Growth model of Reversed Taper during Early Stage of D.C. Etching on Aluminum Oriented to (100)

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The tunnel growth mechanism of aluminum foil was studied in order to control the etching morphology. The growth of tunnels with a reversed taper followed by the tapered tunnel growth was observed only in acid solution. We proposed a model of the self-corrosion of aluminum for the reversed taper growth, and verified it by comparison of the current efficiency with the measured value made by ICP-ES to the simulation obtained from the results of the reversely tapered tunnel structure. From results of the early tunnel growth with a reversed taper, we discussed the relation between the limit length of the tunnel and width of the tunnel. It was expected that a uniform length of the tunnels should be obtained by controlling the width at the tunnel mouth to the same size.

Key Words : Aluminum, Dc Etching, Reversely Tapered Tunnel

1 Introduction

Etch tunnels are produced by the dc etching of highly oriented aluminum foils (100) in a hot chloride solution. The tunnels are ~1 μm in width and a few tens of μm in length, and are arranged in a random distribution at the density of several 10 cm−2. Tunnels grow by dissolving a square tip surface in the <100> direction. The tip surface is flat with a (100) orientation.1 During the dc etching, the tunnel tip dissolves and the sidewalls are passivated, resulting in a microscopic narrow structure with a high aspect ratio. The technology of the dc etching has been widely used for making electrodes for aluminum electrolytic capacitors with an increased surface area. Control of the etched structure in the tunnel structure and density on aluminum is required for improving the capacitance of the electrodes.2

Tunnels develop through the following morphological steps initial hemispheric pit → half cubic pit → tunnel.3,4 During the initial stage of the dc etching, small hemispheric pits develop at a period of an initial potential transient, followed by a constant etch potential. The potential at the initial transient is more anodic than the constant etch potential. At the constant etch potential, the hemispheric pits grow into crystallographic half cubic pits. The sidewalls of the half cubic pit then are passivated, and only the bottom surface dissolves. This is tunnel initiation. Tunnels grow with tapering at the dissolving tip surface, which depends on the etchant temperature and composition.5,6,7 Alwitt et al. first reported that increasing the temperature significantly enhanced the tunnel taper, and suggested that the tunnel taper was determined by a balance between the dissolution rate at a bottom surface and passivation rate at the side-walls.11 Goad showed that the hydrochloric acid and sulfuric acid concentrations increase the tunnel taper.9,10 Hebert proposed in his paper a model of the tapered tunnel growth based on equations for mass transport and potential control of a dissolving surface.7 The authors reported that the tunnel taper was affected by the cation species (Al3+, H+, Li+, Na+, and K+) contained in the etchant, and showed that the tunnel taper was remarkably enhanced only in solutions containing aluminum chloride.3 The characteristic structure of the pits and tunnels and an observation technique using a scanning electron microscope allowed these detailed studies to provide fundamental information about the localized anodic dissolution phenomenon of aluminum.

In acid solution, the width of tunnels near mouths expands with increasing length, followed by the tapered tunnel growth ; i.e., “reversed taper growth of tunnels”9,10 We showed in a previous study that the reversed taper disappeared in neutral solutions of lithium chloride, sodium chloride and potassium chloride, and proposed a model of the self-corrosion, which is chemical dissolution in acid solution, of aluminum during the reversed taper growth from results of the tunnel width vs. depth from the tunnel mouth.9,10 In this study, to verify the self-corrosion model, a measurement of the change in the current efficiency with etching time during the reversed taper growth was carried out, and compared to values expected from our model and previous results. Furthermore, a measurement of the width and length of discrete tapered tunnels grown after the reversed taper growth was carried out, and then we discussed the change in the tunnel structure from the tunnel initiation to the tapered tunnel growth via the reversely tapered...
tunnel.

2 Experimental

The aluminum foil used in this study was of 99.99% purity.\textsuperscript{80} 100 \(\mu\)m thick, and fully annealed with a high cubicity texture of more than 90% (100) orientation. The foil is used for manufacturing electrodes for aluminum electrolytic capacitors.

