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Side Wall Anodization of Aluminum Thin Film on Silicon Substrate

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Abstract−Anodization of aluminum with restricted surface areas is reported in this study. Particularly, the side wall of aluminum thin film is anodized for the purpose of obtaining the confined number of pores with high aspect ratio. It has been observed that side wall anodization does not occur uniformly since the anodization speed is not uniform at the both interfaces and in the middle of the film. For this reason, the resultant pore front profile shows a parabolic shape, which resembles the parabolic velocity profile of fluid flow through two slabs. During the anodization process, the pores tend to break apart and the structure becomes more complex. Side wall anodization is investigated at various applied voltages and the resultant pore structures are shown.

Key words: Anodized Aluminum Oxide (AAO), Aluminum, Anodization, Electropolishing

INTRODUCTION

Anodized aluminum oxide (AAO) has been extensively studied for a long time since it can be used as large area nano-template for nanowires or nanotubes. A number of research efforts have been devoted to obtain the AAO films with regular arrangement of pores or with desired pore sizes. It has been known that the pores have a uniform pore diameter in the range of 4-300 nm, high pore density in the range of 10^9-10^{11} cm^{-2} and that an aspect-ratio of over 100 is easily obtained. In order to control the pore size and density without sacrificing the regularity, a two-step anodic oxidation method has been normally applied with various anodization conditions such as anodic voltage, kind of electrolyte, temperature of electrolyte, anodization times [Thompson, 1997; Jessensky et al., 1998; Hwang et al., 2002; Chae et al., 2005].

The formation of AAO film has been exclusively studied for the aluminum open surface of aluminum foils or aluminum thin films deposited on a substrate. A current major issue on using the AAO film is a nano-template for metal or ceramic nanowires [Nielsch et al., 2000; Rabin et al., 2003; Sauer et al., 2002], which might have potential applications in electronic, optoelectronic and magnetic nanodevices. To expand the applicability of AAO films, the pattern formation has also been studied on the AAO surfaces so that the nanowires could be arranged with the pattern of AAO film.

In this report, we present some experimental results on the anodization of aluminum with confined surface area. For an aluminum surface of large area, the anodization is uniform and regular for the area since there is no restriction in any direction around the anodization area. However, if there is a restrictively exposed area of aluminum surface, the anodization could be affected by the interfaces formed during anodization. For a confined surface of aluminum, the side wall surface of aluminum thin films is studied for the anodization. The confinement could be on the surface or side wall of aluminum film. The side wall anodization was studied for obtaining a small number of long horizontal pores in one direction. Because the thickness of thin film could be easily controlled, the number of pores also could be controlled in the direction normal to the substrate surface.

EXPERIMENTAL

Pure aluminum was deposited on a (100) silicon wafer substrate on which a 200 nm thick silicon oxide layer was formed by thermal annealing for 1 hour at a temperature of 1,100 °C. The thickness of aluminum deposited by an e-beam evaporator was about 1 μm. Subsequently, after a 30 minute thermal annealing at 400 °C, a chemical cleaning process was carried out with acetone and alcohol.

The aluminum film was anodized in 0.3 M oxalic acid at a voltage of 40 V at 15 °C after a short electropolishing period. The widening process after anodization was carried out in 5 wt% phosphoric acid solution at a temperature of 30 °C for 20 minutes. The electropolishing step was applied as well for etching out the sidewall of aluminum film vertically. The composition of electro-polishing solution was ethanol : perchloric acid=4 : 1 (vol%), and a voltage of 40 V was applied for 1 minute at 7 °C.

RESULTS AND DISCUSSION

In Fig. 1(a), the SEM image is shown for an AAO layer on surface-oxidized silicon wafer after anodization and widening with the aforementioned experimental conditions. The formed AAO layer is uniform in large area and the pore are formed straight vertical to the silicon wafer surface. When an area of aluminum surface is exposed and the rest of surface is covered with photo resist (AZ4330, positive) by a photolithographic process, anodization of the sample results in a gradual increase (or decrease) of pore depth around the boundary between exposed and unexposed surfaces.

