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Novel Structure of AAO Film Fabricated by Constant Current Anodization**

By Shiyong Zhao,* Karen Chan, Arthur Yelon, and Teodor Veres*

Since Masuda and Fukuda's study of self-ordered porous alumina membranes by a two-step replicating process,^[1] anodized aluminum oxide (AAO) membranes have become one of the most common nano-templates for the preparation of nanowires,^[2–5] nanotubes,^[6] ordered arrays of nanoparticles,^[7] nanorings and nanocones.^[8] These AAO films are also widely used as filters,^[9] and as 2D photonic crystals.^[10]

The usual electrochemical method for producing the AAO film is the anodization of high purity Al plates at constant voltage, which provides only limited control over the pore spacing using different anodization conditions:^[11] 66 nm (0.3 M H₂SO₄, 25 V), 100 nm (0.3 M oxalic acid, 40 V), and 500 nm (0.1 M H₃PO₄, 195 V) and leads to a hexagonal pore array. Attempts have been made to create nano-porous AAO membranes with symmetries other than hexagonal packing.^[12,13] Krishnan et al.^[12] prepared AAO alumina membranes with a square arrangement of nanopores on Si substrates by using a square array of indentations. These were made by patterning and chemical wet etching of sites for forced anodization. Sun et al.^[13] obtained an AAO membrane with a square lattice of square nanopores using an anodized Aluminum film deposited on a photoresist-grating pattern developed on a silica substrate. Both approaches use indirect methods (mechanical indentation or lithography) in order to pre-process the substrates prior to anodization.

Nielsen et al.^[11] proposed a method for the fabrication of self-ordered porous alumina with the interpore distance customized using a 10 % porosity rule. They reported that long range ordering is possible if the applied potential, the main

determinant of the interpore distance, and the pH value of the electrolyte, which provides the primary control of the pore radius, are adjusted so that the membrane porosity is 10 %. Ono et al.^[14] reported that high current density or high electric-field strength is the key factor for the self-ordering of AAO films. Recently, Chu et al.^[15,16] and Li et al.^[17] have reported the fabrication of ordered AAO films with various interpore distances by using high fields and H₂SO₄ or H₃PO₄–H₂O–C₂H₅OH solutions. Lee et al.^[18] have recently proposed the so-called 'hard-anodization' approach^[19–22] for fast fabrication of AAO films, on which potentials of 100–150 V are applied in oxalic acid solution. To suppress breakdown effects and to permit uniform oxide film growth, an oxide layer (thickness > 400 nm) was formed on the surface of the aluminum substrate before the hard-anodization was carried out. Mosaic nanowire arrays fabricated with AAO templates would be very useful for functional electrodes, sensors, model catalysts and optical devices. For example, Masuda et al.^[23] have prepared ordered mosaic nanocomposites of Au and Ni in AAO film by pretexturing the aluminum. In this paper, we present a constant current method for producing AAO membrane, in which high current density was applied over the entire anodization time in order to prepare an ordered AAO film. This process leads to the formation of a novel AAO membrane with a six-membered ring symmetry co-existing with the usual hexagonal structure. The pore sizes of this structure can be tailored by changing the processing conditions. These new pore structures have great potential applications in nanomaterials fabrication, particular in the mosaic nanowire arrays.

Usually only low voltage (and low current) can be used for stable anodization in H₂SO₄ solution because of the occurrence of breakdown or 'burning' of the AAO film due to corrosive acid attack under a high electric field. Chu et al.^[15] found that the critical high anodizing potential, i.e., the breakdown or burning potential of AAO films in the electrolyte system adopted, increased with the ageing of the solution after a long period of anodization. By adjusting the state of H₂SO₄ solution by ageing the solution over a long period of anodization (10–20 A h l^{–1}), they obtained uniform AAO films in H₂SO₄ solution under a high electric field of 40–70 V and current density of 1600–2000 A m^{–2}. Considering that the ageing of H₂SO₄ solution results in the replacement of H⁺ by Al³⁺, we have used a solution of H₂SO₄ + Al₂-(SO₄)₃ instead. We have used a constant current method with current density of 160 mA cm^{–2}. The constant current promises the constant growth rate of AAO film, in contrast with that reported by