Foil specimens were pretreated by chemical polishing in a mixed phosphoric acid and nitric acid solution at 85-88 \(^\circ\)C for 2 min to obtain a smooth surface without the original surface oxide film and contamination. The thickness of the aluminum removal is about 8 \(\mu\)m by this conditioning. After rinsing with double distilled water, the specimens were immersed in 1M NaOH at room temperature for 10 min. The thickness of the aluminum removal is about 1.5 \(\mu\)m. After rinsing with double distilled water again, the specimens were immersed in 7 wt% HNO\textsubscript{3} at 50 \(^\circ\)C for 3 min for neutralization of the specimen surface. The time of the water rinse is 10 min. Etching was carried out at a constant dc current density of 100 mA cm\textsuperscript{-2} in hydrochloric acid or sodium chloride solutions at 70-90 \(^\circ\)C. The etching time is 0.25 s-15 s. The specimen was masked using an acrylic holder having an exposed area of 10 cm\textsuperscript{2}, and the cathode was a graphite plate. Observation of the tunnels was carried out using the oxide replication technique by scanning electron microscopy (SEM, JEOL, JSM-5500) as previously stated.\textsuperscript{80} The specimens were embedded in epoxy resin, and then mechanically polished perpendicular to the surface after curing the epoxy resin. The metal was then electrochemically polished in a perchloric acid-methanol solution at 60 V with an aluminum cathode. This technique allows measuring the tunnel width with depth from the tunnel mouth. For all etching conditions, 100 tunnels were randomly sampled, and measured.

The current efficiency with time was calculated from the concentration of the dissolved aluminum in the etchant measured by ICP-ES (Shimadzu, ICPS-7500).

3 Results and Discussion

3.1 Observation of tunnels near surface

Figure 1 shows SEM images of the tunnels after the dc etching in 1 M HCl and 1 M NaCl at 90 \(^\circ\)C. In 1 M HCl, the tunnels with a reversed taper are observed in Fig. 1(a). The tunnel width increases with increasing depth from the tunnel mouth to around a 4 \(\mu\)m depth, followed by a decrease in the width. In a neutral solution of 1 M NaCl, we do not see the tunnels with a reversed taper, as shown in Fig. 1(b). In our previous study,\textsuperscript{40} it was found that the reversed taper was enhanced with increasing concentration of H\textsuperscript{+} in mixed solutions of HCl and NaCl at the fixed Cl\textsuperscript{-} concentration. In the measurement of the current efficiency of the anodic Al dissolution obtained from a weight loss of Al before and after the 5 s etching, a high current efficiency was seen in the acid solution, which produced tunnels with a reversed taper. Based on these results, we proposed the self-corrosion reaction, i.e., the local cell reaction, of Al with H\textsuperscript{+} that might occur in a tunnel near the mouth. In this previous study, however, tunnels grew to a 30 \(\mu\)m length, and therefore, the values of the current efficiency included a range of tapered tunnel growth after the preceding tunnel growth with a reversed taper (around 4 \(\mu\)m length). In this study, therefore, we attempted to exactly measure the current efficiency during the stage of reversed taper growth of the tunnels in 1 M HCl. In 1 M HCl and 1 M NaCl at 90 \(^\circ\)C, the tunnel growth rate was then measured to obtain the required etching time to form the reversely tapered tunnel. It was known from Fig. 2 that the growth rate was 6.0 \(\mu\)m s\textsuperscript{-1} in both the acid and neutral solutions. We then measured the tunnel length of \(l_{\text{max}}\) defined by the length from the tunnel mouth to the largest width in depth as shown in Fig. 3(a). Figure 4 shows the \(l_{\text{max}}\) distribution in 1 M HCl.
Fig. 3  Schematic drawing of the tunnel growth (a) and the reversely tapered tunnel growth (b) in acid solution containing chloride ion. (The width is logarithmically expressed), $W_0$: tunnel width at tunnel mouth, $l$: tunnel length, $W_l$: tunnel width at $l$, $W_{\text{max}}$: maximum tunnel width, $l_{\text{max}}$: tunnel length at $W_{\text{max}}$, $a_i (n = 1, 2, 3)$: taper, $I_{\text{dis}}$: Al dissolution rate by applied current, $I_{\text{disc}}$: Al dissolution rate by self corrosion, Hatched area: Al dissolution by local cell reaction.

Fig. 4  Distribution of the tunnel length ($l_{\text{max}}$) at the maximum tunnel width in 1 M HCl. 
Current density: 100 mA cm$^{-2}$, temperature: 90 °C, etching time: 5 s. 
A hundred tunnels were randomly sampled and measured.

