FABRICATION OF UNIFORM SQUARE-SHAPED TUNNEL PITS BY ELECTROCHEMICAL ETCHING ON ALUMINUM FOIL

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1.Introduction

Capacitor, one of the most widely electronics components, have been developed for many electronic such as mobile phone, computer and digital appliances. Recently in automotive electronics, the need for high power capacitor increased largely due to the development of hybrid electronic(HEV) and fuel cell vehicle[1-3]. Among the currently existing capacitor, aluminum electrolytic capacitor which has been used for industrial motor inverter application is basically composed of anode foil with dielectric layer of barrier-type anodic aluminum oxide(AAO) and cathode foil with an organic electrolyte-impregnated separator sandwich in between. At aluminum capacitor, As you know, it is important to maximize the surface area of electrode because the capacitance C is directly proportional to the etched aluminum surface area S as well as to the permittivity ε of dielectric oxide, and inversely proportional to the oxide thickness d ($C= \varepsilon S/d$)[4-6]. In this work, we fabricate the uniform tunnel pits and regular intervals and avoiding an excessive dissolution of the Al surface using polyimide materials as Mask layer. The goal of this experiments increase vertically the aluminum surface area S through the etched tunnel pit on Al foil and was to inspect the controllability of the etching tunnel, and this was confirmed through the selective electrochemical etching with the patterning on aluminum foil.

2. Experimetal

The formation of the selectively etched tunnel is processed in the order shown in the Fig.1. Photolithography process with a pattern that has a diameter of 5 μm and a distance of 10 μm were fabricated as follows: I) Picomax Co.'s Polyzen-150p, which is a type of polyimide and would serve as the etching mask, is spin-coated on the aluminum foil and went through the hardening process. When the curing process of the polyimide is done, a 1.4 μm thick patterning photoresist is coated on the polyimide. The patterning is processed by the photolithography technique. As a result, the top side of the aluminum foil is structured to have the etching mask polyimide layer and the patterning mask photoresist layer. Throughout these processes, the pattern of the thin aluminum foil was found to be 5 μm.

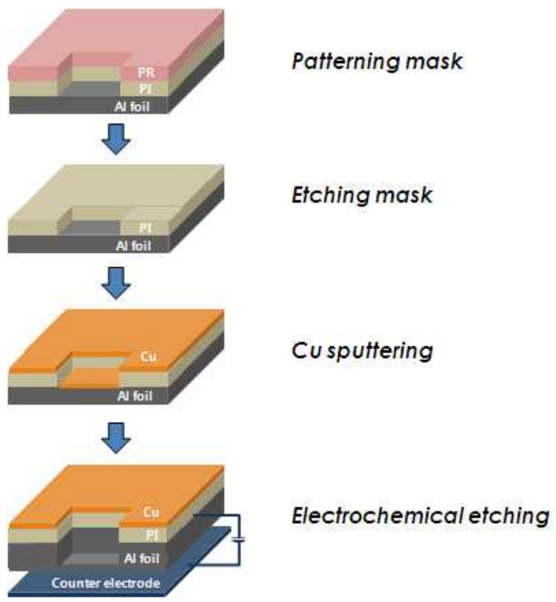

Fig.1 Schematic of formation of Al tunnel using photolithography and electrochemical etching

After the patterning process of the polyimide etching mask layer on the thin aluminum foil, 1 nm of a thin Cu layer is deposited using sputtering equipment. Finally, the electrochemical etching is conducted on the polyimide etching mask layer and an aluminum etching layer that has the selectively formed etching tunnel is made. For the uniformity of the etching tunnels, the current density was selected to be 300 mA/cm^2 and the temperature was chosen to be 50 ºC. Moreover, the size, the shape of the etching tunnel, and process has been studied while controlling the time parameters with 20, 30, 40 and 50 seconds. After electrochemical etching, polyimide etching mask layer on aluminum is removed by etching solutions.

3. Results and Discussion

The effect of electro-polishing produces a uniform tunnel pit as decrease surface roughness. As shown in Fig.2, Surface roughness can be decrease around up to 50nm by using electro-polishing conditions. The electrochemical etching of high-purity Al has been widely used to produce a large surface area on a Al anode for electrolytic capacitors. For the production of high-voltage electrolytic capacitor, Al foils predominantly composed of the (100) plane is etched under a DC condition in chloride-condition in chloride-containing electrolyte. This process produces fine tunnel pits oriented along the <100> direction of Al.

