EFFECT OF THE ELIMINATION OF THE BARRIER LAYER PERIOD IN PRODUCTIVE PROCESS AND ITS SIMULATION OF ABSORPTION SPECTRA FOR ANODIC ALUMINA MEMBRANE

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An anodic alumina membrane is produced in two levels by performing the anodization process in various type of acidic electrolyte. Holes are characterized by hexagonal structure of varying diameters (from 40 to 420 nm). The heat and chemical stability as well as the regularity of the formed holes make the membranes appropriate for use in gas separating process, drug delivery and for fuel cell membrane applications. Detachment of the membrane from the aluminum base is the most important step in the membrane production process. In this research, initially, the synthesis of the aluminum based layer omitted the use of $CuSO_4$ and HCl. In the second step, the barrier layer at the end of the holes was removed via treatment with an aqueous phosphoric acid solution. The aim of this work is to analyze the effect of time upon the barrier layer removal process and, assuming that we have added gold to the alumina membrane, i.e. the alumina membrane has its empty pores filled with gold, simulations were done in order investigate its absorption spectra. Simulations were done using the FDTD method for all structures evaluated. The values for the structures' absorption and their spectra were calculated and plotted. In the case when the aluminum membrane pores are filled with gold, the curve of gold absorption spectrum has the highest absorption, so in practical terms, this means that making this membrane can have different applications.

Keywords: Anodizing, Alumina, Membrane, Absorption spectra, Removal of the barrier layer and Simulation.

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1. Introduction

The initial use of anodized aluminum occurred in the last century. The anodic behavior of aluminum was intensively investigated to obtain protective and attractive films on its surface. Currently, anodizing is defined as an electrochemical process of converting metal (usually aluminum) to metal oxide on the metal surface. The electrochemical anodizing cell consists of a cathode, an anode (the metal substrate to be converted to metal oxide) and a direct current (DC) power supply. The anodic aluminum oxide thin film starts to grow at the anode (aluminum surface) as the anodic current or voltage is applied [1, 2].

An anodic alumina membrane (AAM) can provide a simple template for the deposition and growth of various materials with ordered structure. A new bi-level method of anodizing for the synthesis of porous aluminum oxide with regular structure in oxalic acid was invented by H. Masuda in 1995 [3]. Since then, scientists have tried to discover new ways to synthesize this structure with different features.

The success of anodic alumina membrane is owed to its attractive physical and chemical properties: its ceramic temperament involves high thermal strength (up to several hundred degrees) and excellent chemical insensitivity in many environments (within the pH range of 5 to 9). It has highly-ordered nanopores with controllable and uniform dimensions arranged in a close-packed hexagonal framework. Anodic alumina membranes with pore diameters ranging from 4 nm to 420 nm, density as high as 10^{11} pores/cm², and film thickness variable from 0.1 μ m to 300 μ m has been obtained using two-step anodization or nanoimprint methods. These materials can be synthesized in slightly soluble electrolytes such as sulfuric, phosphoric and oxalic acids [4, 5].

The synthesis of nanomaterials such as polymeric nanowire, metallic nanowire [6], 3D nanodots [7], polymeric [8] and metallic nanotubes [9] and others provides many potential research directions for anodic alumina membrane, also because it can be used as membrane in various applications such as gas separation [10], drug delivery [11], membrane in solid acid fuel cell [12] and solar cells [13].

A key difficulty encountered in the above-mentioned applications is how to attain through-hole porous anodic alumina which is previously produced on an alumina barrier layer covering aluminum substrate in the anodization process. Wet chemical etching, based on H₃PO₄, is commonly viewed as the most reliable method for custom pore opening of AAM [14, 15]. The difficulty of this method is that the process of pore opening is controlled by the etching time, usually from 50–90 minutes. Different etching conditions such as concentration of H₃PO₄ (5–10 wt %), temperatures (25–50°C) have been reported for pore opening of AAM, but there are no details on how these variations affect the pore diameters of AAM [14,15]. One aim of this work is to analyze the effect of time on the barrier layer removal process. Another aim is to perform simulations assuming that gold has been added to the membrane, i.e. the empty pores are filled with gold, in order investigate its absorption spectra. The morphological modifications were monitored by Scanning Electron Microscopy (SEM) and Clemex software.