Here, the $l_{\text{max}}$ indicates a region of tunnel growth with a reversed taper, and more than 80% of the tunnels have a value of $l_{\text{max}}$ from 3-6 μm. The dispersion was independent of the etching conditions of temperature, applied current density, and etching time. Taking 6 μm s$^{-1}$ of the growth rate in the acid and neutral solutions into account, the duration of the tunnel growth with a reversed taper is considered to be less than 1s. Therefore, measurement of the current efficiency of the Al dissolution was carried out at the etching times of 0.5-2.5 s. The current efficiency was obtained using the volume of the dissolved Al in the etchant after the dc etching and the applied electricity (Fig. 5). The calculated values indicate the mean current efficiency at the end of the etching times. It was determined from Fig. 5 that the current efficiency in 1M HCl is much higher than that in 1 M NaCl. The 0.5 s etching time in 1M HCl corresponds to the duration of the reversely tapered tunnel growth. On that time, the current efficiency was the very high value of 300%. This fact shows that the self-corrosion reaction of Al significantly progresses.

The tunnel shape is controlled by a balance of the Al dissolution rate at the tip of the tunnel and the passivation rate at the sidewalls. Based on the results of the current efficiency measurement, the reversely tapered tunnel growth is interpreted by the self-corrosion reaction of Al. Fig. 3(b) shows a model of the reversely tapered tunnel growth near the tunnel mouth. When applying the current ($I_{\text{dis}}$) in neutral solution, tunnels grow by maintaining parallel sidewalls having a width at a tunnel mouth, since during tunnel growth, the dissolution occurs at only the tunnel tip and then the sidewalls immediately are passivated. In contrast, in acid solution, the local cell reaction ($I_{\text{disc}}$), i.e., the self-corrosion reaction, occurs near the tunnel mouth, i.e., the Al dissolution rate is $I_{\text{dis}} + I_{\text{disc}}$, then the reversely tapered tunnel grows.

3.2 Estimation of current efficiency of Al dissolution in a tunnel

We have confirmed that during the tunnel growth with a reversed taper, the tunnel shape is given by the following equation:

$$W_l = W_0 b_n \exp(a_n \cdot l) \quad (n = 1, 2, 3)$$  \hspace{1cm} (1)

where the constant $b_n$ indicates ($W_l/W_0$) at a 0 μm tunnel length, $W_0$ is the tunnel width at the tunnel mouth, $l$ is the tunnel length, and $W_l$ is the tunnel width at the tunnel length $l$ μm, shown in Fig. 3(a). The constant $a_n$ represents an indication of the tunnel width change with the tunnel length, when the tunnel width is logarithmically expressed. The $a_n$ value has been measured under various conditions as a parameter of the tunnel taper. For example, $a_1$, $a_2$, and $a_3$ were $8.5 \times 10^{-2}$, $-2.8 \times 10^{-2}$, and $-3.5 \times 10^{-2}$, respectively, when the etching conditions
included a current density of 100 mA cm$^{-2}$, temperature of 90°C, and etching time of 30 s in 1M HCl. Here, the value of the tapers, $a_1$, $a_2$, and $a_3$, has been considered as follows. Up to the tunnel length $l_{\text{max}}$ at the maximum tunnel width $W_{\text{max}}$, the dissolution rate of Al is sufficiently higher than the passivation rate because the local cell reaction current ($I_{\text{local}}$) due to the self-corrosion reaction of Al is added to the applied current density ($I_{\text{applied}}$). Therefore, the reversed taper, $a_2$, appears. When the tunnel length exceeds $l_{\text{max}}$, $I_{\text{local}}$ is considered to become small. The positive taper of $a_3$ then occurs. From the tunnel length $l$, where the local cell reaction does not occur, the larger taper of $a_3$ than $a_2$ appears. In a model of the reversely tapered tunnel growth shown in Fig. 3(a), the change in the current efficiency with tunnel length is simulated from the measured tunnel parameters, and compared to the quantity of dissolved Al measured by ICP-ES. In this simulation, the assumptions are as follows: tunnel density does not change during the etching time, tunnels with the same length grow, and all the applied current is used for the tunnel growth (there is no surface etching).

