# Nanostructure of the nanopores in anodic aluminum oxide films used as template to fabricate Ag nanowires

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Well-ordered nanoporous anodic aluminum oxide (AAO) templates have been prepared on aluminum substrates by a two-step anodization process. A voltage-controlled branching method was successfully used to thin the barrier layer of the AAO template. The nanostructures of the pores, the branched subpores, and the barrier layer in the AAO template were studied in association with the anodization process and barrier layer thinning methods. Results demonstrate the voltage-controlled branching method is a facile and effective way to thin the barrier layer. Uniform silver nanowires can be easily fabricated using alternating current (ac) electrodeposition into the pores of AAO after redressing the barrier layer.

## I. INTRODUCTION

In recent years, ordered nanoporous anodic aluminum oxide (AAO) has become a popular versatile template for the fabrications of nanoscale materials, such as ordered arrays of nanorods,[1,2] nanowires,[3,4] and nanotubes.[5–7] It is well known that porous AAO templates can be prepared with a normal electrochemical method by anodizing high-purity aluminum foils at certain anodic bias in various electrolytes. By 1995, Masuda and Fukuda[8] found highly ordered AAO templates could be easily obtained by a two-step anodization process, the pore size, pore density, and the thickness of the AAO template can be controlled by changing their anodization conditions.[9]

Compared to other porous templates that are self-assembled by surfactants and polymers, AAO is an ideal template because it consists of highly aligned nanopores with uniform shape and size.[10,11] However, to use such an AAO template to fabricate nanomaterials by the electrodeposition method, these pores array in the template should be in electronic conduct. However, in the anodization process, with the growth of porous oxide film on aluminum substrate to form AAO template, one thick barrier film also forms as a semispherical oxide layer on the bottom of the pore,[12] as illustrated in Fig. 1. This thick barrier layer is completely resistive, thus it is not possible to deposit metal inside the pores directly by electrochemical method.[13] Usually, there are two methods to improve this shortcoming caused by the barrier layer; one is to detach the AAO template from the aluminum substrate and subsequently remove the barrier layer by a chemical etching process.[14] Before electrodepositon, one metal layer is coated on one side of the free-standing AAO template and serves as a contact between template and electrolyte. The metal layer should be thick enough for handling. This method is best for materials longer than several hundred nanometers because the thin membranes needed for short nanomaterials are difficult to detach from the aluminum substrate intact. Another method is to thin the barrier layer at the bottom of the pores in the AAO template and provide a more preferential site for the metal to nucleate. The AAO template still remains on the aluminum substrate.[15] In this case, how to thin the barrier layer for electrical contacts, more specifically for electrical contacts formed of low resistance, is important to facilitate uniform electrodeposition of nanomaterials.

In this work, we describe a facile and effective method to thin the barrier layer through forming multi-branched subpores at the bottom of each pore by reducing the anodizing voltage in steps. Scanning electron microscopy (SEM) was used to evaluate the nanostructures of the pores, the branched subpores, and the barrier layer of the AAO template. The thickness of the barrier layer studied is associated with barrier layer thinning methods and nanowire growth. With the assistance of barrier layer thinning, uniform silver nanowires can be successfully deposited into the pores of AAO by alternating current (ac) electrodeposition.

## II. EXPERIMENTAL

The AAO templates were prepared with a modified two-step anodization process similar to the one found in Ref. 14. The high-purity aluminum sheets (99.999%)

