

## Preparation of Porous Alumina Film on Aluminum Substrate by Anodization in Oxalic Acid

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**Abstract:** Self-ordering of the cell arrangement of the anodic porous alumina was prepared in oxalic acid solution at a constant potential of 40V and at a temperature of 20°C. The honeycomb structure made by one step anodization method and two step anodization method is different. Pores in the alumina film prepared by two step anodization method were more ordered than those by one step anodization method.

**Keywords:** Porous alumina film, anodization, oxalic acid.

With the development of the nanoscale material research, porous alumina was paid increasing attention because it is a good template to fabricate nanometer-sized fine structures. The geometry of anodic porous alumina film may be schematically described as a honeycomb structure, which is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate, as shown in **Figure 1**<sup>1</sup>. The film has the following main merits: (1) easy preparation with self-organized by anodizing an aluminum substrate; (2) high uniformity and controllability of nano-parameters of samples by anodizing conditions; (3) a variety of depositable materials into the nanopores as catalyst for preparation of nanoscale structures<sup>2</sup>.

Masuda<sup>3,6</sup>, Jessensky<sup>4</sup> and W.Y. Zhou<sup>5</sup> *et al* have reported that a highly ordered honeycomb structure with an almost ideal hexagonal arrangement can be obtained over relatively large areas under a specific anodizing condition in oxalic acid solution. The condition of the self-ordering of the cell arrangement was characterized by the application of a constant anodizing potential and a long period anodized for more than 10 hours at low temperature about 0°C<sup>3-6</sup>. In this paper, we indicate that the ideal honeycomb structure can be prepared at a higher anodization temperature and within a shorter period in oxalic acid.

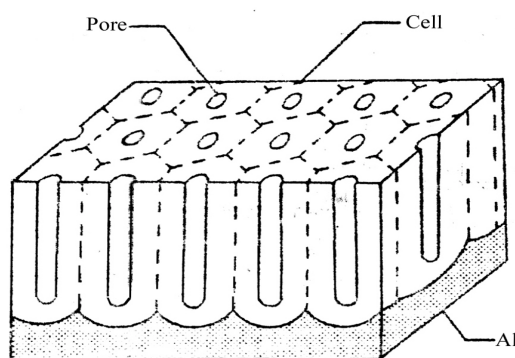
An aluminum sheet (99.999% purity, 20×30×0.3mm) was annealed at 500°C for 4 h in order to eliminate the elastic strain during the rolling process and to obtain coarse grains in the aluminum and homogeneous condition for pore growth over large areas. Then the aluminum sheet was cleaned in a mixed solution of CH<sub>3</sub>COOH, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>COCH<sub>3</sub> by supersonic oscillation. To enhance the surface quality of the substrate, the specimen was electropolished in a mixed solution of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>O.

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Anodization was divided into two steps which was similar to that reported by Masuda and Satooh<sup>7</sup>. In this work, aluminum anodization was conducted under a constant cell potential 40 V in 0.3 mol/L oxalic acid as electrolyte. Plumbum sheet was chosen as cathode in the experiment. The temperature of the electrolyte was maintained constant at 20°C during the anodization. After the specimen had been first anodized for 40 min, the anodic oxide layer was then eroded in a mixture of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 65°C for 10~20 min. Thus numerous flat pores were obtained in the surface of the Al substrate, which will be propitious to nucleate for the second step anodization. The specimen got after erosion was anodized in 0.3 mol/L oxalic acid for another 2 hours. After the second step anodization, the specimen was dipped into the 5 wt.% phosphoric acid at 50°C for broadening the pores.

