



Nano porous alumina template with funnel pores structure

Scientific research paper

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ARTICLE INFO

Article history:

Received 23 June 2023

Revised 10 September 2023

Accepted 24 September 2023

Available online 22 November 2023

Keywords

AAO template

Nano porosity

Electrical capacitance

Anodization

Electrochemical method

ABSTRACT

In this research, we fabricated a porous alumina template with nano meter funnel pores using two anodizing steps with different voltages by the electrochemical method. FE-SEM analysis was used to determine the pores morphology of the templates that shows the funnel pores which are formed as a result of voltage reduction in the second anodization. In this process, by creating funnel pores, we were able to increase the porosity and the specific surface area of the porous alumina template which can increase the electrical capacitance of the template as a capacitor dielectric from 6 pF to 50 pF at a frequency of 50 kHz. Use of this template as a capacitor dielectric would be a more effective method to improve the capacitance of capacitors. Also, by measuring the electrical capacity and loss of the samples the conductivity at different frequencies were calculated.

1 Introduction

Nanotechnology research based on the nanoscale devices fabrication in a controlled way is very interesting. Among nanomaterials, the unique properties of metal oxide nanostructures make them the most diverse group of materials [1]. The porous anodic aluminum oxide (AAO) template used to form nanometer structures have been highly attracted by industry and nanometer systems [2]. AAO template, with hexagonal cells structure and self-organized parallel cylindrical nanopores produced by electrochemical anodizing, is widely used as a flexible model for the fabrication of one-dimensional nanostructures, including nanowires and nanotubes [3-7]. Among the various methods used to fabricate one-dimensional nanomaterials, AAO templates synthesis is a low-cost and high-efficiency method. The structure of AAO layers, formed by the 2-step anodization of aluminum foil, consist of hexagonal cells arrays with

nanopores in the center [8]. Nanoporous anodic aluminum oxide with hexagonally arranged pores, which had the diameter from tens to few hundreds of nanometers, are fabricated by two-step anodization of aluminum in acidic electrolyte [9-11]. The main advantage of the alumina template is that all structural features such as pore diameter, interpore distance, barrier layer thickness, and oxide layer thickness, can be arranged by the anodizing conditions such as voltage, temperature, time, and etc. [12,13]. Also, the temperature of the electrolyte has an effect on the barrier layer thickness [10]. By controlling applying voltage in a constant voltage regime or the current density under constant current anodization, the pore diameter and the interpore distance can be adjusted [14]. In other words, the interpore distance changes linearly with the anodizing potential [15]. It has been reported that the pore diameter is not related to the anodizing time so that even in a long process, small pores can be observed near the oxide/electrolyte surface [15]. The time parameter in

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DOI: 10.22051/jitl.2023.44113.1090

the anodization step causes the formation of more regular pores. In the first anodization, the primary oxide is weak and the pores are irregular, while in the second anodization, regular pores are formed by extending the time [6]. Controlling the dimensions and configuration of the structure of the pores allows the creation of material properties for a specific application [4].

One of the issues that have been considered by nanotechnology researchers in the recent years is the use of AAO template with control of geometric features in capacitors, which are essential components of electronic equipment. Therefore, due to the increasing demand to reduce the size and weight of electronic devices, small capacitors with high capacitance are required [16]. With the result obtained by Zhang et al., there are two methods to increase the capacity of the alumina template: 1) Increasing the specific surface area of aluminum 2) Increasing the dielectric constant which increases the electrical capacitance [17]. It has been reported that the dielectric constant can be increased by adding materials such as TiO_2 [15], ZrO_2 [1], BaTiO_3 [13], MnO_2 [17], inside the pores of AAO template.

In this research, we have investigated the effect of increasing the second anodization voltage in fabrication of an alumina template with funnel pores and analyzed their role in increasing of the surface area of the templates. Also, we have investigated the electrical capacitance of the capacitors by increasing the specific surface area of the alumina template as a capacitors dielectric constant.

Therefore, by fabricating alumina template with funnel pores as a dielectric constant, we could have capacitors with higher energy storage and electrical capacity in a smaller dimension.

2 Experimental

The fabrication of anodic aluminum oxide was performed on 1 in 3 cm aluminium sheets with a purity of 99.5%. For the electro polishing process, the mixture of perchloric acid and ethanol (1:4 vol) as an electrolyte, and a steel plate as the cathode, and an aluminium plate as the anode was used.

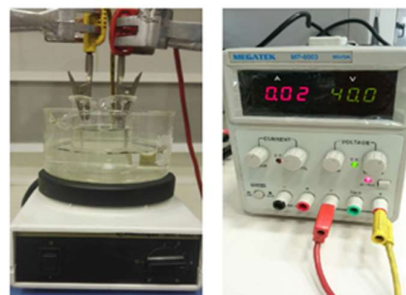


Figure 1. Image of the experiment setup of anodization.