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Chu et al. In their work, the potential was kept constant during anodization while the current varied. Figure 1 shows the voltage-time curves of our constant current anodization. In the 0.8 M $\text{H}_2\text{SO}_4 + 0.1 \text{ M Al}_2(\text{SO}_4)_3$ solution, the voltage first increases gradually from 24 V to a maximum of 90 V at 27 min. Then, it decreases to 40 V. However, if the anodization is performed without $\text{Al}_2(\text{SO}_4)_3$, the anodic dissolution of Al in the 0.8 M H_2SO_4 solution is very fast. Even at a current of 160 mA cm^{-2} , the voltage stays at about 3 V. In that case, no ordered AAO film can form on the aluminum surface. Figure 2a is a bottom-view SEM image of an AAO film anodized in a solution of $\text{H}_2\text{SO}_4 + \text{Al}_2(\text{SO}_4)_3$ for 30 min at 1°C . The remaining aluminum substrate was removed in a mixed solution of HCl/CuCl_2 for 20 min. From Figure 2a it may be seen that the pores are closed and covered by hemispherical shaped caps, evenly distributed on the surface, in a hexagonal structure. This indicates that anodization with a constant current can be used to obtain ordered AAO templates. This is consistent with the results of Chu et al.^[15] The interpore distance is 85 nm. However, when the immersion time in HCl/CuCl_2 was extended to 40 min, smaller pores (diameter of 15 nm) located at all junctions of three cell boundaries (triple points) were found (Fig. 2b). These pores are arranged as a six-membered ring structure with an interpore distance of 50 nm. This structure has never been reported in AAO nanoporous membranes. The size of the pores can be controlled (increased) by increasing the immersion time (Fig. 2c, immersing time 60 min, diameter of 25 nm). The larger pores cannot be opened by immersion in the HCl/CuCl_2 solution. This can be done in H_3PO_4 solution. The SEM image of an AAO film is shown in Figure 2d after immersion in 5% H_3PO_4 solution at 30°C for 20 min. The entire barrier layer has been removed and two networks of nanopores are revealed. We can observe that each of the large pores (55 nm diameter) of the usual hexagonally packed network is surrounded by six smaller pores, arranged in a six-membered ring structure.

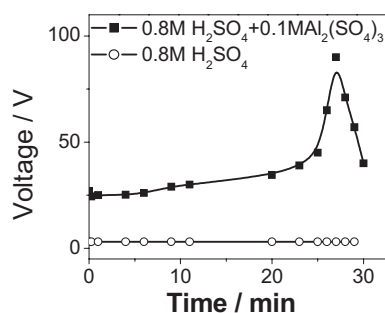


Figure 1. Voltage-time curves during the constant current anodization of Al with a current density of 160 mA cm^{-2} .

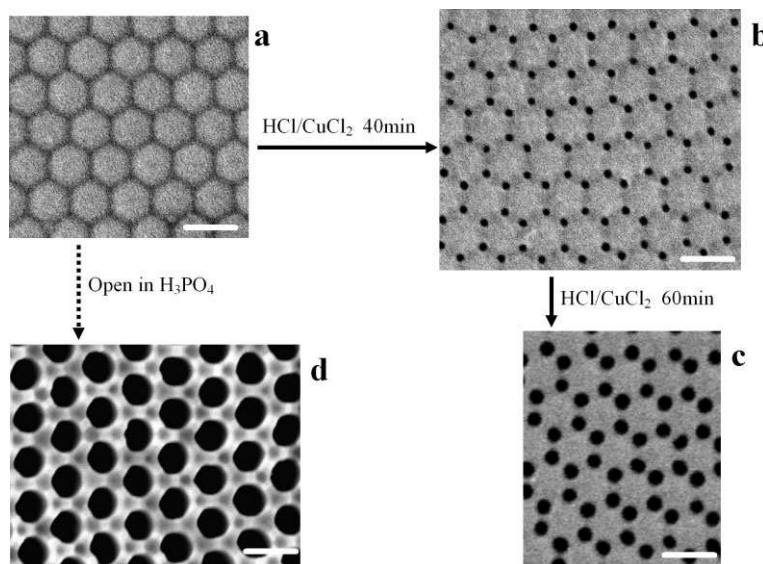


Figure 2. SEM of AAO with novel structure. a) Bottom view just after removal of the Al substrate in a mixed solution of HCl/CuCl_2 (immersion for 20 min), nanopores are closed; b) small (15 nm diameter) pores arranged in six-membered ring are revealed after a 40 min immersion; c) extending the immersion time to 60 min, the size of the pores increases to 25 nm; d) after immersion in 5% H_3PO_4 , the usual hexagonal structure of nanopores with 55 nm diameter and 85 nm inter-pore distance is revealed. The scale bar in the figures is 100 nm.