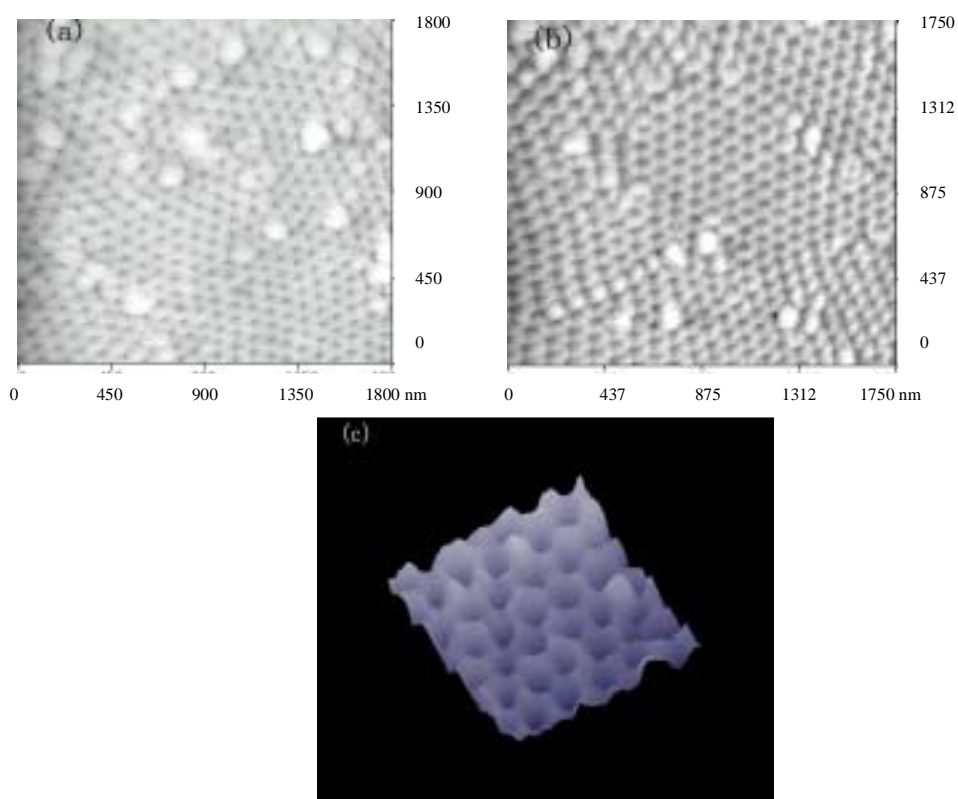
**Figure 1** Schematic model of ideal porous structure of anodic alumina



**Figure 2(a)** and **2(b)** show the atom force microscope (AFM) images of the top view of the porous alumina after the first step anodization and the second step anodization, respectively. **Figure 2(c)** shows the tridimensional surface image after the second step anodization. From **Figure 2(a)**, **2(b)** and **2(c)**, honeycomb structure characterized by close-packed array of columnar hexagonal cells could be observed. The pore arrangement is highly ordered in the domain, but the arrangement is different in adjacent ones, which relies on the difference of the texture in differently oriented domains. There are not hexagonal cells in the boundary area of two adjacent domains.

The pore density and main diameter can be calculated about  $1.52 \times 10^{10}/\text{cm}^2$  and 40 nm from **Figure 2(a)**, and about  $1.36 \times 10^{10}/\text{cm}^2$  and 50 nm from **Figure 2(b)**. The reduction in pore density from **Figure 2(b)** to **2(a)** indicated that some pores which appeared in the one step anodization might be diminished during the second step anodization. Pores nucleated randomly and grew homogeneously during the one step anodization. But after erosion of the anodic oxide layer formed during the one step anodization, the pores nucleated in some places which were in favor of nucleus and grew with high speed. Therefore, some nuclei were not propitious to nucleation growth in the other places and finally stopped growing when they collapsed with the wall of the existing columnar cells. It causes the decrease in pore density during the second step anodization.

**Figure 2** AFM micrographs of anodic porous alumina in 0.3 mol/L oxalic acid at 20°C.



(a) One step anodization, (b) Two step anodization, (c) Tridimensional surface micrograph after two step anodization.

Anodic porous alumina with highly ordered honeycomb structure could be prepared in oxalic acid solution. Two step anodization method is more congruent to prepare honeycomb structure than one step anodization method. Because the pore is nanometer scale in diameter and various metals can be deposited in the pores, the ordered anodic porous alumina obtained in oxalic acid solution can be used to fabricate oriented carbon nanotubes (CNTs) and nanometer-scale composites.

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