Calculation of the current efficiency by the simulation is as follows. The current efficiency is given by Eq. 2.

$$\text{C.Eff(\%)} = \frac{\text{Amount of Al Dissolution by } (I_0 + I_{\text{local}})}{\text{Amount of Al dissolution by } I_{\text{applied}}} \times 100$$ (2)

Figure 6 shows the scanning electron microscopic image of the Al surface electropolished to a 10 μm depth from the sample surface. From the image, we assumed that a dissolving tunnel shape is square with the width $W$. And a dissolving tunnel tip is flat. Figure 7 is a schematic drawing of the appearance of a tunnel with a reversed taper. Since the relationship between the tunnel width $W_i$ and tunnel length $l_i$ is given by Eq. 1 at $n = 1$, the surface area of a dissolving tunnel tip for the length $l_i$ is given by Eq. 3.

$$W_i^2 = W_0^2 \cdot b^2 \cdot \exp (2a_i \cdot l_i)$$ (3)

As the dissolving tunnel tip is square as stated above, the current efficiency at length $l_i$ is obtained by $(W_i^2/dV)/(W_0^2/dV) \times 100\%$ as shown from Fig. 7. At tunnel length $l_i$, the total volume of the Al dissolution $(W_i^2/dV)$ is calculated by integrating Eq. 3 with the length from 0 μm to $l_i$ μm. For the applied current, the volume of the Al dissolution $(W_0^2/dV)$ is calculated by $W_0^2 \cdot l_i$, since the current makes the tunnel with parallel sidewalls having an initial tunnel width $W_0$ grow. At tunnel length $l_i$ the current efficiency is then obtained from the two volume calculations. In our etching experiments, the surface etching is seen at 90°C, and the tunnels are widely dispersed in length. All the current is not converted into the vertical tunnel growth at 90°C, resulting in an unsuitable condition for the simulation of the current efficiency. Therefore, the simulation value compared with the measured values at 70°C, which produces tunnels of

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**Fig. 6** SEM image of electropolished surface at 10 μm depth from original surface. Current density: 100 mA cm$^{-2}$, temperature: 70°C, etching time: 15 s, etchant: 1 M HCl.

**Fig. 7** Schematic drawing of the tunnel shape near the mouth surface. (The width is logarithmically expressed)

**Fig. 8** Change in current efficiency with the tunnel length ($I$). Current efficiency is given by Eq. 2. Etchant: 1 M HCl, current density: 100 mA cm$^{-2}$, temperature: 70°C. ○: measured value, ■: simulated value.
relatively uniform length and less surface etching comparatively over a short etching time. Figure 8 shows that the simulation is in good agreement with the measured values at 0.5 μm in length, of which the reversely tapered tunnels are observed. Over 6 μm, a deviation in the simulation value from the measured value is observed because the tunnel growth condition becomes more inconsistent with the assumptions of the simulation. Thus, within the tunnel growth stage with a reversed taper, the agreement between the simulated value from the model in Fig. 7 and the measured value of the current efficiency verifies the hypothesis of the generation of the self-corrosion reaction of Al during the reversely tapered tunnel growth.

3.3 Limit length of tunnel

In the previous section, we discussed a mechanism for the growth of tunnels with a reversed taper formed by the dc etching in acid solution. During the dc etching manufacturing process for producing electrodes of Al electrolytic capacitors, the design of an etched structure of the electrodes is required for obtaining a high surface area and mechanical strength, i.e., tunnel width, length, and density. For example, there is a suitable tunnel width for the thickness of the dielectric oxide film, and a tunnel length control is required to get a high mechanical strength, and so on.

It is known that the tunnel growth progresses at a constant rate, and then the Al dissolution at the tunnel tip surface abruptly stops. Alwitt et al. showed that in 1 M HCl at 90°C, tunnels grew with an etching time to 30 s, while at more than 30 s, the length was almost constant at 80 μm. This is the limit length of the tunnel (l_u). Uchi et al. investigated the tunnel length at various etching temperatures and sulfuric acid concentrations in the etchant, and showed that the limit length of the tunnel was related to the mean tunnel width. In this study, we measured the length and width of discrete tunnels. The tunnel width was measured at 10 μm from the tunnel mouth. This width was defined as the bottom width W_{bo}. The 10 μm length is beyond the region of the reversed taper growth. Etching is performed in 1 M HCl at 90°C for 60 s, which is the condition for the presence of many tunnels including the limit length after an abrupt dissolution stop. Figure 9(a) shows that the relation between the limit length and width indicated by the solid line, although the tunnel width and length are dispersed in the range of 0.5-3.5 μm (width) and 10-90 μm (length), respectively. This fact shows that a specified limit length exists for any tunnel width. Data points below the line indicate the presence of growing tunnels initiated during applying anodic constant current. Moreover, from Fig. 9(b), the relation between the limit length and width was known to be given by the following logarithmic function.

\[
\ln \frac{l_u}{l} = A \cdot \ln B
\]

where the constant B indicates temporarily \( W_{bo} \) at a 0 μm tunnel length, and the constant A is an index of the limit length of the tunnel for \( W_{bo} \). With increasing A, the limit length of the tunnel becomes short.

