Metal dissolution and passivation in etch pits and tunnels on aluminum

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Metal dissolution and passivation in etch pits and tunnels on aluminum

Wiersma, Bruce John, Ph.D.

Iowa State University, 1990
Metal dissolution and passivation in etch pits and tunnels on aluminum

by

Bruce John Wiersma

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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1. INTRODUCTION

Aluminum and its alloys are frequently used as structural materials because of their resistance to corrosion. Once aluminum is exposed to a source of oxygen a protective oxide film forms over the surface, thereby controlling the rate of corrosion. Other materials such as stainless steels also exhibit similar behavior. However, if this oxide film becomes damaged and cannot repair itself, active metals such as aluminum and chromium (the active metal in stainless steels) corrode quite rapidly. Often the film becomes damaged at specific sites allowing the metal to undergo local attack. A general name for this type of attack is localized corrosion. The problem of localized corrosion has caused one corrosion engineer to lament, "localized corrosion is responsible for 90% of the failures of metals by corrosion [1]."

Localized corrosion takes on many forms such as intergranular corrosion, stress corrosion cracking, crevice corrosion, and pitting. The means by which the oxide film breaks down distinguishes the type of localized corrosion that occurs. For example, crevice corrosion occurs in restricted areas where the concentration of dissolved oxygen has been depleted. The differential concentrations of oxygen or ions result in the initiation and propagation of crevices [2]. Pits, which are small localized holes that are usually a few millimeters in diameter, on the other hand, initiate at metallurgical defects such as scratches, emerging dislocation steps, or compositional heterogeneities.
Although the type of localized corrosion depends on the mechanism by which the oxide film breaks down, the propagation of corrosion structures by metal dissolution or the repair of the oxide film by repassivation are common occurrences. This work will focus on the mechanisms for metal dissolution and repassivation.

Because of the number of environmental factors which influence localized corrosion and the new and stronger alloys which have been developed, fundamental investigations of localized corrosion have become cost effective. Electrochemical and surface science techniques used to characterize localized corrosion have been well documented by Szklarska-Smialowska [3] and Galvele [4]. However, because of complications such as large potential and concentration gradients within the corrosion structure or irregular geometries, the mechanisms for metal dissolution and repassivation are difficult to distinguish. This problem could be alleviated by studying a system which has a simple solution chemistry and structure geometry. Alwitt et al. [5] found that aluminum etched at a constant applied current in chloride solutions at temperatures above 60°C produces approximately $10^7 \text{cm}^{-2}$ cubic etch pits and etch tunnels. Cubic etch pit are approximately 0.1-1.0 μm wide and are bounded by the (100) planes. At a size of 1-2 μm the pit walls become passivated by an oxide film while the base of the pit continues to penetrate the metal. As the metal continues to dissolve at the tip, the oxide film occupies the side walls preventing lateral expansion. This structure is referred to as an etch tunnel and is illustrated in Figure 1.1. Tunnels have been observed to maintain their linear and crystallographic shape to depths of 100 μm. In the past, tunnel etching of aluminum has been used primarily in the production of electrolytic capacitors. Research has therefore focused on parameters
which will increase the capacitance gain. It has been observed that tunnel growth is
strongly influenced by foil composition [6], temperature, chloride ion concentration,
and applied current density [7]. The linear shape of these structures allow for the
calculation of potential and concentration gradients and hence the potential at the
tip surface, where both active and passive surfaces are present.

Passivation is of general interest because it determines the stability of localized
metal dissolution. This work will consider the mechanism for a particular system, the
tunnel etching of aluminum.
Figure 1.1: Scanning electron micrograph of an oxide replica of the tunnel profile. magnification 10,000 X
2. LITERATURE REVIEW

Much of the passivation literature is concerned with the environmental factors which either prevent or promote the formation of a protective oxide film over an active metal surface. This problem of stability requires both electrochemical and morphological information on the metal dissolution and repassivation reactions. It is of particular interest in this work to determine how these processes occur simultaneously on the metal surface within individual pits and tunnels. Thus this review will focus on previous observations and proposed mechanisms for these processes as they apply to the initial development of pits and tunnels.

2.1 Observations on Pit and Tunnel Stability

The repassivation potential is the potential above which the active surface will continue to dissolve and below which the active surface will repassivate. The most influential environmental factor on this potential is the concentration of the "aggressive" anion (i.e., Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), etc.) in the electrolyte. It has been shown that the repassivation potential (\(E_r\)) is a linear function of the logarithm of the halide anion concentration of the solution adjacent to the pit surface.

\[
E_r = a - b \ln [X^-]
\]  

(2.1)
In this equation a and b are empirical constants and $X^-$ represents the halide anion. The most prevalent halide anion in industrial situations is the chloride ion. The value of b in this relationship is typically greater than $RT/F$.

There have been several mechanisms proposed to describe the conditions necessary for repassivation. Galvele [8] has suggested that pit stability relies on the maintenance of a critical pH value near the active surface. There are three processes which control the pH near the active surface: 1) hydrogen ions are produced by a hydrolysis reaction between dissolved metal cations and water, 2) hydrogen ions are consumed by cathodic reduction, and 3) hydrogen ions diffuse away from the surface into the bulk solution. If the metal dissolution current density, which produces the metal cations, is high enough, the electrolyte solution next to the surface may become locally acidified. Based on the thermodynamics of bulk phases, metal oxides are thermodynamically unstable below a certain critical pH value [9]. Therefore, as long as the pH remains more acidic than a certain critical value, the metal will continue to dissolve. However, if the potential changes so that the current density is reduced, the hydrogen ion production will decrease and result in a higher pH. When the pH exceeds a certain critical value, a thermodynamically stable oxide film may form over the active surface. It is evident from this description that the repassivation potential is not an equilibrium potential for a repassivation reaction. It is merely a function of the kinetic processes which produce the acidity near the active surface.

Beck assumes that the active surface area is covered by an adsorbed salt layer [10]. The existence of a thin salt layer present at the active surface has been shown for aluminum [11] and iron [12]. The presence of the adsorbed layer prevents water from
coming in contact with the metal surface. The thickness of the salt layer depends on the relative rates of two processes. The thickness increases due to an electrochemical reaction at the interface between the adsorbed layer and the bare metal surface.

\[ Al + 3X^- \rightarrow AlX_3 + 3e^- \] (2.2)

The equilibrium potential for this reaction is assumed to be the critical pitting potential. This adsorbed salt layer is not in equilibrium with the solution at the salt/solution interface. Thus at this interface the adsorbed layer dissolves into the solution and the corrosion rate is determined by the mass transport of metal ions away from the surface. A third process that occurs simultaneously is the diffusion of water through the adsorbed layer. If the potential shifts so that less metal salt is produced, the thickness of the layer will decrease. The thinner layer allows water to diffuse to the bare metal surface where it reacts to form a metal oxide. Therefore pit stability is determined in part by kinetic processes.

A third mechanism for repassivation proposed by Kolotyrkin [13] and Uhlig and Böhni [14] that passivation occurs as a result of competitive adsorption between the chloride ion and oxygen at the metal surface. The repassivation potential is associated with the minimum potential at which oxygen can reversibly replace the chloride ion at the metal surface. The adsorption of oxygen on the surface results in the formation of a passive oxide film as shown by the following reaction.

\[ Al(Cl)^3^- + \nu_0 H_2O + 3e^- \rightarrow Al(OH)_2\nu_0 + \nu_- Cl^- \] (2.3)

where \( \nu_0 \) and \( \nu_- \) are stoichiometric coefficients. The equilibrium potential for this reaction is hypothesized to be equal to the repassivation potential. The equilibrium
potential for this reaction decreases with an increase in chloride ion concentration in the same manner as the critical potential. This observation coincides with the decrease in the potential of zero charge at a metal electrode surface as the chloride ion concentration in solution increases. The potential of zero charge is the critical potential above which anion adsorption occurs. Variations in the potential of zero charge are attributed to the specific adsorption of an ion to the metal surface. This theory is difficult to test as the chemical potential of the adsorbed species is unknown.

As mentioned previously the complexities surrounding localized corrosion make it difficult to distinguish between these mechanisms. Thus, in this work kinetic information on the metal dissolution and the passivation velocity from the pit and tunnel morphology and electrochemical measurements will be used to elucidate these mechanisms. For this reason, potential transients from constant current and step current reduction experiments will be examined. Therefore, it will be of interest to review previous results from galvanostatic experiments.

2.2 Observations of Galvanostatic Transients

Potential transients at short times, in response to small constant currents (0.03-30 mA/cm²), have been measured for Fe-16Cr [15], stainless steel [16], zinc [17], and aluminum [18]. The transients showed three distinct regions: 1) A rapid increase from the open circuit potential to a very high noble potential, 2) a decline in the potential, and 3) the establishment of a constant potential. Szklarska-Smialowska and Janik-Czachor assert that the maximum potential is a nucleation potential, while the constant potential is the passivation potential. They suggest that the potential re-
response is due to the tendency of the system to maintain the total active area constant and independent of time. They did not, however, suggest the nature of the current source (i.e., capacitive, metal dissolution, etc.) which supplies the applied current. An understanding of these sources would not only serve to explain the transient, but may also give insight into how the pits grow or passivate in their initial stages of development.

The Al/HCl system has also been used to investigate the initial growth of etch pits [19]. A constant applied current density of 10 mA/cm² was applied for times less than 100 ms. This study focused primarily on the initial region of the transient. Current and charge balance equations, calculated at different times within the initial region, allowed for qualitative interpretations of the processes that occur on the surface. There were two major results:

- At the peak potential the applied current density is supplied by the metal dissolution current density from the pits.

- An estimate of the amount of charge passed, based on the total volume of the pits, is much greater than the actual amount of charge passed during the current pulse. The large pit sizes may indicate that the pits either nucleate at large sizes or grow to these sizes via a currentless mechanism.

It was proposed that in the initial region the applied current density was supplied by a capacitive charging current density and the metal dissolution current density from the pits. In this work it was desired to make a more accurate assessment of these processes at different times within the initial region.
The potential transients at later etch times from constant current or step current reduction experiments have been used to study repassivation in tunnels. Hebert [20] observed two conditions which appear to control the tunnel shape. It was found that after a step current reduction the width of the tunnel decreases to a value that is proportional to the change in the current density. Since the metal dissolution current density had been shown to be constant and independent of tunnel length, it was concluded that the system controls the total current from the aluminum by constricting the tunnel tip area. Hebert also established experimentally that the potential at the tunnel tip does not change with tunnel length. Gehlsen and Hebert [21] investigated the hypothesis that passivation is controlled by a critical potential at the metal surface. As discussed above, this hypothesis is in agreement with the competitive adsorption mechanism of passivation. From this assumption, and with the use of mass transport equations, they predicted that the potential at the surface remained within 1 mV of the repassivation potential. These results suggested a possible mechanism for repassivation. During steady tunnel growth the potential at the tip remains poised at the repassivation potential. The tip area is reduced, and hence the total current density is controlled, when the potential at the active surface decreases below the repassivation potential. Conversely, an increase in the surface potential above the repassivation potential would halt the repassivation reaction and allow the active surface to expand. In this work it will be hypothesized that small negative departures from the repassivation potential provide the driving force for the repassivation reaction. It will also be investigated whether this potential drop is due to ohmic, concentration or surface overpotentials.
3. EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus and procedure for the experimental segment of this work will be described in this chapter. The description will explain the design of the apparatus and outline the base case experiments.

3.1 Apparatus

The aluminum foil used in the etching experiments was Toyo (F) type which was 99.99 % pure and had grain sizes of approximately 100 \( \mu \)m. This foil is particularly useful as it is manufactured with a "high cubicity" structure which exposes predominantly (100) crystal planes at the metal surface. Previous work has shown that in hot chloride solutions an anodic current pulse will produce more than \( 10^5 \text{ cm}^{-2} \) pits on the foil. The cubic shape of the etch pits facilitated measurement and modeling of transport processes. The design and dimensions of the electrode holder, shown in Figure 3.1, are similar to those used by Alwitt et al. [5]. The holder was constructed of two glass plates with a 5 cm\(^2\) circular window in the top plate. The recessed design assures that there is a uniform current density over the electrode surface. Previous experiments have shown no variation in the pit density between the edge and center of the window. No evidence of significant crevice corrosion between the glass plates has been observed either. The semicircular platinum counterelectrode was fixed to
the holder to ensure that the ohmic drop in the electrolyte was constant with time and reproducible for each experiment.

The experiment was performed in a 1000 ml beaker which contained about 600 ml of HCl. For the base case, reagent grade (36-38 wt. %) HCl was diluted with deionized water to prepare an electrolyte with a 1 N concentration. This concentration was chosen to coincide with previous etching experiments. A hot plate (Corning PC-351) was used to heat the electrolyte to a constant temperature. The relatively large volume of solution maintained the temperature within 1°C of the desired value. A Ag/AgCl/4 M KCl reference electrode was positioned in the beaker so that it was at infinity with respect to the working electrode when the galvanostatic transients were measured.

A schematic of the experimental set up is shown in Figure 3.2. Current was applied to the working electrode via a PAR Model 273 Potentiostat/Galvanostat. A Z-158 (Zenith) personal computer was used to store the current waveform in the potentiostat’s memory and to send commands which modulate the waveform. Communications software for this process was developed by Joel Benson (ISU graduate student). The galvanostatic transients were measured by a Keithley 194A high speed voltmeter. The digital voltmeter was capable of reading 30,000 data points with a resolution time of 10 µs. The potential transients were retrieved and processed by the computer with the aid of the ASYSTANT software package [22].

A JEOL-JSM 840 scanning electron microscope (SEM) at the Materials Analysis Research Laboratory, Iowa State University, was used to view the tunnels and pits. The magnification of the upper stage of the microscope was calibrated with metal
Figure 3.1: Front and side view of the electrode holder
Experimental Set-up

Figure 3.2: Schematic drawing of the experimental apparatus set up
3.2 Base Case Procedure

Prior to the etching experiment the sample was pretreated. For the base case, the aluminum was cut into pieces that fit into the holder and then stored in a vacuum desiccator for several hours. Before etching, the sample was immersed in 1 N HCl at room temperature for five minutes. Another pretreatment that was used was to immerse the aluminum in 1 N NaOH for 20 minutes. The sample was then rinsed with 500 ml of deionized water and stored in the desiccator for 6-8 hours. The effect of the pretreatment was to change the structure and composition of the oxide film. In this work the effect of the pretreatment on the pit and tunnel morphology will be observed.

After the pretreatment, the foil is placed in the holder for etching. A solution temperature of 65° C was chosen for two reasons: 1) a good distribution of tunnels form only at temperatures above 60° C [7] and 2) metal dissolution current densities may be measured from the tunnel growth rates. There were two types of etching experiments performed. For the first, a constant anodic current density of 12.89 mA/cm² was coordinated so that it coincided with the immersion of the aluminum electrode into the electrolyte. The etch times for the pit studies were typically less than 100 ms, while for tunnels they were as long as 30 s. Current reduction experiments were performed to study the passivation kinetics. The etch time at the initial current density was typically 50 ms and the percent current reduction was between 10-60 %.
After the etch, the electrode was quickly removed from the electrolyte and rinsed with deionized water for two to three minutes. This process washes away any residual chloride that may remain on the aluminum. The sample was then mounted on a 1” graphite stub for viewing under the SEM. Variations in the base case such as an increase in the applied current density, use of AlCl₃ as an etchant solution and changes in the etchant bath temperature are noted in the Results and Discussion chapter.

