Site Control of Tunnel Etching of Al for Electrolytic Capacitors Using Pretexturing by Mold

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(Received August 14, 2002; CL-020694)

Highly ordered arrays of etched tunnel pits were formed using an Al foil pretexturing process. Shallow concaves formed by imprinting Al using a mold with ordered convexes led to the formation of tunnel pits, and generated an almost ideally ordered array of etched tunnel pits propagating along the (100) plane. The obtained ordered tunnel pits were straight and perpendicular to the surface. The present process will be useful for optimizing the surface area of the electrode for electrolytic capacitors.

Etching of high-purity Al has been widely used as a process for producing a large surface area on an Al electrode for electrolytic capacitors. For applications to high-voltage electrolytic capacitors, an Al foil is etched under the constant DC current condition in chloride-containing electrolyte, which produces fine tunnel pits oriented along the ⟨100⟩ direction.[1–3] In these capacitors the surface area of Al electrodes basically determines the obtained capacitance. A number of studies concerning the effect of the Al surface condition on the etching properties of Al have been reported to maximize the surface area of the Al electrode. For this purpose, the control of the concentrations of impurities of Al, which can act as initiation sites for the tunnel pits, has been adopted.[4] However, precise control of the initiation site of pitting has not been explored so far. The tunnel pits obtained by conventional anodic etching are not uniformly distributed across the Al surface. The precise control of the initiation sites of pitting is essential for maximizing the surface area of Al electrodes. For the maximization of the surface area, the uniform-sized tunnel pits should be arranged at uniform intervals. The theoretical calculation of the capacitance in the ideally etched Al foils has been reported by other researcher.[5] In the present letter, we describe the precise control of the initiation site of tunnel pitting of Al, based on pretexturing of Al using an imprinting process. In the present process, tunnel pitting was initiated by the concaves formed by the imprinting process using a metal mold with an ordered array of convexes on the surface. This process was previously employed for the preparation of a porous type of anodic alumina with an ideally ordered hole configuration.[6] This is the first report of the application of the imprinting process for the precise control of the initiation sites for the anodic etching of metals.

Figure 1 shows the schematic of the process for the precise control of the initiation sites of tunnels during anodic etching used in the present study. The specimen was 110 μm-thick Al foil of 99.99% purity (Toyo Aluminum), which is predominantly composed of (100) plane (>95%). The specimen was electrochemically polished in a solution of perchloric acid and ethanol after cleaning with acetone. The imprinting of the Al was performed using a Ni mold that has an ordered array of convexes in the surface. The interval and height of the convexes were typically 10 μm and 2 μm, respectively. The process for the Ni mold preparation was as follows. After the coating of a thin Pt/Pd layer on a glass capillary plate by a sputtering apparatus, Ni of 200 μm thickness was deposited electrochemically on the surface of the glass capillary plate[7] using the Ni plating solution. After the plating, the metal layer was mechanically removed from the glass capillary plate template.

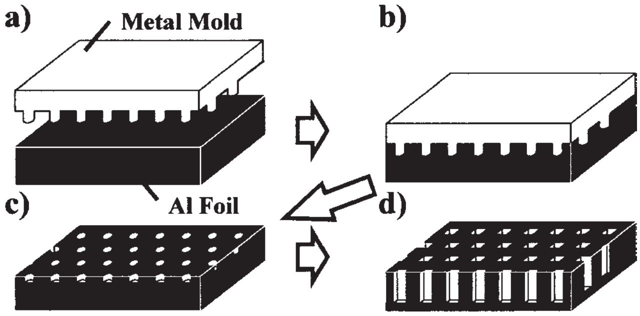

Figure 1. Schematic of control of the site of etched pits based on the pretexturing process: metal mold (a), imprinting of Al foil (b), textured Al with ordered array of concaves (c), ordered array of tunnel pits after anodic etching (d).

The Ni mold was placed on the Al foil and was pressed using an oil press. The pressure for the press was from 100 to 200 kg cm^{-2}. The Ni mold was stable after the imprinting and could be used more than several tens of times. After the imprinting, the specimen was anodically etched in 5 M HCl solution under the constant current condition of 50 mA cm^{-2}. The morphology of the specimen after etching was observed using a scanning electron microscope (SEM: JEOL JSM-6100). A replica technique was also used for the observation of tunnel morphology with high aspect ratios.

Figure 2 shows an SEM micrograph of the Al surface after the pretexturing process. An ordered array of concaves with uniform interval was observed over the sample. The interval of the concaves is 10 μm in the sample shown in Figure 2. The depth of the concaves was measured to be ca. 1 μm under the imprinting pressure of 200 kg cm^{-2} from the oblique SEM image.

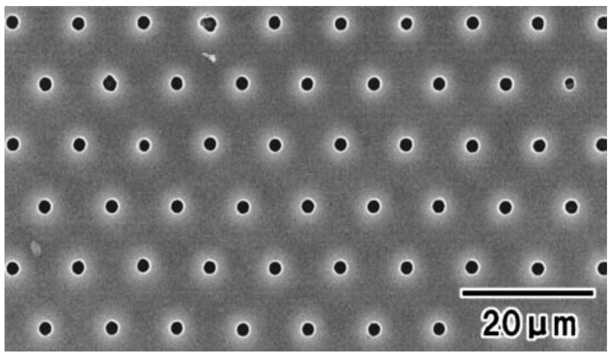

Figure 2. SEM micrograph of pretextured Al foil. The pressure for imprinting was 200 kg cm^{-2}.

