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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 etchant from the clamped area can be a feasible cause to have the upward pores grow in the notches of the unpolished surface. This leakage hypothesis has been disproved by the leakage blocking and triple layers laminate experiments. It is further inferred that the non-uniformity of the thickness or material properties of the aluminum foil causes non-uniformed anodization rate along the sample surface. The fast oxidized areas create a pathway for leakage such that a shorter porous array from the back side is observed. Experiments with the process time being reduced by two hours validate this inference

Keywords Anodic aluminum oxide · Foils laminate approach · Non-uniformed anodization

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 be no pore at the bottom surface of the upper aluminum sheet. It was intuitively deduced that leakage of etchant between the foils may be 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.

The purpose of this research is conducting experiments to verify the leakage hypothesis and have deeper investigations on the bi-directional growing mechanisms.

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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 h, 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

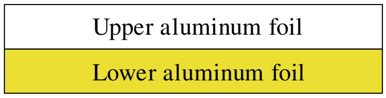

Fig. 1 Schematic illustration of the aluminum foils clamping

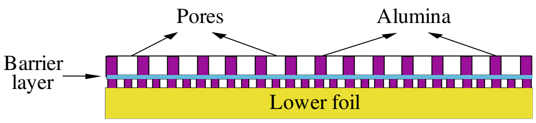

Fig. 2 Anodized aluminum foils

degrease the surfaces. Clamp two aluminum foils tightly together with a Teflon clamper as schematically illustrated in Fig. 1.

(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 h and being stirred by a magnet. After anodization (Fig. 2), the sample is rinsed again with DI water, and then is dried with ethanol.

(5) Aluminum foils separation Take apart the lower foil to obtain a patterned nanopore alumina (Fig. 3). 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 echant are much longer than the bottom one that is likely to grow upward from the laminating interface. It was intuitively assumed that leakage of etchant from the clamped areas into the laminating interface induced the upward pores. However, this leakage hypothesis requires more severe evidence to confirm.

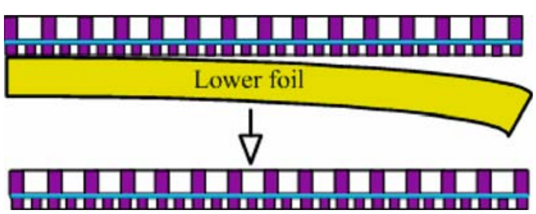

Fig. 3 Aluminum foils separation

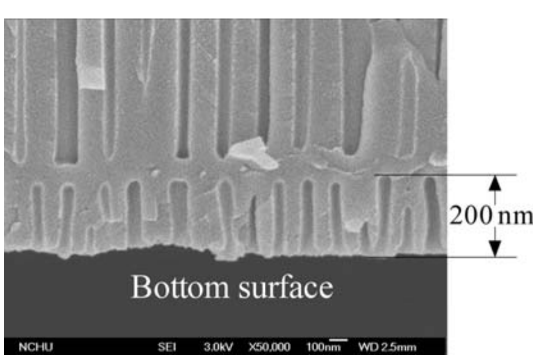

Fig. 4 Bi-directional porous pattern growing from both the top and bottom surfaces

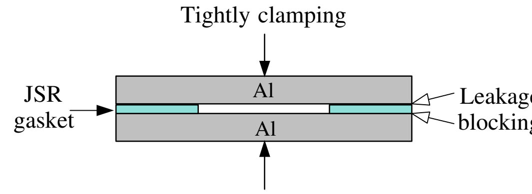

Fig. 5 Schematic illustration of the gasket inserting scheme

Experimental investigation of the leakage hypothesis

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

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 (Fig. 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.