Figure 1 shows the experimental setup. The first anodizing process was carried out at a constant voltage of 40 V in 0.3 M oxalic acid solution at 17 °C for 3h. The first anodization is used as a pre-pattern, while by increasing the anodization time, more organized pores are obtained. Therefore, the oxide layer created in the first anodization is removed via chemical etching in the mixture of 6% wt. phosphoric acid and 1.8% wt. chromic acid at the 60 °c for 3 h. The second anodization was carried out in the same experimental condition as were used in the first step, but the applied voltage was changed to the 25v. Also, we prepared two other samples in this way with 30v and 40v applied for the second anodization. Afterward, to increase the pore diameter, chemical etching of the Aluminium barrier layer was performed in 5% wt. phosphoric acid solution at 30 °c and for 30 minutes.

3 Results and Discussion

FE_SEM images of samples with different second anodizing voltages are shown in the three panels of Fig. 2. Figure 2a shows an AAO template with an organized porous structure with a 50nm pore diameter in a second anodization voltage of 40 v. In this research, we have made a type of alumina template with funnel pores by reducing the voltage in the second anodization compared to the first anodization voltage, and obtained a higher specific surface area with an increase of electric capacitance. Figs. 2b and 2c refer to the template with applied voltage 30v and 25v for the second anodization, while the first anodization voltage for all three templates is 40v. The applied voltage affects the pore diameter and their depth, which also affects the specific surface area of the template [18]. With the constant voltage in the first step, changing the voltage in the second step significantly affects the form of pores. It has been reported that if the voltage of the second step would be lower than the voltage of the first

step, some new small pores are formed at the bottom of the large pores formed on the alumina surface. In other words, the large pores are at the top and the smaller pores are at the bottom, creating a spiral structure [17]. As we see in Figs.2b and 2c related to the samples that were made in this study, pores with a smaller diameter are formed at the bottom of the pores with a larger diameter as pores have funnel shape. By using Measurement software, we determined the average diameter of pores for different second anodizing voltage, 40 V, 30 V, 25 V are 54 , 56 , 57 nm, respectively. in Fig. 2b, which is made with a second anode voltage of 30 volts, the diameter of the smaller pores was equal to 37 nm, while in Fig. 2c which is related to the sample that the second anodization voltage is 25 V, the diameter of the smaller pores is 29 nm.

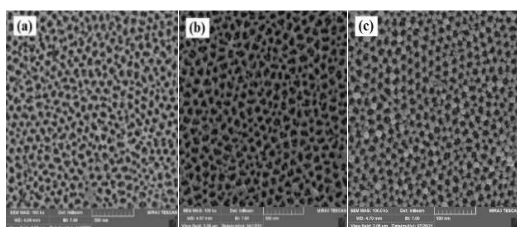


Figure 2. FE_SEM images of samples prepared under (a) 40 V, (b) 30 V, (c) 25 V in the second anodization.

The geometric parameters of the templates are reported in Table 1.

Table 1. Geometric parameters of the prepared templates

Second anodization voltage	Sample (a)_40 volt	Sample (b)_30 volt	Sample (c)_25 volts
Porosity (%)	27.2	37.9	40.8
Wall thickness (nm)	22.2	12.4	10.5
The thickness of the barrier layer (nm)	31.3	17.4	14.7
Density of holes (mm) ⁻²	59.3	61.5	63.8

Among the factors affecting the diameter of the pores and the distance between the pores are temperature, time, and anodization voltage [5]. Applying different

voltages in the second anodization with the voltages applied in the first anodization has created funnel pores on the surface of the alumina template.

According to the values in Table 1, it can be seen that the porosity and density of holes for samples (b) and (c) have increased compared to sample (a), which is due to the difference of the second anodization voltage in these samples and causes the formation of smaller pores at the end of the larger pores. The diameter of the small pores formed at the bottom of the larger pores increase by increasing the voltage in the second anodization (from 25_40 V). As we mentioned, the pores diameter is affected by the anodization voltage, as the voltage increases, the pores diameter also increases [19,20]. As the anodizing time is constant, by reducing the voltage in the second step compared to the first step anodization, funnel pores are formed and therefore have a larger specific surface area than the sample obtained with normal pores. Other positive effects of decreasing the second anodization voltage compared to the first voltage, are decreasing wall thickness and barrier layer thickness, and increasing porosity.

By using the formula $P = 0.91(D_p/D_c)^2 \times 100$, the porosity of the samples were calculated [14] and the results for all the three samples are given in Table 1.

