Fabrication of Nanoporous Alumina Films and Optimization of Anodizing Process Parameters

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ABSTRACT — ***The electrolyte temperature and anodizing voltage effect on the pore structure and their penetration depth of pores in nanoporous alumina (NPA) films were investigated. The pore sizes, the distance between them and the film thickness were changed by varying anodizing voltage and electrolyte temperature. It was found that NPA films have more ordered pores if fabricated at low electrolyte temperature (4 °C). For better control over the pore propagation, anodizing voltage was reduced after getting desired thickness of alumina film. For this technique, optimum parameters of anodizing process (0.4 M oxalic acid $(COOH)_2$, voltage U=30-100 V, electrolyte temperature T=4-8 °C) were determined. Proposed method reduces the pore opening time while maintaining the mechanical integrity of the film.***

Keywords – nanoporous alumina, anodizing, atomic force microscopy, scanning tunnel microscopy.

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1. INTRODUCTION

Fabrication of aluminum-based porous materials is great interest due its strong potential for novel nanostructured materials development using porous alumina layers as a mask or as a template [1-2]. Various nanostructured materials can be prepared using nanoporous alumina with their relatively low cost and ease of manufacture.

An anodic nanoporous alumina film consists of self-organized hexagonally packed cells with pores oriented perpendicularly to the anodizing front. In the anodizing process, aluminum is partially dissolved in the solution and an alumina film is formed assisted by the release of gaseous oxygen at the anode. In this process, an electrostatic field created by the applied voltage will sustain continued growth of the oxide film. Two types of alumina film scan be obtained: a porous film and a barrier film [3]. Which exactly layer can be obtained, depends on the electrolyte used in the anodizing process (oxalic ($(COOH)_2$), sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids are most commonly used as electrolytes [4]).

The main stage in the preparation of nanostructured materials is obtaining of membranes with specific characteristics. The membrane formation occurs in several stages: 1 – aluminum dissolution and its conversion to oxide, 2 – porous structure formation, 3 – pore propagation through the aluminum substrate, 4 – pore opening on the backside of the substrate [5-9]. Since the parameters of nanostructured materials grown using nanoporous membrane as a mask or as a template will depend on the parameters of the membrane itself, great attention has to be paid to the process of anodizing and continuous pore propagation through the membranes. By changing the anodizing process parameters, the pore diameters, the distance between them, and the film thickness can be adjusted.

The process of porous NPA formation can best be monitored by optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). Optical microscopy helps monitoring the aluminum removal from the back side of the film and makes it possible to estimate the thickness of a porous membrane. Atomic force microscopy as opposed to scanning electron microscopy enables examination of porous film surface without resorting to the process of coating the surface by conductive film. Finally, SEM allows us to investigate structural characteristics of the oxide films with high resolution. Furthermore, it allows performing elemental analysis, which is necessary when growing nanostructured materials in the membrane pores.

In this work, we investigated the electrolyte temperature and anodizing voltage effect on the pore structure and their propagation through the alumina films.

The NPA films fabricated were investigated using optical microscope Leica DM 6000 M (Leica), Atomic Force Microscope Ntegra Therma (NT-MDT) and scanning electronic microscope Quanta 3D 200i (FEI Company).

2. EXPERIMENTS

An anodic nanoporous alumina (NPA) was obtained by two-step anodizing. Membrane fabrication process starts with anode oxidation of aluminum foil (99.99 % purity) previously annealed in the muffle furnace at T=500 °C for 3 hours. The oxidation was carried out in 0.4 M oxalic acid $(COOH)_2$ in custom made electrochemical cell. The process of anodizing was carried out in the voltage range of 30-100 V. The first stage of anodizing was 3 hours. Then, after detachment of an oxide layer in a $H_3PO_4/CrO_3/H_2O$ solution at of 70-80 °C, the second stage of anodizing was carried out for one hour. Here, the pores grow through the substrate. Finally, the pores were open on the back side of the substrate using 5% phosphoric acid (H_3PO_4).

The pores begin to form on the surface, and then grow randomly in depth during the first step in the anodizing process. Only after a certain time the pores begin to grow parallel to each other and perpendicular to the aluminum substrate. After this, the oxide layer is removed using a solution ($H_3PO_4/CrO_3/H_2O$) at 70-80 ° C. This process should be implemented to carry out the second step of anodization for parallel and aligned pores production. Next, the second process stage is carried out under the same anodizing conditions as in the first stage. In order to get through the membrane aluminum should be removed from the back side and open pores. So aluminum has been removed by using hydrochloric acid, previously dissolved therein copper plate. Then in the 5% aqueous solution of phosphoric acid pores were opened. The pores have been opened during 45-55 minutes at a voltage of 30-40V (volt).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the AFM images of NPA surface at different stages of anodizing process along with cross-sectional sketches of NPA membrane.