A hemispherical shell with homogeneous thickness known as the barrier layer develops at the bottom of every nanopore during the anodization process. To date, this barrier layer has not attracted much attention in the literature, even though many applications require its removal to create through-hole membranes. Examples for such applications include energyefficient gas separation and pattern-transfer masks for e-beam evaporation, [16] reactive ion etching, [17] or molecular-beam epitaxial growth. [18] Through a carefully controlled barrier layer etching process, one can systematically prepare a tunable pore opening. Three methods have been used to open the barrier oxide layer: wet chemical etching, [3,20] ion milling, [19] and plasma etching. [17] Of these, the wet etching has been regarded as difficult to control and only ion milling has received more detailed analysis in the literature. [19] Both ion milling and plasma etching have the advantage of maintaining intact pores after barrier layer removal, but require expensive equipment, and a typical setup allows only a small area around 1 x 1 mm to be removed at any given time and, thus, they are cost- and time-intensive. Wet chemical etching, when properly controlled, can be used to etch samples with larger dimensions (for example, 2 x 2 cm) and is fast, convenient, inexpensive, and reliable. This method has been used routinely in our laboratory for opening the barrier layers of AAO membranes. Experimental results show that if the chemical etching is done with proper control, 10– 95 nm openings in the barrier layer can be obtained systematically for AAO membranes generated in oxalic acid. In addition, very interesting double hexagon nanostructures were observed for the first time through AFM imaging before complete removal of the barrier layer. These nanostructures reveal the impurity distribution in the membranes that bear significant implication for catalysis and sensing applications [21].

During anodization, a U-shaped aluminum oxide layer or barrier layer with a thickness of 30–40 nm forms at the bottom of every nanopore. A protective polymer layer made of a mixture of nitrocellulose and polyester resin was coated on the top surface of the AAO membrane that is opposite to the barrier layer to prevent overetching of the surface structure and uneven diffusion of acid into the nanopores.[22]

2. AAO Barrier Layer

2.1. AAO Barrier Layer Opening

In addition, the membrane was then immersed in 200 mL of 5.00 wt% phosphoric acid at 30.0°C for different periods of time, rinsed with distilled water, and dried under ambient conditions. The barrier layer removal and pore widening process was then studied with use of atomic force microscopy (AFM) (Digital Instruments, Dimension 3000 with a type IIIa controller and TESP Si cantilevers) and SEM (Hitachi S-4700-II). Effective pore diameters were determined by analyzing the total pore area of each image using Scion Image based on NIH Image to ascertain the average area per pore and, hence, the average pore diameter [21].

This study utilizes a freestanding anodic aluminum oxide (AAO) film with a protective polymer layer made of a mixture of nitrocellulose and polyester resin on the porous side of the film [22]. The polymer layer is used to block the pores and thus prevent uneven etching of the AAO barrier layer from inside, which may be caused by the uneven acid diffusion through the AAO pores. The presence of the protective layer also focuses the etching process on the bottom side of the barrier layer, which is comprised of a hexagonally close packed array of hemispherical domes that are 120 nm in diameter and 27 nm in height (Fig. 1a). The domes begin to shrink both in diameter and height once the etching process starts. After 18 min of etching, the domes have decreased in size to approximately 100 nm in diameter and 24 nm in height (Fig. 1b). It is interesting to note that, at this early stage of the etching process, the walls of each individual cell are becoming more pronounced, which suggests that the area in-between individual domes is not etched as quickly as the domes themselves. This trend continues through 30 min of etching, with the domes continuing to decrease in size (85 nm in diameter and 16 nm in height) and the hexagonal cell walls becoming clearly visible to form a double hexagon nanostructure (Fig. 1c). After 40 min of etching, the barrier layer is finally breached by the acid (Fig. 1d). Note that the initial opening is uneven across the surface. The majority of the cells have an opening of ~ 10 nm, while some of the cells remain closed. While the aluminum surface used to create the AAO membrane was annealed and electropolished before anodization, the surface still maintains a certain degree of roughness. This roughness translates into a subtle variation in the thickness of the barrier layer [23]. Those domes that are thinner would obviously be etched through earlier. It should also be noted that the walls of each individual cell have become distinct enough to completely encircle each dome. Once the domes have been breached initially, the openings begin to widen to generate a unique surface topography which combines a hexagonal cell wall surrounding each opened dome. This process can be used to create membranes with a wide range of pore diameters with fixed pore-to-pore distance, from sub-10 nm, to 34 nm, to 48 nm, and to 70 nm just by terminating the etching process at 40, 50, 60, and 70 min, respectively (Figs. 1d-1f and Fig. 2a). The pronounced hexagonal walls persist through the entire procedure, even after the barrier layer has been completely removed at 70 min of etching [21].



