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Preparation of Porous Alumina by Anodization

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Abstract: The characteristics of porous alumina produced by anodization in both oxalic acid and sulfuric acid solution have been studied. The diameter of the pores for oxalic acid as electrolyte is about 60 nm and for sulfuric acid as electrolyte is about 30 nm. The morphologies of the pores have been improved by two-step anodization process. It has been observed that the temperature and operation voltage are two of the most important factors in the fabrication process of porous alumina films.

Introduction

Anodic porous alumina, a typical self-ordered nanochannel material formed by aluminium in an appropriate acid solution [1], has recently attracted interest because of their potential application in nanometer scaled electronic, magnetic, optical and chemical devices [2-3]. The high stability of the material in aqueous solution makes it well suited for biological applications [4-5]. Generally high ordered nanowire or nanotube arrays are essential to obtain functional devices through template synthesis [6]. The anodic alumina membrane is a good choice for a template since the pores are self-aligned and the diameter of the pores and the porosities can be controlled by the temperature, operational voltage and electrolyte. Well-aligned oxide semiconductor nanowire array, such as ZnO [7] and SiO_2 [8], has been fabricated by electro-deposition and oxidation by using anodic alumina as template.

Generally the porous alumina is prepared by the method of two-step anodization since the single step method results irregular pore arrangement. During the anodization, the electrolytes can be any acid with low concentration, such as, sulfuric acid, oxalic acid, boric acid, and phosphoric acid, where the voltage will be different alternatively responding to the concentration of hydrogen ions. In this paper, the porous alumina membranes have been prepared in both sulfuric acid and oxalic acid electrolytes. The characteristics and the formation process of alumina in one single step and two-step anodization have been investigated.

Experimental

The porous alumina is prepared by anodization. Firstly high purity (99.999%) aluminium plates with 0.5mm of thickness was annealed under vacuum of about 10^{-3} Pa at 450 ^{o}C for 5 hours and then washed with acetone then electrochemically polished (0.4 M KOH), in order to remove the oxide in the surface. The aluminium was used as anode, and a graphite wafer was used as cathode. The first step of

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anodization was processed in 0.3 M oxalic acid and sulphuric acid under 40 V and 20 V, respectively. The second step was carried out after removing the light yellow layer by phosphoric acid, which fabricated in the first step. The experiments were operated at around $5^{o}C$, $10^{o}C$ and room temperature. As the aluminium oxide is slightly attacked by the electrolytes, and as this attack is strongly dependent on the electric field, small fluctuation in the oxide thickness are instable and lead to pore growth [9].

Results and discussions

Fig. 1 shows the scanning electron microscopy (SEM) images of an alumina membrane prepared in oxalic acid at room temperature. After the first step of anodization for 10 hours, the pores on the surface was quite irregular and many pores interconnected with each other, as shown in Fig. 1(a). The second step of anodization for 12.5 hours was carried out after the first layer alumina was removed in 0.6 M H_3PO_4 for 18 hours. From the SEM image of the sample [Fig. 1(b)], the pores were still irregular although the porousity was increased.