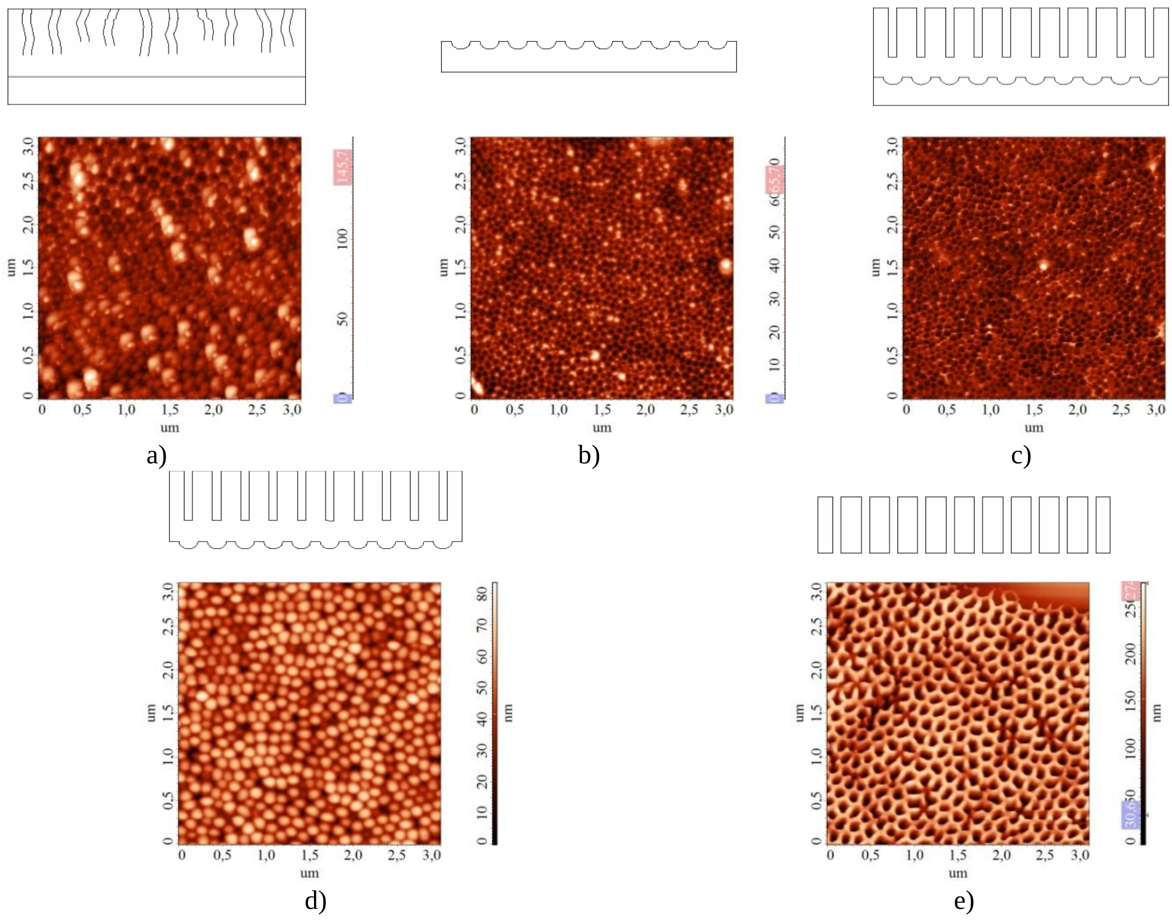


Figure 1: AFM images (scan area 3×3 µm) of NPA films at different stages of formation; on top of each image, a membrane cross-section sketch is given: a – 1st step of anodizing; b – after removal of an oxide layer; c – 2nd step of anodizing; d – after removal of an aluminium substrate; e – after opening the pores on the back side

The electrolyte (oxalic acid) temperature strongly influences the alumina film quality. In the anodizing process used oxalic acid, which is weaker than phosphoric acid and sulfuric acid. The acidity of the oxalic acid was 1 pH. That also allows you to get a steady process. It was found that NPA films fabricated have more ordered pores at low electrolyte temperatures. In Fig.2, one can see that the pores opened at 4 °C are more uniform than at 22 °C. In Fig.2 b (NPA prepared at 4 °C), the distance between the centers of the pores and the pore diameter over entire film surface are uniform, which is not observed in films prepared at room temperature (Fig. 2 a). Furthermore, a series of experiments on NPA fabrication at various electrolyte temperatures showed that anodizing process is more stable at lower electrolyte temperatures.

