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A kind of double-sided porous anodic alumina membrane fabricated with the three-step anodic oxidation method

ZHANG Chen[1], WANG KaiGe[1*], GAO ZeYang[1], WU JunJun[1], REN JunYing[1], ZHANG LiangLiang[2], GU ChangZhi[3] & BAI JinTao[1]

[1] *Institute of Photonics & Photo-Technology, Northwest University, Xi'an 710069, China;*
[2] *State Key Laboratory for Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710069, China;*
[3] *Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

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The porous anodic alumina membranes (PAAMs) have been successfully used as templates for the fabrication of functional nano-materials due to their outstanding regularity and physicochemical properties. In this paper, a transparent double-sided anodic alumina membrane with ultra-thin aluminum substrate was fabricated with the three-step anodic oxidation method in the oxalic acid electrolyte. The characters such as the top-surface morphology, membrane thickness, and depth of nanopores of this three-layer (Al_2O_3-Al-Al_2O_3) sandwiched nano-structure were controllable through regulating the main anodic oxidation conditions, e.g., anodic oxidation time of various steps, coating remove process. The experiments data revealed that the aluminum substrate is exponential declined with the oxidation time when it was approximately reduced by a few micrometers. This new double-sided anodic alumina membrane can be used as the high-quality functional field emission materials and templates.

double-sided porous anodic aluminum membrane, three-step anodic oxidation method, controllability, anodic oxidation rate

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1 Introduction

In recent years, the porous anodic alumina membrane (PAAM) has attracted a great deal of attention due to its unique nano-structures, mechanical properties, corrosion resistance and transparency. Owing to the nanoscale holes distribution, independent PAAM can be employed as a nanofilter for molecules separation [1]. PAAM has been used as capacitive humidity sensor because of the porous structure which gives a large surface area for absorbing water vapor [2], and it also has been applied as the photonic crystal [3]. More to the point, PAAMs can be used as templates to make various functional nano-materials [4]. Some researchers have succeeded in preparation of various functional nanowires and nanorod arrays [5–7]. The organic polymer membranes with nano-constructors have been obtained through using organic polymer materials to copy these templates's morphology, and these materials of special structure have been applied to improve the surface hydrophobicity [8,9], detect DNA molecules [10–12], and to many other fields [13–15].

In practical applications, the large-area ordered PAAM templates are more ideal, and have a wider range of potential applications. For this purpose, scientific and technical workers proposed many methods and techniques. In 1995, Masuda et al. [16] invented a new method of PAAM prepared by secondary oxidation method, greatly improving the PAAM nanopore's ordered area. In 2001, Mikulskas et al. [17] molded the aluminum by using ordinary grating, and

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*Corresponding author (email: wangkg@nwu.edu.cn) got the PAAM. In 2009, Kwon et al. [18] used electron beam lithography technology to imprint template where the square array had two types of aperture and cycles on the silicon nitride, and then obtained PAAM with matrix pore array structure. In 2011, Chen et al. [19] employed focused ion beam (FIB) to etch concave with different hole spacing, and made the high-quality PAAM. Then they found that the aperture size was proportional to the hole spacing, after that, they also used the FIB technology to produce a kind of anodic alumina membrane with the moire fringe [20]. However, whether it is the nano-imprinting technology or the FIB etching technology, these guidance methods for PAAM have disadvantages such as relatively high cost, complex process and low efficiency.

In this paper, based on the standard three-step anodic oxidation method, combined with the working conditions regulation, we reported one kind of three-layer (Al_2O_3-Al-Al_2O_3) sandwiched nano-structure which includes two sides of PAAM and a middle layer of ultra-thin aluminum substrate, and found out the changing relationship between the aluminum substrate thickness and the third step oxidation duration when there is only a few micrometers thickness of middle aluminum substrate.

2 Experiment platform

In all of the following work, high purity aluminum foil (purity 99.99%, thickness 0.1 mm) was used, and the purity of other chemical reagents were analytical grade. The sample pretreatment of aluminum could be briefly described as that: firstly, the block aluminum foil was cut into 15 mm×4 mm× 0.1 mm strip. Secondly, the aluminum foil was annealed at 600°C under the nitrogen environment for 5 h, to eliminate the impurities and defects, and increase the grain size. Then, the sample foil was ultrasonically cleaned in the deionized water (SMART-N, Heal Force, China), ethanol and acetone for 10 min. Subsequently, the aluminum foil was put into 5 wt% NaOH solution for 10 min to remove naturally formed alumina on aluminum surface. After that, the preparative aluminum strip was electrochemical polished at a constant voltage of 3 V in a mixture of chromic acid and phosphoric acid and sulfuric acid (2:5:20 in quality) at 60°C for 20 min.

