodeposition of metals, gold layer has to be sputtered on the back side and short Au electrodeposition has to be performed. As it is seen, many steps are involved in whole process of AAO template fabrication from AAO sample after anodization. Electrochemical barrier layer thinning (BLT) is a suitable alternative for methodology described above. During BLT process, right after the second step of anodization, exponential decrease of voltage is applied and then the barrier layer is being thinned [10]-[12]. After the last step of the BLT process, the pores are opened at their bottoms, thus bare aluminum, is exposed to the electrolyte what makes AAO suitable for further electrodeposition. With the use of BLT method, hexagonally arranged arrays of nanowires made of Ag [12], Au [13], Bi [14], Co [15], Cu [16], Fe [15], Ni [14], [15], [17]-[21], were formed. Moreover, BLT AAO post-treatment method allows also forming efficiently nanowires made of semiconductors like CdS [22]. Furthermore, with the use of BLT approach metallic nanotubes made of Au [23] and Au-Ni segments [24] were formed. Therefore, AAO post-treated with BLT method opens unlimited opportunities in nanofabrication of hexagonally arranged nanowires and nanotubes formed via electrodeposition.

In recent paper various barrier layer thinning processes have been applied and compared to make AAO suitable for further nanofabrication.

II. Experimental Section

AA1050 0.5 mm thick foil was cut into size 4 cm x 2 cm coupons and degreased in C_2H_5OH and H_3CCOCH_3. Next,

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samples were electropolished ($HClO_4$: C_2H_5OH 1:4 vol., at 0.5 A/cm^2, 10°C, 60 s). Then the samples were rinsed twice with C_2H_5OH and twice with DI water. To provide constant surface area of the working electrode (4 cm^2) back and edges of the samples were painted with acid resistant paint.

Self-organized, two step anodization was carried out in 0.3 M oxalic acid at the temperature of 30°C and at the voltage of 50.0 V. Platinum grid (6 cm^2) served as the cathode. After the first, one hour long step of anodization, poorly organized oxide was chemically removed (6 wt.% H_3PO_4 and 1.8 wt.% H_2CrO_4 at 60°C for 90 min) and the second step of anodization was conducted at the same set of operating conditions like the first step, but was lengthened up to 2 hours and 40 minutes to obtain thicker oxide layer (ca. 50 µm).

Anodization current density curves were recorded with APPA 207 multimeter (Technology Corporation, Taiwan).

Characterization of the morphology of the obtained nanoporous alumina was done using Quanta 3D FEG (FEI, USA) field emission scanning electron microscope (FE-SEM).

To investigate whether electrochemical barrier layer thinning process was successful, the cross section images were taken. To check whether pore bottoms are opened, anodic alumina with remaining aluminum was immersed in 0.1 M $CuCl_2$ in HCl to remove selectively aluminum.

III. Results and Discussion

Fig. 1 shows two applied strategies of electrochemical barrier layer thinning (BLT) in 0.3 M oxalic acid. The BLT was performed subsequently after the second step of anodization at 50.0 V. For both strategies, the process is controlled by the applied voltage and its increment (ΔU) depends on the value of the voltage, namely while for given step the voltage is U, for the next one is it 95% of the previous value. Another important value in BLT process is the period for which the voltage is applied (Δt). For the first approach (Fig. 1 (A)) Δt is fixed and equals 30 s, what provided quasi exponential decrease of the voltage, similar to one recommended by [10]. The second approach is more complex – in this case, the voltage is changed while current density reaches 75% of the value of the current density recorded for previous voltage. Thus, in this case Δt is varied and depends strictly on the recorded current density.