Next, chemical purity of aluminum film affects the formation of a porous oxide film. The use of high purity aluminum foils in the anodizing process gave better results. The process of opening pores has revealed that dissolving more chemically pure aluminum in hydrochloric acid is slower than in the case of less chemically pure aluminum, hence better control over the pore opening can be achieved. Fabrication process was optimized by varying the electrolyte temperature from room temperature (20-22 °C) down to 4-8 °C.

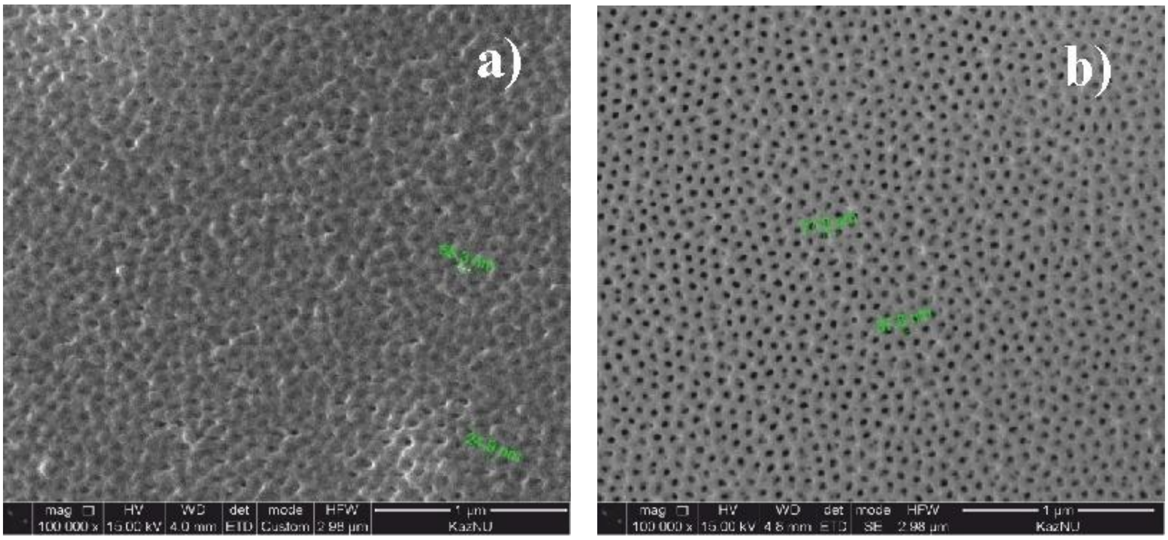


Figure 2: SEM image of porous NPA: a) at T=22 °C; b) at T=4 °C

The process of opening the pores was monitored by AFM and SEM. Figure 3 shows the oxide barrier layer and the beginning of the process of opening the pores after 40 minutes processing in the 5 % orthophosphoric acid. The AFM images show the dissolution of the barrier oxide film and the beginning of pores opening process. In Fig.3 the after some time (after 40 minutes and more) convex regions appear to be smoother and pores open in several locations.