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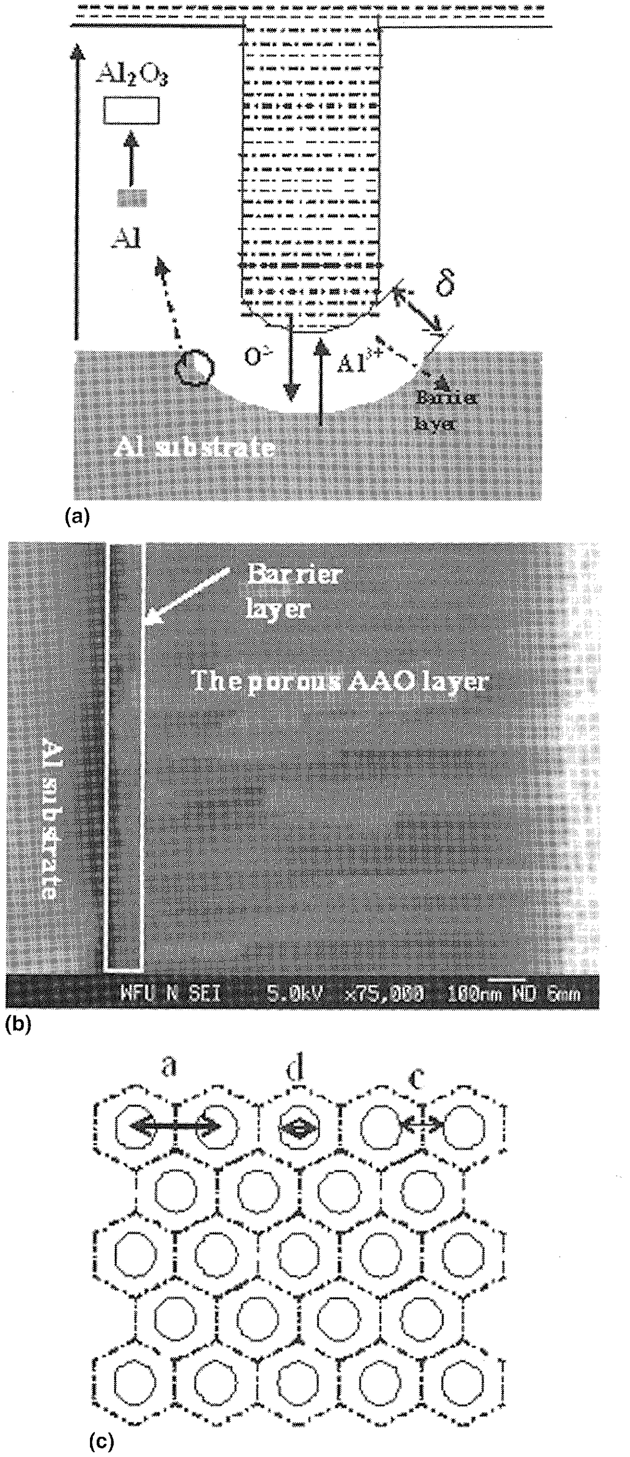


FIG. 1. (a) Model of the formation of a single nanopore. (b) SEM image of the cross section of AAO membrane with semispherical barrier layer at each pore bottom. δ, barrier layer thickness. (c) Schematic diagram of two-dimensional hexagonally ordered AAO pore array. *a* = interpore distance, *d* = pore diameter, *c* = 2× cell-wall thickness.

were cleaned, degreased, annealed at 400 °C for 3 h, and then electropolished in a 1:3 volume mixture of perchloric acid and ethanol at a current density of 100 mA/cm$^2$ and a temperature of 1 °C for 2 min. The aluminum is mirrorlike at the end of electropolishing. In the first anodization step, the electropolished aluminum sheet was anodized in a 0.3 M oxalic acid solution at 40 V and at 0 °C for 20 h. This preliminary oxidization layer creates dimples in the Al substrate that results in ordered pores during the second anodization. This AAO layer was removed by immersing the sample in a solution of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) until the AAO was totally etched and a shiny aluminum surface was obtained. The second anodization was carried out at 1 °C for about 1 h under the same conditions as the first anodizaion step. A highly ordered porous AAO template can be obtained by this two-step anodization process.

After the second anodization, the barrier layer was chemically etched by immersing the sample into a 5 wt% $H_3PO_4$ at 30 °C for 30 min. This process also etches the pore walls and results in larger pore diameters. The pore-widened AAO template was then anodized in a 0.3 M $H_2SO_4$ electrolyte at gradually reduced voltages to form multibranched structures.