When it was required to observe the depth of the pits, a technique developed by Dunn and Bolon [23] was used to make an oxide replica of the metal surface. The anodizing solution used for this procedure was ammonium phosphate monobasic (1.4 g/l). The sample was masked with scotch tape during anodizing so that approximately 2 cm² were exposed. A 50-75 V anodic film (60 - 85 Å) was formed at 1 mA/cm². After anodizing the samples were cut into 1 cm squares and placed on microscope slides with the etched side down. The slide was then placed in a beaker at a tilted position in a crystallization dish. A bromine/methanol solution (10% bromine by volume) was then poured over the sample. The reaction, which was done at room temperature beneath a ventilation hood, strips away the aluminum and leaves the oxide replica. The oxide replica was placed on a 3/8” graphite SEM stub by floating the replica off the slide with an eyedropper filled with methanol. The replica was allowed to dry and then fixed on to the stub with carbon conducting paint. The oxide replica was then sputter coated with gold to provide a conducting surface for the SEM.
4. RESULTS AND DISCUSSION

The experimental results are presented and discussed in this chapter. The focus of this chapter will be fourfold: 1) The initial growth and nucleation of etch pits, 2) the kinetics of repassivation, 3) the prediction of the potential transient based on the repassivation kinetics, and 4) the prediction of the pit and tunnel morphology determined by the repassivation kinetics. It will be of particular interest to understand the mechanism for the transformation of the etch pit into the etch tunnel.

4.1 An Investigation of the Nucleation and Growth of Etch Pits in the Initial Region of the Transient

4.1.1 Description of the transient

The galvanostatic transient for the base case experiment is shown in Figure 4.1. It is observed that immediately after the current pulse the potential rises quickly at an average rate of 100 V/s to a maximum voltage of 0.8 V in approximately 15 ms. Although there are small 2-3 mV fluctuations in the potential at this time, it remains near this maximum for approximately 2-3 ms. The potential then decreases at an average rate of 85 V/s to a value of -0.72 V at 35 ms. This portion of the transient will be referred to as the initial region. At this time a minimum in the potential
Transient is observed before the potential returns to a nearly constant value. Figure 4.2 magnifies this region and shows that the potential declines to a minimum of -0.770 V and then increases to a nearly constant value. This event occurs in approximately 5 ms. It is also observed that the potential in this region declines at a faster rate (88 V/s) than it rises (10 V/s). After the minimum, the potential goes through another maximum at -0.712 V before the transient is damped to a nearly constant value of -0.720 V. These final two sections of the transient will be referred to as the region of the minimum potential and the constant potential region respectively. Efforts to reproduce the transient showed that the maximum potential in the initial region varied between 0.3-0.8 V and the time for this region ranged between 25-40 ms. Also the difference between the constant potential and the minimum potential ranges between 10-60 mV. The final constant potential was between -0.72 V to -0.79 V. Despite these differences, it is significant that the general shape of the features in the transient is very reproducible.

The shape of the potential transient will be investigated at different times along the transient to gain an understanding of the mechanisms of pit initiation, growth and repassivation which occur during an etching experiment. It was hypothesized that the rate of repassivation is controlled by changes in the surface overpotential (see literature review). It is therefore necessary to distinguish changes in the surface overpotential from changes in the measured potential. In the next section resistances which may cause a change in the measured potential will be investigated.
Figure 4.1: Galvanostatic transient for the base case experiment, \( i_a = 12.89 \) mA/cm\(^2\), \( t = 100 \) ms, \( T = 65^\circ \) C, E vs. Ag/AgCl/4 M KCl
Figure 4.2: Galvanostatic transient for the base case in the region of the potential minimum, E vs. Ag/AgCl/4 M KCl
4.1.2 Ohmic potential control in the constant potential region

The measured potential, $E$, in the constant potential region does not represent the actual potential at the dissolving surface. It is desired to demonstrate that the measured potential is rather a combination of the surface potential and overpotentials due to resistances between the surface and the reference electrode. These resistances are shown in the potential balance written in Equation 4.1.

$$E = \eta \Omega_{in} + \eta \Omega_{out} + \eta_c + \eta_s + E_r$$

The first two terms in the potential balance account for the ohmic potential drop in solution between the surface and the reference electrode at infinity. An ohmic potential drop may be calculated from Ohm's law:

$$\eta \Omega = \frac{iA}{\kappa l}$$

where $\eta \Omega$ is the ohmic potential drop, $i$ is the current density, $A$ is the area of the surface from which current flows, $l$ is a length scale, and $\kappa$ is the solution conductivity. The first term, $\eta \Omega_{in}$, represents the ohmic drop associated with individual pits. This ohmic potential drop is proportional to the dissolution current density, $i_d$, and inversely proportional to the conductivity of the pit solution and the length scale of the individual pits. The second term, $\eta \Omega_{out}$, is associated with the ohmic potential drop in the bulk solution far from the aluminum surface. It is proportional to the applied current density, $i_a$, and inversely proportional to the conductivity of the bulk solution and the length scale of the electrochemical cell. The third component, $\eta_c$, is the concentration overpotential. This overpotential is due to concentration gradients in the solution between the reference electrode and the pit surface. Since
the bulk solution is stirred, the gradient would be confined to a small diffusion layer near the surface. An equation for this overpotential, assuming a one dimensional concentration gradient and that the solution near the pit may be approximated by a binary electrolyte, is given by [24]:

\[ \eta_c = \frac{\nu RT \ell^2_+}{z_+ \nu_+ F} \ln \left( \frac{(Cf_+)_p}{(Cf_-)_b} \right) \]  

(4.3)

where \( \nu \) is the stoichiometric coefficient, \( \ell^2_+ \) is the transference number, \( z_+ \) is the charge on the positive ion, \( f_+ \) is the mean activity coefficient, \( R \) is the gas constant, \( T \) is the temperature, \( F \) is the Faraday constant, \( C \) is the electrolyte concentration. The subscripts + and - refer to the cation and anion respectively and the subscripts \( p \) and \( b \) refer to the solution near the pit surface and and in the bulk. \( E_r \) is the repassivation potential which would be measured in a solution that has the same composition as the solution adjacent to the active surface. \( \eta_s \) is the surface overpotential with respect to the repassivation potential. the combination of \( E_r + \eta_s \) represents the potential at the active surface.

Estimates can be made of \( \eta_c \), \( \Omega_{in} \) and \( \Omega_{out} \) for etch pits at these short times. To calculate \( \eta_c \) it will be assumed that the cubic pit can be approximated by a hemispherical pit. It is also assumed that the flux of \( \text{Al}^{3+} \) is controlled by steady state diffusion and is equal to the tunnel dissolution rate. Newman et al. [25] have solved the Laplace equation for this geometry and a constant flux boundary condition. The change in concentration between the bulk and the pit bottom is given by:

\[ C_p - C_b \approx \frac{3i_d \ell^2_+}{nFD} \]  

(4.4)

where \( D \) is the diffusion coefficient of the binary electrolyte. Given that \( i_d = 6.15 \)
A/cm^2, r, the depth of an average pit, is 0.5 μm, t^0 = 0.79 [21], n = 3, and D = 2 \times 10^{-5} \text{ cm}^2 \text{ the concentration difference is } 0.13 \text{ M. It will be assumed that the mean activity coefficient is the same in the bulk and near the pit and the binary electrolyte near the surface is AlCl}_3. \text{ Given that } \nu = 4, \nu_+ = 1, t^0_+ = 0.21, T = 338 \text{ K}, z_+ = 3 \text{ and } C_b = 1 \text{ M the concentration overpotential is approximately } 1 \text{ mV. This value is approximately the same as the potential fluctuations in the transient.}

Newman et al. [25] also solved the Laplace equation for the normalized value of \eta \Omega_{in}. \text{ For an individual pit this overpotential is given by:}

\[ \eta \Omega_{in} \approx \frac{3ri_d}{\kappa} \]   \hspace{1cm} (4.5)

Given that \kappa = 0.531 \text{ Ω}^{-1} \text{ cm}^{-1}, r is 0.5 μm and \text{i}d is 6.15 A/cm^2 \text{ \eta} \Omega_{in} \text{ is calculated to be } 1.7 \text{ mV. This value is also the same order of magnitude as the potential fluctuations.}

Polarization curves performed with the reference electrode at infinity show that above the critical repassivation potential the current responds linearly to a change in potential. This result may indicate that the constant potential region is controlled by the ohmic drop in solution. Step current reduction experiments were done at short times to verify this hypothesis. These experiments were performed at different applied current densities, current reductions, temperatures, and bulk solution concentrations as is shown in Table 4.1. An example of one of these experiments is shown in Figure 4.3. A 200 mA/cm^2 applied current density was reduced to 100 mA/cm^2 at 50 ms. The difference between the two constant potentials, defined as ΔE_1, is assumed to be equal to \eta \Omega_{out}. \text{ If the potential is under ohmic control, a plot of } \eta \Omega_{out} \text{ vs. } \Delta i_d/\kappa \text{ should be linear with a slope equal to the geometry parameter A/\ell. From Figure 4.4
it is seen that the plot is linear and has a slope of 1.15 cm. A previous attempt to
determine the cell constant [26], given the same cell geometry, gave a value of 1.0
cm which shows good agreement with the present value. Therefore the measured
potential is under ohmic control.

Table 4.1: Summary of the solution conductivities [27]

<table>
<thead>
<tr>
<th>Concentration (N)</th>
<th>Temperature (C)</th>
<th>Conductivity (ohm$^{-1}$-cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 N HCl</td>
<td>65</td>
<td>0.0603</td>
</tr>
<tr>
<td>0.5 N HCl</td>
<td>65</td>
<td>0.276</td>
</tr>
<tr>
<td>1.0 N HCl</td>
<td>65</td>
<td>0.531</td>
</tr>
<tr>
<td>1.0 N AlCl$_3$</td>
<td>65</td>
<td>0.107</td>
</tr>
<tr>
<td>2.0 N AlCl$_3$</td>
<td>65</td>
<td>0.119</td>
</tr>
<tr>
<td>6.0 N AlCl$_3$</td>
<td>25</td>
<td>0.185</td>
</tr>
<tr>
<td>6.0 N AlCl$_3$</td>
<td>65</td>
<td>0.20</td>
</tr>
<tr>
<td>6.0 N AlCl$_3$</td>
<td>75</td>
<td>0.22</td>
</tr>
<tr>
<td>6.0 N AlCl$_3$</td>
<td>90</td>
<td>0.25</td>
</tr>
<tr>
<td>9.0 N AlCl$_3$</td>
<td>65</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Although this is a significant resistance, for constant current experiments in a
solution with a constant conductivity, $\eta \Omega_{out}$ does not change with time. Thus for
short etch times in constant current experiments, changes in the measured potential
are due to changes in the surface potential. In the next section a current balance
model will be developed to explain the shape of the potential transient in the initial
region in terms of nucleation and growth of the etch pits.

4.1.3 Current balance calculations in the initial region of the potential
transient

In previous work [19] it was suggested that in the initial region of the transient
two current sources, a capacitive current and a metal dissolution current, were present
Figure 4.3: Potential transient for a step current reduction at 50 ms from 200 mA/cm$^2$ to 100 mA/cm$^2$. 
Figure 4.4: Plot of $\Delta E_1$ vs. $\Delta ia/\kappa$
and could be represented by the following equation:

\[
i_a = C_d \frac{dE}{dt} + \frac{i_x n_p A_p}{\varepsilon}
\]  \hspace{1cm} (4.6)

In this work experiments were done to verify the current balance equation in the initial region of the potential transient. It was desired therefore to determine values for the capacitance, the pit density and the pit size distribution at these times. These results will allow us to evaluate the assumptions about pit growth which are contained in the model.

4.1.3.1 Pit morphology studies of the base case In order to calculate the active area of a pit, it will be necessary to confirm the geometry of the etch pit. Figure 4.5 is a SEM micrograph, taken at 10,000 X, of the etch pits on the aluminum surface. The etch pits are the dark rectangular or square shaped regions with sharply defined edges. SEM micrographs, taken at 20,000 X, of oxide replicas of etch pits were used to determine the pit depth. As is shown in Figure 4.6, tilting the specimen 45° reveals the depth of the pit. From this figure it is apparent that the pits have a cubic shape.

The oxide replicas may be used to evaluate the shape of the active area. The ratio of the length of the two sides \((l_1, l_2)\) to the pit depth, \(r\), was determined for 20 etch pits. The average ratio, \(l_1 : l_2 : r\), was found to be 1.0:0.88:0.51 and thus the general shape of the pit is a half-cube. This observation is consistent with the assumption that all the walls of the pit are active and dissolve at a uniform rate. This result also enables one to calculate the active area based on measurements of etch pits on the aluminum surface. A pit depth which provides an area equal to the
Figure 4.5: Scanning electron micrograph of cubic etch pits which form during the base case experiment, magnification 10.000 X
Figure 4.6: Scanning electron micrograph of an oxide replica which shows the pit depth. magnification 20.000 X
rectangular or square region was determined for each pit. Thus the area per pit could be calculated as 12 r^2.

The aluminum samples were randomly scanned with the SEM to determine their pit size distributions and densities. At a magnification of 10,000 X, 150 micrographs of the sample were taken. Previous calculations based on cluster sampling techniques [19] demonstrated that this number of micrographs was sufficient to approximate the pit size distribution. Pit size distributions were determined at times of 1, 8, and 20 ms. Each of the distributions were repeated to evaluate their reproducibility. Figures 4.7-4.9 are frequency distributions of the pit radius for these times.

The depths of the pits were determined to be between 0.05-0.7 \mu m with the greatest proportion of them between 0.05 and 0.3 \mu m. A few large pits were observed, however they were neglected as they comprised less than 1% of the distribution. Figure 4.10 demonstrates that the 8 ms distribution may be approximated by a log normal distribution. For this case the mean value of the ln r was -1.85 (r in \mu m) and the standard deviation was 0.57 \mu m. The distributions at other times were also found to exhibit this characteristic. Thus distribution averages and variances will be calculated based on this approximation.

A sample which had been pretreated and then immersed in 1 N HCl at 65° C for 5 s with no applied current was also examined for etch pits. Figure 4.11 shows the pit size distribution for this case. It is seen that the pit sizes are the same as for the etched samples. Since the pit density (see Table 4.2) for this sample was on the same order of magnitude as the density for the etched samples, it was necessary to determine whether the pretreatment and immersion steps contribute a significant
Figure 4.7: Pit size distribution after a 1 ms etch at base case conditions
Figure 4.8: Pit size distribution after an 8 ms etch at base case conditions
Figure 4.9: Pit size distribution after a 20 ms etch at base case conditions
Figure 4.10: Log-normal approximation of the pit size distribution after an 8 ms etch at base case conditions.
fraction of the measured pit area.

Since the metal dissolution current density depends on the active area, \( r^2 \) was calculated for each pit. Table 4.2 shows the mean square depth, \( r^2 \), for each distribution along with its standard deviation. The mean square depth was calculated from the log normal distribution parameters with the following equation:

\[
r^2 = \exp(2(\mu + \sigma^2)) \tag{4.7}
\]

where,

\[
\mu = \text{the mean of } \ln r, \text{ } r \text{ in } \mu\text{m} \\
\sigma = \text{the standard deviation of } \ln r, \text{ } \mu\text{m}
\]

The values for \( r^2 \) range from 0.023-0.062 \( \mu\text{m}^2 \). It was decided to test whether the differences in the mean square depths were significant. It was assumed that all the distributions were sampled from the same population and therefore the mean and standard deviation may be estimated from all the data points. The mean square radius was calculated to be 0.0407 \( \mu\text{m}^2 \) and the standard deviation was 0.0316 \( \mu\text{m}^2 \).