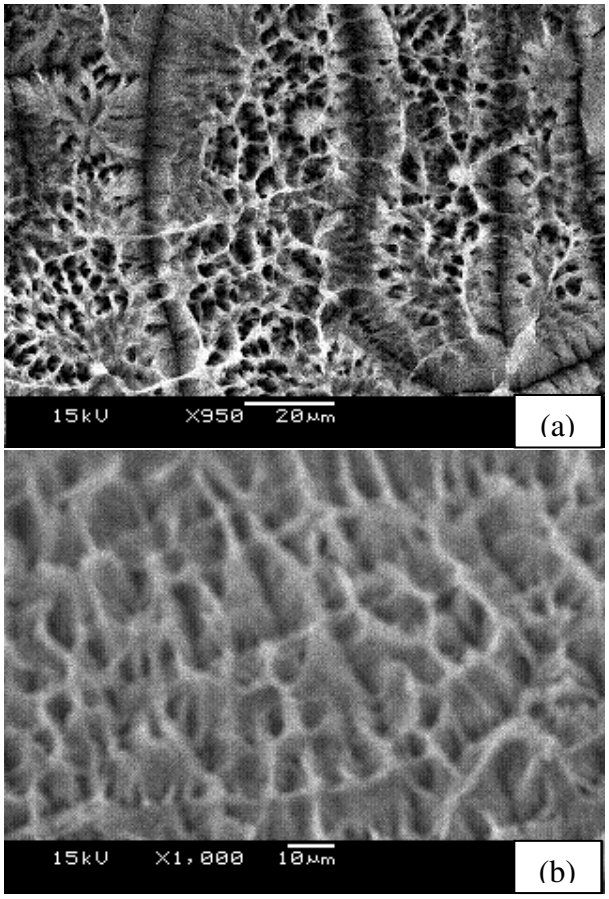

Fig.1 SEM images of anodised alumina membrane surface fabricated in 0.3M oxalic acid at room temperature, (a) by one step for 10 hours, and (b) by two steps, the first step was the same with (a) and the second step was carried out for 12.5 hours after the first layer alumina was removed by keeping it in 0.6 M H_3PO_4 for 18 hours.

Fig. 2 shows the images of the alumina surfaces anodised in oxalic acid at $5^{o}C$ by by single-step and two-step methods. It is clearly seen from Fig. 4 the regular pores with hexagonal shape after the second anodization for 10 hours. The diameter of pores was about 60 nm. It is noted that the first step anodization process for 10 hours resulted in a dense but irregular porous pattern, and the second step anodization resulted in more regular pore arrays.

Comparing Fig. 1(b) and Fig. 2(b), the anodization was conducted in almost the same condition except the temperatures. This indicated that the lower temperature was beneficial to form the regular pore array. The activity of H^+ ions at the pore bases will become stronger under high temperature. Pores opening towards the surface have been attributed to the chemical dissolution of the pore walls by the electrolyte during anodization [10].

Fig 3 shows the SEM images of the alumina membrane surface fabricated in sulphuric acid solution by two-step method. The first layer which was formed in H_2O_4 at of 5 ^{o}C for 10 hours oxide was removed 0.6M H_3PO_4 solution under room temperature, followed by the anodization in the same condition as above for 22 hours.

Fig. 4 compares the morphologies of the nanopores of the anodised alumina fabricated in oxalic acid and sulphuric acid with the same concentration. Both of the anodization processes were carried out at 20 V for sulphuric acid and 40 V for oxalic acid, respectively. The diameter for oxalic acid as