All the experiments were implemented using self-made setup which was sketched in Figure 1(a). The three-step anodic oxidation method was employed to produce the double-sided PAAM in oxalic acid solution at a constant voltage of 40 V under 5°C. As for the working details, the first oxidation step and second step are the same as the general anodic oxidation procedure [21]. In our three-step experiments, the time of former two steps was 6.5, 13 h, and the third-step oxidation time changed from 0 to 7 h. Before the second and the third steps of oxidation, the alumina layers were stripped away by a mixture of 0.6 mol/L phosphoric acid and 0.15 mol/L chromic acid at 60°C. After the third step anodization, the pores were widened with the phosphoric acid for 1 h. It is important to note that during the anodizing process, the sample aluminum foil must be immersed into the electrolyte entirely, and the aluminum foil was parallel to the electrode in the center of the electrolytic cell as far as possible, as shown in Figure 1(a).

After the three-step anodic oxidation, the prepared samples were cleaned with deionized water about 20 min, and dealt with the cross section by $CuCl_2$ solution, and dried naturally. The morphologies of the sample were characterized with the field emission scanning electron microscopy (FE-SEM, Japan Hitachi, su-8010).

3 Results and discussion

Figure 1(b) shows the schematic diagram of the double-sided PAAM, that is, the aluminum foil is oxidated from both sides at the same time under the same condition, thereby forms one kind of the three-layer (Al_2O_3-Al-Al_2O_3) sandwiched nano-structure. During the anodic oxidation process, the sample aluminum strip was entirely submerged into the oxalic acid; both sides of the aluminum foil were fully contacted with the electrolyte, which led the two sides of aluminum to oxidation and obtaining a layer of nanoporous alumina film respectively.

It is well known that the quality of PAAM is influenced seriously by the oxidizing conditions such as the local

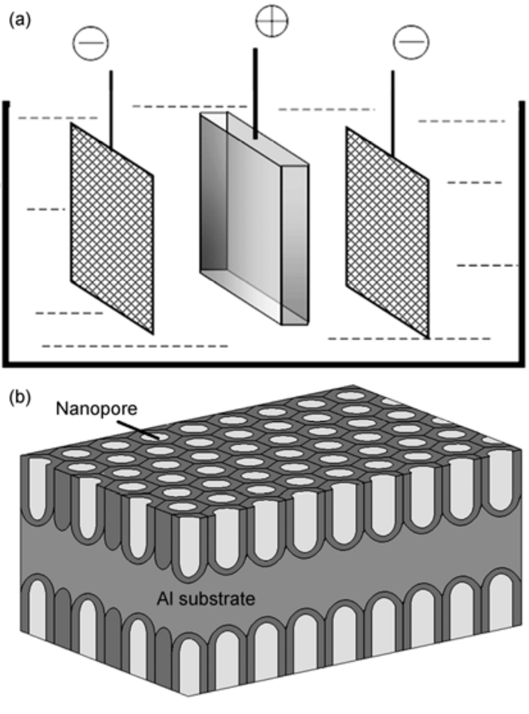

Figure 1 Schematic diagram of (a) experimental setup, (b) double-sided nanoporous anodic alumina membrane.

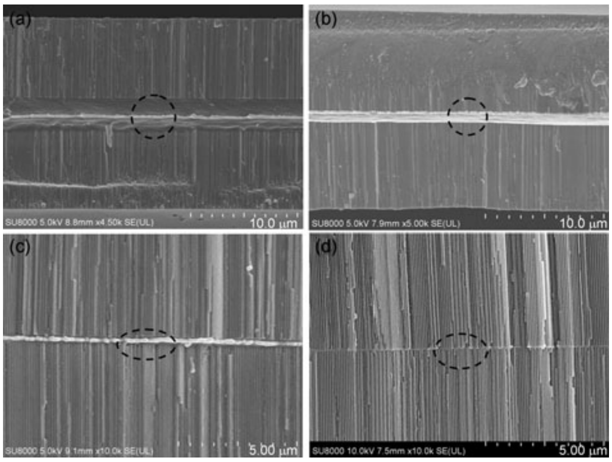

Figure 2 Cross-sectional SEM images of the double-sided PAAM. All the samples have the same oxidation time of the first step and the second step, as 6.5 and 13 h, while the third-step time is different, as (a) 3.5 h, (b) 5 h, (c) 6 h, (d) 7 h, respectively. The black dashed-line circles are just to guide the eyes.

electrolyte concentration around the aluminum surface.

