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EXPERIMENTAL INVESTIGATION ON THE BI-DIRECTIONAL GROWING MECHANISM OF THE FOILS LAMINATE APPROACH IN AAO FABRICATION

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ABSTRACT

The foils laminate approach can be implemented to grow bi-directional porous pattern from both the top and bottom surfaces of an aluminum foil. It was intuitively inferred that leakage of the etchant between the foils may a feasible cause to have the upward pores grow in the notches of the unpolished surface. The leakage blocking and triple layers laminate experiments were conducted to verify this hypothesis. Experimental results disprove this leakage hypothesis. It is further inferred that the applied electric field pulls the oxygen ions of the electrolyte in penetrating the constant thickness barrier layer to oxidize the aluminum metal and fabricate the bottom porous array. Experiments with the process time being reduced by two hours validate this inference.

1. INTRODUCTION

Anodic aluminum oxide (AAO) membrane, having nano-size porous array of regular hexagonal-shaped cells with straight columnar channels, has been widely used as the template in fabricating one-dimensional nano materials which have controllable orientation [1-5]. However, applications of an unpatterned AAO membrane are restricted due to its densely packed pores. The recent focuses of the AAO techniques have been on growing desired patterns on the porous array [6-10].

Wang and Peng [11] developed a laminate foils approach to bi-directionally grow pores from both the top and the bottom surfaces of an aluminum foil.

Ideally, the bottom surface was tightly clamped together with the top surface of the lower aluminum sheet; therefore, there should not be pore at the bottom surface of the upper aluminum sheet. It was intuitively deduced that leakage of the etchant between the foils may a feasible cause to have the upward pores grow in the notches of the unpolished surface. However, the leakage hypothesis needs to be further confirmed.

2. FOILS LAMINATE METHOD [11]

The foils laminate procedures include aluminum foil preparation, electropolishing, aluminum foils clamping, anodization, and aluminum foils separation.

(1) Aluminum foils preparation

The aluminum is annealed at 400 °C for 3 hours, vibrated by a supersonic vibrator for 1 min, then was cleansed with ethanol to degrease the surfaces.

(2) Electrolytic polishing

The aluminum foil is dipped into a bath solution in which the aluminum metal is electrically anodic.

(3) Aluminum foils clamping

The polished aluminum foil is vibrated with a supersonic vibrator for 1 min, and then is cleansed with ethanol to degrease the surfaces. Clamp two aluminum

foils tightly together with a Teflon clumper as schematically illustrated in Figure 1.

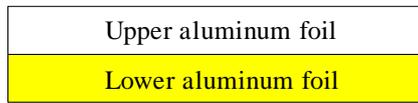


Figure 1. Schematic illustration of the aluminum foils clamping

(4) Anodization

Anodization is carried out under conditions of constant voltage 60 V in a 0.3 M oxalic acid solution at 0 °C for 7 hours and being stirred by a magnet. After anodization (Figure 2), the sample is rinsed again with DI water, and then is dried with ethanol.

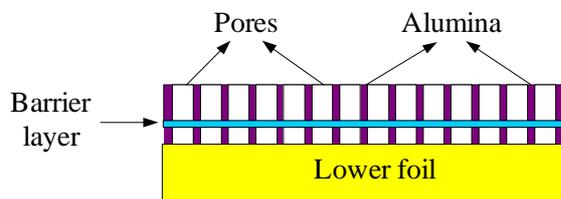


Figure 2. Anodized aluminum foils

(5) Aluminum foils separation

Take apart the lower foil to obtain a patterned nanopore alumina (Figure 3).

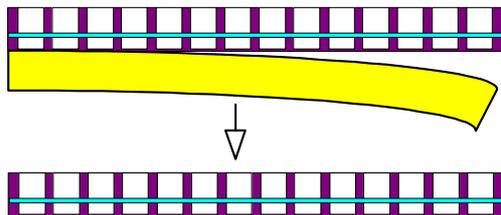


Figure 3. Aluminum foils separation

Figure 4 depicts the cross section SEM image of the upper foil. It can be observed that a bi-directional porous pattern growing from both the top and bottom surfaces. The top porous array that grows down from the surface directly contacting with the etchant are much longer than the bottom one that is likely to grow upward from the laminating interface. It was intuitively assumed that the leakage of the etchant into the laminating interface induced the upward pores. However, the leakage hypothesis requires more severe evidence to confirm.

Two approaches, leakage blocking and triplex foils laminate, are proposed to effectively investigate the leakage hypothesis.

3.1 Leakage Blocking Experiment

If the etchant can be completely blocked from contact with the laminate foils except the anodic surface, there should be no upward pores according to the leakage hypothesis. The leakage blocking can be ensured by inserting an elastic gasket between the foils and thoroughly sealing the anodizing fixture.