Figure 3a is a sectional image of the AAO sample, confirming that normal AAO nanopores (as shown by the arrows) having an interpore distance of 85 nm are closed, while the smaller pores (as shown by the open arrows) at the triple cell

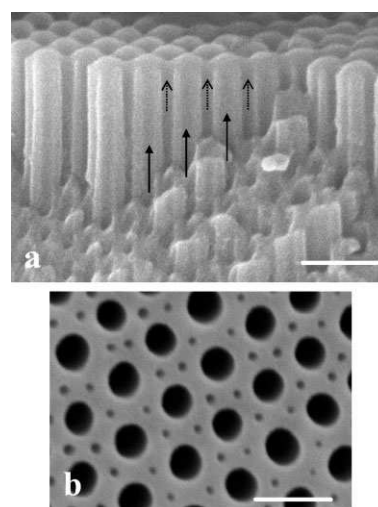


Figure 3. a) Cross-sectional SEM image of the AAO sample after immersion in a mixed solution of HCl/CuCl_2 for 40 min. This reveals that the six-membered ring structure pores are opened at the triple cell junction (indicated by the open arrows) of the hexagonally packed normal nanopores (arrows) which are still closed. b) SEM image of the top surface of an AAO film after immersion in 5% H_3PO_4 for 15 min at 30°C . The normal nanopores (40 nm diameter) are opened and circled by six small pores (15 nm diameter). The bars are 100 nm.

junction are already opened. The small pores belonging to the six-membered ring structure are formed at the bottom surface as observed in Figure 2 but span over the whole thickness (50 μm) of the AAO film as confirmed by the AAO top surface SEM image shown in Figure 3b.

In the work of Choi et al.,^[24] it was reported that the formation of new pores in AAO templates can be guided over a large area by pre-patterning of the Al film by imprint lithography. In preparing alumina nanotubes, Pu et al.^[25] found that after anodization with a high electric field (40 V in 15 % H_2SO_4 solution), voids were often observed at the junction of the cell boundaries. Chu et al.^[15] inferred that the aluminum oxide at the triple cell junction may not be as dense as the other parts of the cell walls, due to the circularly distributed expansion force (a repulsive force arising from volume expansion during film growth) from the centers of the alumina cells, leading to preferential dissolution of the triple junction. Mei et al.^[26] found that with high voltage anodization (40 V in 15 % H_2SO_4 solution), there is some hydrated aluminum oxide (e.g., $\text{Al}(\text{OH})_3$ or AlOOH) in the alumina nanotube walls. In 1991, Ono et al.^[27] had already found that the voids are only located at triple points in the AAO membrane and that the voids increase in size with increasing anodizing voltage. Macdonald^[28] proposed that the voids are produced by cation vacancy condensation below regions in the barrier film (triple points) characterized by high cation vacancy diffusivity, due to the high degree of lattice disorder. As the applied voltage is made larger, vacancy condensation will occur more rapidly, thereby resulting in larger voids.

Based on these reports, the formation of the symmetric six-membered ring structure can be explained as follows: during the constant current anodization process employing high current density or high voltage, voids are easily and rapidly formed at the triple cell junction site (Fig. 4Aa). Many voids are formed successively at the same triple point (Fig. 4Ab). These merge into a small pore (Fig. 4Ac), thus leading to the

formation of the six-membered ring of small pores (shown in Fig. 4Ba). Some voids or hydrated oxide should remain in the barrier layer of a small pore at a triple cell junction site. This hydrated aluminum oxide is easily dissolved in aqueous HCl/CuCl_2 solution; while the alumina barrier layer of the large pores is not. Thus, upon immersion in HCl/CuCl_2 the small pores opened and the six-membered ring of small pores observed, while large pores remained covered with the hemispherical barrier layer (Figs. 2b, c, 3a, and 4Bb). When the barrier layer of the large pores was removed by immersion in H_3PO_4 solution, the hexagonal cell structure of large pores was also revealed, with each large pore surrounded by six small pores as shown in Figures 2d and 4Bc.

The novel structure, with high pore density described here, may be used in the preparation of nanomaterials for sensing applications such as nanostructured SERS (surface enhance Ramen spectrum) and SPR (surface Plasmon spectrum) active surfaces for which the creation of ordered and closely packed arrays of metal (Ag, Au) nanodots is desired. We have developed an application of AAO films for the preparation of ordered nanoring and nanocone arrays using the conical openings of an AAO film as a mold.^[8] Figure 5 shows the AFM image of an Ag film e-beam evaporated onto and subsequently detached from the surface of an AAO film such as shown in Figure 2c. The nanopores are hexagonally ordered; around every nanopore, there are six nanodots which have the six-membered ring structure symmetry.