It is shown in Fig. 1(b), which resembles a bird's beak shape in the LOCOS (Local Oxidation of Silicon) among many microelectronics processings [Wolf and Tauber, 2000]. Near the boundary, the anodization rate should be greatly reduced compared to the area exposed to the anodization solution because the supply of anodization solution should be well short of aluminum to be anodized. En-

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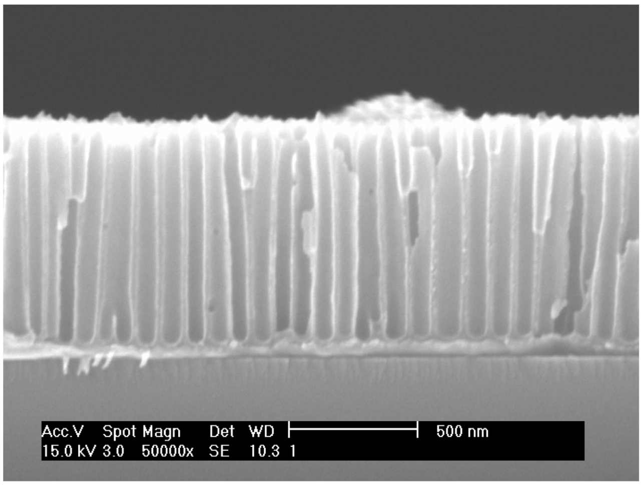
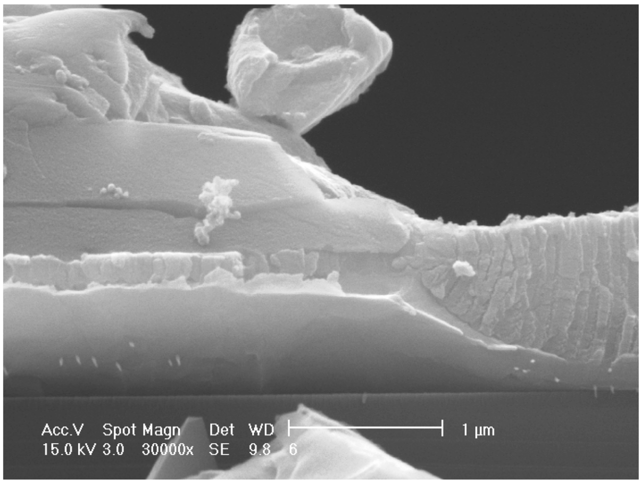


(a)



(b)

Fig. 1. SEM (scanning electron micrograph) cross-section images of (a) an anodized aluminum film on Si substrate and (b) an anodized aluminum film of which left side is blocked by patterning the photo-resist.

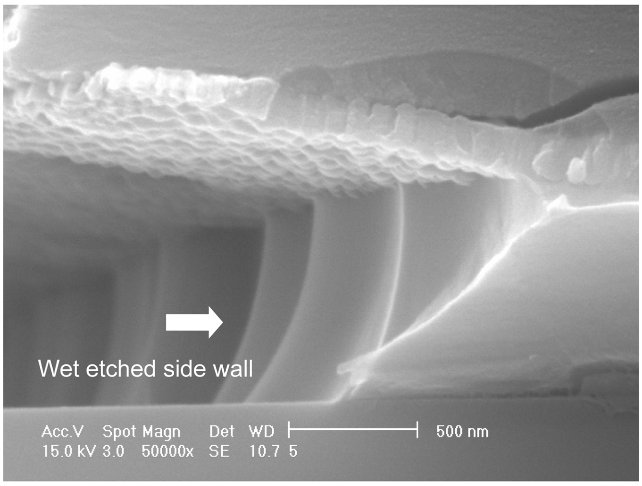


Fig. 2. An SEM image of side wall of aluminum thin film after wet etching, showing tilted side wall.

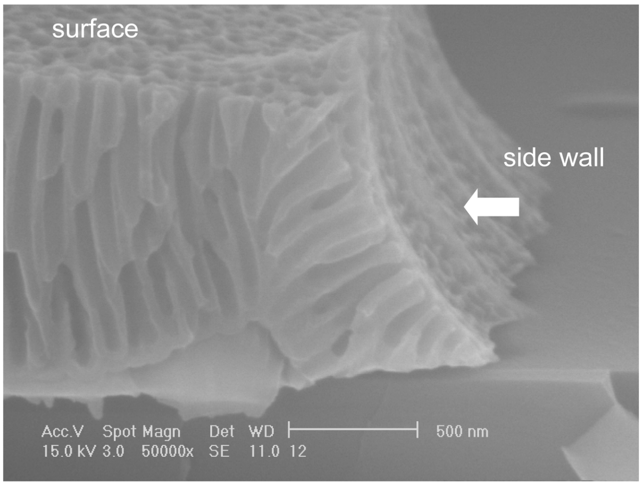


Fig. 3. An SEM image of aluminum thin film edge, showing isotropic anodization.

croachment of the solution between the photo resist and aluminum film could make the phenomena more conspicuous. As a result, the interface boundary between aluminum and anodized alumina looks like a bird's beak and the pores tend to bend to the direction where the pore depth is shallower.

