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SELF-ORGANIZED FORMATION OF HEXAGONAL NANOPORE ARRAYS IN ANODIC ALUMINA*

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Conditions for a self-organized formation of ordered hexagonal structure in anodic alumina were investigated, using oxalic or sulphuric acid as an electrolyte. Highly-ordered nanopore arrays with pore densities of 9×10^{9}–$6.5\times10^{10}\mathrm{cm}^{-2}$ and high aspect ratios over 3000 were fabricated by a two-step anodization process. The array exhibits characteristics analogous to a two-dimensional polycrystalline structure of a few micrometres in size. The interpore distance can be controlled by changing the electrolyte and/or the applied voltage. The formation mechanism of ordered arrays is consistent with a previously proposed mechanical stress model, i.e., the repulsive forces between neighbouring pores at the metal/oxide interface promote the formation of hexagonally ordered pores during the oxidation process.

Keywords: anodic alumina, nanochannel array, self-organization, porous film
PACC: 6146, 8160

I. INTRODUCTION

Porous anodic alumina is a widely studied material used for corrosion protection of aluminium surfaces or as a dielectric material in microelectronics applications. For more than 40 years, porous alumina has been the subject of extensive investigations[1]. It exhibits an homogeneous morphology of parallel pores which grow perpendicularly to the surface with a narrow distribution of diameters and interpore spacings. Meanwhile, the pore size can easily be controlled from ten to a few hundreds of nanometres. Because of these properties, it has been applied as a template for the fabrication of nanometre-scale composites[2–4]. Self-organization during pore growth leading to a densely packed hexagonal pore structure has been reported recently[5–8]. The self-organized arrangement of neighbouring pores in ordered hexagonal arrays can be explained by a repulsive interaction between the pores during growth. Mechanical stress due to the volume expansion during aluminium oxidation has been proposed by the authors to be the origin of these repulsive forces[6]. However, the ordered pore arrangements are formed under some specific anodizing conditions after a long anodization time, and as a result, they can only be observed on the bottom of the films. Masuda and Satoh[3] first showed that straight nanoholes could be formed in a thin membrane of porous alumina by stripping away the thick oxides resulting from the initial long anodization and subsequently anodizing it for a short time. Nevertheless, ordered nanopore arrays with high aspect ratio (ratio of depth to diameter) have been scarcely prepared and the arrangement morphology of the arrays has been less studied[9]. In this paper, we report on the formation of regularly arranged and parallel nanopore arrays with a high aspect ratio in anodic alumina, and show the arrangements of the ordered nanopore arrays in differently oriented domains.

II. EXPERIMENTAL

High purity (99.999%) aluminium foils were degreased in acetone and cleaned in a mixed solution of HF, HNO_3 and HCl acids, and then annealed at 500°C for 4 h in order to enhance the grain size in the metal and to obtain homogeneous conditions for pore growth over large areas. To smooth the surface morphology, the substrates were electropolished. Anodization was conducted under a constant cell potential condition in a sulphuric or oxalic acid. The temperature of the electrolyte was maintained constant at 1°C during anodization using a cooling system.

To fabricate ordered nanopore arrays in which the holes are straight and regularly arranged throughout

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the film, a two-step anodizing process similar to that reported by Masuda and Satoh[3] was used. During the first anodization process, the pore nucleate at the surface at almost random positions, and as a result pores on the surface form randomly and have a broad size distribution. However, under some specific anodization conditions,[5−8,10] hexagonally ordered pore domains can be obtained at the bottom of the layers. After the first anodization of more than 10 h, the anodic oxide layer with a partially distorted surface was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60°C for about 10 h. Thus a textured pattern of concaves was obtained on the surface of the Al substrate, which acts as a self-assembled mask for the second anodization process. An ordered nanopore array could be obtained after anodizing for the second time by using the same parameters as in the first step.

After the second anodization, the surface was protected against etching using a coating layer made of a mixture of nitrocellulose and polyester resin in ethyl acetate, butyl acetate and heptane. The Al layer was removed in a saturated $HgCl_2$ solution. Then the bottom part of the anodic porous alumina membrane, i.e. the barrier layer, was removed in 5 wt% phosphoric acid at 30°C, after which the coating layer was dissolved in acetone to form a through-hole membrane.

