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Passivation behavior of pure aluminum and sputtered non-equilibrium Al-Cr and Al-Ta alloy films

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The Ohio State University, 1993
PASSIVATION BEHAVIOR OF PURE ALUMINUM AND
SPUTTERED NON-EQUILIBRIUM Al-Cr AND Al-Ta ALLOY
FILMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School of
The Ohio State University

By

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* * * * *

The Ohio State University
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Dedicated to my Dad and his vision
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CHAPTER I

INTRODUCTION

Aluminum has a very good general corrosion resistance in neutral solutions but poor localized corrosion resistance. This can be inferred from the Pourbaix diagram (1) (fig.1) that indicates the presence of a thermodynamically stable passive film on the metal surface at neutral pH but corrosion at low and high pH values. As localized corrosion resistance requires the presence of a surface film that is stable at acidic pH present in occluded cells at the localized corrosion sites, it is understandable that aluminum has a poor localized corrosion resistance. Most passivity enhancing elements like Cr, Mo, W etc. have very little solid solubility in the aluminum matrix. Therefore attempts to alloy aluminum with these passivity-enhancing elements result in the formation of second-phase precipitates, whose interface with the matrix act as pit initiation sites. Also the second phase could establish an active microgalvanic cell. Therefore conventional alloying techniques result in little improvement or loss in the localized corrosion resistance of pure aluminum. In order to overcome these limitations and to improve the localized corrosion resistance of aluminum,
Figure 1: Potential-pH diagram for the system aluminum-water at 25°C.
several studies have focused on developing non-equilibrium aluminum alloys through sputter deposition or ion implantation (2-10). The primary benefit from such alloying techniques is the ability to contain the solute elements in solid solution within the primary aluminum phase in a supersaturated state. This has shown to result in a considerable enhancement of the pitting potential of the alloys compared to that of pure aluminum. A brief review of such investigations will be presented in chapter 2. Several models have been proposed to explain the mechanism causing the enhanced localized corrosion resistance in the non-equilibrium aluminum alloys (2-4, 7-10). However, these mechanisms lack universal applicability and are inconsistent with some experimental observations.

The objective of this study is to better understand the mechanism by which the sputtered non-equilibrium Al-Cr and Al-Ta alloy films exhibit a significantly higher localized corrosion resistance than pure aluminum.
CHAPTER II

LITERATURE REVIEW

The present study is an attempt to better understand the passivity and pitting characteristics of pure aluminum, and the nature of the passive film on metastable aluminum alloys prepared by sputter deposition. The techniques used were Electrochemical Impedance Spectroscopy (EIS) and Ellipsometry. The literature relevant to this study is therefore reviewed under the following headings.

1. Passivity Models
2. Passivation and Pitting Characteristics of Pure Aluminum
3. Passivation Characteristics of Metastable Aluminum Alloys
4. Ellipsometry Studies on Pure Aluminum
5. EIS Studies of Passivation and Pitting (Aluminum and Other Materials)

4
2.1. PASSIVITY MODELS:

The discussion of passivity models presented here is not meant to be exhaustive in nature. Selected models are chosen as they provide significant fundamental insights into the nature and kinetics of passivation. Although most models discussed here lead to kinetic expressions for film growth, the model by Cahan and Chen, discussed in this section, does not lead to kinetic expressions. However, this model is discussed due to the importance it attaches to the electronic characteristics of the passive film. The current study also investigated the electronic properties of passive films.

2.1.1 MOTT-CABRERA MODEL:

One of the earliest models relating to the growth kinetics of passive films was presented by Cabrera and Mott in 1948 (11). It was assumed that the rate limiting step for passive film thickening was interfacial reaction at the metal/film (M/F) interface. Passive film growth was thought to be the result of cation transport from the M/F interface to the film/solution (F/S) interface by a high field mechanism. The passive film growth kinetics correspond to a thermally activated process assisted by the electric field. It is assumed that the electric field is a constant throughout the film. The model predicts the film growth rate \( \frac{dL}{dt} \) as:

\[
\frac{dL}{dt} = N \Omega_0 \exp \left[ \left( -W + qa\Phi_f / 2L \right) / kT \right]
\]  

where
L is the film thickness, N the # of mobile ions per unit surface area, \( \Omega \) the molecular volume per cation, \( \nu \) the vibration frequency, \( W \) the activation energy for the rate controlling step, \( q \) the charge on the cation, \( a \) the jump distance, \( kT \) the thermal energy (Boltzman constant times the absolute temperature), and \( \phi_f \) the total potential drop across the passive film.