In order to anodize the side wall of 1 μm-thick aluminum film, the aluminum surface was spin-coated with a photo resist material and patterned photolithographically. Upon a wet etching of aluminum film patterned by the photolithography, the side wall of aluminum film can be exposed as a result. Since the wet etching is inherently isotopic, however, the exposed side wall should not be vertical, as shown in Fig. 2. The aluminum anodization and pore formation is known to occur following the direction normal to the surface, so that the isotropically etched surface should not deliver a pore structure horizontal to the film surface.

The eave shown in Fig. 2, which has the embossed bottom surface, is 200 nm-thick AAO film. The film was formed by aluminum anodization for 2 minutes at a voltage of 40 V at 15 °C before photolithography. The thin AAO film plays an important role for protecting the penetration of anodization solution along the interface between the photoresist and aluminum. Without the AAO film, the anodization of aluminum film occurs rather vertically soon after the short initial anodization to the horizontal direction (Fig. 3).

In order to achieve a directional anodization to the horizontal direction from the side wall of aluminum thin film, it is critical to prepare the vertical etching of aluminum thin film. We obtained the vertical side wall of aluminum thin film by electropolishing the side wall using ethanol and perchloric acid solution. The vertical side wall with a thin AAO eave on the top surface is shown in Fig. 4.

The vertical side wall was subjected to anodization and widening at various voltages and anodization durations. At a voltage of 10 V, two hour anodization of the side wall leaves relatively small pores on the side wall surface and yields the highly porous AAO of about 700 nm in depth (Fig. 4). As shown in the figure, all the pores proceeded horizontally, but the pores in the middle grew straight and the pores close to top (or bottom) bent toward interfaces as the anodization continued. As a result, the parabolic profile of the pore

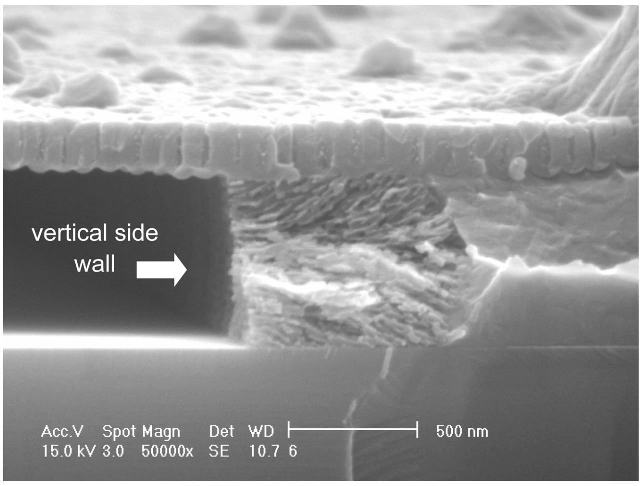


Fig. 4. A side-view SEM image after the side wall anodization of aluminum thin film at 10 V for 2 hours. The side wall of aluminum thin film prior to anodization has been extropolished to be vertical.

front settles. The profile looks like the Poiseuille velocity profile of a fluid flowing between two parallel slabs in fluid mechanics [Den, 1980]. Such as the case of fluid flow, at both interfaces of top and bottom the pore formation velocity (fluid velocity in the fluid case) could be considerably retarded by stresses exerted by the surfaces. Remarkably, the volume expansion during anodization was not noticeable, contrary to the case of anodization of open aluminum surface. Since the pores continue to grow with curvature toward the top and bottom surfaces, the pores in the middle of the film keep branching to end up a complex structure. The pore formation velocity was measured to be quite slow, about 350 nm an hour, compared to vertical anodization. It should be noted that there was no sign of penetration of anodization solution and the anodization proceeds only from the vertical side wall.