FIG. 1. Stages of chemical etching process of the anodic aluminum oxide barrier layer. Etching progress after (a) 0 min, (b) 18 min, (c) 30 min, (d) 40 min, (e) 50 min, and (f) 60 min [21]

Note that the two techniques give fairly consistent results, especially before the complete removal of the barrier layer. From 40 to 90 min of etching, the pore opening rate is about 1.3 nm/min, but the following pore expansion rate is much slower, at about 0.5 nm/min. This is attributed to the fact that the barrier layer is the growth front of the anodization process; [24] it is constantly building up and redissolving. This action allows the oxalate



FIG. 2. AFM topography and phase images of the AAO membrane after (a and b) 70 min and (c and d) 90 min of etching

anion (Ox), $C_2O_4^{2-}$, and H_2O to be mixed with the alumina within the barrier layer, leading to a less dense composite material, Al_2O_3 mixed with $Al_2(Ox)_3$ [21].

The results, as seen in Figure 3(measured by SEM), show that there are also two different regimes. The first regime, which runs from 10 to 60 min, shows the pore diameter increasing at a rate of 0.93 nm/min, which means the cell walls are etched at a slower rate than the domes of the barrier layer (1.3 nm/min). As can be seen from Figure 3, the change in diameter versus time is fairly linear. The second regime, which begins at 60 min, has an etching rate of only 0.17 nm/min. The two different etching rates clearly indicate that the cell wall is comprised of two different material layers. Earlier studies of AAO have suggested that there is a measurable difference in the alumina of these two areas arising from the entrapment of conjugated base anions in the alumina near the pore [25].

Figures 4a and 4b show the section analyses of the AAO membranes just before (30 min etching) and after (50 min) the barrier layer was breached, respectively. The doubledip features with 25 nm separation and 2.5 nm height at the 30 min etching (Figure 4a) and 31 nm separation and 2.9 nm height at the 50 min etching (marked in Figure 4b) are clearly observed in both figures and indicate the boundary of pure alumina between the cells as depicted schematically in Figure 4c. In addition, the two types of alumina as indicated in the cell wall of Figure 4c can be observed from the AFM phase imaging technique, which is sensitive to changes in elastic modulus and surface hardness of the AAO membrane. The



FIG. 3. Etching of the barrier side (\bullet , SEM; O, AFM) and front side (*, SEM) of AAO membranes in 5.00 wt % H₃PO₄ at 30.0°C

cell wall nanostructures can be observed from both topography (Figure 1c-1f) and phase imaging (not shown here). At the early etching stage (18 min, Figure 1b) and just after the barrier layer has been removed (70 min, Figure 2a), while topography imaging simply showed the actual cell size and shape, phase imaging continued to reveal the underlying cell wall nanostructures. As shown in pseudo color (Figure 2b, 70 min), the contaminated alumina is indicated with light blue next to the dark blue pore, while the pure alumina of the cell wall, which is harder than the alumina near the pore, is indicated as pink. As the pores are etched further (90 min etching, Figure 2c), this contaminated layer is quickly removed, leaving behind only the pure alumina wall indicated as blue walls in Figure 2d and empty pores in green [21].

2.2. Implications of the Barrier Layer

If the barrier layer was made of concentric layers of the same material throughout the whole curvature, the whole barrier layer should be etched away all at once under homogeneous etching without diffusion limit, which is not supported by the aforementioned observation. It is quite obvious from Figure 1d-1f that the barrier layer is first breached at the very top or center of the domes, and then the small opening is gradually enlarged and eventually the whole dome is etched away as the chemical etching process proceeds. Based on our etching results, the barrier layer cannot consist of simple concentric layers with different purities [21].

