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1998 Jpn. J. Appl. Phys. 37 L1340

(http://iopscience.iop.org/1347-4065/37/11A/L1340)

Jpn. J. Appl. Phys. Vol. 37 (1998) pp. L 1340–L 1342
Part 2, No. 11A, 1 November 1998

Self-Ordering of Cell Configuration of Anodic Porous Alumina with Large-Size Pores in Phosphoric Acid Solution

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(Received August 20, 1998; accepted for publication September 16, 1998)

Large cell-sized anodic porous alumina with long-range ordering was fabricated using phosphoric acid solution. Self-ordering of the anodic alumina took place under long-period constant voltage anodization at 195 V, which generated the self-ordered anodic porous alumina with a cell size of 500 nm.

KEYWORDS: anodic porous alumina, channel array, self-ordering, phosphoric acid

Anodic porous alumina, which is formed by the anodic oxidation of aluminum has attracted much interest as a starting material for the fabrication of several kinds of functional devices with nanometer dimensions due to its naturally occurring nanometer-order channel array structure with a high aspect ratio.[1–7] The geometrical structure of anodic porous alumina is schematically shown as a hexagonally packed array of cylindrical cells at the center of which a straight hole is located (Fig. 1).[8,9] However, the cell configuration of the anodic porous alumina obtained under usual anodizing conditions is far from ideal; it has many irregularities and imperfections, and the degree of periodicity is low.[10] Improvement of the ordering of the cell configuration of anodic porous alumina is essential so that the performance of fabricated functional devices can be optimized.

In our previous reports, we described that cell configurations with long-range ordering are formed in anodic porous alumina under specific appropriate anodization conditions.[11,12] Several groups have also reported similar results concerning the self-ordering conditions for anodic porous alumina.[13–15] However, the cell size of the anodic porous alumina obtained by naturally occurring self-ordering has been limited to less than 100 nm, and the conditions for preparing anodic porous alumina with a larger cell size have not been clarified so far. Ordered porous membranes with large cells are important for applying anodic alumina in several areas, especially in the fabrication of optical devices used in the visible-IR wavelength region, *e.g.*, photonic band structures.[16] In the present report, we show for the first time the conditions for promoting the self-ordering of anodic porous alumina with a large cell size of 500 nm formed in phosphoric acid solution.

The cell size of anodic porous alumina, in other words, the pore interval, was determined by the applied voltage used for anodization;[17,18] the cell size has a good linear relationship with the applied voltage, where the proportionality constant of cell size per applied voltage is approximately 2.5 nm/V. In previous surveys, self-ordering has been observed to occur under limited voltage conditions that were specific to the solution used for anodization; self-ordering takes place at 25 V in sulfuric acid solution,[12] and at 40 V in oxalic acid solution,[11] corresponding to cell sizes of 65 and 100 nm, respectively. However, at higher anodization voltages, self-ordering of cell configuration was not observed in oxalic acid solution, and stable anodization of Al was difficult in sulfuric acid solution. In the present experiment, we introduced a phosphoric acid solution as the electrolyte, which is known to meet the conditions for anodization at relatively high applied voltage.

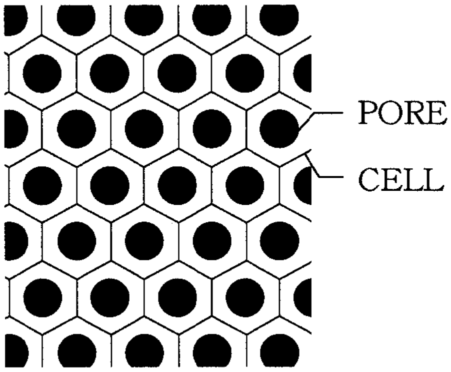

Fig. 1. Schematic drawing of the idealized structure of anodic porous alumina.

An aluminum sheet (10 × 50 × 0.3 mm: 99.999%; Nilaco) was electropolished in a mixed solution of perchloric acid [60%] and ethanol (1:4 in volume) at constant current conditions of 100 mA/cm^2 below 10°C for 4 min [caution: the mixture solution is explosive]. Anodization was conducted at constant voltage conditions using a DC source [Metronix 410A-350]. The temperature of the electrolyte was maintained at 0°C during anodization using a cooling system [EYELA CTP-20]. The solution was stirred vigorously using a magnetic stirrer in order to accelerate the diffusion of the heat that evolved from the sample. This treatment is important for preventing localized temperature increases and to maintain the stable growth of the anodic oxide film. Unless the appropriate level of agitation of the solution was maintained, localized heat generation disturbed the stable oxide growth and destroyed the formed oxide film. The anodization cell configuration was observed using a scanning electron microscope (SEM: JEOL JSM-6100) after removing the Al substrate in saturated $HgCl_2$, and the bottom part of the oxide film, called the barrier layer, in 10 wt% phosphoric acid solution. The pore widening treatment was carried out in phosphoric acid solution to make it easy to observe the cell configuration.