In summary, we have prepared a novel symmetry six-membered ring structure of AAO film by constant current anodization. The interpore distance is reduced from the usual 85 nm to 50 nm and this doubles the pore density. Ordered arrays of nanodots with novel structure have been fabricated by this AAO template. The pore diameter can be easily controlled by the HCl/CuCl_2 immersion time and the solution conditions. The investigations of six-membered ring structure

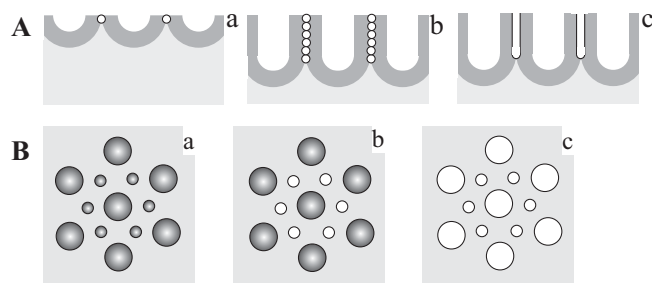


Figure 4. Schematic illustration of formation of A) small pores at the triple cell junction site: a) Voids formed at the triple cell junction site, b) many voids formed successively at the same triple junction, c) the voids formed successively at the same triple point merge into a small pore; B) novel six-membered ring structure of AAO: a) after anodization and removal of the Al substrate the two networks of nanopores are formed, but covered with hemispherical barrier layers; b) the barrier layer of the small pores is removed in a mixed solution of HCl/CuCl_2 , and the six-membered ring is formed; c) the barrier layer of the large pores is removed in a solution of H_3PO_4 , and all the pores are open-through.

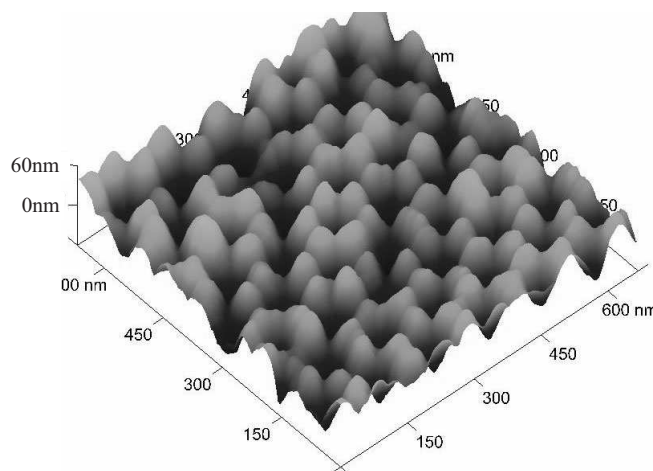


Figure 5. 3D AFM image of the surface of an Ag film e-beam evaporated onto the surface of AAO film with symmetry structure of six-membered rings then detached from the AAO film. The nanopores are hexagonally ordered, and the nanodots have a six-membered ring structure.

of AAO film with interpore distances smaller than 40 nm, and the fabrication of mosaic nanowire arrays with these AAO templates are in progress.

Experimental

99.999 % 0.50 mm Al foils (Goodfellow Cambridge Ltd.) were first degreased with acetone and etched in 1.0 M NaOH(aq) for about 1 min, until bubbles were observed over the surface. This was followed by electropolishing with a voltage of 12 V in a mixture of HClO₄ (70 %) and C₂H₅OH (1:3 v/v). The electropolished Al foils were subjected to anodization for 30 min in a solution of 0.8 M H₂SO₄ + 0.1 M Al₂(SO₄)₃. Anodization was carried out at a constant current density of 160 mA cm⁻². The temperature was kept at (1 ± 0.1) °C by a cold plate (Stir-Kool SK-12D). A big Al plate (3 × 3 cm²) was used as a cathode. After anodization, the remaining Al was removed in a solution of 19 % HCl/0.2 M CuCl₂. Scanning electron microscopy (Hitachi S-4800) was used to image the AAO films and determine their pore diameters and interpore distances. The Ag film was evaporated on the surface of an AAO film by a CMS-18 E-beam Evaporator (Kurt J. Lesker Company) with a voltage of 9.7 kV and a current of 60 mA. The rate of deposition was 0.1 nm s⁻¹. The purity of the Ag source was 99.99 %. The metal films can be detached from the AAO films directly or after immersion of the sample in a solution of 1 M NaOH for 5 min, since the Al₂O₃ film is easily dissolved in a basic solution.

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