Control of Anisotropic Tunnel Etching of Al by Indentation

Kazuyuki Nishio,*[1,2] Kenji Kanezawa,[1] and Hideki Masuda[1,2]
[1]*Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachioji, Tokyo 192-0397*
[2]*CREST, JST, 4-1-8 Honcho, Kawaguchi 332-0012*

(Received July 3, 2006; CL-060748; E-mail: k-nishio@ecomp.metro-u.ac.jp)

Pitting sites on Al foil for electrolytic capacitors were controlled by the deformation of Al using a nanoindenter. During anodic etching of Al in hydrochloric acid solution, pitting was initiated at the edge of a triangular impression, and square pits were grown as a result of anisotropic dissolution of Al. Using this technique, 4 × 4 arrays of square pits were also obtained.

Anisotropic tunnel etching of Al in the direction of ⟨100⟩ in HCl solution has been widely used for the enlargement of the surface area of Al foil used in electrolytic capacitors.[1–17] Control of the tunnel etching sites of Al foils is important to maximize the surface area of the electrode, because the size and density of the tunnel pits must be adjusted considering the thickness of the dielectric layers (Al_2O_3) used for the electrodes. In the previous work, we showed the process of the site control of the anisotropic tunnel etching of Al by imprinting using a mold with ordered convexes.[18] In this process, the textured pattern composed of the ordered array of concaves formed by imprinting using a mold induced the anisotropic etching of Al during anodization in HCl solution. In the present report, we describe the site-controlled tunnel etching of Al by indentation using a nanoindenter attached to a scanning probe microscope (SPM). This process has several advantages for controlling the sites of anisotropic tunnel etching of Al especially for the laboratory-scale study; that is, it allows the pretexturing of Al of a desired pattern without the need for a mold, which, up to now, has required an expensive apparatus for its preparation. In addition, this process enables the quantitative analysis of the influence of the mechanical deformation of Al on the anisotropic etching of Al in HCl solution.

Figure 1 shows a schematic of the site control of anisotropic pitting on Al using a nanoindenter. A 110 μm-thick Al foil (99.99% purity, Toyo Aluminum), predominantly with the (100) plane (>95%), was used. Prior to the indentation, the foil was electrochemically polished in a mixture of ethanol (80 vol %) and 60 wt % perchloric acid (20 vol %) at a constant DC of 100 mA cm^{-2} for 2 min below 10 °C. A nanoindenter (Hysitron, Triboscope) and diamond tip (90°, triangular pyramid) incorporated into SPM unit (Shimadzu, SPM-9500J2) were used in the present study. After the indentation, Al foil was anodically etched in 1 M HCl solution under a constant-DC condition at 70 °C. The morphology of the pits formed on Al was observed by scanning electron microscopy (SEM: JEOL, JSM-6100).

Figure 2 shows the atomic force microscopy (AFM) image of a typical impression formed on Al using the nanoindenter under a load of 3.0 mN. This image was obtained by an AFM (SII, SPI3700/SPA300). In the present study, indents on Al were produced in the load-controlled mode of the instrument at 3.0 mN with a 3 s hold. In Figure 2, it can be observed that a clear impression of an inverse triangular pyramidal shape was formed on the surface of the Al foil. The side length and the depth of the triangular impression were 2 and 0.6 μm, respectively. The impression was slightly shallower than calculated (0.8 μm) on the basis of the geometrical structure of the tip used for indentation. Figure 3 shows SEM images of the Al surface during the growth of the anodic tunnel pits at the impression formed on Al. These images were taken using the samples with impressions formed under identical conditions of indentation. In Figure 3b, the development of small pit is observed at the edge of the triangular impression. This site corresponded to the highest part in the tri-

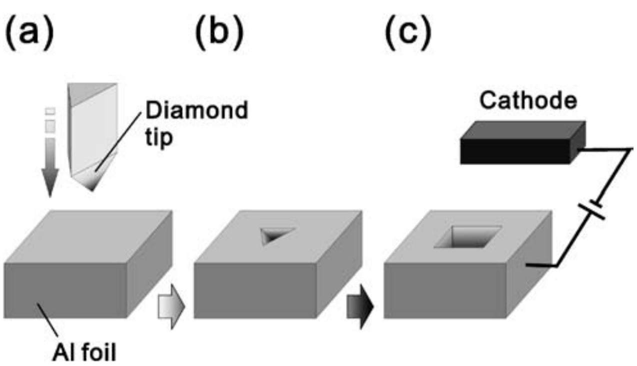

Figure 1. Scheme for control of pitting site on Al using a nanoindenter: (a) indentation on Al foil, (b) inverted triangular pyramidal impression on Al foil, and (c) anisotropic dissolution of Al at the indentation site during electrochemical etching.