The silver nanowires were electrodeposited into the pores of AAO by ac electrodeposition at 20 mA and 167 Hz in a solution of silver nitrate (2 g/L) and boric acid (20 g/L). After electrodeposition, the AAO template with silver nanowires was detached from the aluminum substrate with a solution of saturated $HgCl_2$. The 1.0 M NaOH solution was used to dissolve the AAO template and free the silver nanowires.

## III. RESULTS AND DISCUSSION

The formation mechanism of AAO membranes has been studied in detail for more than 50 years.[13] In the anodization process, an electrical circuit is built between two metal electrodes, in which an aluminum sheet serves as the anode. Figure 1(a) presents a model to describe the pore growth on the anode. During the anodization, a barrier layer forms followed by pore growth, which leads to the formation of the porous AAO array. This barrier layer remains throughout pore growth as a semispherical oxide layer with thickness (δ) at the bottom of each pore [Fig. 1(a)]. Figure 1(b) shows an SEM image of a porous AAO array. It is clearly seen that a semispherical barrier layer exists at each nanopore bottom. There are two active interfaces on the barrier layer, the $Al_2O_3$/electrolyte interface and the $Al_2O_3$/Al interface. The $Al_2O_3$/Al interface is associated with the oxidation of Al to $Al_2O_3$. During barrier layer growth (i.e., before pore formation), the $Al_2O_3$/electrolyte interface is associated with the dissolution of $Al_2O_3$ to the electrolyte and oxidation of $Al^{3+}$ ions that have migrated to the electrolyte interface. Pores grow perpendicularly on the surface. Under a constant applied voltage, when the $Al_2O_3$ dissolution at the $Al_2O_3$/electrolyte interface on the pore bottom is in

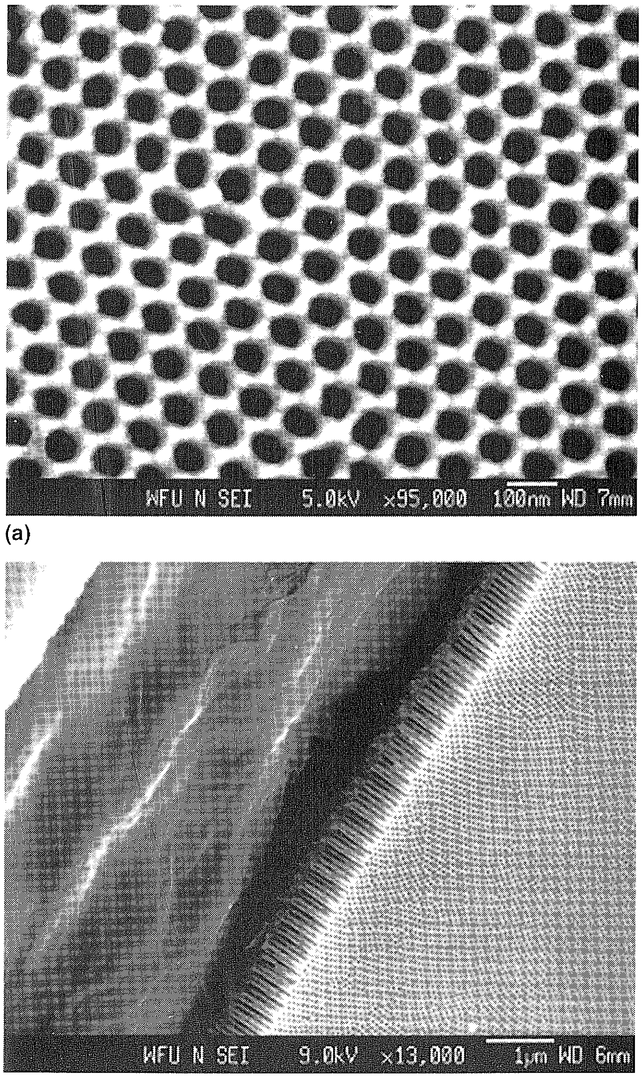


FIG. 2. (a) Top view and (b) cross-sectional view of pore structure in AAO template.

equilibrium with the formation of $Al_2O_3$ at the $Al_2O_3$/Al interface, the pore growth will reach a steady state with the same diameter and be self-organized in a two-dimensional hexagonally packed pattern, as shown in Fig. 1(c).