Figure 2 shows a SEM micrograph of the anodic oxide membrane with the typical self-ordered cell configuration which was formed under the most appropriate conditions in phosphoric acid solution. This micrograph was observed from the bottom side of the membrane after removing the Al and barrier layers sequentially. From this figure, an almost ideally arranged hexagonal cell configuration with a cell size of approximately 500 nm was observed.

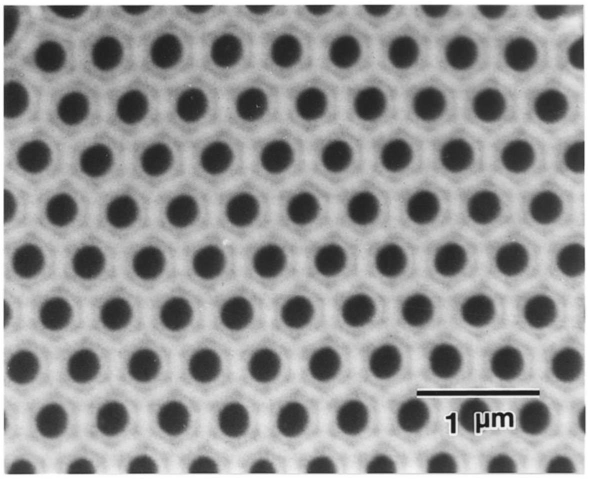

Fig. 2. SEM micrograph of the self-ordered hole configuration of anodic porous alumina obtained in phosphoric acid solution at 195 V. Pore widening treatment was carried out for 240 min in 10 wt% phosphoric acid.

The most appropriate conditions for the self-ordering obtained through the present experiment are summarized in Table I. The most important parameters for self-ordering were the period of anodization, and the applied voltage.

In Fig. 3, the dependence of the ordering of the cell configuration upon the time of anodization is shown. Self-ordering proceeded through the rearrangement of the cell configuration with anodization time. The cell configuration changed gradually from a random configuration at the initial stage of anodization (Fig. 3(a)) to a partially ordered configuration after steady-state cell growth (Fig. 3(b)), and an almost saturated configuration was obtained after anodization for 16 h (Fig. 3(c)).

The ideally ordered area of the cell configuration obtained after long-period anodization showed a domain structure at the boundary of which accumulated imperfections were observed. The size of the ordered area increased with the anodization time, taking in surrounding disordered cells, and attaining an almost saturated size in an area over 5 μm. The manner of change in cell configuration during self-ordering in phosphoric acid solution was similar to that in oxalic and sulfuric acid solutions except that the size of the ideally ordered area was larger than that in the other two acid solutions due to the difference in the size of a single cell.

Self-ordering of the cell configuration was also dependent on the applied voltage. The most appropriate anodization voltage was found to be 195 V. Figure 4 shows the cell configuration obtained under anodization voltages below 195 V. The thickness of the samples was adjusted to almost the same value (*ca.* 60 μm) as that of the film formed at 195 V (shown in Fig. 3(c)) in order to exclude the influence of the thickness on the ordering. At higher anodization voltages, stable long-period anodization was difficult because of the large amount of heat generated by the sample. In the anodization at 150 V, no self-ordering was observed (Fig. 4(a)), and the degree of self-ordering was low even on anodization at 180 V (Fig. 4(b)). This result implies that self-ordering takes place at a specific anodization voltage, and little or no ordering was observed without the appropriate voltage conditions. It is noteworthy that the appropriate anodization voltage in phosphoric acid solution was different from those in other solutions; the appropriate voltage is higher than in oxalic or sulfuric acid solutions. This property brought about the ordered porous alumina with large cells. Although the detailed mechanism for explaining the dependence of the ordering on the applied voltage is not clear at the present stage, strain-free cell growth is thought to take place under anodization at this voltage in phosphoric acid solution.

Long-range ordering of anodic porous alumina with a cell size of 500 nm was obtained using phosphoric acid solution. For membranes with straight through-holes, a two-step anodization process is available, which comprises a first long-period anodization for a highly ordered cell configuration, and a second anodization after the removal of the anodic ox-

Table I. Most appropriate anodization conditions for self-ordering in phosphoric acid solution.