The following equation was used to construct 95% confidence intervals on each of the distribution means [28].

\[
Pr[\exp \left(2(\mu - \frac{z\sigma}{\sqrt{n_i}} + \frac{\sigma^2(n_i - 1)}{x_i^2}) \right) \leq r^2 \leq \exp \left(2(\mu + \frac{z\sigma}{\sqrt{n_i}} + \frac{\sigma^2(n_i - 1)}{x_i^2}) \right)] = 1 - \alpha
\]

\[
Pr[\exp \left(2(\mu - \frac{z\sigma}{\sqrt{n_i}} + \frac{\sigma^2(n_i - 1)}{x_i^2}) \right) \leq r^2 \leq \exp \left(2(\mu + \frac{z\sigma}{\sqrt{n_i}} + \frac{\sigma^2(n_i - 1)}{x_i^2}) \right)] = 1 - \alpha
\]

(4.8)

If the mean square depth of the overall population was within the confidence limits of each of the distribution means, the hypothesis that the means were equal would be
Figure 4.11: Pit size distribution after pretreatment in 1 N HCl at room temperature followed by immersion in 1 N HCl at 65° C
accepted. From Figure 4.12 it is observed that the overall mean is within or near the confidence limits for most of the distributions. The error in each distribution mean may be calculated by comparison of the confidence limits and the mean. The error was found to range between 20-50%. Thus the overall population mean was accepted as a good estimate for the mean square depth.

Table 4.2: Summary of the pit size distribution parameters and density for different etch times in 1 N HCl at 65°C

<table>
<thead>
<tr>
<th>Etch time (ms)</th>
<th>( r^2 ) (( \mu m^2 ))</th>
<th>( \sigma ) (( \mu m^2 ))</th>
<th>( np \times 10^5 ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0544</td>
<td>0.0404</td>
<td>3.43</td>
</tr>
<tr>
<td>1</td>
<td>0.0627</td>
<td>0.0497</td>
<td>4.35</td>
</tr>
<tr>
<td>8</td>
<td>0.0603</td>
<td>0.0477</td>
<td>5.77</td>
</tr>
<tr>
<td>8</td>
<td>0.0365</td>
<td>0.0275</td>
<td>6.70</td>
</tr>
<tr>
<td>20</td>
<td>0.0475</td>
<td>0.0361</td>
<td>7.43</td>
</tr>
<tr>
<td>20</td>
<td>0.0369</td>
<td>0.0265</td>
<td>8.0</td>
</tr>
<tr>
<td>20</td>
<td>0.0231</td>
<td>0.0183</td>
<td>12.2</td>
</tr>
<tr>
<td>30</td>
<td>0.0367</td>
<td>0.0272</td>
<td>7.62</td>
</tr>
</tbody>
</table>

This result seems reasonable based on what is known about the growth rate in tunnels. Given that the growth rate is the same in pits as it is in tunnels (2.12\( \mu m/s \)), and a current pulse that is 20 ms in duration, the pit depth would be expected to increase by 0.04 \( \mu m \). For micrographs taken at 10,000 X this change would be difficult to detect.

The pit density was also estimated from 150 micrographs at 10,000 X. At short etch times, these pits tended to locate in isolated clusters on the aluminum sample. Oxide replicas revealed that certain crystal grains had been preferentially etched while some grains gave little evidence of pitting. The pit clustering is shown in Figure 4.13 which is a map of the aluminum surface after a 100 ms etch. The map was constructed
Figure 4.12: 95% confidence interval on the mean square pit depth of pit distributions after etch times between 1-20 ms
by scanning along parallel lines spaced about 0.3 cm apart. Every 0.1 cm along a
given line an area of approximately 6600 μm² was examined for pits. The density
of the clusters ranged from 0-1.35 x 10^6 pits/cm². It appears that there is a high
probability that at a given point on the surface one will not observe any pits.

The pit densities at times within the initial region are also shown in Table 4.2.
They range from 4.3 x 10^5 cm⁻² at 1 ms to about 1.22 x 10^6 cm⁻² at 20 ms.
Although there are differences in the pit density at 20 ms, it appears that there is
continuous nucleation of new pits in the initial region.

In addition to the pit density estimates from the initial region, estimates were
made from samples which had been etched between 40 ms and 30 s. Between 100-150
micrographs at 10,000 X were examined for this purpose. Figure 4.14 shows that the
log of the pit number increases almost linearly with the log of the etch time. Although
there is some error in these measurements, it should be observed that the pit density
consistently increases with time. The slope of this line will give an expression for
the pit nucleation rate. A linear least square analysis was performed on the data
with IMSL routine RLINE [29] and the nucleation rate was given by the following
equation:

\[
\frac{dn_p}{dt} = 4.464 \times 10^5 t^{-0.69}
\]

From this equation the pit nucleation rate at 1 ms was calculated to be 5.24 x 10⁷
cm⁻²s⁻¹ and at 30 ms the rate had decreased to 4.27 x 10⁴ cm⁻²s⁻¹.

Small 2-3 mV fluctuations in the potential are observed at different times along
the transient. These fluctuations are illustrated in Figure 4.15 which magnifies the
potential transient near the maximum potential in the initial region. Bertocci et
Figure 4.13: Pit map of the aluminum surface after a 100 ms etch at base case conditions; the pit number at a given location on the sample is indicated.
Figure 4.14: Plot of log pit number vs. log etch time
al. [30] and Williams et al. [31] have attempted to correlate these fluctuations with either changes in the ohmic drop or capacitive current density that are associated with the sudden nucleation and repassivation of pits. The frequency of the fluctuations may be an indication of the nucleation rate of the pits while the amplitude of the fluctuations may be associated with changes in the ohmic drop or capacitive current density. These relationships were investigated by measuring the peak to peak time and amplitude of the fluctuations. Approximately 100 points were used to determine the average peak to peak amplitude and time. Table 4.3 is a summary of these average values at different etch times. The average peak-to-peak time was found to be between 28.9-33.3 $\mu$s and the average peak-to-peak amplitude was between 2.15-2.78 mV. The frequency of the fluctuations is approximately 32 kHz and is relatively independent of the etch time. If it is assumed that each peak is associated with the birth of a pit the nucleation rate would be $3.2 \times 10^4$ cm$^{-2}$s$^{-1}$. In the initial region, at a time of 15 ms, the nucleation rate calculated from Equation 4.10 is $8.1 \times 10^6$ cm$^{-2}$s$^{-1}$. It is apparent from this result that at this time there is not a direct one-to-one correlation between the fluctuations and the nucleation rate. At a later time, for example 15 s, the nucleation rate has decreased to $6.9 \times 10^4$ cm$^{-2}$s$^{-1}$. Although the latter nucleation rate is approximately the same as the frequency of the fluctuations, the decrease in the nucleation rate from the initial region to later times is not accompanied by a decrease in the frequency of the fluctuations. The amplitude is approximately the same magnitude as the sum of $\eta_c$ and $\eta_{in}$ (2.7 mV). Heusler and Fischer [32] observed current fluctuations with an iron electrode after chloride ions were introduced into a sodium borate-boric acid electrolyte. However it was
shown that these fluctuations occurred independent of whether there were any pits on the surface. This result brings into question whether current from pits, which produces an ohmic drop, is responsible for the amplitude of the fluctuations. Thus arguments for a correlation between the fluctuations and the birth of pits do not appear to be complete.

<table>
<thead>
<tr>
<th>Etch time (s)</th>
<th>Average Amplitude (mV)</th>
<th>Average time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>2.78</td>
<td>32.3</td>
</tr>
<tr>
<td>0.016</td>
<td>2.52</td>
<td>32.3</td>
</tr>
<tr>
<td>0.030</td>
<td>2.51</td>
<td>28.9</td>
</tr>
<tr>
<td>0.300</td>
<td>2.57</td>
<td>32.1</td>
</tr>
<tr>
<td>5.000</td>
<td>2.15</td>
<td>33.3</td>
</tr>
<tr>
<td>15.00</td>
<td>2.25</td>
<td>31.0</td>
</tr>
</tbody>
</table>

All the parameters necessary to calculate the measured active area have been determined. In order to estimate the active area from the potential transient, the capacitive current density must be calculated. The next section will be concerned with the determination of the capacitance of the surface.

4.1.3.2 Determination of the capacitance of the surface Current interruption experiments have been used previously by Ord [33] to determine the capacitance of the surface. These experiments were performed with iron immersed in a sulphuric acid solution. The current was interrupted after a steady state potential had been achieved and the slope of the potential transient after the interruption was used to determine the capacitance. It was found that as the steady state potential
Figure 4.15: Potential fluctuations near the maximum potential in the initial region
was varied from -0.1 V to 0.8 V the capacitance decreased by a factor of 4. If the same trend is true for the capacitance in the initial region of the transient, it may have a significant effect on the capacitive current density.

Current interruption experiments were used to determine the capacitance in this work. The base case conditions were used for these experiments and the applied current was interrupted at times between 1 and 20 ms. The potential transient was monitored so that the response to the interruption could be analyzed. Figure 4.16 shows the potential transient for the case where the applied current was interrupted at 8 ms. The potential at the time of interruption is approximately 0.8 V which is well above the open circuit potential of -0.84 V. It should also be realized that at these conditions the potential is not at a steady state value.

The current balance equation can be used to calculate the capacitance. The equation can be written for the transient before and after the current interruption:

\[ i_{a1} = C_d \frac{dE}{dt} \bigg|_{1} + \frac{d^n p A_p}{\varepsilon} \] (4.10)

\[ i_{a2} = C'_d \frac{dE}{dt} \bigg|_{2} + \frac{d^n p A_p}{\varepsilon} \] (4.11)

where subscripts 1 and 2 refer to the slope of the transient before and after the interruption respectively. Immediately after the interruption there is a discontinuity in the transient due to a change in the ohmic potential drop. Therefore the slope was determined after the discontinuity. If it is assumed that the active area does not change significantly in the short time span after the interruption, equations 4.11 and 4.12 may be equated and solved for the capacitance:

\[ C'_d = \frac{i_{a1} - i_{a2}}{\frac{dE}{dt} \bigg|_{1} - \frac{dE}{dt} \bigg|_{2}} \] (4.12)
Figure 4.16: Potential transient after a current interruption at 8 ms under base case conditions
The results of these calculations are illustrated in Figure 4.17. The potential at the time of interruption ranged from a value of 0.1 V at 1 ms to 0.8 V at 8 ms. The capacitances varied between 9-14 \( \mu F/cm^2 \) with the average value being 11.6 \( \mu F/cm^2 \). Thus it is concluded that the capacitance is independent of the potential in this potential range.

The capacitance was also measured with the use of a capacitance bridge. In this experiment two pieces of pretreated aluminum were placed in separate cell holders and connected to the bridge. The electrodes were at the open circuit potential (\( \approx -0.84 \) V) and were immersed in 1 N HCl at 65° C. The capacitance was monitored for two minutes and was found to increase from an initial value of 9.6 \( \mu F/cm^2 \) to a final value of 60 \( \mu F/cm^2 \). The increase in the capacitance may be a result of oxide film growth which occurs due to a reaction between the metal and water. It was desired to measure the potential as quickly as possible so as to limit this effect. The operation of the apparatus required a few seconds to measure the capacitance; therefore the capacitance may be slightly higher than the initial value. Because of the uncertainty in determining the capacitance with this method, it was decided to use the values determined from the current interruption experiments.

It should be noted at this point that the other experimental parameters in the current balance equation have also been determined. The current density in the pit, \( i \), is proportional to its growth rate.

\[
i = \frac{\rho n F}{MW} \frac{dr}{dt} = 2.9 \frac{dr}{dt}
\]  

(4.13)

It will be assumed for the current balance equations that the growth rate in the pits is equal to the growth rate of tunnels. At 65° C in 1 N HCl the growth rate of tunnels
Figure 4.17: Plot of $C_d$ vs. etch time
was 2.12 μm/s (see sec. 4.1.7.3) which would give a value for \( i_d \) of 6.15 mA/cm². The value for the current efficiency has been experimentally determined by Alwitt et al. [5] to be approximately 1.15. The excess metal dissolved during the etch has been correlated with the hydrogen that is evolved at the electrode surface. With all of the experimental parameters determined, current balance calculations may be done to verify the model.

4.1.3.3 Current balance calculations of the active pit area  The size distributions and pit densities from the 1, 8, 20 ms cases were used to calculate the measured active area. The active area may be calculated from the following equation:

\[
A_p = 12npr^2
\]  

Equation 4.6 was used to calculate the active area from the current balance equation. The potential transients from each of the corresponding distributions were used for these calculations.

The comparison between these two active areas is shown in Figure 4.18. The uncorrected data represent the measured active areas calculated from the pit densities in Table 4.2. These values are approximately 1.5-2 times greater than the active area from the current balance equation. It was mentioned earlier that a significant number of pits form during the pretreatment and immersion stages of the experiment. However, in potentiostatic etching experiments at -0.4 V, the initial current is near zero [26]. Thus it may be concluded that these pits are inactive. Since it has been shown that these pits have the same mean square depth as those from the etching experiments, it can be reasoned that the density of the etched samples should be
corrected to eliminate the influence of the pretreatment and immersion. The corrected densities range from $0.92 \times 10^5$ at 1 ms to $8.8 \times 10^5$ at 20 ms. From the figure it appears that this correction allows for good agreement between the two values. The difference in the values is approximately 20-30 % which is within the experimental error encountered for the measurement of the pit density and size distributions.

The agreement of these two values confirms two assumptions inherent in the calculations. First, all sides of the pit are active, i.e., there has been no repassivation. This result is not surprising as the potential is always above the critical repassivation potential. It has also been shown that the average current density at the active surface is equal to the current density within tunnels.

The potential transient can be used to illustrate how the two current sources, capacitive and metal dissolution, supply the constant applied current. Initially there are not enough active pits to supply the applied current by metal dissolution alone. An anodic capacitive current density (i.e., $\frac{dE}{dt} > 0$) must be present to supply the additional current. As more pits are nucleated, the metal dissolution current-density supplies a greater fraction of the applied current. At the maximum potential, where $\frac{dE}{dt} = 0$, the applied current is supplied by metal dissolution alone. After the maximum potential, the nucleation of new pits means that the metal dissolution current will exceed the applied current. A cathodic capacitive current (i.e., $\frac{dE}{dt} < 0$) must then be present to maintain the constant applied current. At the base of the transient the cathodic capacitive current is abruptly reduced from a value of 2.3 mA/cm\(^2\) to 0 mA/cm\(^2\). In order to maintain a constant applied current either a new cathodic source must be present or part of the active area must be repassivated.
Figure 4.18: Total pit area calculated from the current balance equation and the pit size distribution
It has been shown that the average current density inside a pit is equal to that in tunnels (6.15 A/cm²). It was also shown that pit growth due to metal dissolution is negligible during the initial region of the transient. This result poses a question as to how the pits attained their relatively large initial sizes. The apparent current density, $i_{app}$, in a pit may be calculated from Equation 4.13. Given that a majority of the pits grow to a minimum depth of 0.1 μm in 1 ms, the apparent current density is 290 A/cm². This value is approximately 50 times greater than the current density in tunnels. Pit volume calculations will be done in the next section to investigate this discrepancy further.

4.1.4 Studies of the apparent initial current density in etch pits

In order to investigate the high apparent current density, it is necessary to determine whether the pits could have grown to their large sizes by electrochemical metal dissolution alone. If this assumption is true, the total charge applied during an etch can be directly related to the total volume of the pits by Faraday’s law. In this section a comparison will be made between the measured and faradaic pit volumes for the different etch times.

For these calculations it will be assumed that the pits are half-cubic and that only metal dissolution and capacitive charging supply the applied current density. The faradaic volume may be calculated from the total amount of charge that is passed that is used for metal dissolution.

$$V_{far} = \frac{\varepsilon |iat - C_d(E - E_{oc})|MW}{nF\rho}$$  \hspace{1cm} (4.15)
The measured pit volume is calculated from the following equation:

\[ V_m = 4n_pr^3 \]  

(4.16)

where \( r^3 \) is the mean cube depth. The volume present due to the pretreatment and immersion was subtracted from this value to obtain the actual etched volume.