This expression leads to an inverse logarithmic growth law upon integration:

\[
\frac{1}{L} = A - B \ln t \quad \text{--------------------------} \quad 3.2
\]

where \( A \) and \( B \) are constants.

2.1.2 SATO AND COHEN'S MODEL:

Based on several galvanostatic and potentiostatic experiments on iron in pH 8.4 borate buffer solution, Sato and Cohen (12) arrived at the following kinetic expressions:

\[
i = C \exp (\beta E - Q_T/B) \quad \text{--------------------------} \quad 3.3
\]

where \( i \) is the passive current density, \( C, \beta, \) and \( B \) are constants explained below, \( E \) the passivation potential, and \( Q_T \) the total charge passed which is proportional to the film thickness.

\[
C = \frac{2FkT}{h} \sqrt{N_{\text{f}}} \left( \frac{\nu N_{\text{f}}}{2} \right)^{1/\nu} \exp \left( \frac{nE_{\text{f}} - \left( W_m - W_q + 0.5nW_{\phi} \right)}{2\nu RT} \right)
\]
where $N_s$ is the total no. of surface sites available for OH- adsorption on the oxide surface,

$N_{Fe}$ is the no. of Fe ions on the oxide surface,

$n$ is the ionic valence of the Fe ions in the oxide,

$v$ is the no. of times the rate determining step occurs when the overall reaction occurs once where the overall reaction is;

$$2Fe + nOH^- = Fe_{2O_n} + nH^+ + 2ne$$

$E_0$ is the difference between the potential drop across the metal/oxide/solution interface system and the applied potential,

$W_m$ is the activation energy for the transfer of Fe from the metal to the oxide,

$W_o$ is the activation energy for the transport of Fe ions in the oxide lattice

$W_s$ is the activation energy for the incorporation of oxygen into the oxide,

$R$, $T$, $F$, $K$ and $h$ have their usual meanings

$$\beta = \frac{nF}{2vRT}, \quad \frac{1}{B} = \frac{l^2W_o}{4neRT}$$

and $l$ is the lattice distance of oxygen in the fcc unit cell.

At a constant potential, the above expression indicates that the activation energy for the passive film thickening process is linearly related to the film thickness. In order to account for this the authors proposed a place exchange mechanism. According to this mechanism, all the layers in the passive film, including an adsorbed layer of oxygen ions on the F/S interface, change places simultaneously. This is indicated schematically in
Figure 2. As the activation energy for this place exchange process is the sum of the energy required to activate all the layers in the passive film, the activation energy is proportional to the thickness of the passive film. This model is more rigorous than the Cabrera-Mott model as the electric field at the metal/film (M/F) interface is assumed to be different from that across the passive film. The rate determining step is assumed to be the transfer of oxygen from the adsorbed OH\textsuperscript{-} to the oxide lattice in the passive film.

Sato (12) has hypothesized that as the film thickness increases the activation energy increases until the activation energy for the place exchange process exceeds that for other thickness-independent processes. An example of such a thickness-independent process is lattice diffusion of cations or anions by a vacancy mechanism in a high electric field. It was later pointed out that integration of the current expression under potentiostatic conditions
results in the logarithmic expression for the increase in film thickness with time.

\[ L = A + B \ln (t + t_0) \] 3.4

where \( L \) is the film thickness, \( t \) is time, and \( A, B, \) and \( t_0 \) are constants.

2.1.3 VETTER AND GORN'S ANALYSIS:

The kinetics of the film growth process and corrosion rate through the passive film on iron have been studied extensively by Vetter and Gorn (13). The analysis is an extension of the Mott-Cabrera model with particular attention to the film/electrolyte interface. Film growth and corrosion reactions are assumed to be rate limited at the F/S interface, and hence the potential drop at the F/S interface (\( \phi_{f/s} \)) provides the driving force for both reactions. Experimental observations indicate that the corrosion current density (\( i_c \)) through the passive film on iron does not depend on the applied potential. This is evident from the constant stationary (steady-state) current density observed during anodic polarization over most of the passive range. Also, experimental observations indicate that \( i_c \) does not vary during the instationary period after a step change in the applied current density in a galvanostatic experiment, even though the potential changes in a linear fashion. Based on these observations, the corrosion current density (\( i_c \)) and the film formation current density (\( i_f \)) are written as an exponential function of \( \phi_{f/s} \).