Concentration of phosphoric acid	0.3 M
Temperature	0°C
Anodization voltage	195 V
Anodizing time	16 h

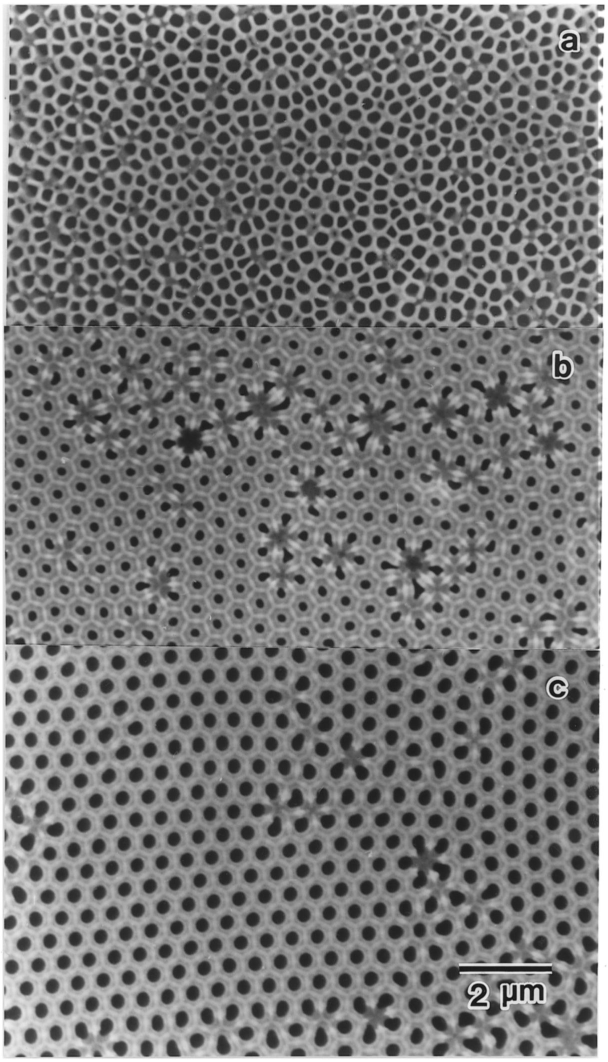

Fig. 3. Dependence of the self-ordering of the hole configuration on the time of anodization; 0.5 h (a), 4 h (b), and 16 h (c). The anodizing conditions were the same as those described in Table I.

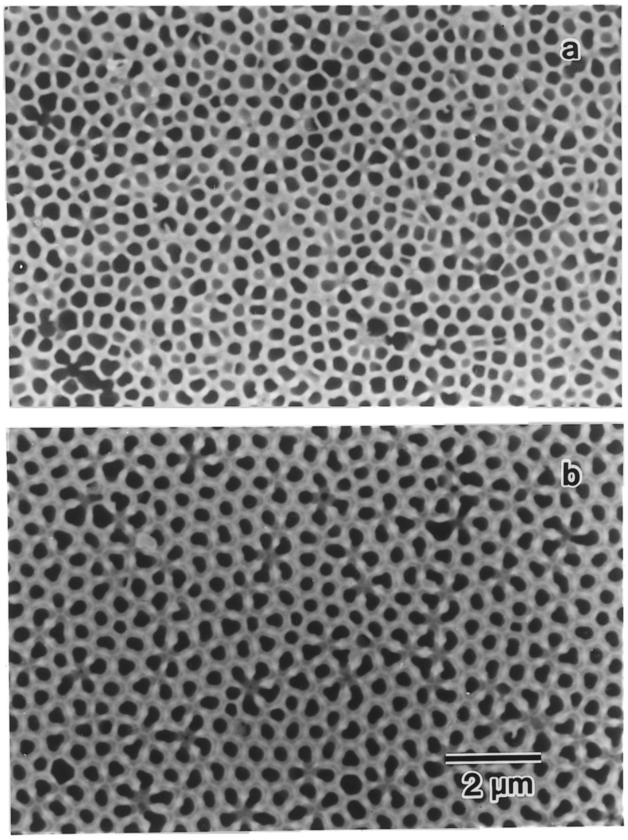

Fig. 4. SEM micrographs of the cell configuration of the anodic alumina formed at 150 V (a) and 180 V (b).

ide film that generates the ordered array of dimples on the Al surface, to introduce the development of an ordered array of holes.[19)]

The conditions for self-ordering described in the present report have much importance in the application of the naturally occurring structure of anodic alumina to the microfabrication of large cells where ordered anodic alumina has not previously been available. In addition, the present finding will contribute to the clarification of the detailed mechanism for self-ordering of anodic porous alumina.

Acknowledgement

This work was partially supported by a Grant-in-Aid in Priority Area of Electrochemistry of Ordered Interfaces (No. 225) and Scientific Research C (No. 10650813) from the Ministry of Education, Science, Sports and Culture.

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