Figure 3 shows the SEM micrograph of the surface view of the typical Al foil after the anodic etching. The low-magnification view in Figure 3a shows that the tunnel pits are arranged regularly over the sample. The interval of the tunnel pits corresponded to that of preformed concaves caused by imprinting. From the enlarged SEM view in Figure 3b, the etched tunnel pits were observed to be square in cross section due to the partial anisotropic dissolution along the ⟨100⟩ directions and were about 3 μm wide. All the pits observed in Figure 3b have the same orientation. The results shown in Figure 3 confirmed that the pretextured concaves act as initiation sites for the controlled development of tunnel pits. The highly controlled arrangement of etch tunnels could be observed only under the low temperature of around 30 °C. It is noted that the anodic tunnel etching was usually performed in HCl solution above 60 °C to increase the density of nucleation sites of etching.[3] In the case of the pretextured Al, the etching under the high temperature condition generated a large number of fine pits, and could not yield a well arranged array of tunnels. This is because the higher temperature increased the number of nucleation sites and thus brought about the development of an excessively large number of etching tunnel pits that prevented the selective ordered growth of the tunnels.

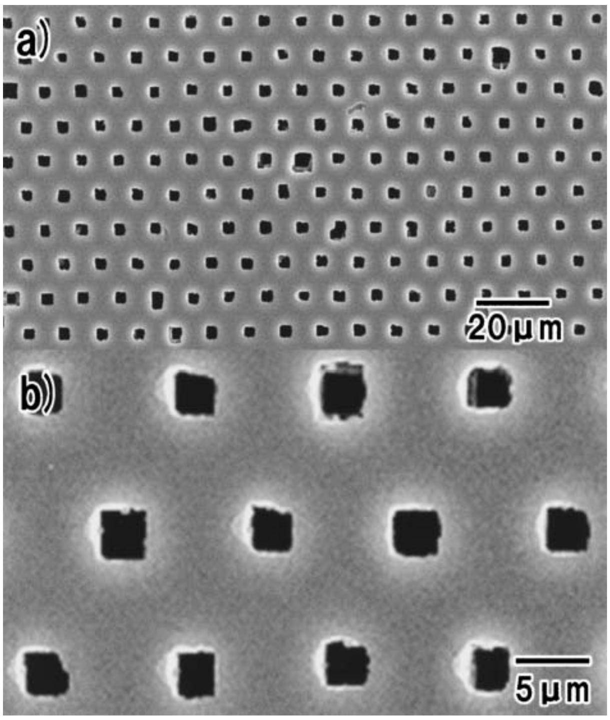

Figure 3. SEM micrographs of anodically ethed Al foil: low (a) and high (b) magnifications. Etching was carried out in 5 M HCl at 30 °C under the constant current of 50 mA cm^{-2} for 90 s.

Metal replicas of the tunnel pits were made by evaporation of the metal layer into the tunnel and subsequent electrochemical deposition of Ni in the plating solution, and then selectively removing Al in NaOH solution. From the SEM micrograph of the obtained replica in Figure 4, it is confirmed that the tunnels were straight and tapered. The depth of the tunnels was almost uniform at 15 μm. In the case of etching of Al with the (100) plane, the dissolution of Al proceeds along the ⟨100⟩ direction, while the side walls of the tunnel are passive. Alwitt et al. reported that the width of the tunnel near the opening does not increase with increasing etching time, yielding the tapered tunnels.[2] The results obtained in the present pretexturing process shows good accordance with those obtained in usual tunnel growth by the anisotropic etching of (100) Al foils. This means that the tunnel pits propagated in a controlled fashion and yielded the saturation depth even in the pretextured Al, similarly to that in the usual anodic etching. Although the detailed mechanism of the introduction of tunnel pits by the pretexturing of Al is not clear at the present stage, the defects in the Al lattice introduced by mechanical imprinting are thought to cause the selective etching during the anodic electrolysis of Al.

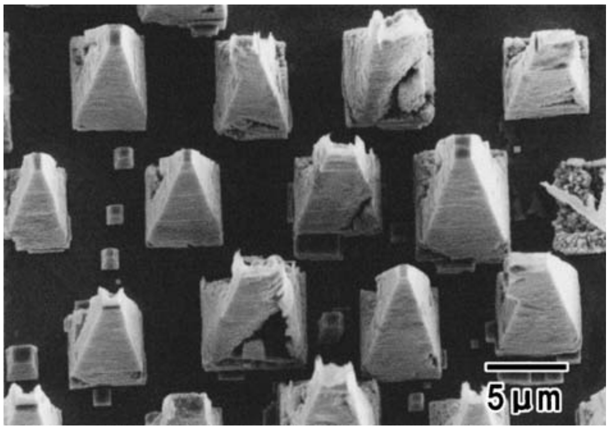

Figure 4. Oblique SEM view of replica of tunnel pits. The conditions for sample preparation were the same as for Figure 3.

The precise control of the initiation sites for tunnel etching of Al foil could be successfully achieved based on the pretexturing of Al using a metal mold. This process will be useful for the improvement of the capacity of the electrolytic capacitors. In addition, the highly ordered fine structure of the Al foil will be applied to several fields that need highly ordered fine structures, such as those involving sensors, batteries, and so on.

References

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