When the anode oxidation happens, the electrolyte concentration will suddenly drop down in an extremely short period, while the solution temperature will rise up rapidly before the new solution is supplied without stirring. Therefore, in our experiments, the electrolyte quantity around both sides of the aluminum foil greatly affected the response speed of solution supplement, and then affected the procedure of anodic oxidation on the aluminum surfaces. Different electrolyte concentrations will lead to inconsistence of nanopore diameter and interval, and subsequently changes the oxidation rate. With the increase of electrolyte concentration, the nanopores' diameter increased gradually, nanopores' density decreased, and the ordering increased firstly and then decreased. In order to solve the above issue, the sample aluminum foil was put as possible as perpendicular to the direction of electric field in the middle of the electrolytic cell as shown in Figure 1(a). During the experiments, the electrolyte environment around both sides of sample aluminum was kept constant assisted with the refrigerated circulator system and the magnetic bead stirring technology.

Figure 2 displays the cross-sectional SEM images of the double-sided PAAMs using the three-step anodic oxidation method with the different third-step time which changes from 3.5 to 7 h. After oxidizing with different duration, all the original aluminum foils have the sandwich structure, Al_2O_3-Al-Al_2O_3. It is clearly that the thicknesses of aluminum substrate in the middle of samples are different from Figure 2(a) to Figure 2(d). It can be also found that as the third-step oxidation time increasing, the aluminum substrate thickness is decreased gradually until it almost disappears (thickness from 3.9 μm to 50 nm), while the nanopores grow continuously.

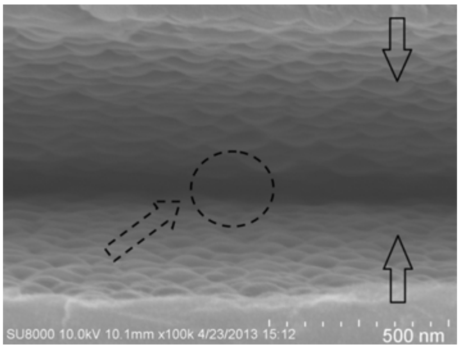

Figure 3 SEM image of double-sided nanoholes barrier layers. The arrows represent the growth direction and the black dashed-signs are only for guiding the eyes.

Figure 3 is the SEM profile image of the double-surfaced PAAM, where the aluminum substrate is chemically etched with CuCl2 solution entirely, and it clearly shows the intersection of two nanoholes' barrier layers. In Figure 3 we can find that the two-layer cap structure of barrier develops continuously in the interior of PAAM. The upper surface's barrier layer grows down and the lower surface's one grows up. In Figure 2(d), the double-sided PAAM has already grown together and there is almost no metal aluminum, the cap-structure barrier layers on two sides have nearly contacted with each other.

In order to understand well the changing regularity of the aluminum substrate thickness (when it has become a thin one) during the anodic oxidation, we systematically studied the sample double-sided PAAM growth situation when the aluminum substrate was about to be used up. By measuring and counting the samples' thickness in our experiment, the curve correlating the thickness of ultra-thin aluminum substrate inside the double-sided PAAM with the third-step oxidation time was drawn as Figure 4. It is noticed that when the thickness of the aluminum substrate was very thin about a few microns, the consumption of aluminum reduced rapidly as the third step oxidation time increased.

The thickness (H) of middle aluminum substrate reduced with the third-step oxidation time (t) as an exponential decay relationship which can be described as the following equation:

$$H = 20.19\mathrm{e}^{-t/2.04} - 0.70. \tag{1}$$

Eq. (1) indicates that the anodic oxidation rate of the double-sided PAAM continuously decreased until it became nearly extinction when the aluminum substrate was vanished almost. The reasons inducing this phenomenon might be that the fluid flowability of oxalic acid at the bottom of the nanoholes became weaker as the nanoholes grew longer which caused the concentration of the electrolyte to get down, and more, the electric current density changed to be non-uniform because the thickness of the aluminum substrate became thinner and thinner.