Figure 2 displays the SEM morphologies of the AAO template. Figure 2(a) is an SEM image of the top view of an AAO template showing the hexagonal pore arrangement. Figure 2(b) is a cross-sectional view of the template. The structural features of the porous AAO template (e.g., pore diameter, pore spacing, and thickness of the barrier layer) are highly dependent on the anodization voltage, electrolyte, and temperature. Figure 2(a) shows that the AAO template fabricated under our experimental conditions had pore diameters of about 50 nm and interpore distances of about 110 nm.

It is well known that porous AAO membranes on aluminum have a double-layered structure. A thicker porous layer is formed on the top, whereas a barrier layer is formed on the bottom at the interface between the aluminum and the oxide layer, as shown in Fig. 1(a). Efficient electrodeposition of a metal (e.g., silver) into the pores requires that the metal ions in the electrolyte are able to pick up an electron from the appropriate electrode. However, this barrier layer provides electrical resistance of AAO films, even for ac electrodeposition, electrons cannot form through such a thick resistant barrier layer into the pore; therefore, it is impossible to electrochemically deposit silver metal inside the pores. As discussed previously, the thickness of the barrier layer is one of the important dimensions of the oxide cell, which is proportional to the applied cell voltage. During the anodization process, the oxide dissolution and formation rate are in equilibrium in the barrier layer, thus the barrier layer thickness remains stable.

Usually, the barrier layer of alumina can be thinned a little by chemical pore widening and current limited anodization process. Here, we propose a convenient way to thin the barrier layer by dividing the stem pore into multiple branched subpores under consecutively reduced anodization voltages at the end of the second anodization process, and then followed by chemical pore widening. It is found that the barrier layer on the bottom of the branched pore structure can be easily thinned, which highly improves the electronic contacts between the pore and the substrate, and silver metal can be easily electrodeposited into the pore.

The ideal pore diameter is proportional to the applied voltage, but the relationship varies a lot with practical anodization conditions, such as using different acid electrolytes, running at different acid concentrations, and temperatures.[16] It must be pointed out that it is impossible to get highly ordered pore array by applying an arbitrary voltage. Different electrolytes have their own voltage region to produce ordered pore array.[17] As known, in oxalic acid a highly ordered pore array can be prepared between 40 and 50 V. However, in sulfuric acid the optimal anodization voltage is from 10 to 25 V. Under the same concentration of the electrolyte, the pore diameter anodized from oxalic acid at 40 V is about 45 nm,[11] whereas anodized from sulfuric acid at 25 V, the pore diameter is 20 nm.[18] Even at the same anodization potential, the pore diameter of the AAO membrane prepared from oxalic acid electrolyte is also different from that anodized from sulfuric acids.[19] For AAO template anodized from sulfuric acid electrolyte, its pore diameters were much smaller, the same as the thickness of the barrier layers at the bottom of the pores. In this work, we changed the electrolyte from oxalic acid to sulfuric acid to form the branched pore structures. The starting anodization voltage was 25 V for several