Figure 5 schematically illustrates the gasket inserting scheme. The negative photoresist JSR that is spin-coated and photolithographic patterned on one of the aluminum foils (Figure 6) serves as the gasket. The other aluminum foil is electrolytically polished to assure the flatness of the contact surface. Since the JSR is an elastic polymer, it can tightly adhere with the aluminum foils when the fixture is closely fastened such that the etchant can be prevented from leaking in between the laminate foils.

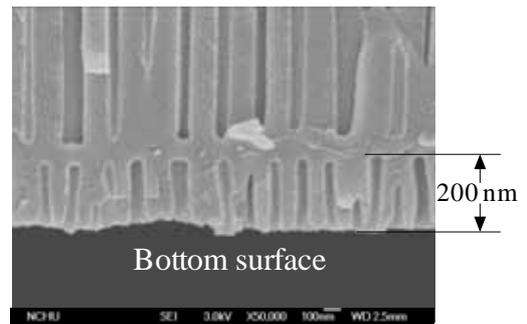


Figure 4. Bi-directional porous pattern growing from both the top and bottom surfaces

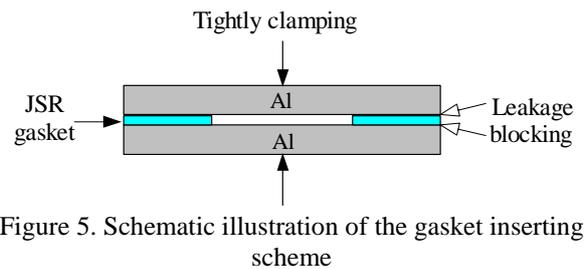


Figure 5. Schematic illustration of the gasket inserting scheme

3. EXPERIMENTAL INVESTIGATION OF THE LEAKAGE HYPOTHESIS

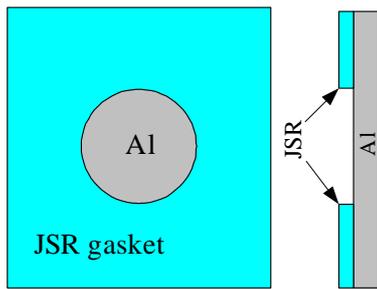


Figure 6. Spin-coated and photolithographic patterned JSR gasket

Figure 7 depicts the fixture sealing arrangements to thoroughly block the etchant. Firstly, the screw threads of the fixture are wound around using Teflon sealing tape. Following, the gasket inserting foils laminate is placed in the fixture. The fixture is then tightly locked. Finally, all contact surfaces are completely sealed with AB glue.

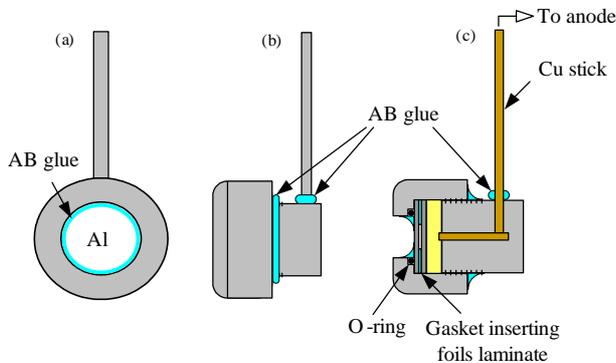


Figure 7. Schematic illustration of the fixture sealing arrangements
 (a)Front view (b)Side view (c)Cross section view

Figure 8 is the cross section SEM image of the upper aluminum foil under the leakage blocking experiment. The bi-directional porous array still can be observed. It conflicts with the leakage hypothesis.

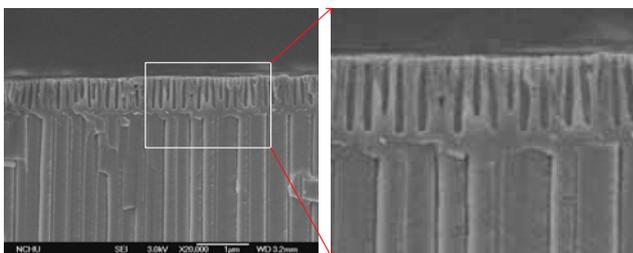


Figure 8. The cross section SEM image of the top aluminum foil under the leakage blocking experiment

3.2 Triplex Foils Laminate Experiment

Figure 9 shows the setting up of the triplex laminate foils. Under the leakage hypothesis, the etchant should

leak into both the interfacing surfaces between foils. Therefore, the porous array should be observed on both the middle and bottom foils. The SEM images of the top surfaces of the middle and bottom foils are presented in Figure 10(a) and (b), respectively. It is observed that the porous array only grew on the middle foil (Figure 10(a)). No pore appears on the bottom foil.