\[ i_c = i_{c,0} \exp \left[ \alpha_c^+ \frac{F}{RT} \phi_{f/s} \right] \] 3.5
\[ i_1 = i_{1,0} \left( \exp \left[ \alpha f^+ \frac{F}{RT} \phi_f/s \right] - \exp \left[ - \alpha f^- \frac{F}{RT} \phi_f/s \right] \right) \]  

where \( i_c \) is the corrosion current density, \( i_1 \) the film formation current density, \( i_{c,0}, i_{1,0} \) the exchange current densities for the above 2 reactions \( \phi_f/s \) the potential drop at the film/electrolyte interface, \( \alpha_{c^+} \) the apparent charge transfer coefficient for the corrosion reaction, and \( \alpha f^+, \alpha f^- \) the apparent charge transfer coefficient for the film formation and dissolution reactions, respectively.

The reverse reaction is not considered for the corrosion reaction as the concentration of dissolved cations is negligible compared to that required for reprecipitation. The expressions for the 'apparent' transfer coefficients \( \alpha_{c^+}, \alpha f^+, \alpha f^- \), and the interrelationship between \( i_c \) and \( i_f \) are then developed. The analysis is done by considering a different sequence of steps. The 'apparent' transfer coefficients are determined from the valence of the species transported across the F/S interface in the rate determining step, from the actual transfer coefficient, and from the valence of the species transported across the F/S interface in equilibrium steps prior to the rate determining step. The current densities \( i_c \) and \( i_f \) are then combined by eliminating \( \phi_f/s \). The resulting expression:

\[ i_1 = i_{1,0} \left[ \left( \frac{i_c}{i_{c,0}} \right)^{\alpha_f^-/\alpha_f^+} - \left( \frac{i_c}{i_{c,0}} \right)^{-\alpha_f^-/\alpha_f^+} \right] \]  

\[ \text{---------} \]  

\[ 3.7 \]
is experimentally verified. The experiments were conducted in a sulfate solution and the kinetics of the corrosion reaction were found to depend on the sulfate concentration. This was rationalized by the formation of a FeSO$_4^+$ adsorbed intermediate. The reaction order in sulfate and H$^+$ was determined.

Kirchheim (14) has presented an extension to the Vetter and Gom model by combining the high-field transport mechanism of Mott-Cabrera and the analysis by Vetter and Gom (13). The transient behavior of the potential response to a step change in the current density in a galvanostatic experiment (Figure 3) is explained in terms of the modified model. The instantaneous increase in potential is attributed to the change in the potential drop in the passive film due to a change in the electric field, and due to an increase in $\Phi_{fs}$. The electric field in the passive film changes due to a change in the current density as predicted by eqn. 1. The linear increase in potential with time is due to the linear increase in film thickness. This arises from the increased potential drop at the film/solution (F/S) interface causing film growth according to eqn. 6. The distribution of the potential drop at the working electrode surface into its components at the M/F interface, across the passive film, and at the F/S interface, along with their variation with time are illustrated in Figure 4. The predictions from such an analysis are shown to fit the experimental results of Sato and Cohen (12). An analysis is also presented for the potentiostatic case.

In another paper Kirchheim (15) has modeled the transient behavior of the potential response of the passive film upon a step change in the applied current density in a galvanostatic experiment. The transition from the initial sharp increase in potential to the steady linear increase is predicted based on
Figure 3: Change of potential (lower figure) for the galvanostatic experiments of Vetter and Gom (13), where the current was changed at \( t=0 \) from its stationary value \( i_{CO} \) to \( i \) and decreased after \( t=t_0 \) to \( i_{CO} \). \( i_c \) and \( i_i \) are the two components of \( i \) for corrosion (metal dissolution) and film formation. During the instationary period the potential changes first instantaneously by \( \Delta \epsilon_i \) and then linearly by \( \Delta \epsilon_2 \). For \( t>t_0 \) a permanent change of \( \Delta \epsilon_2^0 \) remains. Transient changes are shown by dashed dotted lines and are discussed later (14).