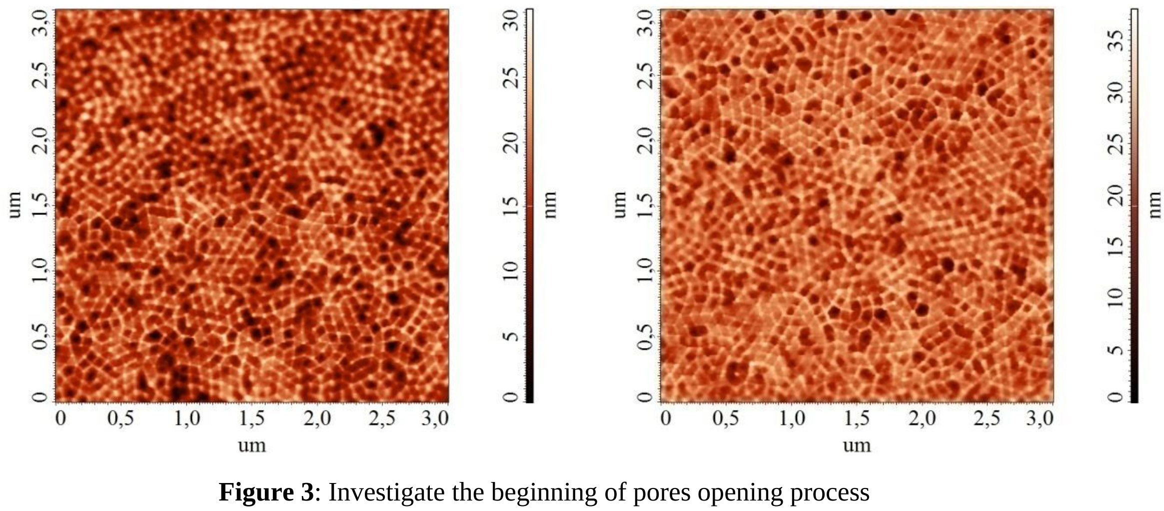
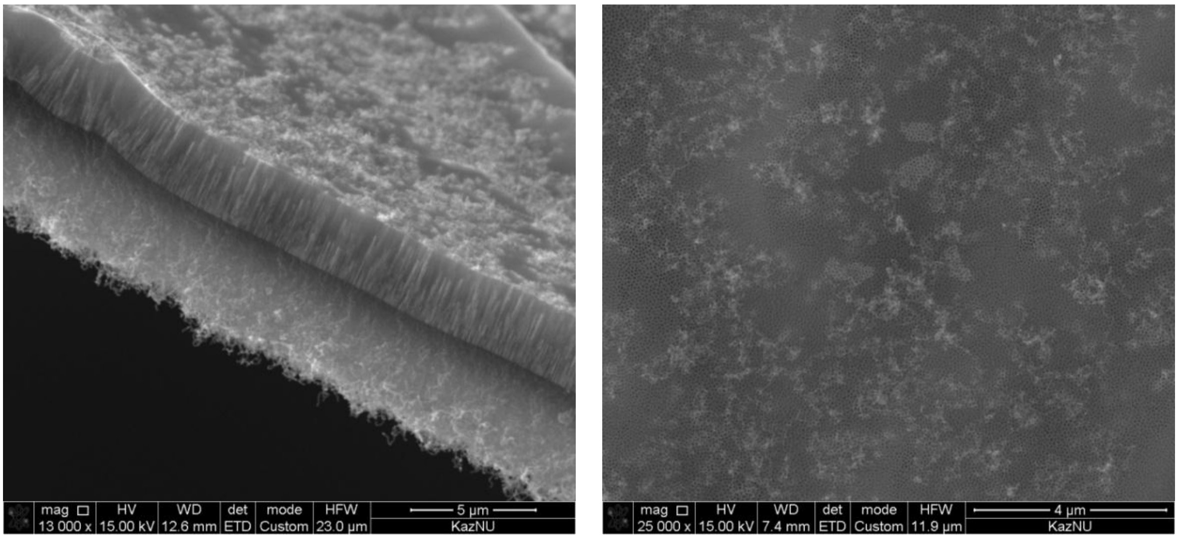


Figure 3: Investigate the beginning of pores opening process
using AFM images (scan area 3×3 µm): after 40 minutes and more

Two values of anodizing voltage have been used: a) 30 V, and b) 70-100 V. At 30 V, the growth of nanostructures in the pores with diameter between 30 and 40 nm did not occur (Figure 4). However, some problems occurred with opening the pores at high voltages. With increasing voltage, the thickness of barrier layer increased (Table 1) and the process of opening pores took more time than at low voltages (2 to 6 hours against 45-55 min, respectively). At such a long time, destruction of the NPA film and reduction of its thickness was observed. In Fig. 5, an AFM image of NPA film after 2 hours of anodizing at 70 V is shown. One can see that some pore walls have been thinned down and disappeared due to over etching. Thus, longer pore opening time leads to the destruction of the oxide film and therefore complicate the growth process of nanostructured materials in the pores.