The morphologies of the nanopore arrays of anodic porous alumina were observed using a scanning electron microscope [(SEM), Hitachi S-4200].

III. RESULTS AND DISCUSSION

After anodization, the remaining aluminium was removed in a saturated $HgCl_2$ solution. Figures 1(a) and 1(b) show scanning electron microscopy (SEM) images of the top and the bottom views of the alumina after dissolution of the aluminium following the first anodization step. Although the pores start growing at the upper surface at almost random positions shown in Fig.1(a), nearly perfectly ordered densely packed hexagonal structures can be observed at the bottom of the layer shown in Fig.1(b). This ordered structure is accompanied by a smooth lower surface and an homogeneous depth of neighbouring pores. The pore density in ordered pore arrays was found to be typically about 20%–30% lower than that at upper surface of the alumina, indicating that part of the pores stop growing either shortly after their nucleation or during the self-organization process.

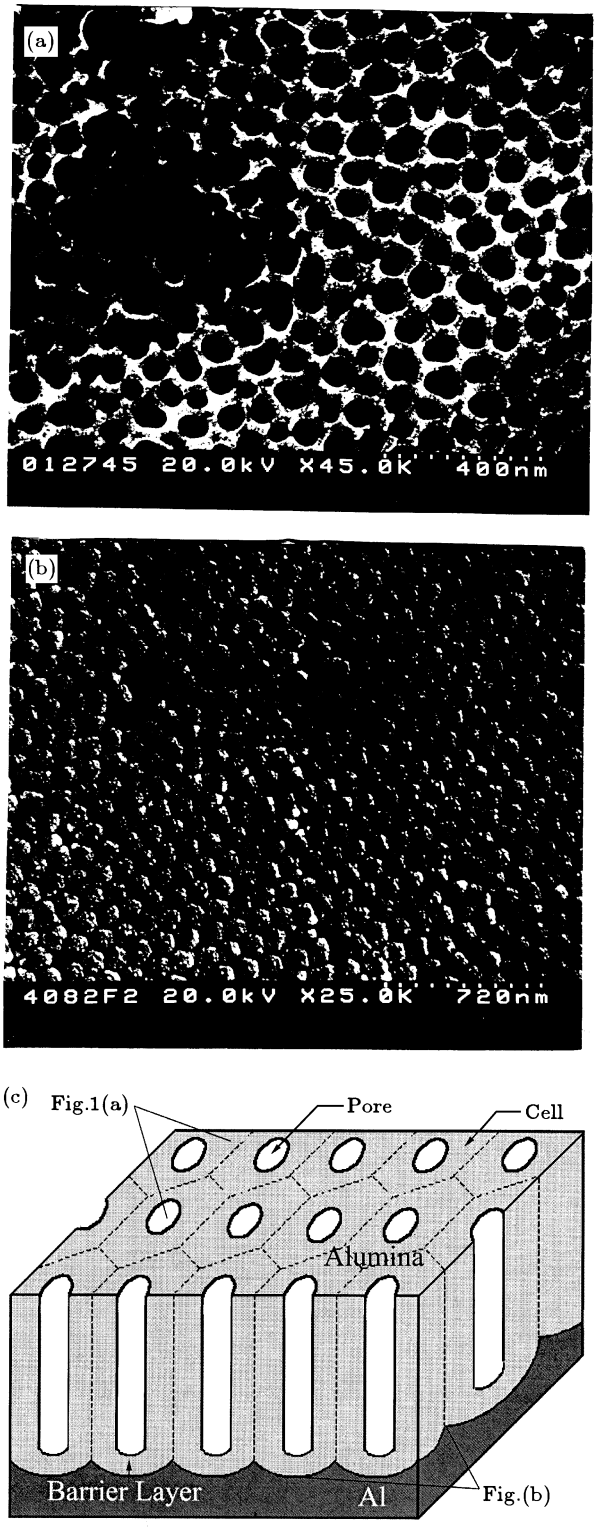


Fig.1. SEM images of the top view (a) and the bottom view (b) of the alumina after dissoluiton of the aluminium following the first anodization step. Anodization is conducted in 0.3 M oxalic acid at 1°C and 40V. (c) Schematic diagrams of the ideal porous structure of anodic alumina, showing the typical diagrams corresponding to (a) and (b).