We attempted to understand the relation between the limit length of the tunnel (\( l_u \)) and the tunnel width at the tunnel mouth (\( W_{bo} \)) in order to investigate the effect of the tunnel shape near the surface, i.e., reversed taper, on the etched morphology. We measured the tunnel length \( l \) and the width \( W_o \) of discrete tunnels. Three etchants with the same Cl− concentration were used: 3 M HCl, 3 M NaCl, and 1 M HCl + 0.67 M AlCl3 at 90°C. The etching time was 15 s that is enough time to see tunnels with the full length under this condition. The measured tunnels were sampled at random. Figure 10 shows the presence of the limit length of tunnels (\( l_u \)) with \( W_o \) in each etchant. The data plots below the straight line indicate

![Fig. 9](image)

**Fig. 9** Relation between the bottom width (\( W_{bo} \)) and the limit length of tunnel (\( l_u \)) drawn by (a) normal expression and (b) semi logarithmic expression.

Etchant: 1 M HCl, current density: 200 mA cm², temperature: 90°C, etching time: 60 s.
the presence of growing tunnels initiated during applying anodic constant current as seen as Fig. 9.

On the other hand, after the tunnels sufficiently grew, the relation between the tunnel length \( l \) and width \( W \) was given by Eq. 5.\(^{10}\)

\[
(W/W_0) = b \cdot \exp (a \cdot l)
\]

We found the same relation as Eq. 5 for the tunnel width at a tunnel mouth \( W_0 \).

\[
(W/W_0) = b_3 \cdot \exp (a_3 \cdot l)
\]

Therefore, from Eqs. 5 and 6, the relation between \( W_0 \) and \( W_0 \) is given by

\[
W_{10} = W_0 \cdot (b_3/b) \cdot \exp [(a_3 - a)\cdot l]
\]

where \( X \) indicates \( W_0 \) at a 0 \( \mu \)m tunnel length, and \( Y \) is the index of the limit length of the tunnels \( l \) for \( W_0 \) and depends on the temperature and composition of the etchant. There, \( X \) is \( W_0 \) when length limit of the tunnel \( l \) decides. For example, for increasing \( Y, l \) decreases. Thus, Eq. 9 indicates that the limit length of the tunnel \( l \) is determined by the width at the tunnel mouth \( W_0 \). As we already know all the parameters of \( X = (b \cdot B/b) \) and \( Y = (A + a - a_3) \) in 1M HCl at 90 °C,\(^{10}\) we compared the measured data of tunnel length \( l \) and width \( W_0 \) with the simulated data of the limit length of tunnel \( l_0 \) and width \( W_0 \) from Eq. 8 as shown in Fig. 11. The measured limit length of the tunnel values agreed very well with the simulated values. Namely, it was proved that Eq. 8, then Eq. 9, were correct. Consequently, we propose from an industrial view point that a uniform limit length of tunnels, \( l_0 \), should be obtained if the width at the tunnel mouth, \( W_0 \), is controlled with the same size.

4 Conclusions

We studied the morphology of the tunnel near the surface that is an influential factor on the etched structure. Furthermore, we discussed the self-corrosion model by comparison of the experimental data to the simulated values. As a result, it was clarified that

1) “tunnels with a reversed taper” were observed only in acid solution, and we found that the current efficiency was 300% at the time at which the reversed taper was formed. We proposed the model of the self-corrosion of aluminum by \( H^+ \) for the mechanism of reversely tapered tunnel growth.

2) We simulated the current efficiency of the Al dissolution from the mean morphology of the tunnel and the model of the reversed taper growth, and compared it with the experimental results. As a result, it was determined that the geometric model of the reversely tapered tunnel was correct, because the simulation
and experimental values were in good agreement within the stage of tunnel growth with a reversed taper.

(3) From the results of the measurement of the tunnel structure, it was revealed that the limit length of tunnel \( l_d \) was determined by the width at the tunnel mouth \( W_0 \). It was then expected that the uniform length of the tunnels should be obtained by controlling the width \( W_p \) with the same size.

References