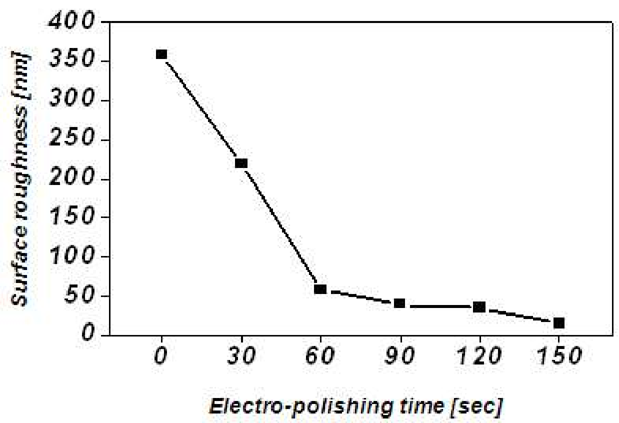

Fig.2. Effect of electro-polishing.

A Picomax Polyzen-150p polyimide is used for the etching mask due to its strong resistance against acid. However, because the Polyzen-150p is a non-photosenstive polyimide, after the polyimide is coated, a separate patterning of the photoresist should be performed. Fig.3 is plane-view SEM images of photo lithography after PR removal.

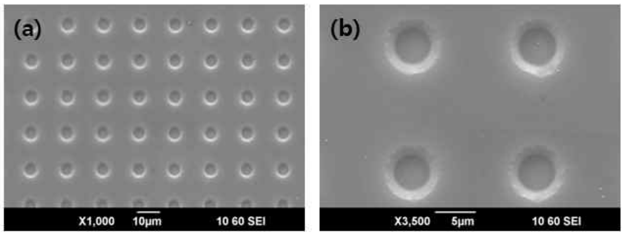

Fig.3. Plane-view SEM images of photo lithography after PR removal : polyimide / aluminum foil

Fig.4 shows the surface state containing the aluminum pit resulted from the removal of the polyimide on the aluminum foil.

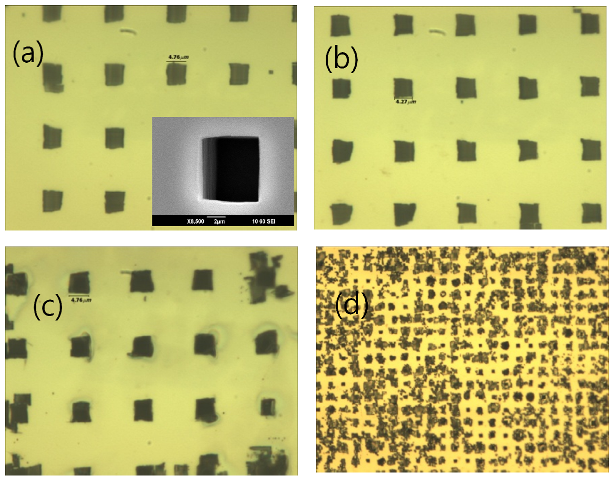

Fig.4 Plane-view SEM images of etch tunnel at 50 ºC/300 mA/cm^2 after polyimide removal: (a) 20's (b) 30's (c) 40's (d) 50's

By inspecting the images of the aluminum foil processed for 20, 30, 40 and 50 seconds captured by the electron microscopy, one can see that the surface has little loss and uniform etching tunnels have been formed in the images (a) and (b). On the other hand, in the images (c) and (d), one can observe that the loss of the surface starts to appear. To know how deep the tunnels are etched, the sample was cut such that the cross section is exposed, and the depth of the etching tunnel was measured. Fig.5 is microscope images showing the etching depth of the aluminum for etching times of 20, 30, 40, and 50 seconds. As can be seen in the images (a) and (b), the initial growth of the electrochemical etching of the aluminum foil is kept vertically in cubical shapes. On the other hand, as can be seen in the images (c) and (d), although the diameter of the bottom part does not show a big difference from the images (a) and (b), when the etching tunnel is longer, the diameter becomes narrower as it goes deeper into the film. In other words, (the fact that the tunnel becomes narrower as the etching tunnel grows means that) the resistance of the electrolyte increases due to the space formed between the outside of the tunnel and the cross section of the corroded tunnel. Hence, the corroding rate of the chlorine ions is reduced and the corroded area is diminished, and this results in overall decrease of size of the tunnel pits toward the etching direction. As the etching proceeds deep enough into the aluminum foil, the influence of the current density become smaller at the sites where the texturing is not well-formed from the rolling process, and we believe that this results in a loss of the directionality of the etching process.