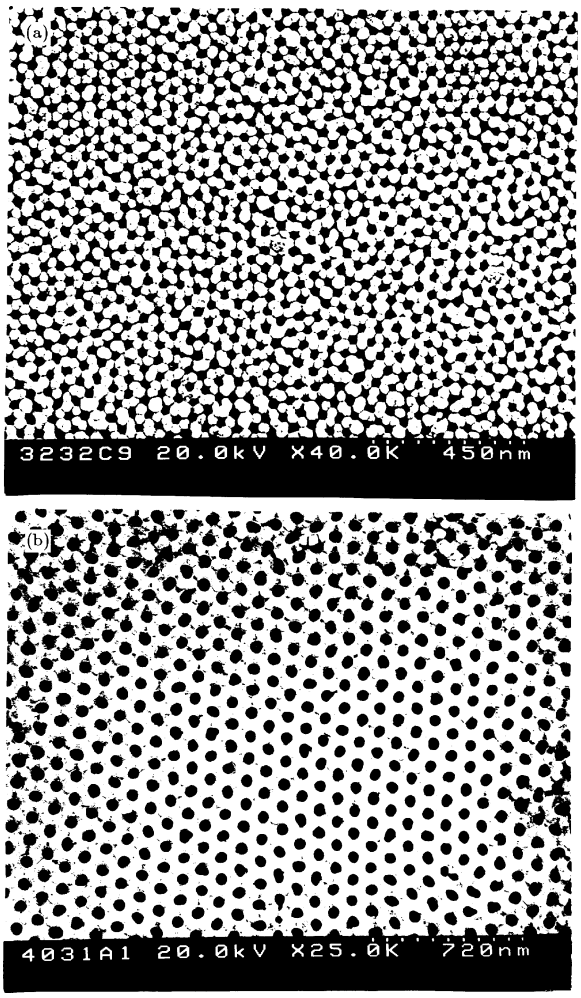


Fig.2. Top view of nanopore arrays in anodic alumina prepared by two-step anodization. (a) Anodization is conducted in 10 wt% sulphuric acid at 1°C and 19 V. (b) Anodization is conducted in 0.3 M oxalic acid at 1°C and 40 V. The first and second anodization time are 24 and 95 h, respectively.

As clearly shown in Fig.1, at the initial stage of anodization of aluminium, the points of pore initiation are spread randomly over the aluminium surface. Ordering of the cell arrangement proceeds with the anodizing time after a steady state in the growth of the porous structure is established. Therefore, for the fabrication of symmetrical films with straight holes throughout the entire film, a two-step anodization process was used here. In this process, the concave texture of the Al surface which is formed by selective removal of the film after the first anodizing step can induce ordered formation of pores even at the initial stage of anodization in the second anodizing step. Figure 2 shows an SEM top view of nanopore arrays in anodic alumina prepared by two-step anodization. (a) Anodization is conducted in 10 wt.% sulphuric acid at 1°C and 19 V. (b) Anodization is conducted in 0.3 M oxalic acid at 1°C and 40 V. The first and second anodization time are 24 and 95 h, respectively. The pore density is about 9×10^9 for oxalic acid and 6.5×10^{10} for sulphuric acid. Therefore, the interval of pores not only increases in proportion to the applied voltage during anodizing but can also be controlled by changing electrolyte.

Dimensions of the porous structure of the anodic alumina depend on the conditions of anodizing and subsequent etching treatment. This etching process also leads to some pore widening, so the observed pore diameters do not reflect the intrinsic properties of the anodization process. On the other hand, this etching process can also be used to adjust the ratio of the pore depth to the diameter in a certain range, especially for the thin porous membranes. Figure 3 shows the SEM image of a partially etched surface of an anodic alumina.