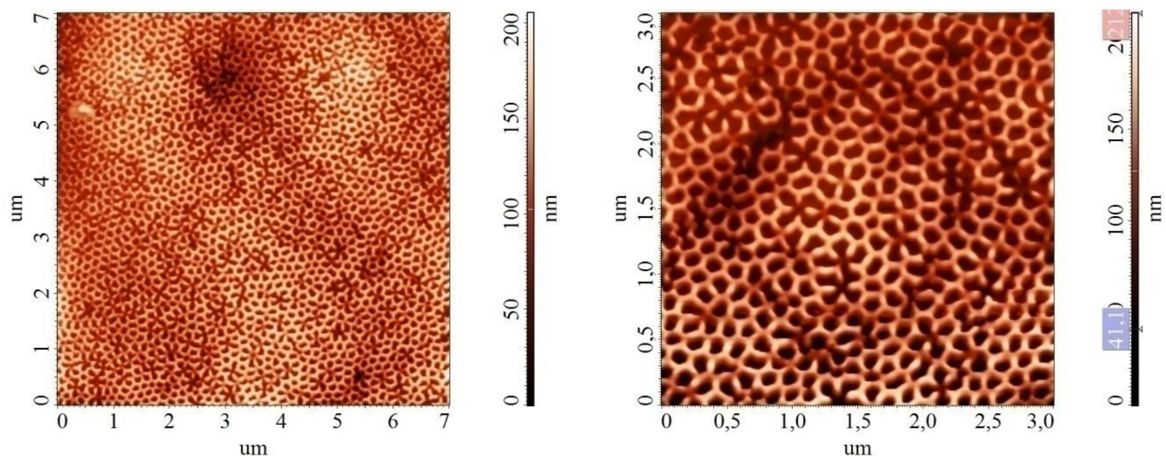


a) b)

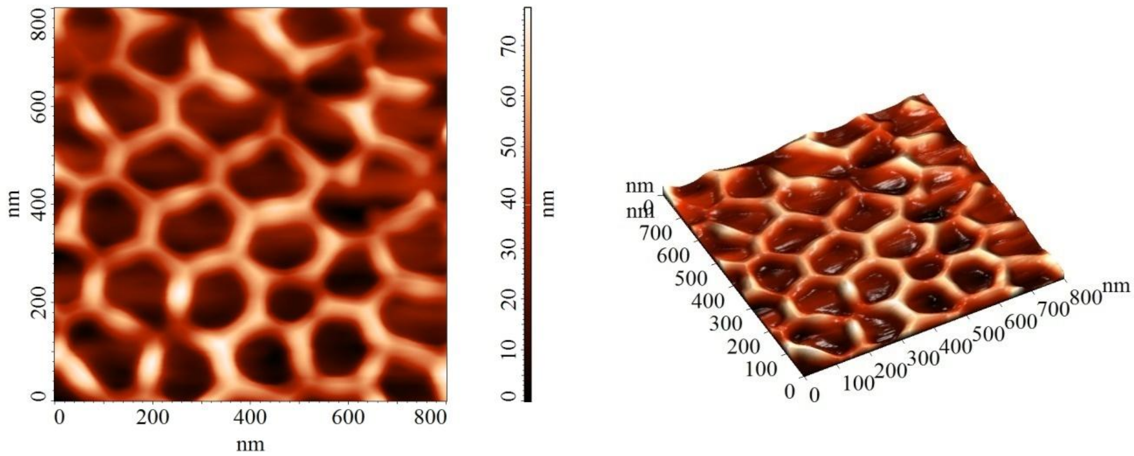
Figure 4: SEM images of NPA after the formation process of nanotubes in NPA pores:
a – on the cleavage; b – on the surface

Table 1 Effects of voltage on thickness of NPA

PARAMETERS OF ANODIZATION PROCESS				Film thickness (µm) (mean value)
Voltage (U, V)	Electrolyte	Temperature (T, °C)	Time of anodization process (t, min)	
40	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	4-5
50	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	8-9
60	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	13
70	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	17
80	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	37
90	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	180	44
100	Oxalic acid $(COOH)_2$ (0.4 M)	10-11	120	40



a)



б)

Figure 5: AFM images NPA after process of opening the poresfor two hours (anodizing voltage, U=70 V);
a – 30x30 µm scan area; b – 800x800 nm scan area

To solve these problems, we proposed a new method based on the voltage reduction during the anodizing. In this method, high voltage (70-100 V) was initially applied, then after getting desired thickness of alumina film, the voltage was reduced to 30-40 V. Thus it turned out to be possible to reduce the pore size to 30-40 nanometers and open the pores within 45-55 minutes, while keeping the film mechanical integrity.