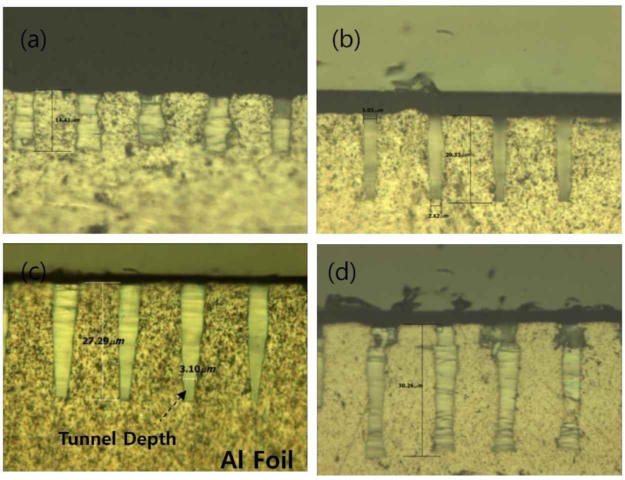

Fig.5. Plane-view SEM images of etch depth : (a) 20 sec (b) 30 sec (c) 40 sec (d) 50 sec

Resultingly, as can be seen from Fig. 6, the etching depth increases continuously from 15 µm for after initial 20 seconds to 36 µm when 50 seconds have passed.

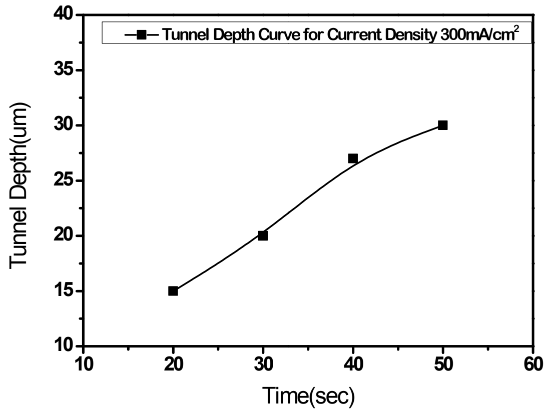

Fig.6. Tunnel depth curve for current density 400mA

However, as the etching depth is being deeper as shown in the Fig.6 (d), the width of the etching tunnel becomes narrow. To solve this problem, changing current density step by step over time might be necessary.

4. Conclusion

In this experiment, a research was performed to increase the capacitance of the aluminum capacitor, which has been spotlighted for its rapid development into electronic components. The goal of this experiment was to inspect the controllability of the etching tunnel, and this was confirmed through the selective electrochemical etching with the patterning on aluminum foil. To find out the best patterning conditions on the aluminum foil, various patterning techniques had been tried, and the photolithography was found to give the best result and was selected for the patterning method. To acquire the condition for uniform etching of the patterned aluminum foil, current density and electrolyte temperature were kept constant while the etching time was being changed to find out the optimal condition. To optimize the number of defect sites and the condition of distribution, which would act as the corrosion starting points during the electrochemical etching process, the trace of the fluid used during the rolling process and the oil film on the rolled aluminum foil were removed. however, by inspecting the shape of the etched fits on the surface, it was found out that although the distribution of etching tunnels is uniform as the current density increases, if the current density exceeds its threshold values, excessive concentration of current occurs, resulting in the etching mask detachment and some consequent surface corrosions due to the high current density. Throughout these tests, 400mA/cm2 was found to be the best condition for that the diameter of the etching tunnel is not much reduced from the original patterning size and the etching tunnels are formed uniformly on the surface.

References

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