Of course, applied BLT strategy has significant influence on the morphology of AAO. While strategy with fixed Δt is applied (Fig. 1 (A)), values of diameter of the pores on the top and bottom are similar (Fig. 2). However, on the AAO top the pores, due to the relatively long immersion in the acidic solution, are strongly widened, or individual even connects with neighboring ones. Moreover, after detachment of AAO from aluminum substrate, it was found that not all the pores are opened (Fig. 2 (B)). Therefore, too long exposure to the acidic electrolyte and not enough efficient BLT are major disadvantages of the applied approach. While different approach is applied, where duration of the voltage step is determined by the current density (Fig. 1 (B)), the whole BLT procedure is shorter and the formed nanoporous oxide is not exposed for such a long time to the electrolyte (this procedure is over 4 times shorter than the first one). It is easily seen that the pores on the top are well ordered and not damaged by the secondary reaction with the electrolyte. On the other hand, all the pores at the bottom are opened; nevertheless, these are much smaller than on the top. These are Y-branched while transforming into narrower ones and whole phenomenon has been studied in details in [25]. Experiments described above show that with the second approach, a through-hole membrane suitable for AAO template assisted nanofabrication can be obtained. Such template is suitable for electrodeposition due to the provided electric conductivity at the pore bottoms. The only disadvantage is lack of the pore diameter uniformity along the whole cross-section of the pore. On the other hand, in particular situations, such shaped template may be advantegous while gradient diameter of formed nanowires is required i.e. in nanoelectronics. For example such geometry was desired by Zaraska et al. however he did post-treated AAO with BLT approach, but after step-wise voltage drop, he removed chemically Al and chemically opened pore bottoms for further electrodepotision [26]. Therefore, our approach is much more time and cost efficient.

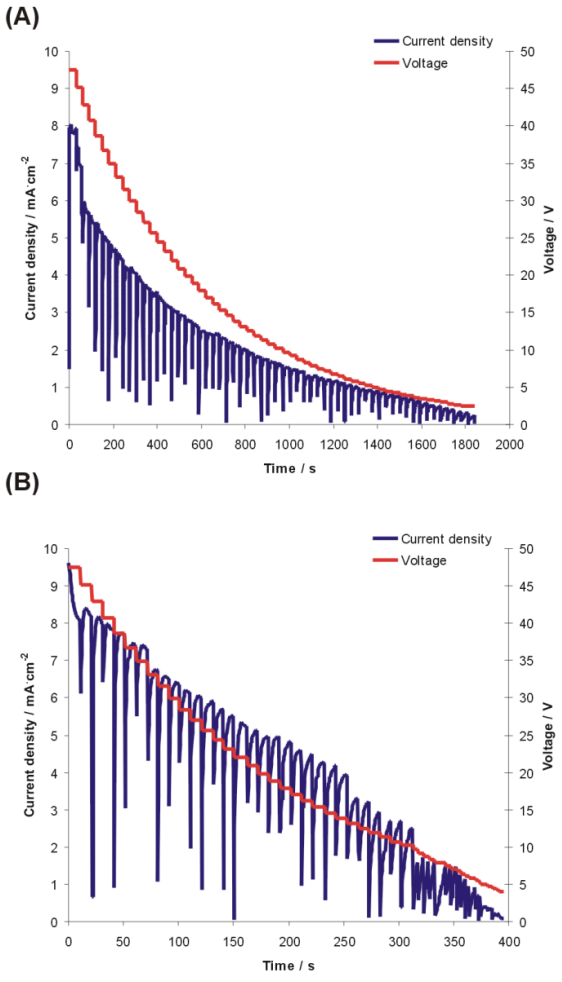

Fig. 1 Current-time and voltage-time curves of barrier layer thinning process of anodic alumina with fixed (A) and varied (B) duration of the voltage step