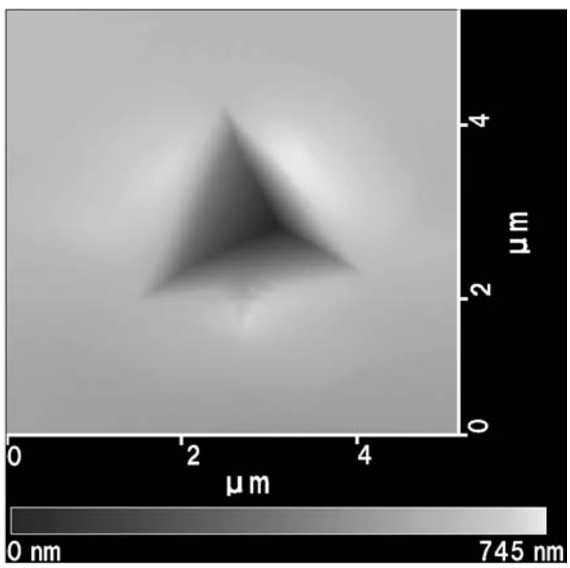

Figure 2. AFM image of an indent impression on Al formed by indentation at 3.0 mN.

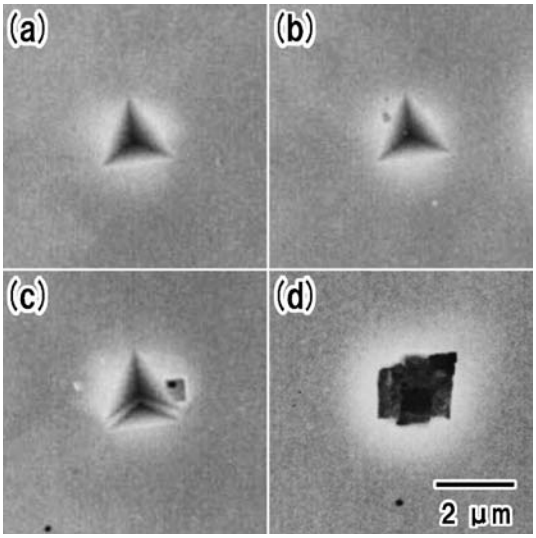

Figure 3. SEM images showing growth of anisotropic pit at indentation site: (a) an indent impression with inverse triangular pyramidal shape on Al foil, (b) onset of pitting corrosion at the edge of impression, (c) development of pit into cubic shape, and (d) extension of anisotropic pit over the impression. Each image was obtained from a different indentation site. Onset of pitting corrosion is observed on the left side of impression in Figure 3b. Anodic etching was carried out in 1 M HCl at 70 °C at constant DC of 50 mA cm^{-2}.

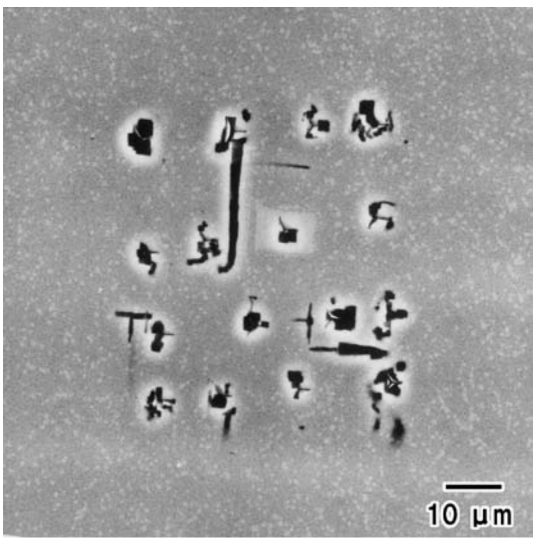

Figure 4. SEM image after anodic etching of Al foil with 4 × 4 array of indent impressions.

angular impression shown in the AFM image in Figure 2. This pitting occurred because that this part contained the largest deformation around the impression and initiated the tunnel pitting at the initial stage of anodic etching of Al. The small pit grew with etching time and generated the cubic pit due to the anisotropic etching of Al in the direction of ⟨100⟩ (Figure 3c). With the growth of the tunnel pit, the square pit extended over the impression (Figure 3d).

Figure 4 shows a SEM image of a two-dimensional array of tunnel pits on Al, in which impressions were formed in a square lattice (4 × 4) with a spacing of 10 μm. From Figure 4, it can be confirmed that each impression acted as an initiation site for tunnel pitting leading to a square tunnel pit. This result indicates that pretexturing of the Al foil by indentation enables the site-controlled anisotropic tunnel pitting of Al foil with a desired pattern. Line-like pits also grew on Al because of lateral anisotropic dissolution in the direction of ⟨100⟩ during electrochemical etching. Although the controllability of the tunnel etching is relatively low at the present stage, this problem will be improved by adjusting the etching conditions.

Site-controlled tunnel pitting of Al could be achieved using a nanoindenter incorporated into a scanning probe microscope. This technique can be used for the formation of site-controlled tunnel pits in Al foil. The obtained ordered microstructures will be applicable for the preparation of several types of functional devices which require ordered hole arrays of micrometer scale, in addition to electrolytic capacitors.

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