A comparison between the measured and faradaic volumes are shown in Table 4.4. For the base case experiments the ratio of the measured volume to the faradaic volume ranged from 100:1 at 1 ms to 4:1 at 20 ms. The table also shows the effect of pretreatment of the aluminum on the measured and faradaic volumes at an applied current density of 200 mA/cm\(^2\). The samples which had been pretreated again showed a significantly larger measured volume in comparison with the faradaic volume. However, for the untreated samples the values for the two volumes are close. It may be concluded from these results that for the pretreated samples the rapid initial growth occurs by a currentless mechanism. The decrease in the ratio of the measured volume to the faradaic volume indicates that the currentless mechanism is initially very fast, but then decays at later times. In contrast, pit growth for the untreated sample is by an electrochemical mechanism alone. The effect of the pretreatment on the mechanism for pit growth will be examined in the following paragraphs.

In order to explain the effect of the pretreatment, it would be useful to know how aluminum interacts with HCl at room temperature; however, no such investigations could be found in the literature. Pretreatment in HCl followed by immersion in the 65\(^\circ\) C electrolyte at the open circuit potential produced approximately 3 x 10\(^5\) cm\(^{-2}\) pits; while no pits were formed at open circuit on the sample which had not been pretreated. When water was substituted for HCl in the pretreatment, the
pit density after the pretreatment and 5 s immersion in 1 N HCl at 65° C was $1.7 \times 10^5 \text{ cm}^{-2}$. Conversely, pretreatment of the sample with HCl followed by immersion in water at 65° C produced an insignificant number of pits. It is evident that exposure of aluminum to water at room temperature, followed by immersion in HCl, also produces a significant number of pits. This result suggests that water, which is incorporated into the oxide film during pretreatment, is a cathodic reactant for open circuit pitting. It has been shown that at higher temperatures, excess water is first incorporated into the oxide film and then reacts with aluminum to thicken the film [34]. Although it is not known to what extent this process occurs at room temperature, it seems reasonable that some water becomes incorporated in the oxide film during the pretreatment. It is possible then that these pits formed at open circuit may be a result of a similar currentless mechanism that produced the large initial pit growth rates under an applied current.

A fraction of the electrons produced by the anodic aluminum reaction in pits are consumed at the oxide surface by a cathodic reaction. A possible cathodic reaction is the reduction of water to hydrogen gas. As suggested previously, the water reaction may occur due to the incorporation of water in the oxide film. For the untreated sample this cathodic reaction would be suppressed. For this mechanism the apparent dissolution current density, $i_d$, is the sum of the apparent current density and the cathodic current density divided by the pit area. It is evident then that $i_d$ would be a net anodic current density and would not actually be the metal dissolution current density. It is possible that the true dissolution current density is 290 A/cm², and that pretreatment enhances the rate of the cathodic reaction. Ford, Burstein and
Table 4.4: Comparison of the measured and faradaic pit volumes for the no pretreatment and pretreatment cases

<table>
<thead>
<tr>
<th>$i_d$ (mA/cm$^2$)</th>
<th>Etch Time (ms)</th>
<th>$V_m$ (cm$^3$/cm$^2$)</th>
<th>$V_f$ (cm$^3$/cm$^2$)</th>
<th>$V_m/V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.89</td>
<td>1</td>
<td>$5.0 \times 10^{-9}$</td>
<td>$1.5 \times 10^{-10}$</td>
<td>33</td>
</tr>
<tr>
<td>12.89</td>
<td>1</td>
<td>$1.3 \times 10^{-8}$</td>
<td>$1.4 \times 10^{-10}$</td>
<td>93</td>
</tr>
<tr>
<td>12.89</td>
<td>8</td>
<td>$1.8 \times 10^{-8}$</td>
<td>$3.1 \times 10^{-9}$</td>
<td>5.8</td>
</tr>
<tr>
<td>12.89</td>
<td>8</td>
<td>$2.2 \times 10^{-8}$</td>
<td>$3.1 \times 10^{-9}$</td>
<td>7.1</td>
</tr>
<tr>
<td>12.89</td>
<td>20</td>
<td>$3.6 \times 10^{-8}$</td>
<td>$8.5 \times 10^{-9}$</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>8</td>
<td>$2.6 \times 10^{-7}$</td>
<td>$5.5 \times 10^{-8}$</td>
<td>4.7</td>
</tr>
<tr>
<td>200</td>
<td>8</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$5.5 \times 10^{-8}$</td>
<td>2.9</td>
</tr>
<tr>
<td>200†</td>
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<td>$5.4 \times 10^{-8}$</td>
<td>0.26</td>
</tr>
<tr>
<td>200†</td>
<td>8</td>
<td>$5.1 \times 10^{-8}$</td>
<td>$5.4 \times 10^{-8}$</td>
<td>0.94</td>
</tr>
</tbody>
</table>

† untreated aluminum sample
Hoar [35] observed that for bare aluminum alloy surfaces the dissolution current densities can be very high. However, since \( i_d \) is the same current density that was calculated from tunnel growth rates, it seems likely that it represents the true metal dissolution current density. Therefore it is suggested that another currentless process in parallel with the metal dissolution current is responsible for the large initial growth rates.

It is possible that the pits grow to sizes of 0.1 \( \mu \)m by a vacancy condensation mechanism. In this mechanism water, which has been absorbed into the oxide film, reacts with aluminum at the oxide/metal interface.

\[
\text{Al} + 2 \text{H}_2\text{O} \rightarrow \text{AlOOH} + \frac{3}{2} \text{H}_2
\]  

(4.17)

This reaction is known to be rapid at temperatures approaching 100\(^\circ\)C [34]. The aluminum atoms are removed from the lattice and then incorporated into the oxide film leaving vacancies behind at the surface. The reaction may therefore create a supersaturation of vacancies in the metal near the oxide/metal interface. Doherty and Davis [36] have shown that thermal etch pits form as a result of a supersaturation of vacancies at the metal surface followed by vacancy diffusion to a nucleation site. It is proposed that this situation is analogous to the etching experiments. The growth rate of the pit would depend on the flux of vacancies to a nucleation site. The flux may be estimated by assuming that pit growth is a result of steady state diffusion to a hemisphere within a semi-infinite medium.

\[
N_v = \frac{D_v C_v \rho}{r MW}
\]  

(4.18)

In this equation \( C_v \), the mole fraction of vacancies at an infinite distance from the pit, is controlled by the rate of reaction between water and aluminum and the rate at
which vacancies can diffuse in aluminum. The pit growth rate is related to the flux by the following equation:

\[ 2\pi r^2 N_v = \frac{2\pi r^2 \rho \frac{dr}{dt}}{MW} \]  

(4.19)

From these two equations the pit growth rate may be determined.

\[ \frac{dr}{dt} = \frac{D_v C_v}{r} \]  

(4.20)

If it is assumed that \( D_v C_v \) is constant, the growth rate of the pit would decrease as \( r \) becomes larger. This result agrees with the observation that the apparent growth rate decreases at later times. In order to verify this mechanism it will be necessary to determine the kinetics of the aluminum oxide reaction and the diffusivity of vacancies in the metal near the oxide/metal interface.

It has been shown that in the initial region of the transient that two current sources are present: a capacitive charging current density and a metal dissolution current density. It has also been shown that for the pretreated sample there are two independent growth mechanisms; one due to metal dissolution and the other due to a currentless mechanism. It would be of interest to demonstrate that these observations are consistent for etches done under different experimental conditions. In the next sections the influence of the pretreatment, applied current density, and etchant bath temperature on the potential transient and the pit morphology will be explored.

4.1.5 The effect of the pretreatment on the initial stages of etch pit development

For this set of experiments the aluminum sample was untreated prior to being etched at 12.89 mA/cm² in 1 N HCl at 65° C. As shown in Figure 4.19, the shape
of the potential transient is altered by the change in pretreatments. The slope in
the rising section of the transient for the case where the sample was not pretreated is
greater than that for the base case and results in a maximum potential of 1.05 V. The
potential remains near this maximum for 15-20 ms before declining to about -0.35 V
at 35 ms. The potential minimum is not seen in this case, but rather a slow potential
decay to -0.42 V is observed over the next 60 ms. The large difference between the
constant potentials for the two cases was unexpected. Since the experiments were
done in the same solution, the difference cannot be explained by a change in the
ohmic drop in solution. Evidently another resistance is present at the surface for the
untreated sample that is not present for the base case.

The pit morphology and density was also influenced by the change in pretreat-
ment. SEM micrographs taken of untreated samples that had been etched between
1-16 ms at 12.89 mA/cm² revealed large (0.3-1.4 µm) irregularly shaped pits. It was
observed that pits less than 0.2 µm were conspicuously absent. The average mean
square depth for these pits, assuming a half-cubic shape, was 0.35 µm² and the stan-
dard deviation was 0.28 µm². The pit density ranged between 1.5 x 10³ cm⁻² at
1 ms to 5.8 x 10³ cm⁻² at 16 ms. The pit density after immersion of an untreated
sample was determined to be 5 x 10³ cm⁻². From these pit densities it is observed
that there is not a significant difference in the pit density of an etched sample and the
pit density of a sample which had only been immersed in the hot electrolyte solution.

4.1.5.1 The effect of NaOH pretreatment on the initial stages of etch
pit development In this experiment an aluminum sample was pretreated with
NaOH for 20 minutes, rinsed with de-ionized water and then stored in a vacuum
Figure 4.19: Comparison of the galvanostatic transients for pretreated and untreated samples
desiccator for 6-8 hours. Afterwards the sample was pretreated in 1 N HCl for 5 minutes and then etched under base case conditions. A comparison between the potential transients for the base case and the NaOH + HCl pretreatment is shown in Figure 4.20. The maximum potential for the NaOH pretreatment is approximately -0.3 V and the initial region lasts for nearly 80 ms. A small 5 mV minimum is observed before the potential becomes constant at -0.72 V. The significant alterations in the shape of the potential transient suggest again that the pretreatment, and hence the initial condition of the oxide film, may be important in the initial growth of the etch pits.

4.1.6 The effect of the applied current density on the initial stages of etch pit development

For the experiments in this section the applied current density was increased from 12.89 mA/cm² to 200 mA/cm². Pretreated and untreated samples were used for this case while all other base case conditions were retained. From Figure 4.21 it is seen that the potential transients for the 200 mA/cm² etches have features which were not present for the base case. The transient from the pretreated sample rises very rapidly (less than 1 ms) and is observed to pass through maxima near 1.7 V. The potential remains near the maximum for approximately 12-15 ms before beginning to decline. At about 1.2 V the potential goes through an inflection point before declining rapidly to a constant potential of -0.35 V at 20 ms. The inflection may be due another electrochemical reaction that occurs at the oxide surface. The potential minimum is about 10 mV below the constant potential. For the untreated sample it is observed
Figure 4.20: Comparison of the galvanostatic transients for the base case pretreatment and the NaOH pretreatment.
that both the maximum potential (2.4 V) and the constant potential (-0.15 V) are
greater than that for the pretreated sample. The inflection occurs at approximately
1.6 V but again no potential minimum is observed near the constant potential region
for the untreated sample.

Figure 4.22 shows the pit size distribution for a pretreated sample which had
been etched at 200 mA/cm² for 8 ms. A high density of small pits were observed
for this case. The mean square depth of the distribution was 0.0224 µm² and the
standard deviation was 0.0218 µm². The pit density was approximately 5.83 x 10⁶
cm⁻². The pit size distribution for an untreated sample which had been etched
for 8 ms at 200 mA/cm² is shown in Figure 4.23. The mean square depth of the
distribution was 0.52 µm² and the standard deviation was 0.64 µm². It is observed
again that there are no pits below 0.2 µm and that there is a significant number of
large pits. The pit density was approximately 2.8 x 10⁴ cm⁻². From these results
it is apparent that the pit sizes do not increase significantly with an increase in the
applied current density. The pit density on the other hand was observed to increase
by a factor of 10.

4.1.7 Effect of the Etchant Bath Temperature on the Base Case Results

For this section, the base case experiments were repeated except that the etchant
bath temperature was varied between 25-90° C. The potential transient and pit mor-
phology will be analyzed by the same procedures as above.

4.1.7.1 Galvanostatic transient results The potential transients for the
different etchant bath temperatures are shown in Figure 4.24. There are several
Figure 4.21: Comparison of the galvanostatic transients for pretreated and untreated samples at different applied current densities
Figure 4.22: Pit size distribution after an 8 ms etch at 200 mA/cm$^2$; pretreatment with 1 N HCl at room temperature
Figure 4.23: Pit size distribution after an 8 ms etch at 200 mA/cm$^2$; no pretreatment.
changes in the features of the potential transient. It is observed that the maximum potential decreases with an increase in temperature. The three lower temperatures have approximately the same maximum potential, 0.8 V, while at 90°C the maximum potential is almost 0.3 V lower. The time required to reach the maximum potential decreases from 60 ms at 25°C to 22 ms at 90°C. The time to reach the constant potential from the maximum potential also decreases with an increase in temperature (28 ms to 9.5 ms). The potential minimum feature of the transient is observed to disappear as the temperature decreases. Finally it is seen that the value of the constant potential increases as the temperature is decreased; this potential is determined by the repassivation potential and the ohmic resistance.

The changes observed in the initial region of the potential transient may be related to changes in the experimental parameters in the current balance equation. It is of interest then to see how parameters such as the capacitance, pit size distribution and density are influenced by temperature. In addition the temperature dependence of the growth rate in tunnels will be measured. The values obtained will be used to estimate the current density within a pit for that given temperature. The current balance equation will then be tested to see if the assumptions made about the initial growth of etch pits are valid at these temperatures.

4.1.7.2 Pit morphology at different etchant bath temperatures Pit size distributions and densities were again determined at times within the initial region of the potential transient. Etch times of 1, 8, 16 and 20 ms were used at temperatures of 25°C and 45°C while times of 1, 4, and 8 ms were used for the 90°C etch. Initially the size distributions and pit densities were again measured from
Figure 4.24: Comparison of the galvanostatic transients for etchant bath temperatures between 25-90° C.
100-200 micrographs taken at 10,000 X. At the two lower temperatures 25° and 45° C small pits with a depth between 0.05-0.7 μm were again present. It also became apparent, however, that there were a number of pits with depths greater than 0.7μm. As can be seen in Figure 4.25 these pits tended to cluster together and overlap. Oxide replicas of the surface reveal large irregularly shaped structures which are probably associated with these large pits. Their irregular shape make it difficult to estimate the active area of these pits. However, as a first approximation it will be assumed that these pits are also half cubic. In order to view a significant number of these pits a magnification of 2500 X was used. The size and density of these pits may make a substantial contribution to the active area. At 90° C only the smaller pits were present in significant numbers.

The pit size distribution which resulted from a 1 ms etch at 25° C, is shown in Figure 4.26. Approximately 7% of the distribution is comprised of pits that are greater than 0.7 μm. Pit depths as large as 1.8 μm were present. The log-normal distribution parameters were μ = -1.49 and σ = 0.786. The pit size distribution for a 1 ms etch at 45° C is shown in Figure 4.27. Again it is observed that approximately 7% of the pits have a depth greater than 0.7 μm. The log-normal distribution parameters were μ = -1.57 and σ = 0.528. The size distribution for the 90° C etch however contained predominantly small pits. The pit size distribution for a 1 ms etch is shown in Figure 4.28. The log-normal distribution parameters were μ = -2.03 and σ = 0.502.