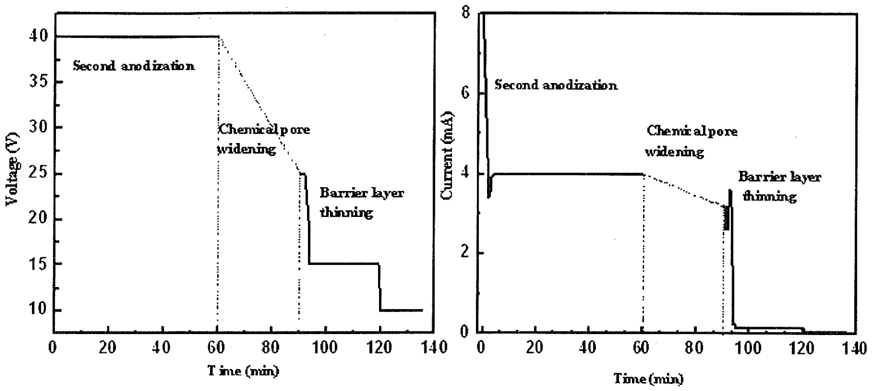
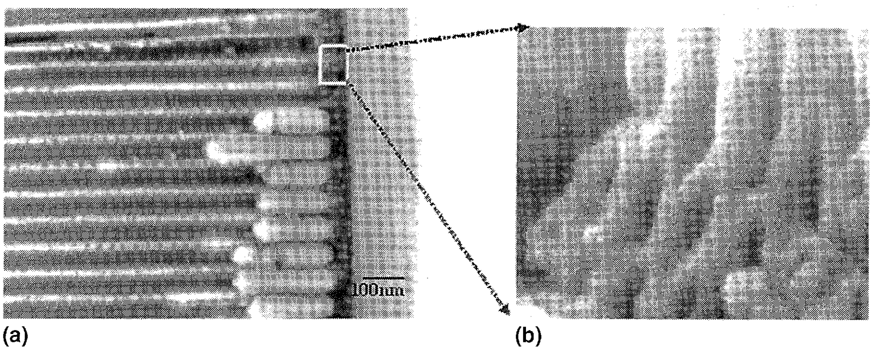


FIG. 3. Voltage-time and current-time curves for the second anodization, pore widening, and barrier layer thinning.



(a) (b)

FIG. 4. Cross-sectional images of pore structures in AAO template. (a) After forming multibranched pores and second pore widening. (b) The multibranched pore structure on the bottom, barrier layer is about 10 nm thick.

minutes, and then voltage was gradually decreased to 10 V, the voltage-time and current-time changes are illustrated in Fig. 3. The pore diameter, cell size, and barrier layer thickness decrease while the anodizing voltage reduces. As anodization proceeds, the process is in an equilibrium state and multibranched pores finally form (Fig. 4). With thinning of the barrier layer by the second chemical pore widening process, many tiny branches can be seen on the bottom of the pores.

Figure 3 shows plots of the voltage and current changes against time during the second anodization, chemical pore widening, and barrier layer thinning process. Initially, the second anodization of the structure is carried out at 40 V for about 1 h, and followed by chemical pore widening for 30 min in 5 wt% phosphorus solution at 30 °C; the pore diameter increases to about 50 nm, whereas the barrier layer decreases from 50 to 30 nm. Subsequently, anodization voltage is reduced gradually to form multibranched pore structures. The AAO template is then pore-widened for another 25 min. It is observed from the current-time curves that the anodizing current drops quickly at the beginning, which implies that there may be a sharp increase in resistance or the growth of a resistant oxide; after 2 min it reaches a minimum. At this point, a thin, nonporous $Al_2O_3$ film is formed on the surface of the aluminum substrate. As the anodization continues, an array of the pores starts to order on the thin, nonporous $Al_2O_3$ surface. The current remains in a steady state. Voltage is exponentially dropped to form the branched pores and thin the barrier layer at the bottoms of the pores. However, such drops let the current take a long time to recover before reaching a steady state. At the end of the thinning process, the current density is low, only 0.034 mA/cm$^2$.

Figure 4(a) gives the cross-sectional view of the pore structure after barrier layer thinning. The thickness of the barrier layer on the bottom of the branched pores finally becomes about 10 nm. It can be seen that each stem pore first divided into two branched subpores, then each branched subpores continuously divided into another two smaller subpores [Fig. 4(b)]. This multibranched pore structure between the alumina pore array and the aluminum substrate favors the formation of nucleation sites in each pore at the beginning of the electrodeposition. Figure 4(a) shows a lot of small bright spots inside the branched pores, which are small silver nanoparticles and are used as seeds for nanowires growth. After modifying the barrier layer, silver can be easily deposited into the formed AAO template by ac electrodeposition.