As the anodization voltage increases, the resulting pore size also increases. As shown in Fig. 5, the number of pores across the thickness of aluminum film is reduced significantly. For an anodization voltage of 60 V, only a few pores are formed across the film thickness. It should be noted that the barrier layer thickness also increases as the distance between pores increases, so as to say that the number of pores reduces. In all cases of 20, 40, and 60 V anodizations, the parabolic profiles of the pore front are settled and the structure complexity increases. For low anodization voltages of 20, 40 V, the alumina pores are more like arranged hexagonally. At higher anodization voltages, however, the pores seem to be arranged rather randomly.

In summary, anodization was investigated by using the restricted surface areas of aluminum in order to observe the anodization behavior. Particularly, the side wall anodization of aluminum thin film was carried out for the purpose of realizing the long horizontal pores. The horizontal pores, however, were found to be unsuccessful because of different anodization speed at the top and bottom interfaces compared with that inside the thin film. The speed of side wall anodization was observed to be much lower than that for bulk aluminum surface.

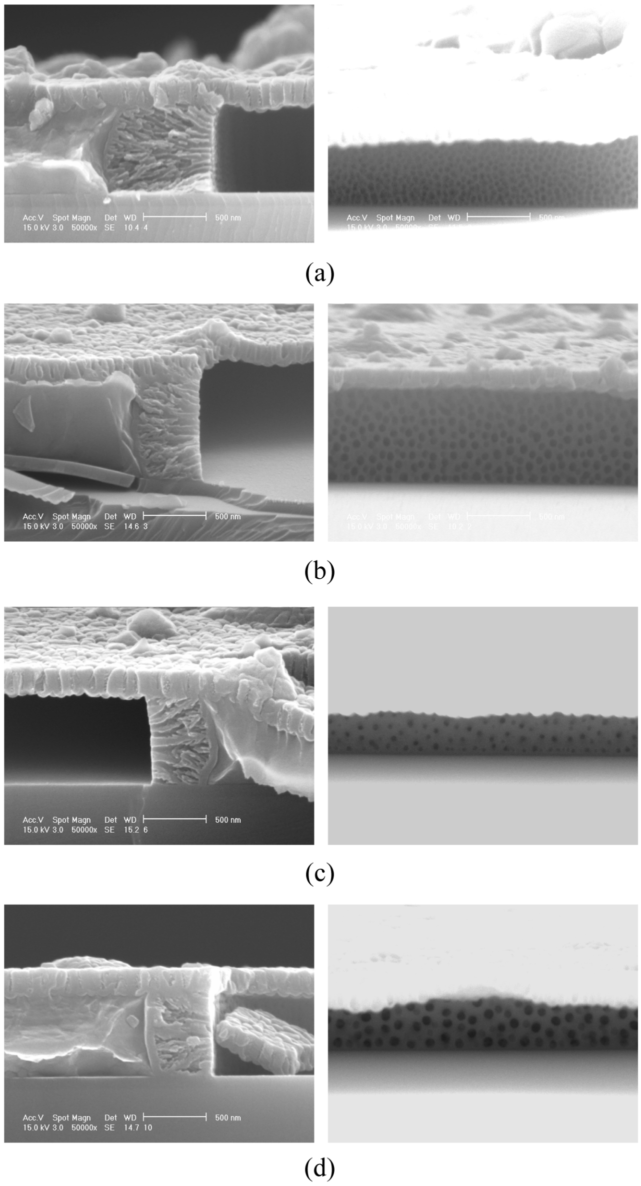


Fig. 5. SEM images after the side wall anodization of aluminum thin film at various anodization voltages, (a) 10 V, (b) 20 V, (c) 40 V, and (d) 60 V. The left images are the side views showing the pore structures and the right images show the surfaces with pore entrances.

CONCLUSIONS

In this study, side wall anodization of aluminum thin film was carried out for the purpose of realizing long horizontal pores. Unfortunately, however, the side wall anodization of aluminum thin film was found to be unsuccessful in obtaining a uniform pore structure because of different anodization speeds at interfaces and in the middle of the film. At interfaces the anodization is slowed compared to that in the middle of the film, so that the resultant pore front profile exhibits a parabolic shape. At higher anodization voltages, larger pores are formed but with lower densities of pores.

ACKNOWLEDGMENT

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