Table 4.5 contains a complete summary of the distribution parameters and pit densities for these experiments. At the lower temperatures, the data at certain times has been decomposed to represent both the distribution of small pits and of large
Figure 4.25: Scanning electron micrograph of large pits which form after an etch at 45° C; magnification 2500 X
Figure 4.26: Pit size distribution after a 1 ms etch, $i_0 = 12.89$ mA/cm$^2$, $T = 25^\circ$ C, pretreatment with 1 N HCl at room temperature.
Figure 4.27: Pit size distribution after a 1 ms etch, $i_a = 12.89 \text{ mA/cm}^2$, $T = 45^\circ \text{C}$, pretreatment with 1 N HCl at room temperature.
Figure 4.28: Pit size distribution after a 1 ms etch, \( i_a = 12.89 \text{ mA/cm}^2, T = 90^\circ \text{C} \), pretreatment with 1 N HCl at room temperature
Among the set of experiments done at a given temperature the mean square depth of the small pits does not appear to change significantly. A statistical analysis, similar to that done previously was done for each distribution. It was estimated that the mean square depths for the population of small pits at $25^\circ$, $45^\circ$ and $90^\circ$ C were 0.0457, 0.0685 and 0.0221 $\mu m^2$ respectively. At each temperature, the mean square pit depth is within the 95% confidence intervals for the distribution means. The confidence intervals at $25^\circ$ and $45^\circ$ C however, allowed for approximately 50-200 % error in the mean square depth. The large error is due primarily to the low number of pits in the distributions. The error in the means at $90^\circ$ C was smaller at approximately 30-60%. The large error in the means suggests that caution must be used when drawing conclusions about the active area. Although the pit density estimates do not exhibit the same consistency that was observed at $65^\circ$ C, they do suggest that pits are continuously nucleating.

Between the distributions at different temperatures two trends became apparent. The mean square depth decreases as the temperature increases while the pit density increases with temperature. The same trends were observed for the comparison between the pretreated and untreated samples. Thus in addition to calculating the active area, it will be of interest to compare the measured pit volume and the faradaic pit volume for the different temperatures. Before these comparisons can be done however, information on the growth rate and capacitance at these temperatures must be obtained.

4.1.7.3 The effect of etchant bath temperature on the current density inside the pit. It was mentioned previously that the current density within the pit
Table 4.5: Summary of the pit size distribution parameters and density for different etch times in 1 N HCl at temperatures of 25°, 45°, and 90° C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Etch time (ms)</th>
<th>Magnification</th>
<th>$r^2$ (μm$^2$)</th>
<th>$\sigma$ (μm$^2$)</th>
<th>np x $10^5$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>10000</td>
<td>0.0652</td>
<td>0.05</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>1</td>
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<td>0.0425</td>
<td>0.0333</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>10000</td>
<td>0.0426</td>
<td>0.0327</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>10000</td>
<td>0.0346</td>
<td>0.0278</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2500</td>
<td>1.441</td>
<td>0.691</td>
<td>0.123</td>
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<tr>
<td></td>
<td>8</td>
<td>2500</td>
<td>2.192</td>
<td>1.767</td>
<td>0.071</td>
</tr>
<tr>
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<tr>
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<td>0.670</td>
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<td>0.0100</td>
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<td>0.0286</td>
<td>0.0227</td>
<td>9.31</td>
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<tr>
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<td>10000</td>
<td>0.0217</td>
<td>0.0175</td>
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</tr>
</tbody>
</table>
is proportional to the growth rate of etch tunnels. Hebert and Alkire [37] have shown that the growth rate demonstrates an Arrhenius dependence upon temperature:

$$\frac{dr}{dt} = v_0 \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (4.21)

They also showed that the growth rate also depends on the type of foil that has been etched. Therefore, growth rate experiments were repeated with the Toyo foil to determine the appropriate pre-exponential factor and activation energy for the Arrhenius expression. The technique used by Hebert and Alkire was used with etchant bath temperatures between 45-90°C. It was previously stated that tunnels form only at temperatures above 60°C. Although the distribution of tunnels at 45°C was poor, the tunnels present showed the wave-like structure that is due to the sawtooth current waveform. No tunnels were evident at 25°C. Figure 4.29 is an Arrhenius plot of the growth rate versus 1/T. The slope of the line, which is equal to \(-\frac{E_a}{R}\), is \(-6730\) K\(^{-1}\) and hence the activation energy is 13.37 kcal/mole. The pre-exponential factor was then calculated to be \(8.8 \times 10^8\) \(\mu\)m/s. These values are quite similar to Hebert's which were 15 kcal/mol and \(6.5 \times 10^9\) \(\mu\)m/s. Table 4.6 is a summary of the growth rates calculated from Equation 4.21, and their associated current densities, at the temperatures used in the previous section. The value at 25°C was extrapolated from the higher temperature data since no tunnels were observed at this temperature. These values will be used in the current balance calculations.

4.1.7.4 Current balance calculations of the active area Current interruption experiments were carried out to determine the effect of temperature on the capacitance. The data indicated that the capacitance is independent of the etchant
Figure 4.29: Arrhenius plot of tunnel growth rates in 1 N HCl
Table 4.6: Growth rates and metal dissolution current density in tunnels at different temperatures

<table>
<thead>
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<th>Temperature (°C)</th>
<th>v (μm/s)</th>
<th>i (A/cm²)</th>
</tr>
</thead>
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</tr>
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<td>45</td>
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<td>1.64</td>
</tr>
<tr>
<td>65</td>
<td>2.12</td>
<td>6.14</td>
</tr>
<tr>
<td>90</td>
<td>7.799</td>
<td>22.61</td>
</tr>
</tbody>
</table>

bath temperature. The average value of the capacitance is 11.3 μF/cm² which is near the value for 65° C. This average value for the capacitance will be used for these current balance calculations.

To calculate the measured active area it will again be assumed that the mean square radius of the population of small pits may be used. At the lower temperatures an area term which includes the mean square radius of the large pits will be included. It will also be assumed that all of the sides of the pit are active and that there is continuous nucleation of pits. The measured area was also corrected for pits which may have nucleated during the pretreatment and immersion.

Figures 4.30-4.32 compare the measured area with the area calculated from the current balance for each temperature. At the lower temperatures the large pits provide a significant fraction of the active area. As can be seen at 25° C the current balance equation predicts an area that is ten times greater than the measured area, while at 45° C the equation predicts an area that is two times greater than the measured area. However, at 90° C the measured area is approximately two times greater than the calculated area. The large uncertainty in the distribution parameters may explain some of the discrepancies. Also due to a higher \( i_d \) at 90° C the total pit current
density is more sensitive to errors in measurement of the pit density. However, the error in pit density measurement does not explain the order of magnitude difference observed at 25°C. This result suggests two possibilities: 1) The metal dissolution rate is equal to that in tunnels and therefore another current source must be present or 2) The apparent growth rate in the pits is approximately 10 times greater than that predicted for tunnels.

Pit volume calculations were again made to determine whether the etchant bath temperature influences the pit growth mechanism. Table 4.7 shows the results of these calculations for temperatures between 25-90°C and for etch times of 1 and 8 ms. Since these samples were pretreated, it was again observed that the measured pit volume is greater than the faradaic volume. It is also seen that the ratio of \( V_m/V_f \) for a 1 ms etch increases from 100:1 at 65°C and 90°C to 550:1 at 25°C. It appears then that the currentless mechanism depends upon the temperature of the etchant bath.

Table 4.7: Comparison of the measured and faradaic pit volume for temperatures of 25°C and 90°C, \( i_a = 12.89 \text{ mA/cm}^2 \), HCl pretreatment

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (ms)</th>
<th>( V_m \times 10^8 \text{ (cm}^3/\text{cm}^2) )</th>
<th>( V_f \times 10^8 \text{ (cm}^3/\text{cm}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1</td>
<td>11.41</td>
<td>0.02</td>
</tr>
<tr>
<td>25</td>
<td>8</td>
<td>11.36</td>
<td>0.29</td>
</tr>
<tr>
<td>90</td>
<td>1</td>
<td>2.13</td>
<td>0.02</td>
</tr>
<tr>
<td>90</td>
<td>8</td>
<td>1.54</td>
<td>0.32</td>
</tr>
</tbody>
</table>

In this section it was attempted to confirm that the current balance equation would explain the effect of the etchant bath temperature on the base case. Although the quantitative results showed some error, some qualitative conclusions were drawn.
Figure 4.30: Total pit area calculated from the current balance equation and the pit size distribution, $T = 25^\circ C$
Figure 4.31: Total pit area calculated from the current balance equation and the pit size distribution, $T = 45^\circ C$
Figure 4.32: Total pit area calculated from the current balance equation and the pit size distribution, $T = 90^\circ \text{C}$.
The growth and nucleation of etch pits in the initial region of the transient has been investigated. It was concluded that shortly after the initial region passivation must occur to maintain the current balance. Eventually it will be desired to use the current balance along with microscopic observations of pits and tunnels to understand the mechanism for the transformation of etch pits into etch tunnels. Before investigating this question, it will be necessary to learn more about the processes which control the total metal dissolution current density. In the next sections electrochemical measurements will be interpreted for this purpose.

### 4.2 An Investigation of the Metal Dissolution and Repassivation Kinetics for Short Etch Times

As shown previously in Figure 4.2, after the initial region the potential goes through a potential minimum near the base of the initial region. The difference between the minimum and the constant potential was between 10-60 mV and the duration of this region was about 5 ms. It was suggested that at 35 ms the total metal dissolution current density is reduced. Figure 4.33 shows a potential transient, at base case conditions, before and after a 25% current reduction at 50 ms. After the current reduction, the potential decays rapidly to a minimum potential in approximately 170 μs. The potential then relaxes back to a constant value after about 6-8 ms. The difference between the constant and minimum potential is about 35 mV. This difference will be defined as ΔE₂. As shown previously, the difference between the potential prior to the interruption and the constant potential was due to the change in the ohmic-overpotential in the bulk solution. The similarity between these
two potential responses suggests that the fundamental processes controlling the total metal dissolution current density are the same. Therefore, current step experiments will be investigated to determine the metal dissolution and repassivation kinetics.

4.2.1 A study of the metal dissolution kinetics in the potential decay region

In this section the decay of the potential to the minimum, following the current step, is considered. Prior to the current reduction, the applied current density is supplied by metal dissolution alone. From the current balance equation it is apparent that at the minimum potential the new applied current density is supplied by metal dissolution alone. Since the applied current density has been reduced at this time, the total current density from the pits has been reduced. There are three means by which the total current may be reduced: a) passivation, b) a decrease in the metal dissolution current density, and c) an increase in the hydrogen evolution rate. Tak and Hebert [38] performed current pulse and alternating current experiments to examine this question. The first step was to use the current pulse experiments to establish a minimum time for passivation to initiate. In these experiments, after an initial etch time of 5 s, the current was reduced to a new value for times between 2-12 ms before being returned to its initial value. It was observed that for the 2 ms pulse the tunnels did not constrict. Since the decay time to the minimum potential is less than 0.2 ms, the active area remains constant during this time and hence there is no passivation. The alternating current experiments were used to determine whether the metal dissolution current density within the pit varies with time as the current,
Figure 4.33: Potential transient following a 25% step current reduction at 50 ms,
\[ i_{a1} = 12.89 \text{ mA/cm}^2 \]
and hence the potential, is rapidly changed. For this experiment a constant current was applied for 5 s and then followed by a series of alternating positive and negative current steps for an additional 5 s. One cycle consisted of holding the current at a low value for 2 ms and then returning to the original value for 4 ms. It was determined that the average growth rate decreased from 2.0 μm/s while the constant current was applied to 1.5 μm/s during the alternating current. The slower growth rate was a result of a variation in the metal dissolution current density as the applied current was cycled. These results indicate that in the decay region the metal dissolution current density decreases.

The potential drop ΔE₂ is associated with changes in the overpotentials within pits or tunnels. It was shown earlier that for small pits (i.e., times less than 50 ms) the concentration and ohmic overpotentials are negligible. It may then be concluded that ΔE₂ is due to a change in the surface overpotential. However, these calculations did not take into account the possibility of an obstruction within the pit or tunnel. Hydrogen bubbles have been observed to evolve from the pit surface during an etch. The presence of these bubbles in the pits and tunnels would increase the resistances to current flow and diffusion. The minimum transient diffusion time for the current step experiments is \( \tau_D = r^2 / D_+ \). Given that \( r = 0.5 \, \mu m \) and \( D_+ = 6.65 \times 10^{-6} \, cm^2/s \) [21], \( \tau_D \) is 0.4 ms. This time is two times greater than the longest time observed for the potential decay. The effect of the obstruction would be to make this time even longer. Therefore during the potential decay to \( E_{min} \) the concentration overpotential remains constant and ΔE₂ may be due to changes in the ohmic and surface overpotentials.
In order to distinguish between the ohmic and surface resistance contributions, the effect of the solution conductivity on $\Delta E_2$ was determined for 50 ms etch times. For these experiments an initial applied current density of 12.89 mA/cm$^2$ was used followed by a 40 % step current reduction. The solution conductivity was varied between 0.0603-0.531 Ω$^{-1}$-cm$^{-1}$. The variation of the bulk concentration of HCl and AlCl$_3$ ensures that there will be significant differences in the pit solution conductivities. Figure 4.34 shows that $\Delta E_2$ is constant at approximately 0.044 V and is therefore independent of the solution conductivity. If hydrogen bubbles are present in the pit, the ohmic potential drop would be approximately 5 times greater than the value of 1.7 mV calculated previously [39]. The lack of any significant change in $\Delta E_2$ with the conductivity demonstrates that $\Delta E_2$ does not exhibit ohmic behavior. It is concluded that $\Delta E_2$ and the potential transient below the constant potential is associated with the change in the surface overpotential necessary to provide a reduced metal dissolution current density. For the repassivation studies the focus will be on the section of the transient below the constant potential. To begin this study, the relationship between the percent change in the metal dissolution current density and $\Delta E_2$ will be investigated.

Values for $\Delta E_2$ were determined from current reduction experiments performed in 1 N HCl at 65° C. The initial applied current was varied from 12.89-200 mA/cm$^2$ and the current reduction percentage ranged from 10-60%. From Figure 4.35 it can be seen that at a constant initial-applied current $\Delta E_2$ increases linearly with an increase in percent current reduction. It can also be observed that for a constant current reduction $\Delta E_2$ increases slightly with an increase in the initial applied current. The
Figure 4.34: Plot of $\Delta E_2$ vs. $1/\kappa$
slope of the lines ranged from 0.124 V at 12.89 mA/cm\(^2\) to 0.164 V at 60, 100 and 200 mA/cm\(^2\). From this figure it is apparent that there is a linear relationship between the metal dissolution current density and the surface overpotential:

\[ i_d = i_o[1 + k(E - E_o)] \quad (4.22) \]

where \(i_o\) and \(k\) are constants. Since \(\Delta E_2\) depends on potential changes associated with individual pits, it should not depend on the applied current density. However it is observed that at the lowest current density, \(\Delta E_2\) is approximately 30 % smaller than at the higher current densities. It was found that at the lowest current density the time for the potential decay to the minimum was approximately 3-4 times longer than that for the higher current densities. Therefore, for the lowest current density, appreciable passivation of the active surface may have occurred. A model will be developed in a later section to investigate this question.