Figure 5(a) displays a top view of a highly ordered alumina pore array filled with silver. The silver nanowires are uniformly arranged in the hexagonal pores

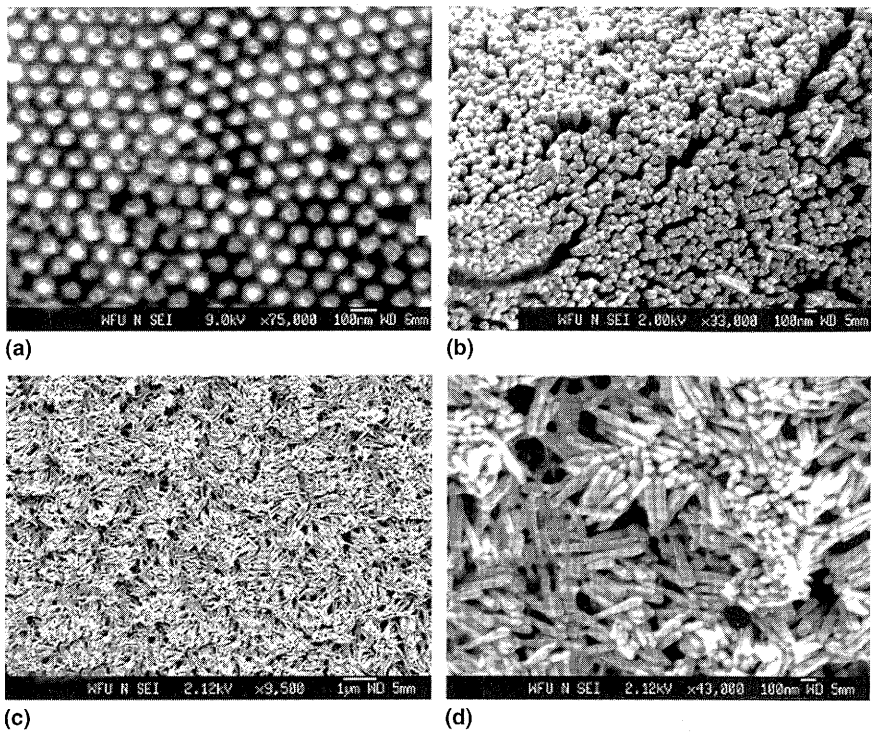


FIG. 5. SEM images of the prepared silver nanowires on the AAO template: (a) the top view of silver nanowires array with 50 nm diameter in the AAO template, (b) view from bottom after removing the barrier layer, (c, d) free nanowires with AAO template removed through etching.

with an average diameter of about 50 nm. Figure 5(b) shows the bottom view of the nanowire after removing the barrier layer. Silver nanowires can be released from AAO template by immersing the sample into 1M NaOH solution, as shown in Figs. 5(c) and 5(d). It can be seen that the length and width of the silver nanowires are uniform. The density of silver nanowires is close to the pore density of the original AAO template; this means almost every pore is filled with silver nanowire. The length of the nanowires can be controlled by the growth time or by raising the pore lengths with a longer second anodization time.

## IV. CONCLUSION

The pore and barrier layer structures in AAO template are investigated with SEM. The voltage-controlled branching method was successfully used to thin the barrier layer of the AAO template. Results show that this method of combining chemical pore widening is a very convenient and effective way to thin the barrier layer. After the barrier layer thinning process, the thickness of the barrier layer can be gradually decreased from 50 to 10 nm, and thus ordered silver nanowire arrays can be easily fabricated into AAO template. The sizes of the nanowires are very uniform. This successful growth of silver nanowires is indebted to the barrier layer thinning technology. Moreover, with the improved voltage-controlled branching method (run a long time in each voltage step), longer multibranched AAO template will be formed, which can be explored to fabricate more promising materials with complex and multibranched nanostructures.

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