The triplex laminate foils experiment once again contradicts the leakage hypothesis.

4. THE BI-DIRECTIONAL GROWING MECHANISM

In Both the leakage blocking and triplex foils laminate experiments disprove the intuitive leakage hypothesis. Therefore, the upward porous by the laminate foils approach should be caused by another mechanism.

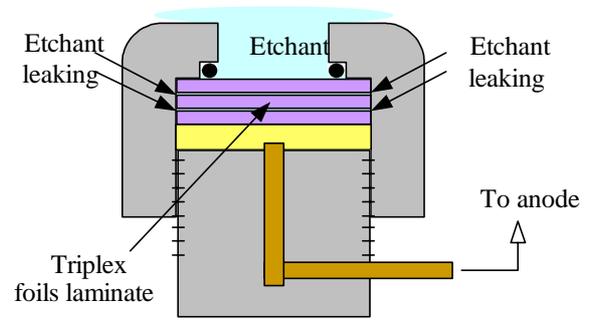


Figure 9. Triplex foils laminate

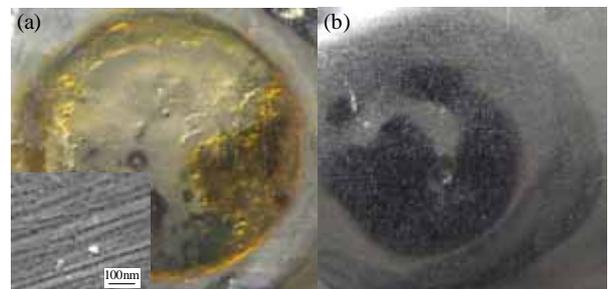


Figure 10. SEM images of the triplex foils laminate experiment (a) Middle foil (b) Bottom foil

During anodization, the electrochemical reaction (oxidation of Al into Al_2O_3) occurs on the aluminum / barrier layer interface, pushing the barrier layer downward. When the rate of alumina dissolution on the electrolyte side equals to the rate of alumina production on the metal side, the thickness of the barrier layer remains constant. It is further inferred that the applied DC voltage pulls the oxygen ions of the electrolyte in penetrating the constant thickness barrier layer to oxidize the aluminum metal, fabricating the bottom porous array (Figure 11).

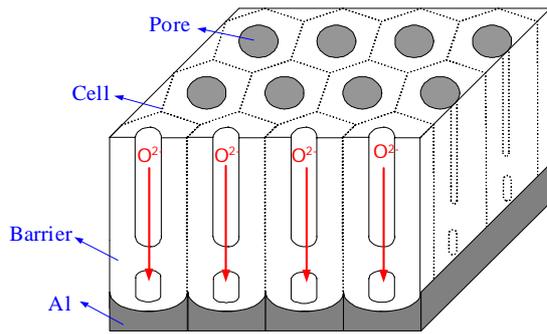


Figure 11. Oxygen ions penetrating mechanism

Based on the ions penetrating inference, the bottom porous array has capsule-like structure (Figure 11) before it reaches the laminate interface. To further verify this inference, the processing duration is reduced from eight hours to six hours. The remaining aluminum is then etched off with etchant $\text{CuCl}_2 \cdot \text{HCl}$.

Figure 12 is the cross section SEM image of the processing time reducing anodization. The expected capsule-like structure confirms the ions penetration inference.

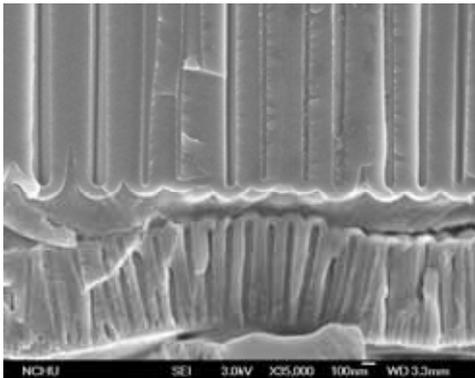


Figure 12. The cross section SEM image of the nano-capsule array

5. CONCLUSIONS

A bi-directional porous array in an alumina membrane can be produced by the laminate foils approach. It was intuitively inferred that leakage of the etchant between the foils may be a feasible cause to have the upward pores grow in the notches of the unpolished surface. The leakage hypothesis is disproved by the leakage blocking and triplex laminate foils experiments being conducted in this research.

It is further inferred that the applied electric field pulls the oxygen ions of the electrolyte in penetrating the constant thickness barrier layer to oxidize the aluminum metal, producing the bottom porous array. This ion

penetrating inference has been verified by the anodization time reducing experiment.

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