The current balance equation after the current reduction may be written as:

\[ i_{a2} = Q_d \frac{dE}{dt} + \frac{n_p A p i_d}{\varepsilon} \quad (4.23) \]

It will be assumed that the decay time is short so that little or no passivation occurs during this time. Therefore, the active area is constant and equal to the active area before the step. After substitution of Equation 4.22, the current balance may be written as:

\[ i_{a2} = C_d \frac{dE}{dt} + i_{a1}[1 + k(E - E_o)] \quad (4.24) \]

where

\[ i_{a1} = \frac{n_p A p i_o}{\varepsilon} \]
Figure 4.35: Plot of $\Delta E_2$ vs. percent current reduction for initial applied current densities between 12.89-200 mA/cm$^2$. 
At the minimum potential \( dE/dt \) is zero, therefore,

\[
\frac{i_{a2} - i_{a1}}{i_{a1}k} = \Delta E_2 \tag{4.25}
\]

The value of \( k \) is the inverse slope of the lines shown in Figure 4.35. Substitution of this equation into the current balance, followed by rearrangement, yields the differential equation:

\[
\frac{dE}{dt} + P(E - E_0) = P\Delta E_2 \tag{4.26}
\]

where,

\[
P = \frac{i_{a1}k}{C_d} \tag{4.27}
\]

The initial condition for this equation is \( E = E_0 \). The differential equation may be solved analytically and the result is that the dimensionless potential, \( \xi \), changes exponentially with time.

\[
-\ln \left( \frac{E_{\text{min}} - E}{\Delta E_2} \right) = -\ln \xi = Pt \tag{4.28}
\]

This relationship will now be used to predict the experimental potential decay observed for the current reduction experiments. The potential decay after a 25% reduction of an initial current density of 12.89 mA/cm\(^2\) is shown in Figure 4.36. From this transient and Equation 4.28 the dimensionless potential may be calculated. An exponential curve fit was performed with the aid of the ASYSTANT software package [22]. Generally only the first 4-8 points of the transient after \( E_0 \) were used. The onset of a significant amount of signal noise made curve fitting difficult near the minimum. This signal noise may also be an indication that other processes such as repassivation are initiating. The slope, \( P \), calculated from the curve fit was defined
as the exponential decay slope. Based on previously determined experimental values for $k$ and $C_d$, a theoretical value for the exponential decay slope may be calculated from Equation 4.27. A comparison of these two decay slopes will be made to verify the model.

Figure 4.37 is a semi-log plot of the dimensionless potential vs. time. The initial applied current density was 60 mA/cm$^2$ and the current reductions were between 10-50%. The line represents the average exponential decay for all the current reduction experiments performed at this current density. It is observed that the exponential decay slope is independent of the amount the current is reduced. This result is expected as Equation 4.27 predicts that the potential depends only on the initial applied current density. The dimensionless potential decay for a sample which had been pretreated with NaOH is also included in the figure. The current reduction for this case was 25%. The agreement with the HCl pretreatment results allows us to conclude that the initial stages of repassivation are similar for both cases.

The theoretical value for the exponential decay slope was calculated from Equation 4.27 and compared with the curve fit values. It will be assumed that the true value for $k$ is determined from the results at the higher current densities (6.1 V$^{-1}$). Figure 4.38 shows the exponential decay slope as a function of the initial applied current density. Again the value from the NaOH pretreatment is included in the figure. Good agreement between the fit values and the theoretical value is achieved. The differences at the lower current densities may be due to a small amount of passivation which occurs in the potential decay region. Since the decay time is 3-4 times longer for an initial applied current density is at 12.89 mA/cm$^2$ than for the higher current
Figure 4.36: Potential transient decay after a 25% step current reduction of an initial current density of 12.89 mA/cm$^2$.
Figure 4.37: Plot of the dimensionless potential vs. time for the decay region
densities, it is possible that some passivation has begun to occur. Therefore, for this case the assumption that no passivation occurs in the decay region may no longer be valid. It should be realized, however, that the primary mechanism for the reduction of the total metal dissolution current density is the reduction of the metal dissolution current density at the active surface.

After the minimum potential, the potential begins to rise and relax back to \( E_0 \). Based on the current balance, and the dependence of metal dissolution current density on the surface overpotential, one would expect that the potential increases in order to supply a higher metal dissolution current density that will compensate for a reduction in active area due to passivation. In the next section a model for the passivation velocity will be coupled with the current balance equation to predict the behavior of the experimental potential relaxation.

4.2.2 A study of the passivation velocity as the potential relaxes to a constant value

Hebert and Alkire [40] performed current reduction experiments with initial etch times between 1.35 s and 10.8 s. The effect of using different initial etch times was to increase the depth at which the constriction was observed from 2.5-20 \( \mu \text{m} \). Their experiments were performed in 1 N \( \text{AlCl}_3 \) at a temperature of 70° C. The initial applied current density was 10 mA/cm\(^2\) and the step current reduction they used was 40 %. They found that the inverse square root of the slope of the relaxation of \( \ln \phi \) with time is linearly related to the tunnel length.

\[
S_t^{-0.5} = S_{t_0}^{-0.5} + (2AD)^{-0.5}t \tag{4.29}
\]
Figure 4.38: Plot of the exponential decay slope as a function of the initial applied current density.
Therefore, they determined that the relaxation is determined by diffusion of the electrolyte out of the tunnel. The intercept was associated with a transport resistance which is independent of tunnel length. It was not considered to be caused by a surface kinetic resistance in series with mass transport in the tunnel. Figure 4.39 shows a plot of $S_t^{-0.5}$ vs. 1 for their experiments. The line indicates the dependence of the potential decay on diffusion in the tunnel. Also included in this figure are the slopes calculated from the current reduction experiments performed with initial etch times between 50 ms and 1.5 s. The time constant, $t_{0.8}$, is defined as the time necessary for the surface overpotential $(E - E_0)$ to achieve a value that is 20% of its initial value $(\Delta E_2)$. It is related to $S_t$ by the following equation:

$$\exp(-S_t t_{0.8}) = 0.2$$  \hspace{1cm} (4.30)

For example at the intercept, $S_t^{-1/2} = 0.159$ s$^{1/2}$, $t_{0.8}$ is 41 ms. Tak and Hebert [38] showed from the current pulse experiments that after 12 ms the tunnel tip areas had been reduced to their final values. Thus it appears that there is no relationship between the time constant for potential decay during tunnel growth and the time for repassivation. However, if the current is reduced at 50 ms, $S_t^{-1/2} = 0.035$ s$^{1/2}$ and hence $t_{0.8} = 2.65$ ms. Therefore it seems more likely that the potential relaxation time for pits is similar to passivation times. Thus the potential relaxation after a current reduction at short etch times will be investigated.

Figure 4.40 shows the potential relaxation for step current reductions between 10-50%. The initial applied current density in each case was 60 mA/cm$^2$ and the etch time prior to the current reduction was 50 ms. The change in potential from the time of the current interruption is monitored. The initial slope of the relaxation is observed
Figure 4.39: Plot of the exponential decay slope as a function of the tunnel length
to increase from 5 V/s for the 10% current reduction to 25 V/s for the 50% reduction. After 4-5 ms, the slopes become equal at approximately 3 V/s. The time necessary to reach the final constant potential is about 8 ms and appears to be independent of the percent current reduction. Often, particularly for the larger current reductions, a potential maximum occurs at about 6 ms. The difference between the maximum potential and the constant potential is between 2-7 mV. The influence of the initial applied current density on the relaxation time was also investigated. Figure 4.41 shows the potential relaxation for a 25% current reduction to initial applied currents between 12.89-200 mA/cm². It is apparent that the time constant for the potential is independent of the initial applied current density.

For etch times less than 750 ms, no constrictions were observed on the etch tunnels. At times greater than 750 ms constrictions were observed. The constrictions are evidence that the extent of passivation was the same for all structures on the surface. Conversely, the lack of constrictions suggest that the structures do not all experience the same extent of passivation.

From Figure 4.42 it is apparent that the tunnel tip passivates from one side. Thus the passivation models were developed to account for two situations. The transformation from etch pit to tunnel has been due to the simultaneous passivation of the pit walls. Therefore, for etch times of less than 750 ms, at which the surface is populated with etch pits, it will be assumed that passivation occurs at a constant rate from all sides of the pit or tunnel. For the NaOH pretreatment and at times greater than 750 ms, it will be assumed that passivation occurs from one side of the tunnel tip. Although the shapes are different for these cases, it may be possible to show that
Figure 4.40: Potential transient relaxation for current reductions between 10-50 %, $i_d = 60$ mA/cm$^2$, etch time = 50 ms
Figure 4.41: Potential transient relaxation for initial applied current densities between 12.89-200 mA/cm², 40% step current reduction, etch time = 50 ms
Figure 4.42: Scanning electron micrograph of an oxide replica which exhibits a constriction after an initial etch time of 1 s, magnification 10,000 X
the potential driving force for repassivation is similar for both cases. Therefore the potential transients after the current reduction for these situations will be analyzed.

The current balance equation may now be used to predict the potential transient in this region. It will be assumed that the passivation velocity increases linearly with the surface overpotential:

\[ v_p = -A_1 \eta_s \]  

(4.31)

This assumption is supported by the view that passivation is controlled by chloride adsorption on the active surface, as will be discussed below.

The metal dissolution current density is proportional to the rate of aluminum oxidation. For heterogeneous reactions it is appropriate to express the reaction rate in terms of the surface concentrations of the adsorbed species. Adsorbed chloride serves to block oxygen species from the metal surface and to facilitate the removal of metal atoms [13], while adsorbed oxygen passivates the metal surface. Chloride ions have a tendency to specifically adsorb on many metals [41,42]. Increasing the anodic polarization from the potential of zero charge increases the coverage of specifically adsorbed anions. Potentials of about 1 V above the potential of zero charge are necessary to achieve monolayer coverage of the adsorbed anion. The extent of the surface coverage of chloride anions at the repassivation potential may be qualitatively estimated. The potential of zero charge for aluminum can be estimated from the work function correlation of Trasatti [43] to be about -0.85 V NHE at 25°C. Given that the repassivation potential is approximately -0.45 V NHE at 25°C [44], it is apparent that there is significant coverage of the surface with the chloride anion. It has also been shown that the potential at a given coverage of specifically adsorbed anion
decreases linearly with the logarithm of the anion concentration in the solution [45]. This response is similar to the dependence of the repassivation potential on the anion concentration in solution.

The current density may be expressed as a function of the chloride surface coverage:

\[ i_d = i_o \frac{\theta Cl^-}{Cl_o^-} \]  

(4.32)

where \( i_d \) is the metal dissolution current density, \( i_o \) is the current density at \( E_o \), \( \theta Cl^- \) is the equilibrium chloride surface coverage at a given potential, and \( \theta Cl_o^- \) is the chloride surface coverage at \( E_o \). It will be assumed that when the potential at the surface is at the critical repassivation potential; that is, when the measured potential is at \( E_o \), the current density within the pit is the same as for etch tunnels. According to Equation 4.32, below the critical repassivation potential chloride ions begin to desorb from the surface and oxide species adsorb to the empty sites. The surface which has been covered by the oxide adsorbates does not dissolve while the metal that remains covered by the chloride ions continues to dissolve at a uniform rate. Therefore since the chloride surface coverage has been reduced, from Equation 4.32 it can be shown that \( i_d \) decreases.

It was assumed that the oxide surface coverage of the aluminum depends on the equilibrium chloride surface coverage at a given potential, \( i.e., \theta_{ox} = 1 - \theta Cl^- \). The oxide coverage at the interface between the oxide film and the bare aluminum surface is determined by the equilibrium between the oxide film and the active surface, and is equal to the surface oxide coverage of the bare aluminum at the repassivation potential. Thus at the repassivation potential the adsorbed oxide is in equilibrium
with the film. As the potential decreases below the critical repassivation potential
the chloride ions desorb instantaneously from the surface and assume a coverage
determined by the adsorption isotherm at a given potential. Oxide adsorbates then
adsorb to the empty sites on the aluminum surface. At this stage the surface oxide
coverage of aluminum exceeds the oxide coverage in equilibrium with the oxide film
surrounding the active surface. To achieve equilibrium at the interface the oxide
adsorbates are transported to the oxide film and then incorporated into the bulk
oxide. The rate at which this process occurs is expressed as:

\[ v_p = kg(\theta ox - \theta ox_0) \quad (4.33) \]

This expression assumes that the oxide surface coverage of the aluminum is uniform
at any given potential. The coverage is determined by the surface coverage of chloride
in equilibrium with the solution at a given potential. The absence of concentration
gradients on the surface assumes that the oxide adsorbates diffuse rapidly to the oxide
film interface. Therefore the only resistance to oxide film coverage over the surface is
at the interface between the oxide film and the active surface.

From the above discussion the oxide surface coverages may be related to the
surface overpotential in the following manner:

\[ \frac{\theta_{C1^-}}{\theta_{C1^0}} = \frac{1 - \theta ox}{1 - \theta ox_0} = 1 + k(E - E_0) \quad (4.34) \]

The final relationship between the passivation velocity and the surface overpotential
may then be written as:

\[ v_p = -kk_1(1 - \theta ox_0)(E - E_0) = -A_1(E - E_0) \quad (4.35) \]
where $A_1$ is a constant.

From the potential transients it is observed that the maximum capacitive current density in this potential region occurs soon after the minimum potential. The maximum capacitive current density for any of the current reduction experiments that were done was approximately 0.5% of the final applied current density. Therefore, as a first approximation, it will be assumed that the capacitive current density is negligible as the potential relaxes. The simulation also included assumptions about the shape of the active area. A square patch was used to represent the active area. Both passivation from all sides of the patch and from one side of the patch are illustrated. It will be assumed that all the patches have the same initial width. The number of patches was determined by the active area necessary to supply the initial applied current density by metal dissolution alone. It is assumed that for times less than 750 ms the pits and tunnels passivated from all sides, while for samples that had been pretreated with NaOH and etched for times greater than 750 ms tunnels appear to passivate from one side of the base. Differential equations which describe the shapes for both situations will be derived. For both cases the rate at which the width, $w$, decreases is given by:

$$\frac{dw}{dt} = -v_p = A_1(E - E_o)$$  \hspace{1cm} (4.36)

Thus a relationship between the area passivated and the potential may be developed. A final assumption that will be made is that initiation of new pits during the relaxation period may be neglected.

The case where passivation occurs from all four sides of the patch will be considered first. After substitution of Equation 4.36, the current balance equation may
be written as:

\[ i_{a2} = \frac{n_{pi0}w^2}{\varepsilon}(1 + \frac{k\,dw}{A_1\,dt}) \]  \hspace{1cm} (4.37)

It will be advantageous to make use of dimensionless variables in order to reduce the number of unknown parameters that are varied. The dimensionless variables are expressed as:

\[ \tau = \frac{k_g(1 - \theta_0x_0)t}{w_f} \]

\[ X = \frac{w}{w_f} \]

where \( w_f \) is the final width which is determined by the percent current reduction. The variables \( \tau \) and \( X \) are the dimensionless time and width respectively. The dimensionless current balance is then written:

\[ X^2(1 + \frac{dX}{d\tau}) = 1 \]  \hspace{1cm} (4.38)

The initial condition for \( X \) is dependent upon the percent current reduction as is shown in the following equation:

\[ X_0 = \frac{1}{\sqrt{1 - \%\text{ reduction}}} \]  \hspace{1cm} (4.39)

The differential equation may be solved analytically to give a relationship between \( X \) and \( \tau \).

\[ \tau = (X_0 - X) + \frac{1}{2} \ln \frac{(1 + X)(1 - X_0)}{(1 - X)(1 + X_0)} \]  \hspace{1cm} (4.40)

The dimensionless potential, \( \phi \), may then be derived from Equation 4.36.

\[ \phi = k(E - E_0) = -\frac{dX}{d\tau} = \frac{1 - X^2}{X^2} \]  \hspace{1cm} (4.41)
Likewise for the one sided passivation case the current balance equation may be written as:

\[ i_{a2} = \frac{n_p i_0 h \omega}{\varepsilon} (1 + \frac{k}{A_1} \frac{d\omega}{dt}) \]  \hspace{1cm} (4.42)

In this equation the variable \( h \) represents the length of the side of the pit that remains constant. The same dimensionless variables that were used previously may be utilized and hence the dimensionless current balance may be written as:

\[ X(1 + \frac{dX}{d\tau}) = 1 \]  \hspace{1cm} (4.43)

The initial condition for \( X \) depends upon the percent current reduction.

\[ X_0 = \frac{1}{1 - \% \text{ reduction}} \]  \hspace{1cm} (4.44)

Again the differential equation may be solved analytically to determine a relationship between \( \tau \) and \( X \).

\[ \tau = (X_0 - X) + \ln \frac{1 - X_0}{1 - X} \]  \hspace{1cm} (4.45)

Finally the dimensionless potential, \( \phi \), may again be derived from Equation 4.37.

\[ \phi = k(E - E_0) = -\frac{dX}{d\tau} = \frac{1 - X}{X} \]  \hspace{1cm} (4.46)

The kinetic parameter for the passivation velocity was calculated from the time constants of the experimental potential transients. The time constant (\( t_{0.8} \)) was determined from the experimental transients manually. This particular time constant was chosen because as the slope of the transient approached zero it became more difficult to distinguish the time at which the small change in the potential occurred. This problem was also encountered for the 10% current reduction. It was observed that the surface overpotential is approximately 20% of its initial value for a time
interval of 0.5 ms. Thus small errors in the value of the time constant may occur at the lower percent current reductions. The experimental time constant was observed to decrease slightly from approximately 3.2 ms at 10% current reduction to 2 ms at 60% current reduction. Given that there was some scatter in the data for the time constant, there may be no significant difference in these values.