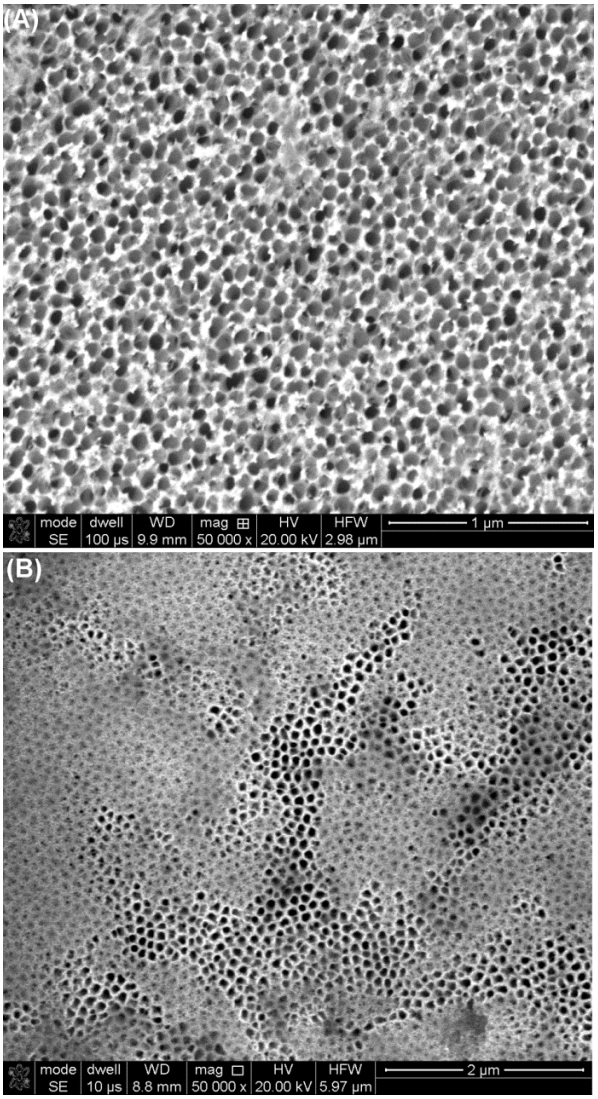

Fig. 2 Top view (A) and bottom view (B) of anodic alumina after barrier layer thinning with fixed duration of the voltage step, equal 30s.

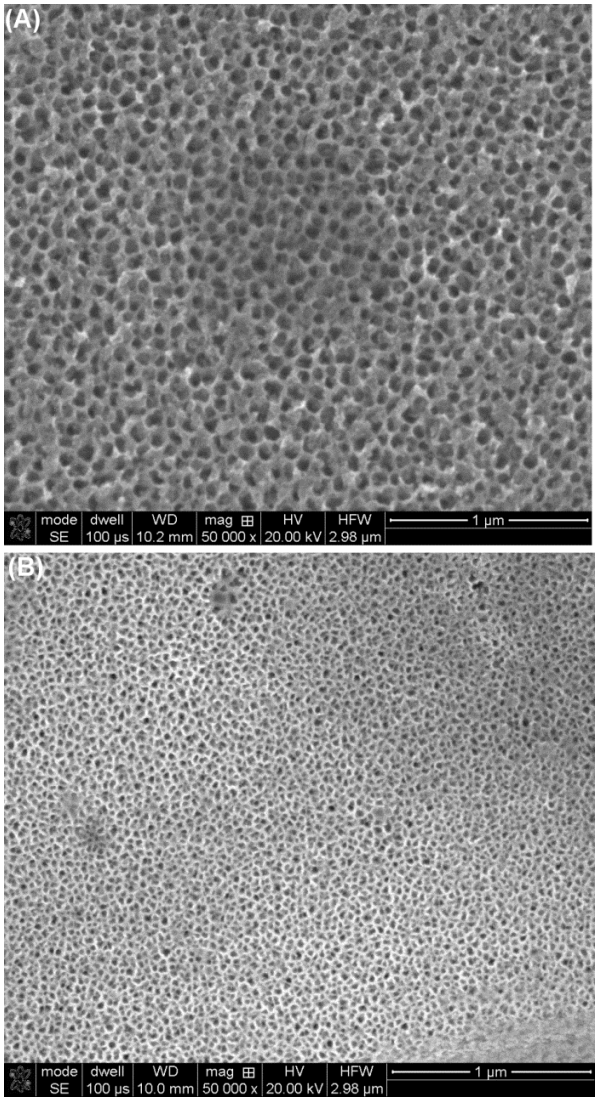

Fig. 3 Top view (A) and bottom view (B) of anodic alumina after barrier layer thinning with varied duration of the voltage step, depending on the value of current density

IV. Conclusion

Presented research have shown that electrochemical barrier layer thinning of anodic aluminum oxide is an elegant, cost and time efficient alternative to the typical multi-step post treatment approach.

It was found that too long electrochemical barrier layer thinning process of anodic aluminum oxide damages the nanoporous array at the bottom. Not optimized parameters of the process lead to only partial pores opening at the bottom what may result in poor filling of the pores during deposition. On the other hand, optimized barrier layer thinning process, where time of whole process is short allows forming AAO with pores opened at the bottoms; however, pore diameter at the bottom is smaller than on top. Such a template is suitable for further nanofabrication with the use of such cost-efficient techniques like electrodeposition.

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