Figure 4: Positional changes of the potential from the metal (1) through the passive film (2) to the electrolyte (3) for different times of the galvanostatic experiment described in figure 2. The electric field within the film should increase during the instationary state according to equation 1, if \( i > i_{CO} \), but it is assumed not to depend on film thickness, \( x_0 \). The instantaneous potential change, \( \Delta \epsilon_i \), shown in Figure 4 is due to a change of both the potential drop within the film, \( \epsilon_2 \), and at the interface, \( \epsilon_{23} \). The latter is independent of the potential for stationary conditions (14).
the change in the vacancy (or interstitial) concentration with the change in the current density (Figure 5). The change in the vacancy concentration with current density is assumed to occur at the film/solution interface, and the time duration of the transient region is estimated from the time required to homogenize the passive film with the new vacancy concentration. The higher the corrosion current density compared to the film formation current density (Fe in acid solutions), the more prominent is the overshoot in potential before the subsequent linear increase. For Fe in neutral solutions, where the film formation current density dominates the corrosion current density, the potential overshoot is minimal and the potential seems arrested at a constant value before the linear increase region (Figure 6). A quantitative analysis is presented to predict the time duration of the transient region. The pre-exponential term in the high field transport expression of eqn. 1 is assumed to be linearly related to the vacancy concentration in the passive film.

2.1.4 CAHAN AND CHEN'S MODEL:

Cahan and Chen (16,17,18) have rejected models that assume that passive films on iron are composed of an inner Fe3O4 and an outer Fe2O3 layer. Based on their ellipsometry experiments they assert that there is no evidence for the presence of an Fe3O4 layer and assume that the passive film is entirely Fe2O3. They propose that the thermodynamic requirement for the presence of Fe2+ at the metal/Fe2O3 interface is satisfied by the presence of Fe2+ as defects in the Fe2O3 lattice.(16) They also state that the passive film does not exhibit characteristics of a classical semiconductor.
Figure 5: Vacancy (squares) concentration and slope of the potential (= electric field) within the film for four different times and total potential vs time during a galvanostatic transient. Case 1 corresponds to a stationary state where the potential and the film thickness are constant. For case 2 the vacancy concentration is not changed and the higher current requires a high electric field. During the time period $0 < t < t_0$ or case 3 the vacancies formed at the oxide/electrolyte interface have migrated the distance $y$, in which a lower field is necessary due to a higher vacancy concentration. Due to a lowering of the overall potential drop through the film the total potential is decreasing (dashed curve). This effect is superimposed on an increase (dashed-dotted curve) because the film becomes thicker during the instationary state. For case 4 the film has a higher vacancy concentration throughout the film and is considerably thicker (15).

Figure 6: In acid solutions the increase of the total potential due to layer formation (dashed-dotted line) is slow, because the corrosion c.d. plays an important role, and therefore, the decrease caused by changing the vacancy concentration (dashed line) dominates, which leads to an "overshooting" of the potential (a). For neutral solutions decrease and increase compensate each other leading to a "rest" of the potential (b) (15).
This is because the Mott-Schottky plots exhibit linearity over a very small potential range, the charge carrier density determined from the M-S plot (10^{20} /cm^3) is too high for a classical semiconductor, and the charge carrier density and flat band potentials are frequency dependent. (17) The above data were obtained from impedance experiments performed at various frequencies and at different anodic potentials. The authors therefore propose a chemiconductor model for the passive film. (18) A chemiconductor is defined as a material whose stoichiometry can be varied by oxidative and/or reductive valence state changes. This non-stoichiometry can then modify the local electronic (and/or ionic) conductivity of the film. The principal band gap (2p-4s transition) in the film is about 5.5 eV. However localized d states exist within the gap. These d states become broadened by the local symmetry variations and by local excesses in protons (Fe^{2+}) and/or deficiencies of protons (Fe^{4+}). These defect states, when present in sufficient concentration, can lead to an enhanced local conductivity and can result in the development of otherwise forbidden d-d, p-d and d-s transitions. The authors propose that the Fe^{2+} concentration falls off exponentially from a fixed maximum value at the metal/oxide interface into the interior of the oxide. At high anodic potential values, the H^+ is removed from the film and Fe^{4+} is introduced. The concentration of Fe^{4+} has a maximum value at the oxide/electrolyte interface and drops off exponentially toward the inside of the film (Figure 7)
2.1.5 THE POINT DEFECT MODEL:

Chao, Lin and Macdonald (19) have proposed a point defect model for the formation and breakdown of passive films in materials. The model makes the following major assumptions:

1. The passive film can be thought of as a crystalline oxide with a high concentration of point defects, with vacancies being the major point defect.
2. The high electric field (~ 10^6 V/cm) in the film keeps it on the verge of dielectric breakdown. The electric field therefore does not depend on the thickness of the film.