The decay of the surface overpotential to a value that is 20% of it original value may be represented by the following equation.

\[
\frac{\phi}{\phi_0} = \frac{X_0^2(X^2 - 1)}{X^2(X_0^2 - 1)} = 0.2
\]

(4.47)

Solving this equation for \(X\) in terms of \(X_0\) will yield:

\[
X = \sqrt{\frac{X_0^2}{0.8X_0^2 + 0.2}}
\]

(4.48)

Finally, substitution of this equation into Equation 4.40 will give a relationship between \(\tau_{0.8}\) and \(X_0\).

\[
\tau_{0.8} = X_0 \left(\frac{\sqrt{0.8X_0^2 + 0.2} - 1}{\sqrt{0.8X_0^2 + 0.2}}\right) + \frac{1}{2} \ln \left(\frac{1 - X_0}{1 + X_0}\right) \left(\frac{\sqrt{0.8X_0^2 + 0.2} + X_0}{\sqrt{0.8X_0^2 + 0.2} - X_0}\right)
\]

(4.49)

Figure 4.43 shows a plot of \(\tau_{0.8}\) vs. \(X_0\) for both passivation cases. It is observed that the dimensionless time constant is about two times larger for the one sided passivation case than for passivation from all sides. This result is not due to a difference in the kinetic parameter for the passivation velocity, but rather a difference in the geometry of the active area. From the dimensionless time variable the kinetic parameter may be estimated by the following equation:

\[
k_g(1 - \theta_{ox}) = \frac{\tau_{0.8}w_0}{X_0t_{0.8}}
\]

(4.50)
Figure 4.43: Plot of $\tau_{0.8}$ vs. $X_o$ for passivation from one side and from all sides
where $w_0$ is the initial width of the patch.

An estimate of the kinetic parameter may be made from the results of the current reduction experiments at 50 ms. A square patch with an active area equivalent to a half-cubic pit has a width of $2\sqrt{3} r$. The initial value for $r$ will be assumed to be the same as the average pit depth from the base case experiments in the initial region, 0.21 μm. As an example, the results from a 40 % current reduction at 12.89 mA/cm² will be shown. The values for $r_{0.8}$ and $t_{0.8}$ were 0.897 and 2.65 ms respectively. From Equation 4.50 the kinetic parameter was then estimated to be 246 μm/s.

Figure 4.44 shows the experimental transient along with the transient from the analytical calculations. The analytical transient used the following parameter values: $w_0$ for pits is 0.727 μm, $X_0$ for a 40 % reduction is 1.291, $k_g (1 - \theta_{oxo})$ is 246 μm/s, $E_o$ for an initial current density of 60 mA/cm² was -0.693 V, and $k$ is 6.1 V⁻¹. Although there is a difference in the initial slope after the minimum, the general shape of the calculated transient shows good agreement with the experimental transient. Therefore, this passivation model, along with the kinetic parameter $k_g (1 - \theta_{oxo})$, may be used to predict the potential minimum observed after the initial region.

Finally, a model for the potential transient was developed in which the capacitance term in the current balance equation was not neglected. It is recalled that the passivation velocity of the oxide film is related to the overpotential by the following equation:

$$\frac{dw}{dt} = k_k (1 - \theta_{ox}) (E - E_o)$$  \hspace{1cm} (4.51)

Insertion of this equation in to the current balance yields:

$$i_{a2} = \frac{C_d}{k_k (1 - \theta_{oxo})} \frac{d^2 w}{dt^2} + n_p i_w^2 (1 + \frac{1}{k_g (1 - \theta_{oxo})} \frac{dw}{dt})$$  \hspace{1cm} (4.52)
Figure 4.44: Comparison of the experimental and analytical potential relaxation, $i_{\text{inj}} = 60 \text{ mA/cm}^2$, etch time = 50 ms
This equation may be expressed in a dimensionless form as:

$$\beta \frac{d^2 X}{d\tau^2} + X^2 \left(1 + \frac{dX}{d\tau}\right) = 1 \quad (4.53)$$

where,

$$\beta = \frac{C_d r_{0.8}}{t_{0.8} k_1 a_2} \quad (4.54)$$

$\beta$ represents the ratio of the capacitive current density to the applied current density.

The initial conditions for this second order differential equation were:

$$X = X_0 \quad (4.55)$$

$$\frac{dX}{d\tau} = 0 \quad (4.56)$$

The dimensionless potential was calculated from the following equation:

$$\phi = -\frac{dX}{d\tau} \quad (4.57)$$

The differential equation was then solved with IMSL subroutine DIVPAG [29], which uses Gear's method to solve initial value problems.

A comparison between experimental values for $\Delta E_2$ and the analytical values are shown in Figure 4.45 as a function of the initial applied current density. The initial current densities were between 2-200 mA/cm$^2$ and a 40 % current reduction at 50 ms was used. At the higher current densities both the analytical and experimental are relatively constant and independent of the applied current density. This result indicates that the system reduces the total current during the decay region of the transient by reducing the metal dissolution current density. However, for current densities less than 50 mA/cm$^2$, $\Delta E_2$ begins to decrease significantly for both the analytical and experimental values. From the analytical results it was found that
significant passivation had occurred during the decay region. Since passivation occurs, the reduction in the metal dissolution current density necessary to supply the applied current density is less than if no passivation occurs. This result supports the model given here which is based on the view that the transient is determined by metal dissolution kinetics and oxide coverage.

In this section the focus has been on extracting information on the kinetics of repassivation from potential transient measurements. In the next section these kinetic parameters will be used to predict features of the potential transient which occur during constant current etching.

4.3 Prediction of the Potential Transient at Times After the Initial Region

In a previous section it was proposed that for a constant applied current density passivation may be initiated near the potential minimum which occurs at 35 ms in Figure 4.2. It will be examined whether the passivation kinetics model, along with the kinetic parameters, may be used to predict the potential transient during etching. The computer simulation for the potential minimum region was done by a procedure similar to that used for the step current reduction experiments. It was assumed that the pits may be represented by a square patch with a width of $2\sqrt{3} \ r$, where $r$ is the pit depth. It was also assumed that the initial size distribution of $r$ was the same as the size distribution for the initial region. It is recalled that the initial size distribution was divided into seven pit classes that are 0.1 $\mu m$ wide. The number of pits was determined by the metal dissolution current density present at the base of the initial
Figure 4.45: Comparison between the experimental and analytical values of $\Delta E_2$ as a function of the initial applied current density.
region. From Figure 4.2 the slope of the transient at this point is approximately -200 V/s which means that given an applied current density of 12.89 mA/cm², the metal dissolution current density is 15.21 mA/cm². The number of pits present, \( n_p \) is then calculated from the following equation:

\[
np = \frac{i_{tot} \varepsilon}{n \sum_{i=1}^{i_d} f_i w_i}
\]

(4.58)

where \( i_{tot} \) is the total metal dissolution current density, \( \varepsilon \) is the current efficiency, \( i_d \) is the current density in a pit, \( f_i \) is the fraction of pits in a given size classification, and \( w_i \) is their initial size. The nucleation rate was assumed to be continuous and equal to the experimental nucleation rate. Subsequent generations of nucleating pits were assumed to have the same size distribution as the initial pits. The simulation is composed of coupled initial value problems. The width of the pit for each classification is determined by the following derivative:

\[
\frac{dw}{dt} = kkg(1 - \theta_0 x_0)(E - E_0)
\]

(4.59)

The passivation is assumed to occur from all sides of the pit. The active area may then be calculated from the width of the square patch. The active area is coupled to the surface overpotential via the current balance equation.

\[
\frac{d\eta_s}{dt} = \left( i_a - \frac{n_p A p_d i_d}{\varepsilon} \right) / C_d
\]

(4.60)

The initial condition for the surface overpotential was \( \eta_s = 0 \). The IMSL subroutine DIVPAG [29], which uses Gear's method to solve for a system of initial value problems, was used for these calculations. The experimental parameters used in the simulation
were:

\[ i_a = 12.89 \text{ mA/cm}^2 \]
\[ C_d = 11.6 \mu\text{F/cm}^2 \]
\[ E_o = -0.722 \text{ V} \]
\[ k = 6.1 \text{ V}^{-1} \]
\[ k_g(1 - \theta_{oxo}) = 0.0246 \text{ cm/s} \]
\[ \varepsilon = 1.15 \]

Figure 4.46 shows a comparison between the experimental potential minimum and that predicted from the computer simulation. It is observed that the time necessary to achieve the minimum potential (\( \approx 0.5 \text{ ms} \)) and the time necessary to return to the constant potential region (\( \approx 5 \text{ s} \)) is predicted from the simulation. However, the experimental minimum potential is approximately 20 mV less than the predicted minimum potential. The depth of the potential minimum was expected to be proportional to the excess current density. \( E_{\text{min}} \) may be calculated from the following equation:

\[ E_{\text{min}} = E_o + \frac{i_a - i_{\text{tot}}}{k_{i_{\text{tot}}}} \] (4.61)

Given the previous values, \( E_{\text{min}} \) would be expected to be -0.747 V which agrees with the predicted value from the simulation. At times just prior to the minimum potential, the whole surface of the pit is active and may be covered by chloride species exclusively. Thus the additional overpotential observed for the minimum potential may reflect the initial adsorption of oxygen species on the active surface.

Additional kinetic information may also be obtained from microscopic observa-
Figure 4.46: Comparison between the predicted and experimental potential transients near the potential minimum.
tions of the pit and tunnel morphology. Based on this information and the results of the passivation kinetic studies an attempt to predict the morphology of pits and tunnels via a computer time simulation will also be made.

4.4 Pit and Tunnel Morphology at Later Etch Times

The profile of a tunnel was briefly described in chapter 1. Given that the metal dissolution rate is known, the profile provides a record of the rate at which the oxide film grows along the walls. In most cases the tunnel walls were nearly parallel from the mouth of the tunnel to its tip. Occasionally the tunnel would widen or narrow at various locations along the profile. However, the width would always return to a nearly constant value. Given that tunnels originate from etch pits, the initial position of the oxide film would be above the pit bottom. Thus, if the passivation velocity of the oxide film is slow compared with the growth due to metal dissolution, the walls of the pit would be expected to expand. The parallel walls near the mouth of the tunnel suggest, however, that the oxide film reached the pit bottom quite rapidly. Once the oxide film reaches the pit bottom, it grows at a rate equal to the metal dissolution rate. The current balance and the repassivation kinetics will be used to interpret these characteristics of the tunnel profile.

It is of interest to determine the minimum pit size at which tunnel growth becomes stable. This question may be investigated with the combined pit and tunnel size distribution. In order to superimpose these distributions, a characteristic length representative of the active areas for each of these structures is needed. Since the tunnel walls do not expand significantly near its mouth, the active area for the tunnel
is $4 r^2$, where $r$ is the initial pit depth. Thus, the distribution of tunnel half-widths may be superimposed on the distribution of pit depths.

The distributions were measured from a sample which had been etched for 30 s under the base case conditions. The tunnel half-widths were determined from SEM micrographs taken at 10,000 X. Approximately 100 tunnels were randomly selected for this distribution. The tunnel half-widths ranged between 0.2-1.1 \(\mu m\) and had an average half-width of 0.455 \(\mu m\). The density of tunnels on the surface was estimated to be $1.14 \times 10^6 \text{ cm}^{-2}$. A large number of cubic etch pits which had not transformed into tunnels were also seen on the replicas. The density of these pits was determined to be approximately $4 \times 10^6 \text{ cm}^{-2}$. Thus only 22\% of the cubic etch pits initiated transform into tunnels. Although a distribution of these pits was not determined, it was observed that a significant number of these pits had a width less than that of tunnels. The proportion of pits in each size classification was assumed to be equal to that for the size distribution in the initial region. The combined pit and tunnel density was then used to determine the proportion of pits and tunnels in each size classification. The distribution is shown in Figure 4.47.

Two conclusions may be drawn from these results about the transformation of cubic etch pits into etch tunnels. Small etch pits (< 0.2 \(\mu m\)) are passivated soon after they are initiated. The lack of expansion at the pit mouth also suggests rapid passivation of the pit walls has occurred. The hypothesis for this work was that small changes in the surface overpotential provide the driving force for repassivation. Given this hypothesis, the distribution suggests that the changes in the surface overpotential experienced by the small pits are sufficiently large to passivate the whole pit.
Figure 4.47: Combined distribution of pit and tunnel widths after a 30 s etch at base case conditions
However, the changes in the surface overpotential experienced by the large pits are only able to passivate the walls of the pit. Beck, Uchi and Hebert [46] have shown that active tunnels are passivated rapidly in response to pit nucleation. Thus the rapid passivation observed in these cases may also be a response to pit nucleation. This rapid passivation is necessarily confined to pits and tunnels located near the nucleating pits since uniform rapid passivation would violate the current balance. The driving force for passivation would be local potential changes induced by nucleation. However, it is also observed that during steady tunnel growth the passivation velocity is uniform and equal to the metal dissolution velocity. The same uniform passivation was observed for step current reductions after the sample had been pretreated in NaOH and after an initial etch time of 750 ms. It remains therefore to examine both local and uniform passivation. Simulations of tunnel structures will be done in the next sections to further investigate the role of uniform repassivation in the development of tunnel structures.