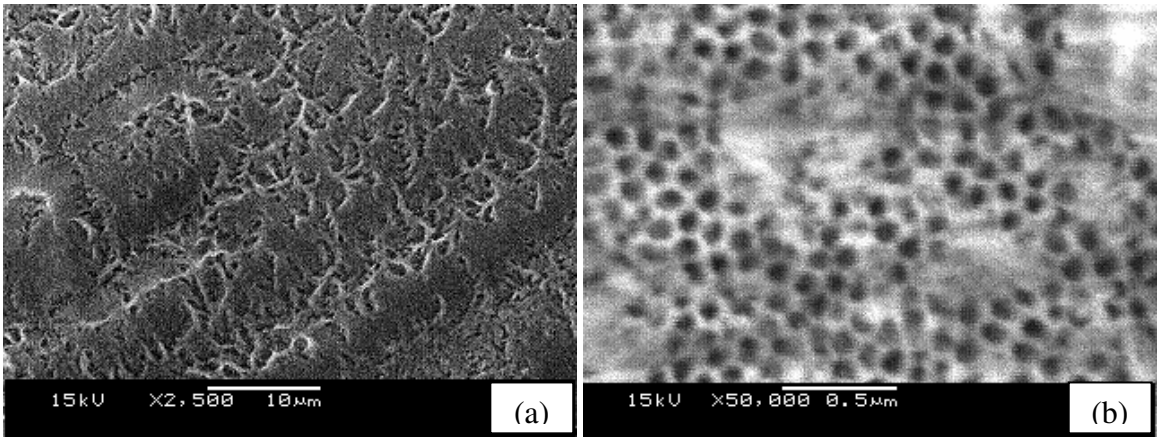

Fig. 2 SEM imgaes of surface of alumina membrane anodised in 0.3M oxalic acid at around 5 ^{o}C, (a) by one step for 9 hours and (b) by two steps, the second step was repeat of the step (a) after the first layer alumina was removed in 0.6 M H_3PO_4 for 18 hours.

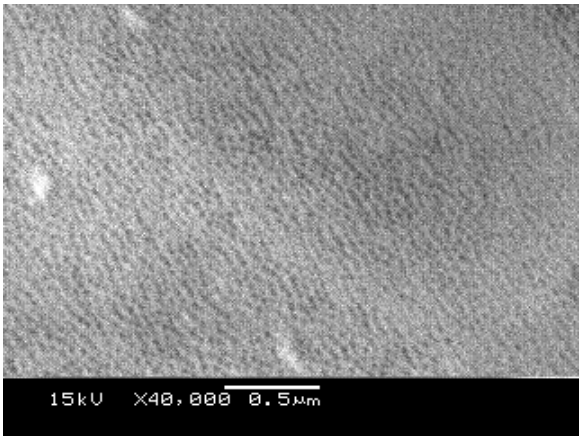

Fig. 3 SEM image P-Al anodised in 0.3M H_2SO_4 of 5 ^{o}C by two-step method. In the first step was for 10 hours, and it was repeated in the second one after the first layer alumina was removed in 0.6 M H_3PO_4 for 22 hours.

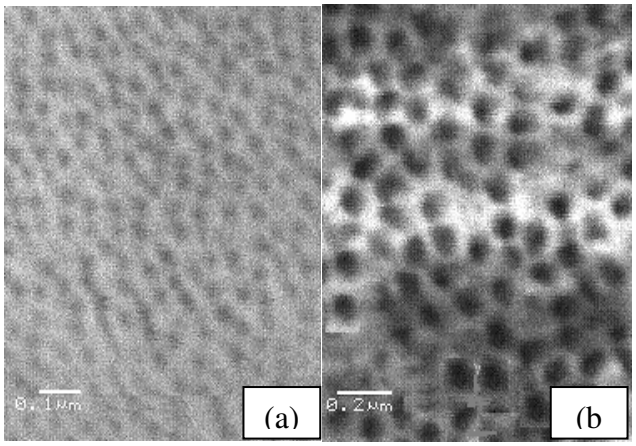

Fig. 4 SEM micrographs of the anodised alumina membranes prepared in (a) sulphuric acid at 20 V and (b) oxalic acid at 40V, repectively. The concentration of the both electrolytes were 0.3M.

anodic agent was about 60 nm, and the diameter for sulphuric acid as anodic agent was about 30 nm. The reported results [11-12] have demonstrated that the size of pore mainly depends on the operation voltage rather than different oxidizing agents. The present results indicated that the lower voltage was beneficial for getting smaller sized pores under the same H^+ ion concentration. It can be seen from Fig. 4 that the pore density for the sample prepared in sulphuric acid is much higher than that prepared in oxalic acid. The result indicates that the higher the density of pore is obtained under the lower operation voltage.

Conclusion

In summary, the voltage of anodization was an important factor that influenced the porosity and the pore size of the anodised alumina membrane. The lower the voltage of anodization was beneficial to

obtain the self-organized porous array with the well-aligned morpholgy and the small diameter. Comparing anodization under two different electrolytes, the sulfuric acid has the advantages for lower voltage operation. To get more regular pore array, the operation temperature was another important factors besides the voltage. The higher operation temperature, the more irregular the expected pore array.

Acknowledgement

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