Figure 7: A schematic representation of the 'chemiconductor' model for passive film at higher anodic potential region (18)
3. Electron transport is rate limited at the metal/film (M/F) and film/electrolyte (F/S) interfaces while vacancy migration is rate limited in the bulk of the film.

4. Film growth occurs at the M/F interface by anion transport through the film and metal dissolution occurs through cation transport.

5. The potential drop at the F/S interface ($\phi_{f/s}$) is a function of the applied potential ($V_{ext}$) and solution pH, but is independent of the anodic film thickness.

$$\phi_{f/s} = \alpha V_{ext} + \beta p\text{H} + \phi_{f/s}^0 \quad \text{------------------ 3.8}$$

where $\alpha$, $\beta$ and $\phi_{f/s}^0$ are constants.

The model predicts the rate of film growth by evaluating the rate of transport of anion vacancies through the passive film under a chemical and electrical potential gradient. The concentration of the anion vacancies at the M/F interface is determined from the equilibrium of the reactions;

$$M = M_M + \chi / 2 \ V_{O^{2-}} + \chi \ e^- \quad \text{------------------ 3.9}$$

and

$$M + V_{M^{\chi-}} = M_M + \chi \ e^- \quad \text{------------------ 3.10}$$

where $M$ is a metal atom, $M_M$ is a metal cation in the oxide lattice, $V_{O^{2-}}$ is an oxygen ion vacancy in the oxide with 2 excess positive charges, $V_{M^{\chi-}}$ is a cation vacancy in the oxide with $\chi$ excess negative charges.
The concentration of anion vacancies at the F/S interface is determined from the following reactions:

\[ \text{VO}^{2-} + \text{H}_2\text{O} = 2\text{H}^+(\text{aq}) + \text{O}_\text{O} \quad \text{-----------} \quad 3.11 \]

\[ \text{Null} = \text{V}_\text{M}^{\chi'} + \chi/2 \text{VO}^{2-} \quad \text{-----------} \quad 3.12 \]

where \( \text{O}_\text{O} \) is an oxygen anion in the passive film.

Upon using the equilibrium constants for the above reactions, the solution pH, and the potential drop at the M/F and F/S interfaces, the anion vacancy concentration is determined at the M/F and F/S interfaces. The rate of anion vacancy transport through the film is then determined using the above concentrations, vacancy diffusivity, and the electric field in the passive film. Upon integration of the rate of growth, the passive film thickness at any time \( t \) is obtained as:

\[ \exp(2KL) - 2KL - 1 = 2KA(B-1) t \quad \text{-----------} \quad 3.13 \]

where \( K \) is \( \text{Fe}/(RT) \), \( \epsilon \) is the electric field in the passive film, \( L \) the film thickness, and \( A \) is given by the equation:

\[ A = KD_{\text{VO}} \exp \left[ -2F/RT (\alpha V_{\text{ext}} + \beta \text{pH} + \phi_{\text{f}/s^0}) + \Delta G_{9^0}/(RT) - 4.606 \text{ pH} \right] \]

\( B \) is given by the equation:

\[ B = \exp \left[ 2F/RT (V_{\text{ext}} + \phi_{\text{R}}) - 2\Delta G_{9^0}/(XRT) - \Delta G_{11^0}/RT + 4.606 \text{ pH} \right] \]

where \( D_{\text{VO}} \) is the diffusivity of oxygen ion vacancies, \( \Delta G_{9^0} \) the standard Gibbs free energy for reaction 2.9, \( \Delta G_{11^0} \) the standard Gibbs free energy.
for reaction 2.11, $\phi_R$ the potential drop at the reference electrode/solution interface, and $F$, $R$, and $T$ have their usual meaning. The other variables were defined earlier.