By chemical etching in 5 wt% aqueous phosphoric acid, opening of the pore bottoms as well as widening of the pores occurs. In Fig.4, an SEM bottom view of a porous alumina layer after dissolution of the pore bottoms is shown at a lower magnification. Perfect hexagonal pore arrays are observed within domains of micron size, which are separated from neighbouring domains with a different orientation of the pore lattice and an irregular shape by grain boundaries, i.e., the ordered pore arrangements show a domain structure analogous to a two-dimensional polycrystalline structure. Some defects, i.e., pores which are not hexagonally arranged, are usually pentagonally or heptagonally arranged at the surrounding. The ordered domains have no correlation with the crystalline grains of the aluminium since the latter are about two orders of magnitude larger. The lattice parameter within the ordered domains was approximately proportional to the forming voltage, in accordance with the literature, where proportionality of both pore and cell wall diameters to the voltage has been established[9,10]. In the present work, the best results were obtained at 40 V anodizing voltage for oxalic acid and 19 V for sulphuric acid. The degree of ordering was reproducible with this set of parameters. Increasing or lowering the voltage leads to a much smaller size of the ordered domains, so that moderate voltages seem to be preferable in order to obtain highly ordered structures.

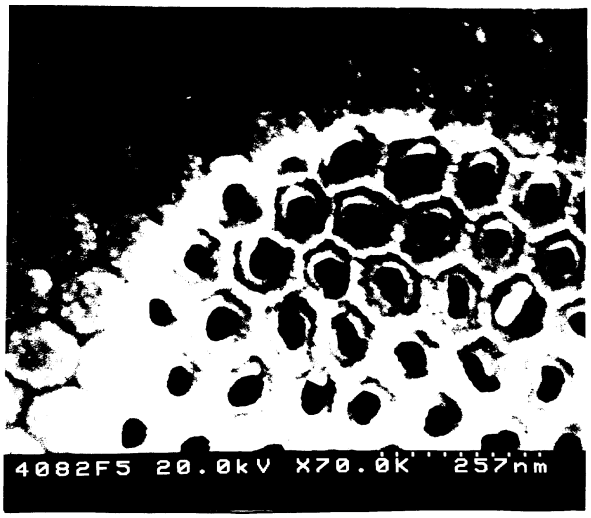


Fig.3. SEM image of a partially etched surface of an anodic alumina.

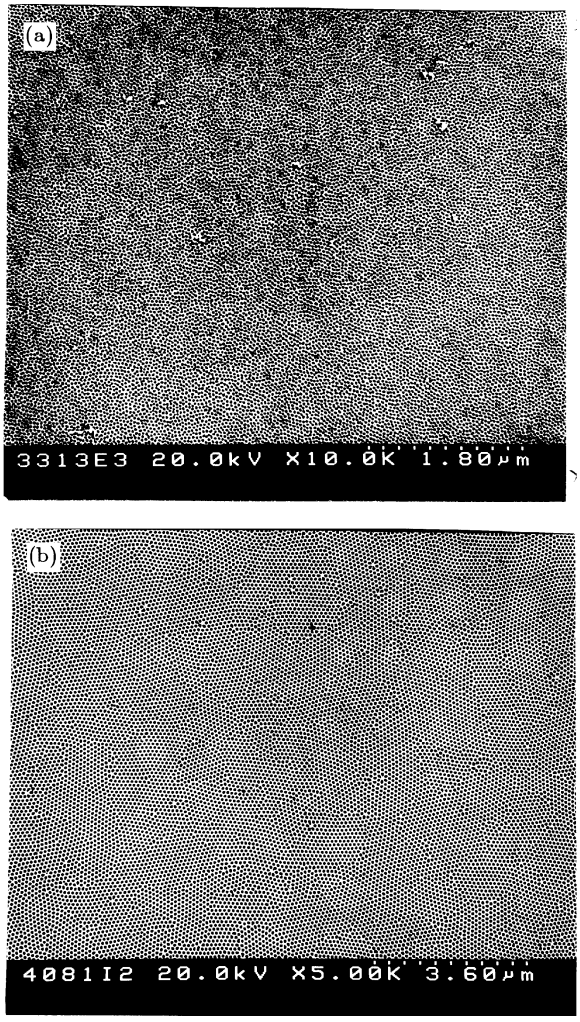


Fig.4. SEM bottom view of a porous alumina layer after dissolution of the pore bottom, shown at a lower magnification. (a) Anodization is conducted in 10 wt% sulphuric acid at 1°C and 19 V; (b) conducted in 0.3 M oxalic acid at 1°C and 40 V.