4.5 The Pit and Tunnel Shapes Predicted by an Extended Time Model

Before discussing the uniform repassivation model and the results of the simulation, details of the computer simulation will be presented. In order to predict the profile, and calculate the metal dissolution current for the current balance equation, it is necessary to develop a relationship between the passivation velocity, \( v_P \), and the profile. The two basic profiles observed at different stages of pit and tunnel growth are illustrated in Figure 4.48. The profiles are defined as pit mode and tunnel mode. The dark lines in the figures represent the length of the oxide film at time \( t'(x) \), while the
dashed lines indicate the active perimeter of the structure. The relationship between \( v_p \) and the profile can be derived from the following equation:

\[
\int_{0}^{t'(x)} v_p \, dt = \int_{0}^{x} \sqrt{\left(\frac{dw_{t}}{dx_{t}}\right)^2 + 1} \, dx \tag{4.62}
\]

The left side of the equation is the distance the oxide film has grown after time \( t'(x) \). The right side is the formula for the arc length traced out by the oxide film. For pit mode the relationship between \( w_{t} \) and \( t'(x) \) is given by:

\[
w_{t} = w_{o} + v(t'(x) - t_{o}) \tag{4.63}
\]

where,

- \( w_{o} \) = initial radius of the oxide film, \( \mu m \)
- \( v \) = growth rate due to metal dissolution, \( \mu m/s \)
- \( t_{o} \) = time at which the pit or tunnel initiates, \( s \)

This equation assumes that bulges occur in the profile when the oxide film is above the active tip and the walls of the pit or tunnel expand at a rate of \( v \). The derivative of this equation with respect to \( x_{t} \) is:

\[
\frac{dw_{t}}{dx_{t}} = \frac{v}{d_{t}'(x)} \tag{4.64}
\]

Substitution of this equation into Equation 4.62 and differentiation with application of the Leibnitz rule gives:

\[
v_{p} \frac{dt'}{dx_{t}} = \sqrt{v^2 (\frac{dt'}{dx_{t}})^2 + 1} \tag{4.65}
\]
Figure 4.48: Basic pit and tunnel profiles: a) pit mode and b) tunnel mode
This equation along with Equation 4.64 will give a differential equation which relates
the position of the oxide film to \( v_p \).

\[
\frac{dw_f}{dx_t} = \frac{v}{\sqrt{v_p^2 - v^2}} \quad (4.66)
\]

Equation 4.62 can be used to derive a similar equation for tunnel mode.

\[
\frac{dx_t}{dw_t} = -\frac{v}{\sqrt{v_p^2 - v^2}} \quad (4.67)
\]

In this situation the oxide film is at the corner between the tunnel tip and the wall.
This profile would describe tunnels with parallel walls or walls that taper. A description
of the setup and procedure for the simulation is listed below.

1. The pits are placed in discrete size categories which correspond to the experimental pit size distribution. The width of each size category is 0.1 \( \mu \)m and the midpoint of each category will be used to calculate the active area. The experimental distribution is determined from the population of pits measured at 65\(^\circ\) C. Initially all sides of the pit are active.

2. The nucleation rate is continuous and equal to the experimental nucleation rate of \( 4.464 \times 10^5 \ t^{-0.69} \ cm^{-2} \cdot s^{-1} \).

3. Subsequent generations of pits are assumed to have the same size distribution as the initial pits. An additional initial value problem was necessary for each size category within each generation. It will also be assumed that at these short times the difference in area between a pit with all of its sides active and one that is partially passivated may be neglected.
4. For a constant applied current density at times greater than 100 ms the capacitive current density is negligible. Therefore, the nucleation of new active area must be balanced by the repassivation of an equal amount of active area. Thus for the simulation the rate at which active area is nucleated will determine the growth rate of the oxide film in each pit.

5. An iterative algorithm was used to determine the passivation velocity in each pit or tunnel. The iteration began by nucleating a new generation of pits. The initial value problems were solved by an iterative Euler technique. A value of \( v_p \) was chosen to calculate the derivatives which determine the position of the oxide film. The active area in each pit and tunnel could then be calculated.

6. The sum of the metal dissolution current densities in the pits and tunnels was compared with the applied current density. If they were not equal a new value of \( v_p \) was chosen. The IMSL subroutine DZBREN [29] was used for this iterative process. This routine uses Brent's method to find real roots of functions which change signs within a given interval.

7. The program also stored tunnel statistics in arrays. The statistics of interest were the length distribution of active and dead tunnels and the maximum width a pit attained prior to transformation into tunnel growth.

The simulation was performed for an etch time of 10 s. Figure 4.49 shows the distribution of active and dead tunnel lengths. It is observed that approximately 66% of the nucleated pits are passivated before they reach a depth of 1 \( \mu \)m. The length of the longest tunnel was about 6 \( \mu \)m. It was also determined that 97% of
the distribution was passivated. These results suggest that all of the pits nucleated at early times were passivated by 10 s, while the more recent generations of pits have been allowed to grow. To gain more information about the shapes of the tunnels, the maximum tunnel width for the active tunnels was plotted against the lengths of the active tunnels. As can be seen in Figure 4.50, the active tunnels have been identified by their initial pit depth. The number of data points for each depth classification corresponds to the number of generations of active tunnels. It is observed that the maximum width of the tunnels, for a given classification, is relatively independent of the time at which the tunnels were nucleated. Therefore the simulation has reached a steady state. The simulation predicts that the tunnel width expands to 3.5 \( \mu m \) at a depth of 3.5 \( \mu m \), and then gradually decreases until a width of zero is reached at 6 \( \mu m \). These tunnel shapes do not resemble the experimental tunnels. The width of the predicted pits expands to a value 6-8 times larger than their initial width. Experimentally, tunnels maintain an approximately constant width from their mouth to their tip.

The influence of the nucleation rate on the predicted tunnel shapes was also investigated. For this simulation a lower nucleation rate of \( 1.8 \times 10^3 \ t^{-0.8} \ cm^{-2} \ s^{-1} \) was used. For this case it was found that approximately 83% of the nucleated pits and were passivated before they reach a depth of 1 \( \mu m \). The percentage of passivated tunnels also increased to 99 observed though that the maximum tunnel length had increased to 21 \( \mu m \). This result indicated that a small fraction of the earlier generations of tunnels remained active. The tunnel shape was also investigated. From Figure 4.51 it is apparent that the maximum width for each pit classification have
Figure 4.49: Distribution of active and dead tunnel lengths predicted from a simulated etch time of 10 s.
Figure 4.50: Plot of the maximum width of active tunnels vs. the length of active tunnels for a simulated etch time of 10 s
increased as the nucleation rate was lowered. The lower nucleation rate has resulted in a slower average growth rate for the oxide film. The slower growth rate allows the pit to expand further. Therefore the predicted shapes have less resemblance to the experimental shapes than the previous case.

It is apparent from these simulations that uniform passivation within pits and tunnels does not explain the rapid transition from etch pits to etch tunnels. Another possibility is that the initial passivation velocity in pits is controlled by local fluctuations in the surface overpotential. Because of local potential changes accompanied by pit nucleation, both rapid passivation of the sidewalls of large pits and complete passivation of the small pits occurs.
Figure 4.51: Plot of the maximum width of active tunnels vs. the active tunnel length for a simulated etch time of 10 s, $dn_p/dt = 1.8 \times 10^3 t^{-0.8}$
5. CONCLUSIONS

In this work, the initial growth of cubic etch pits and their subsequent transformation into etch tunnels was investigated. Constant current and step current reduction experiments were performed and the results from the potential transients and the pit and tunnel morphology examined. Mathematical models were developed to explain these results in terms of mechanisms for the metal dissolution of the active surface and the passivation velocity of the oxide film. The conclusions made from this work are summarized below.

1. During the first 35 ms of the etch, all sides of the cubic etch pit remain active. It was also shown that the current density from the pits was equal to the metal dissolution current density in tunnels.

2. In the initial 35 ms after the current is applied, the current density is supplied by two sources: 1) a capacitive charging current density and 2) a metal dissolution current density. In the rising section of the transient there are not enough active pits to supply the applied current density by metal dissolution; therefore an anodic capacitive current density must be present. In the descending portion of the transient there is an excess metal dissolution current density so that the current balance is maintained by a cathodic capacitive current density. At the
base of this region this capacitive current is abruptly reduced to zero and the metal dissolution current density is greater than the applied current density. It is proposed that at this time the repassivation process initiates to reduce the metal dissolution current density.

3. It was shown that the initial growth rate of pits was much faster than that observed in tunnels. Pit volume calculations revealed that for pretreated samples a currentless mechanism in parallel with the metal dissolution current density is responsible for this fast growth rate. In contrast, it was found that for untreated samples the growth rate was due to electrochemical metal dissolution alone. It was proposed that the currentless mechanism may occur due to incorporation of water into the oxide film during the pretreatment. Vacancy condensation was suggested as a possible currentless mechanism.

4. After a step current reduction at 50 ms, the measured potential responds to changes in the ohmic drop in the bulk solution ($\Delta E_1$) and the surface overpotential ($\Delta E_2$). It was determined that repassivation processes were initiated as the potential transient goes through the region where $\Delta E_2$ is negative.

5. $\Delta E_2$ decreases linearly with the percent current reduction. This result implies that the metal dissolution current density decreases with the surface overpotential relative to $E_F$. A mechanism involving competitive adsorption between chloride ions and oxygen adsorbates was proposed to explain the response of the metal dissolution current density $\Delta E_2$ becomes more negative. At a given potential there is an equilibrium coverage of chloride ions and oxygen adsor-
bates. The metal below the chloride ions dissolves at a uniform rate, while that below the oxygen does not dissolve. Thus, the surface coverage of chloride ions determines the metal dissolution rate. After the step current reduction, as $\Delta E_2$ becomes more negative, the chloride ions desorb from the surface and are replaced by oxygen. The current density adjusts immediately to a lower value at each new potential.

6. The competitive adsorption model assumes that the oxygen adsorbate coverage on the active surface depends upon the chloride ion coverage at a given potential. The passivation velocity is determined by the equilibrium between the oxygen adsorbates and the oxygen at the interface between the active surface and the oxide film. The potential at which the oxygen adsorbates are in equilibrium with the oxygen at the interface is hypothesized to be the re-passivation potential. When the surface coverage of the oxygen is greater than the oxygen coverage at the interface, the oxygen is incorporated into the oxide film. Since the oxygen coverage depends upon the surface overpotential, the passivation velocity would increase as the surface overpotential becomes more negative.

7. These two mechanisms were combined to develop a mathematical model which predicted the time constant for the experimental potential relaxation. From these calculations an estimate of the kinetic parameter for oxide incorporation can be made.

8. A study of the pit and tunnel shapes revealed that small pits ($< 0.2 \mu m$) are passivated rapidly, while only the walls of the larger pits are passivated rapidly.
The rapid passivation is a result of changes in the local potential induced by nucleation of pits.

9. However, uniform passivation was observed during steady tunnel growth and after step current reductions.

10. An extended time model, which assumed uniform passivation, was unable to predict the experimental pit and tunnel shapes.

This work adopted the competitive adsorption model to explain the metal dissolution current density as well as the passivation velocity. Although the mathematical models present a simplified picture of the situation, good agreement between the experimental and theoretical potential transients was achieved. It is also apparent that in order to understand the pit and tunnel morphology, a model which incorporates local changes in the potential induced by nucleation should be developed.
6. LIST OF SYMBOLS

\( A \) area of the surface from which current flows, \( \text{cm}^2 \)

\( A_C \) area corrected for pretreatment and immersion, \( \text{cm}^2 \)

\( A_L \) area due to large pits, \( \text{cm}^2 \)

\( A_S \) area due to small pits, \( \text{cm}^2 \)

\( A_T \) sum of the areas due to large and small pits, \( \text{cm}^2 \)

\( A_p \) active area, \( \text{cm}^2 \)

\( A_1 \) proportionality constant between the passivation velocity and the surface overpotential, \( \text{cm/V-s} \)

\( a \) constant in repassivation potential relationship, \( V \)

\( b \) proportionality constant between repassivation potential and the log of the chloride ion concentration, \( V \)

\( C_p \) concentration of ions adjacent to the pit surface, \( \text{mole/cm}^3 \)

\( C_b \) concentration of ions in the bulk solution, \( \text{mole/cm}^3 \)

\( C_d \) differential capacitance, \( \mu\text{F/cm}^2 \)

\( C_v \) mole fraction of vacancies in metal
D diffusion coefficient of binary electrolyte, cm$^2$/s
D$_v$ diffusion coefficient for vacancies, cm$^2$/s
D$_+$ diffusion coefficient for Al$^{+3}$ ions, cm$^2$/s
E measured potential, V
E$_a$ activation energy, J/mole
E$_h$ constant potential with pretreatment, V
E$_l$ constant potential without pretreatment, V
E$_{min}$ minimum potential after a step current reduction, V
E$_o$ potential for zero passivation rate, V
E$_{oc}$ open circuit potential, V
F Faraday constant, 96500 coul/equiv
f$_{+-}$ mean activity coefficient
f$_i$ fraction of pits in a given size classification
h constant width for one sided passivation case, cm
i current density, A/cm$^2$
i$_a$ applied current density, A/cm$^2$
i$_{a1}$ applied current density prior to step current reduction, A/cm$^2$
i$_{a2}$ applied current density after the step current reduction, A/cm$^2$
i$_{app}$ apparent applied current density, A/cm$^2$
i$_o$ metal dissolution current density at potential E$_o$, A/cm$^2$
\( i_{tot} \) total metal dissolution current density, A/cm\(^2\)

\( k \) proportionality constant between the dissolution current density and the surface overpotential, V\(^{-1}\)

\( k_g \) proportionality constant between the passivation velocity and the excess surface concentration of oxygen, cm/s

\( l \) length scale, cm

\( MW \) molecular weight of aluminum, 27 g/mole

\( n \) number of equivalents per mole, equiv/mole

\( n_p \) surface density of pits and tunnels, cm\(^{-2}\)

\( n_i \) number of pits in a sample

\( P \) exponential decay slope, s\(^{-1}\)

\( R \) gas constant, 8.314 J/mole-K

\( r \) pit depth, cm

\( S_t \) slope of the diffusion controlled potential relaxation, s\(^{-1}\)

\( T \) temperature, C

\( t \) time, s

\( t'(x) \) time at which the oxide film is at position x, s

\( t_o \) time at which a pit initiates, s

\( t_{0.8} \) time for 80% decay of the potential to the steady potential, s
$t^+_o$  transference number of the cation

$t^-_o$  transference number of the anion

$V_{far}$  faradaic equivalent volume, cm$^3$/cm$^2$

$V_m$  measured volume, cm$^3$/cm$^2$

$v$  growth rate due to metal dissolution, cm/s

$v_o$  pre-exponential factor, cm/s

$v_p$  passivation velocity, cm/s

$w$  width of a square patch, cm

$w_o$  depth of a nucleated pit, cm

$w_f$  final width of square patch, cm

$w_t$  distance from central axis of pit or tunnel to the leading edge of the oxide film, cm

$X$  dimensionless width

$X_o$  initial dimensionless width

$x_t$  distance along central axis of pit or tunnel to the leading edge of the oxide film

$z$  normal distribution function

$z_+$  charge on the positive ion

$\alpha$  confidence coefficient

$\beta$  ratio of the capacitive current density to the applied current density

$\Delta E_1$  discontinuous potential change after current step, V

$\Delta E_2$  total potential drop in the potential transient, in
excess of the initial discontinuous potential change, V

\( \varepsilon \)  
current efficiency for metal dissolution during etching, 115 %

\( \eta \Omega_{in} \)  
ohmic overpotential within pits and tunnels

\( \eta \Omega_{out} \)  
ohmic overpotential in the bulk solution, V

\( \eta_{c} \)  
concentration overpotential associated with pits and tunnels, V

\( \eta_{s} \)  
surface overpotential with respect to the passivation potential, V

\( \theta_{Cl^{-}} \)  
equilibrium coverage of chloride at a given potential

\( \theta_{ClO^{-}} \)  
equilibrium surface coverage of chloride at \( E_o \)

\( \theta_{ox} \)  
surface coverage of oxygen at a given potential

\( \theta_{oxo} \)  
surface coverage of oxygen at \( E_o \)

\( \kappa \)  
solution conductivity, \( \Omega^{-1}.\text{cm}^{-1} \)

\( \mu \)  
mean of \( \ln r \), \( r \) in cm

\( \nu \)  
stoichiometric coefficients

\( \xi \)  
dimensionless potential in the decay region

\( \rho \)  
density of aluminum, 2.7 g/cm\(^3\)

\( \sigma \)  
standard deviation of \( \ln r \), cm

\( \tau_D \)  
dimensionless diffusion time constant

\( \tau_{0.8} \)  
dimensionless time constant for 80 % decay

\( \phi \)  
dimensionless potential in the relaxation region

\( \chi \)  
chi-square distribution function
7. BIBLIOGRAPHY


8. ACKNOWLEDGEMENTS

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