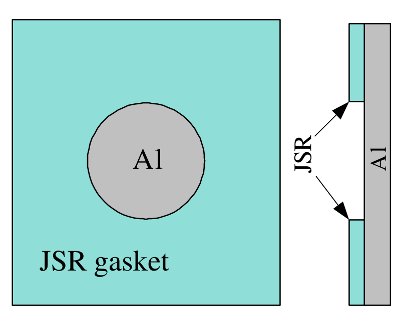

Fig. 6 Spin-coated and photolithographic patterned JSR gasket

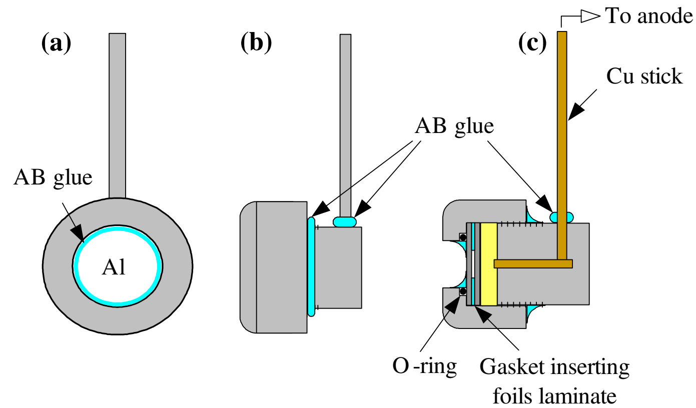

Fig. 7 Schematic illustration of the fixture sealing arrangements

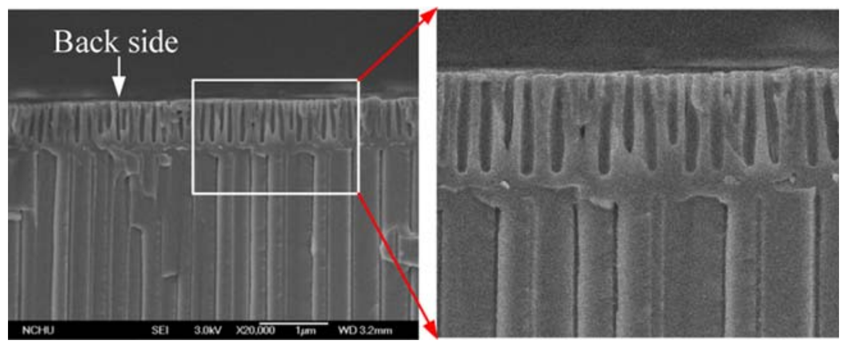

Fig. 8 The cross section SEM image of the top aluminum foil under the leakage blocking experiment

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 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.

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 Fig. 10a and b, respectively. It is observed that the porous array only grew on the middle foil (Fig. 10a). No pore appears on the bottom foil.

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

The bi-directional growing mechanism

Both the leakage blocking and triplex foils laminate experiments disprove our intuitive leakage hypothesis of the bi-directional grown of pores, which was reported elsewhere [11]. Therefore, the upward porous by the laminate foils approach should be caused by another mechanism. We greatly appreciate one of reviewers' comments that the bi-directional growth results from the non-uniform anodization along the sample surface. Fast anodization of selected areas results in the formation of leakage pathway.

During anodization, the electrochemical reaction (oxidation of Al into Al_2O_3) occurs on the aluminum/

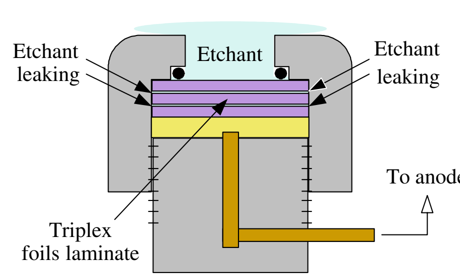

Fig. 9 Triplex foils laminate

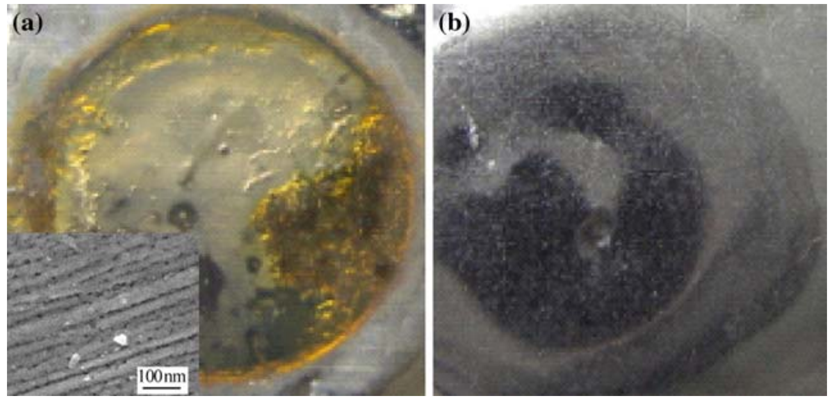

Fig. 10 SEM images of the triplex foils laminate experiment (**a**) Middle foil (**b**) Bottom foil

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 can be further inferred from the experimental results that the anodization process along the sample surface is non-uniformed. Due to the nonuniformity of the thickness or material properties of the original aluminum foil, some areas are anodized fast than the rest of the areas. The fast oxidized areas create a pathway for leakage, allowing porous-type anodization from the back side.

Closely examining on the interpore distance on both the front and back sides may provide further evidence to the above inference. There is a relatively linear relationship between the interpore distance and anodization voltage. The high resistance of the leakage pathway results in a small anodization voltage from the back side and small interpore distance.

Based on the non-uniformed anodization inference, the bottom porous array may possesses capsule-like structure 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 $CuCl_2 \cdot HCl$.

Figure 11 is the cross section SEM image of the processing time reducing anodization. The expected capsule-like structure confirms the non-uniformed anodization inference.

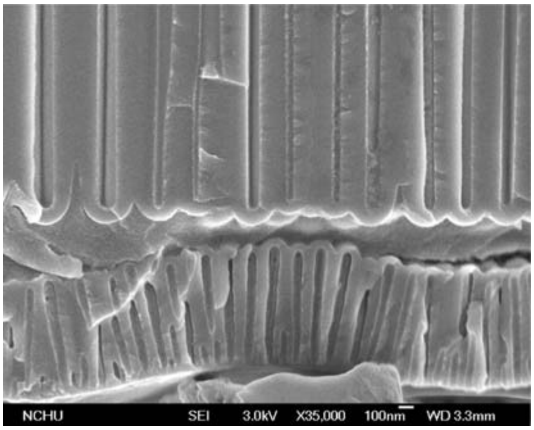

Fig. 11 The cross section SEM image of the nano-capsule array

Conclusion

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

It is further inferred that the nonuniformity of the thickness or material properties of the aluminum foil induces unequal anodization rate along the sample surface. The fast oxidized areas produce a pathway for leakage, allowing porous-type anodization from the back side.

This non-uniformed anodization inference has been verified by the anodization time reducing experiment.

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