It was found out that when high voltage (100 V) was applied in combination with opening technique proposed above, pores with diameter of more than 150 nm were obtained in some experiments. Furthermore, each pore consisted of a few small pores with diameter of 65-70 nm (Fig.6). Based on this structure, novel heterostructure materials can be produced.

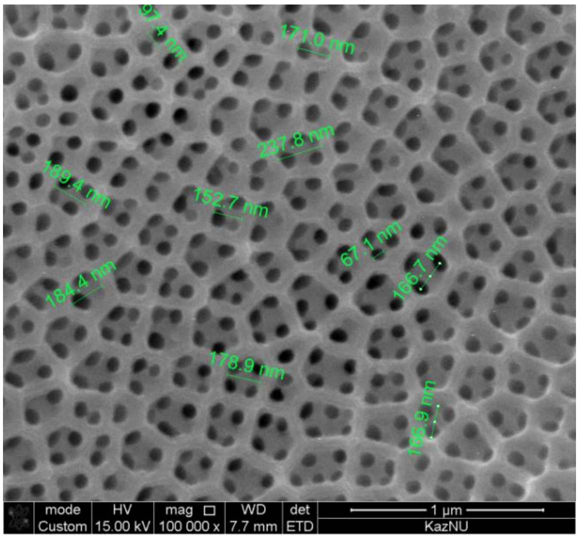


Figure 6: SEM images of NPA

4. CONCLUSION

The electrolyte temperature and anodizing voltage effect on the pore structure and their propagation through the nanoporous alumina films were investigated. It was found that NPA films have more ordered pores if fabricated at low electrolyte temperature (4-8 °C). The experiments showed that the process of anodizing is stable at this temperature. It was also found that the quality of fabricated NPA films depends on the chemical purity of applied aluminum. The pore sizes, the distance between them and the film thickness can be changed by varying anodizing voltage and electrolyte temperature. Novel technique of forming highly ordered structures of nanoporous oxide of aluminum has been demonstrated. For this technique, optimum parameters of anodizing process (0.4 M oxalic acid $(COOH)_2$, voltage U=30-

100 V, electrolyte temperature T=4-8 °C) were determined. Proposed method reduces the pore opening time while maintaining the mechanical integrity of the film.

5. REFERENCES

[1] Keunjoo Kim, Jaeho Choi, Jung Tack Lee. Electric Field Effect on Nanochannel Formation in Electrochemical Porous Structures of Alumina. Transactions on electrical and electronic materials, vol. 11, No. 5, pp. 230-233, 2010.

[2] Shoso Shingubara. Fabrication of nanomaterials using porous alumina templates. Journal of Nanoparticle Research 5, pp.17–30, 2003.

[3] Odel R., Pul R., Herz, Yu-Ming L. and et.al. Formation of Thick Porous Anodic Alumina Films and Nanowire Arrays. On Siliocon Wafers and Glass. Adv.Funct. Mater., No. 8, pp.13, 2003.

[4] Proenca M.P., Sousa C.T., Leitao D.C., Ventura J., Sousa J.B., Araujo J.P. Nanopore formation and growth in phosphoric acid Al anodization. Journal of Non-Crystalline Solids, No. 354, pp. 5238-5240, 2008.

[5] Campos R.P., Cuevas A.C., Muñoz R.E. Fabrication and Characterization of Highly Ordered Porous Alumina Templates by a Two-Step Anodization Process. Materials Science Forum, vol. 755 pp.75-81, 2013.

[6] Lee W., Kim J-C. Highly ordered porous alumina with tailor-made pore structures fabricated by pulse anodization. Nanotechnology, vol. 21, pp. 1-8, 2010.

[7] Lazarowich R. J., Taborek P., Yoo B.-Y., Myung N. V. Fabrication of porous alumina on quartz crystal microbalances. J. Appl. Phys, vol.101, pp. 1-7, 2007.

[8] Ding G.Q., Yang R., Ding J.N. Yuan N.Y., Zhu Y.Y. Fabrication of Porous Anodic Alumina with Ultrasmall Nanopores. Nanoscale Res Lett, vol. 5, pp. 1257-1263, 2010.

[9] Zahariev A.,Girginov A. Formation of complex anodic films on porous alumina matrices. Bull. Mater. Sci., vol. 26, No. 3, pp. 349-353, 2003.