As a comparison, Figure 5 shows one SEM image of the double-surfaced PAAM made by the two-step anodic oxidation

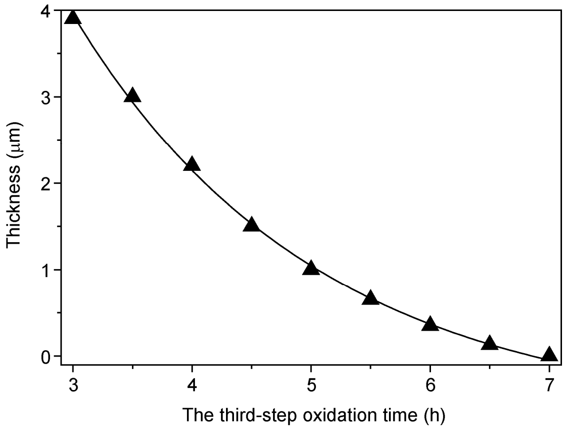

Figure 4 Changing curve, the thickness of double-sided PAAM aluminum substrate with the third-step oxidation time.

method. From the SEM image, it can be found that there were some bifurcation structures at the bottom of the nanopores, which is often said as the heteromorphic structured PAAM. It should be noted that there is no heteromorphy structure in our all three-step oxidation experiments (Figure 2). The reason of appearance of this bifurcation structure might be the duration of the second step anodic oxidation which is too long for the goal to use up the middle aluminum of the double-sided PAAM. This is one of the important reasons why we preferred to use the three-step anodic oxidation method in our experiments. The second reason is that due to the anodic oxidation proceeding on the two sides of the aluminum foil at the same time, the current and local electrolyte concentrations are distributed unsteadily. It causes the morphology of the double-sided PAAM to be worse than the one-sided PAAM. In order to get the better morphology of the template, we increased the number of the oxidation times. Thirdly, because we wanted to study the anodic oxidation rate of the double-sided PAAM with ultra-thin substrate, we chose the three-step anodic oxidation method. By the method, stripping away the top alumina layers twice, we can get the sample with the ultra-thin aluminum substrate faster and better and it will be more convenient to carry out the measurements and the subsequent processing. The formation mechanism about these bifurcations produced in the two-step anodic oxidation method is not entirely understood, and it will be the focus in our future research.

Furthermore, these new sandwich structures have amazing function, which is different from the single side PAAM and enriches the spatial structure of PAAMs, and will have powerful capability to provide us with a conveniently integrated means to work with a complex network of applications on a Lab-on-Chip sensor. In fact, just recently, Hsieh et al. reported their new humidity sensor based on the dual-layer nanoporous anodic aluminum oxide [22], the sensing signals are greatly increased, and the sensitivity is improved for near 4 fold.

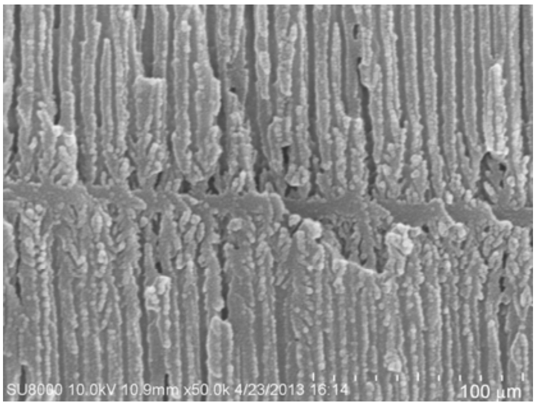

Figure 5 SEM image of bifurcation structure at the bottom of the nanopores produced by the two-step anodic oxidation method.

4 Conclusion

A kind of transparent double-sided nanoporous anodic alumina membrane with ultra-thin aluminum substrate was fabricated with the three-step anodic oxidation method in the oxalic acid electrolyte. In the experiment, we have got the double-sided PAAM with different ultra-thin thickness of aluminum substrate by different oxidation times. The aluminum substrate thickness of these Al_2O_3-Al-Al_2O_3 sandwiched nano-structures was reduced exponentially with the third step oxidation time when the aluminum substrate thickness decreased by several micrometers. It proved that the double-sided PAAM's substrate thickness and the depth of the nanopores were controllable and the anodic oxidation rate will be continuously decreased until stop. The present experiments and results will be beneficial to the future controllable fabrication of functional nanostructure based on various PAAMs and the application in the fields such as the field emitting, solar cells and biological sensors.

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