Pore opening and removal of the oxide barrier layer by wet chemical etching is the last and most critical step in the fabrication of AAO with through-hole pore morphology. The time controlled etching method is dependent on many parameters that can't provide reproducible pore diameters of fabricated AAO. The removal of the AAO barrier layer was performed using a two-half permeation cell assembled with disposable plastic cuvettes with a hole in middle of the cell (Fig. 5.) AAO is sandwiched between the two cells and sealed using flat silicon rubber with a hole that corresponds to the hole in the cuvettes. The cells were then filled, by the etching solution (5 wt % H₃PO₄) for the cell that faces AAO with



FIG. 4. (a) Section analysis of AAO membrane at 30 min etching (same sample as Figure 2c) showing a cross section of the barrier layer and the double-dip feature. (b) Section analysis of AAO membrane at 50 min etching (same as Figure 2e) showing the collapsed dome and the double-dip feature (marked with red arrows). (c) Schematic drawing of the bilayered cell wall (gray area, oxalate contaminated alumina; white, pure alumina), the barrier layer (shown with thicker oxalate contaminated layer), and the double-dip feature observed during etching

oxide barrier layer, and by KCl (0.2 M) for the second cell with front surface of AAO. A small voltage 1.5-2V is applied between two platinum electrodes immersed in both cells, and both solutions were stirred using a magnetic stirrer [26].

To investigate how structural changes during the pore opening process correlate with pore opening curves, a series of SEM images of the barrier oxide layer were taken at different time intervals representing different stages of barrier layer dissolution, and presented in Figure 4. The SEM image (Fig. 4 a) of the barrier layer after about 25 minutes of etching didn't show morphological differences in comparison with structures before etching (Fig. 2 a). Characteristic black spots seen in the middle of the cell verify that the initial dissolution process starts at the top of the convex domes of the barrier layer. These spots suggest that



FIG. 5. Schematic diagram of the method for controlled dissolution of anodic aluminium oxide (AAO) barrier layer that combines wet chemical etching and electrochemical detection of the pore opening

the barrier layer is not homogenous and that dissolution of oxide layer is more extensive at the top than at the edge of AAO cells. Similar results are reported in previous studies describing the underlying black layer as electrolyte-rich alumina [27, 28]. A structure of the barrier layer after 42 minutes of etching or 2 min after the pore opening point was detected is shown in Figure 4 b. From the pore opening curves we expected to see very small holes in the centre of the cell as an indication of the initial pore opening and progressive dissolution of black spots. However, this initial breaching of the barrier layer was not clearly visualized by SEM images, likely due to the limitation of the SEM technique to observe structures less than 5 nm [26].

3. Materials and method

3.1. Anodic alumina membrane production

AA1057 aluminum (diameter 14 mm, thickness 0.3 mm) was used as the starting material. Active surface diameter of the samples was 10 mm. The samples were disc-shaped to minimize both the uneven electric field during Electro Polishing (EP) and anodizing, and the undesirable effects of heat treatment such as remaining stress. Before anodizing, the aluminum was degreased with acetone and then annealed at 450°C for 15 min. During the EP, the aluminum specimens were electropolished in a mixture of ethanol-perchloric acid solution (1:4) at 35V for 1 min. To speed up the anodization, a poly-ethylene chemical reactor was designed to treat 4 specimens simultaneously. The temperature of the electrolyte was maintained at $17\pm0.1^{\circ}$ C by means of isotherm Lauda circular bath (RE106). Anodic alumina membranes were prepared in a two-step anodizing process. In the first step, aluminum specimens were anodized in 0.3M oxalic acid (C₂H₂O₄) electrolyte 40 V and 17°C. After 15 h of anodization, the specimens were immersed in a mixture of 0.5 wt% H₃PO₄ and 0.2wt% H₂CrO₄ at 70°C for 6 h to remove the alumina layers. The aluminum specimens were then anodized again for 24 h under the same anodization conditions used previously.



FIG. 6. SEM images of a bottom surface of anodic aluminium oxide (AAO) with the barrier film before pore opening. AAO was fabricated by anodization at 40 V, temperature -0.5° C in 0.3 M oxalic acid. a-b) Low and high-resolution image of the top topography of barrier layer with an array of highly ordered hexagonal cells. c-d) Cross-sectional images showing internal pore structure with the barrier layer at the top. Bar scale is 100 nm

The Current-Time diagram of the 2nd anodizing at different voltages was drawn using multimeter (Lutron 801) software. The film thickness was measured by using a scanning electron microscope (SEM, XL30, Philips Company). Since the layers are fragile, they are deeply cracked when curved. Hence, the thickness of oxide layer will be observed more easily using Scanning Electron Microscopy. X-Ray Diffraction (XRD) patterns of AAM were obtained by Philips PW1140 system. Using Clemex software, the pore diameter distribution diagram, the average pore diameter and the number of pores per unit surface of samples were measured. A saturated solution of copper sulfate and perchloric acid was used for dissolving the metallic base. Then, the membrane was immersed in 100 mL of 5.00wt% phosphoric acid at 30.0°C for different periods of time (30 min, 60 min and 90 min). Finally, assuming that we have added gold to the membrane, i.e. the alumina membrane has its empty pores are filled with gold, simulations were done in order investigate its absorption spectra.