For film thicknesses exceeding 0.5nm, equation 13 can be simplified to:

$$L = \frac{1}{2K} \left[ \ln 2KA(B-1) + \ln t \right]$$

This has the form of the logarithmic growth law.

The unknown parameters in this model are the constants $\alpha$, $\beta$ (the dependence of the film/solution potential drop on the externally applied potential and solution pH respectively), $\phi_{f/s}^0$, and $\phi_R$. The authors fit experimental film growth kinetics data taken from the literature to this model and show that the resulting values for the above unknown parameters fall within an acceptable range. The model predicts that the current transient varies inversely with time. For very thin films it predicts that the current transient varies inversely with the square root of time. The fraction of the applied potential ($\alpha$ in eqn 8) that appears across the film/solution interface ($\phi_{f/s}$) was found to be 0.743 and is independent of the anion in the solution. The variation of $\phi_{f/s}$ with the solution pH ($\beta$ in eqn. 8), however, is found to depend on the identity of the anion in the electrolyte. The model therefore indicates that a significant fraction of the applied potential goes to altering the drop at the F/S interface compared to the contribution to the drop across the passive film.
Further work with the PDM (20) has led to the prediction of pitting potentials and pit incubation times. This is accomplished by hypothesizing that pitting occurs when the accumulation of vacancies of metal atoms in the metal at the M/F interface leads to their coalescence at weak spots, and subsequent loss of adherence of the passive film at such sites. The rate of accumulation of the cation vacancies at the M/F interface is given by the difference between the rate of vacancy arrival at the M/F interface from the F/S interface through diffusion in the passive film, and the rate of removal of these vacancies into the bulk of the metal. The PDM has also been used to estimate the distribution in the pitting potentials and incubation times under identical conditions using theoretical distribution functions (21). A solute-vacancy interaction model has been proposed to explain the role of trace additions of beneficial alloying elements like Mo (22) in increasing the pitting potential.

2.1.6 SATO'S IDEAS ON PASSIVITY:

Sato has suggested that passivity is induced by the bipolar nature of an ion-selective interfacial layer (23). An inner (next to the metal surface) anion selective layer and an outer cation selective layer is a good rectifier which promotes passivation (Figure 8). This is because the cation selective outer layer would prevent the ingress of damaging halide anions into the film and the anion selective inner layer would prevent the egress of cations from the metal surface. A cation selective layer has a fixed negative charge in the form of anions (or cation vacancies) and the anion selective layer has a fixed positive charge in the form of cations (or anion vacancies). Sato points out
the importance of electronic properties of the passive films on the anodic behavior of different metals. The bipolar model of the passive film may correspond to a sophisticated semiconducting phase where the film can be thought of as a p-n junction with a p-type inner film and an n-type outer film. A more sophisticated model is a p-i-n configuration that has an intrinsic semiconductor in between. Sato states that the chemiconductor model by Chen and Cahan is analogous to this p-i-n model. The applied potential during anodic polarization appears across the passive film, and is accommodated by the bending of the conduction and valence bands. The potential drop across the film/solution interface is determined only by the acid-base dissociation of the surface hydroxyl groups;

\[
\begin{align*}
=\text{MOH (acid site)} & \quad \rightarrow \quad =\text{MO}^- + \text{H}^+ \\
=\text{MOH (basic site)} & \quad \rightarrow \quad =\text{MH}_2\text{O}^+ + \text{OH}^- (\text{aq})
\end{align*}
\]

So

\[
\phi_{f/s} = \frac{RT}{(nF)} (pHpzc - pH) \quad \text{---------------------------} \quad 3.15
\]

This means that the film/solution interfacial drop (\(\phi_{f/s}\)) is independent of the applied potential as long as the surface charge is a constant. The passive current density as a function of applied potential within the passive range is almost constant for iron in acid solutions. It is assumed that the passive current density at steady state is due to corrosion which is governed by the film/solution interfacial potential (\(\phi_{f/s}\)). This observation lends evidence to the suggestion that the film/solution interfacial drop does not vary with potential. According to Sato the magnitude of the band bending in the passive film is therefore identical to the difference between the applied
potential and the flat band potential. However, at a high enough anodic potential (critical bias potential), when the band bending becomes sufficiently steep for either the conduction or valence band edges of the passive film to intersect the Fermi level, a degenerate state is set up at the F/S interface. If the film is thin enough under this condition, electron tunneling takes place and the outermost surface layer converts itself from a semiconductor to a metal-like layer (transpassivity). The variation in band bending with applied potential is illustrated in Figure 9. In the potential range of degeneracy the film/solution interfacial potential drop varies linearly with applied potential.