Figure 3 shows that by increasing the voltage in the second anodization, the average of pore diameter and the average of inter-pore distance of samples were increased. We found that, the linear variation of the inter-pore distance (D_c) (with slope of 2.34 nm/v) are more than the pore diameter (D_p) (with slop of 0.75 nm/V) versus the voltages which confirms the report of Lee et al. [21].

For investigating electrical capacitance of the samples, a potential difference between the two ends of the capacitor with AAO dielectric was applied and the electrical capacitance was measured. In this study, we have measured the electrical capacitance and loss of the samples using the LCR meter model GDM-8261A in the frequency range of 10 Hz to 200 kHz. Also, we have calculated the conductivity by using the relation $\sigma = \epsilon_0 \omega (\epsilon' + i\epsilon'')$ in which σ is conduction, ϵ' is the real part and, ϵ'' the imaginary part of the dielectric function, ϵ_0 is the vacuum dielectric constant $8.85 \times 10^{-12} (C^2/N.m^2)$, and ω is frequency [22].

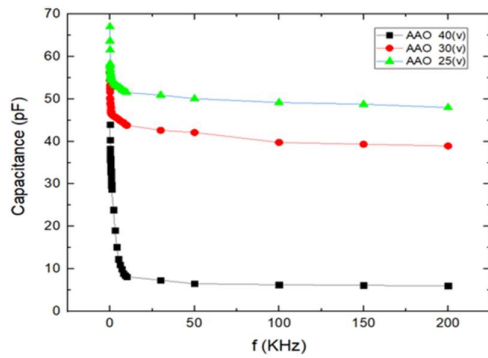


Figure 3. Electrical capacitance of the samples versus frequencies with different second anodization voltage (40, 30 and 25 volts).

Figure 4 shows the capacitance of the samples versus frequency for different second anodization voltages (40, 30, 25 V). As shown in Fig. 4, the maximum electrical capacitance is for the sample with the 25 volts for the second anodization voltage. We also found that the decreasing of second anodization causes the increasing of porosity and the density of pores that increases the electrical capacitance. In other words, an alumina template with funnel pores (sample b and c) have a larger effective surface than the sample (a) with normal pores, so alumina template with funnel pores have higher electrical capacitance, which confirms the work of Wojcieh et al. [23]. Equation (1) can be used to calculate the capacitance with the surface area of the dielectric and also its permittivity.

$$C = \epsilon' \epsilon_0 A/d, \quad (1)$$

where ϵ' is permittivity, A is surface area of the dielectric, d is the dielectric thickness, and C is the capacitance [24,25]. In order to increase the capacitance based Eq. (1) for dielectrics with the same thickness, their surface area or their permittivity should increase. In many reports, they have been able to increase the electrical capacitance by adding materials such as MnO_2 to the AAO template and make nano-composites to increase the permittivity of the sample [17]. In this work, without adding any additional materials and just by changing the voltage of the second anodization the specific surface area of the template and the electrical capacitance are increased. By calculating the permittivity, we found that the permittivity of the sample increased by increasing of the specific surface

area of the template. Also, at the frequency of 50 kHz, the permittivity of sample (a) is equal to 3.5, this value is consistent with the results obtained by Hong et al. [26]. But for sample (c) which has a higher specific surface area, it is equal to 30.6. That means, with increase the specific surface area, the permittivity of the templates and also capacitance of the samples with funnel pores increase.

Figure 4, shows that, at a frequency of 50 KHz, the electrical capacitance of sample (a) (with anodization voltages of 40 V_40 V) is about 6 pF, sample (b) (with anodization voltages of 40 V_30 V) is 42 pF, and sample (c) (with anodization voltages of 40 V_25 V) is about 50 pF.

Figure 5 shows the conductivity behavior versus frequency for the samples with different second anodization voltages. As the frequency increases, the AC electrical conductivity of the samples, increases and the transfer of charge carriers is easier. By comparing Fig. 4 and Fig. 5, it can be seen that the sample with funnel pores has higher capacitance and lower conductivity than the template with normal pores. AAO template due to its low loss and conductivity is used as an insulator for various electronic applications like dielectric gate on transistors [27,28]. Therefore, an alumina template with funnel pores that has lower conductivity than regular template is more practical.

4 Conclusions

We found that different voltages in 2-step anodization of the AAO template causes funnel pores on the aluminum surface. By the formation of funnel pores, the percentage of porosity (from 27.2% to 40.8%), density of pores (from 59.3/mm² to 63.8/mm²) and the specific surface area of the template compared to the normal template increase. Also, we found that the electrical capacitance of the sample increased from 6 pF to 50 pF at frequency of 50kHz.

Acknowledgements

This work was financially supported by Alzahra University.

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