The difference in the morphology of ordered and disordered pore arrays can also be observed at the cleaved edges of the alumina layers. Figure 5 shows the cleaved edge of an ordered sample and a disordered sample, both produced at 40 V anodizing voltage in oxalic acid followed by a pore widening process. Only in the case of ordered structures does the cleavage result in flat edges within the ordered domains. The distance between the pore rows in the ordered structure indicates that the cleavage proceeds through the pore centres along one axis of the hexagonal lattice and represents the nanopore diameter.

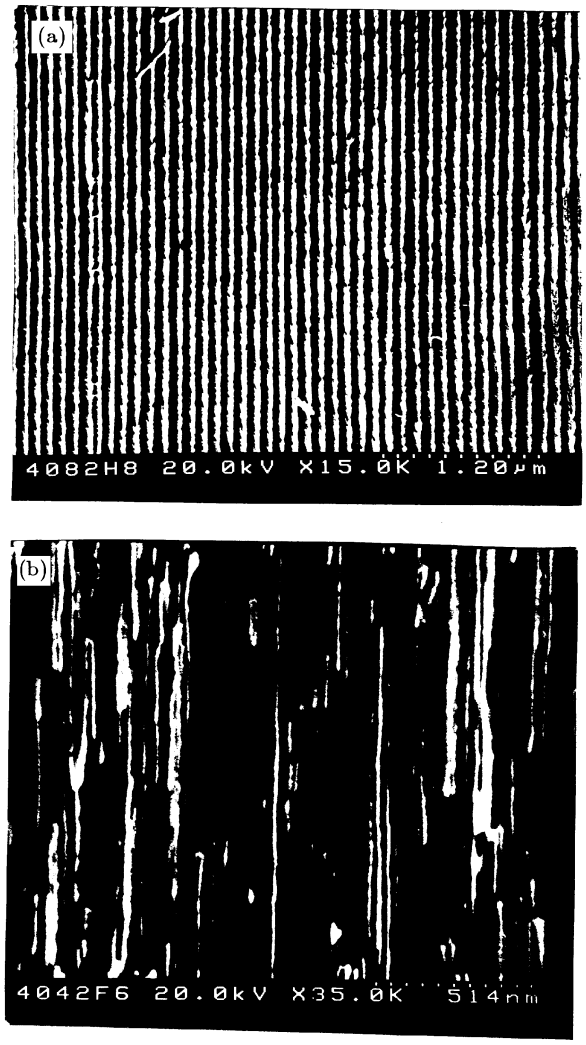


Fig.5. The cleaved edge of an ordered sample (a) and a disordered sample (b), both produced at 40 V anodizing voltage in oxalic acid followed by a pore widening process.

The thickness of the free standing porous alumina layer, which would be gained after removing the remaining aluminium substrate in saturated $HgCl_2$ solution, is proportional to the anodizing time. With oxidation time between two and four days, the layer

thickness between 100 and 200μm and aspect ratios (ratio of depth to diameter) of the pores of more than 1000 up to over 3000 could be obtained. When varying the second anodization period from 1 h to four days, the ordered pore and domain structures do not change. This means that a nanopore array grown from a patterned aluminium surface yields an ordered pore structure which closely resembles the pattern on the aluminium surface from which they grow. This implies that the nanopore arrays can also be grown from a prepatterned aluminium surface by means of electron beam lithography or nanoimprint techniques. The feasibility of patterning the aluminium surface by a molding process and preparing ordered nanopore arrays in the anodic porous alumina has been shown recently[8,11].

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