4. Simulation and results

Further recent work investigated the behavior of gold nanorod arrays coupled with a semicontinuous nanoparticle film developed using AAM substrates as templates. Nonlinear enhancement effects occurred upon plasmonic coupling and interference between a percolating Au nanoparticle film and a free standing Au nanorod array [29]. In this paper, in addition to analyzing the effect of time on the barrier layer removal process, we also performed simulations assuming that the aluminum holes are filled with gold. Simulations were done using the finite-difference time domain (FDTD) method, assuming the alumina membrane has had its empty pores filled with gold. These simulations were performed in order to evaluate the absorption spectrum. In this work, we used a structure with the following properties (Fig. 8):

1. the surface underside had the following dimensions: $X = 10.18 \ \mu m$ and $Y = 6.2 \ \mu m$ depth 1 μm and was made of aluminum.

2. the structure had a total of 71 holes with depth of 0.5 μ m and empty / full of gold.

3. the layer's upper surface , including the walls between the holes, is made of Al_2O_3 .



FIG. 7. Scanning electron microscopy (SEM) images of the barrier oxide layer obtained during different stages of chemical etching process of anodic aluminum oxide (AAO). AAO was fabricated by anodization in 0.3 M oxalic acid at 40 V and -0.5° C. Etching condition was 5 wt % phosphoric acid at 25°C. SEM images of barrier oxide layer after etching of a) 25 min, b) 40 + 2 min, c) 40 +12 min, d) 40+22 min, e) 40+32 min and f) 40+ 52 min. The etching time t = 40 min was determined as the average pore opening point



FIG. 8. Aluminum structure with empty / full of gold holes, a) in the two dimensions and b) in the three dimensions



FIG. 9. Source (Aluminum structure with empty holes)[2D]



FIG. 10. Source (Aluminum structure with empty holes)[1D]

When using the FDTD method, all structures had mesh dx=dy=dz=0.05 μ m and were done with times of 100 fs. Light or Gaussian wave with domain 2, phase 0, pulse length of 45 fs, frequency of 650 THz and a radiation angle of 55° to the surface. All the boundary conditions are perfectly matched layers (PML). The magnitude of the structure's absorption and its spectrum were calculated and plotted. In the empty holes or source state (aluminum structure with empty holes), its spectrum and diagram are shown in Fig. 9 and 10, and field on the aluminum membrane surface[2D] shown in Fig. 11 and 12, also In the state where Au occupies the holes, its spectrum and diagram are shown in Fig. 13 and 14.

In the beginning of the gold absorption spectrum curve, shown in Figure 13 (Wavelengths greater than 20 μ m) the amount of absorption is very trivial and with a slight increase in the wavelength, the absorption increases until it reaches a maximum slightly above 22 μ m. After that maximum, with increasing wavelength, the absorption is reduced, finally reaching



FIG. 11. Field on the Aluminum membrane surface[2D]



FIG. 12. Field on the Aluminum membrane surface[1D]



FIG. 13. Total absorption of the Aluminum membrane according to wavelength



FIG. 14. Total absorption of the Aluminum membrane according to frequency

a plateau for wavelengths greater than 27 μ m, where the absorption values remain fairly low and constant. When comparing the curves of gold absorption spectrum, one can clearly say that in the case when the aluminum membrane pores are filled with gold, the curve of gold absorption spectrum has the highest absorption, so in practicality, this makes the membrane amenable to different applications.

5. Conclusion

Porous alumina membranes were prepared in a two-step anodizing process. In the first step, aluminum specimens were anodized. After 15 h of anodization, the specimens were immersed in a mixture for 6 h to remove the alumina layers. The 2nd anodizing at different voltages was drawn using multi-meter software. The aim of this work was to analyze the effect of time on the barrier layer removal process. Additionally, simulations were performed using the FDTD method, assuming that gold occupied the once-empty pores of the model membrane. This was done in order to investigate its absorption spectra. Adding gold to the holes of an anodic alumina membrane causes its absorption spectrum to change. We note that the absorption spectrum of an anodic alumina membrane will have the greatest absorption by the results of the simulation done when gold was added to the anodic alumina membrane.

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