For the anodic oxide film on aluminum, whose mobility gap (used by Sato for band gap in materials with a high concentration of intermediate...
defect states) is greater than 6 eV, the film thickness before the anodic potential reaches the critical bias potential is high enough to make the electron tunneling probability negligible. Therefore the film surface cannot be converted to a metal like phase. This results in the isolating characteristic of the anodic film on aluminum and thereby the absence of any transpassivity or oxygen evolution. Materials whose energy gap between the Fermi level and the valence band is high (n-type semiconducting passive films like Fe in H$_2$SO$_4$) have a high passive potential range. Materials that have a low energy gap between the Fermi level and the valence band (Ni in H$_2$SO$_4$) have a low passive potential range. The rational for the above argument is that the higher the energy gap between the valence band edge and the Fermi level, the greater is the extent to which the valence band can bend without intersecting the Fermi level, and hence the greater the potential range over which the metal is passive. The above argument is illustrated in Figure 10. In certain cases the transpassive potential is therefore given by the potential where the valence band edge intersects the Fermi level. This argument has to be used within thermodynamic constraints as eventhough electronic processes may indicate the occurrence of a certain reaction, it will not occur if thermodynamics predicts otherwise.

2.1.7 CRITICAL ANALYSIS OF PASSIVITY MODELS:

The major limitations of the Mott-Cabrera model are: (i) It has been shown by several investigators that the passive film growth on iron (and several other materials, e.g., Al, Nb, Ta, W, Zr, Hf, U, Si; ref. 19) occurs by the inward diffusion of oxygen ions to the M/F interface while the model
Figure 9: Electron energy band bending and Helmholtz layer potential $\Delta \phi_H$ at the oxide/electrolyte interface as functions of electrode potential (23)

Figure 10: Anodic polarization curves of nickel and iron in sulfuric acid solution and electron energy band structures of passive oxide films at the flat band potential $E_{fb}$. $E_{tp}$ is the transpassivation potential (23)
assumes that outward diffusion of cations causes film growth. (ii) The kinetic expression for film growth assumes that the activation energy for the interfacial process at the M/F interface is modified by the electric field in the of the passive film. In other words the electric field at the M/F interface is assumed to be the same as the electric field existing in the bulk of the passive film. The point defect model (PDM) (19) does not suffer from the above limitations and its primary advantage is that it provides mathematical expressions for evaluating the passivation kinetics, pitting potential, pit incubation times, and the influence of alloying elements in enhancing passivity. The main point of contention regarding the PDM is the assumption of a crystalline passive film and the several unknowns in the model. The place exchange mechanism proposed by Sato (12) could only be valid at very small film thicknesses (of a few monolayers) as pointed out by Macdonald (19) due to the sharp rise in activation energy with film thickness. Sato's hypothesis that the F/S interfacial drop remains constant within the passive range of iron (23) independent of the applied potential contradicts the result obtained from fitting the point defect model to experimental results. According to the PDM, about 75% of the applied potential appears across the film/solution interface. Upon reviewing the various models, Kirchcheim concludes that the analysis by Vetter and Gom (13) that modifies the Mott-Cabrera model, is the most reasonable depiction of the passivation kinetics (14)

2.2 PASSIVATION AND PITTING OF PURE ALUMINUM:

Davis et al. (24) have made an exhaustive study of the composition of the passive film on pure Al in 0.05M Na2SO4 with and without the presence
of Cl\(^-\) ions using X-ray Photoelectron Spectroscopy (XPS). Experiments were conducted at pH 2, 7, and 10. The samples were exposed for up to 8 days in the Ultra High Vacuum (UHV) chamber to investigate the stability of the film in vacuum. It was observed that some of the oxygen in the film was removed in the 8 day vacuum exposure. However, the same amount of oxygen was found to be removed in the first 3 days and no further removal in the final 5 days. It is therefore concluded that the oxygen lost during the vacuum exposure is present in a physisorbed state on the passive film, and none of the chemisorbed or incorporated oxygen is removed. So all the reported oxygen content is normalized to remove the physisorbed oxygen. Based on this study Surface Behavior Diagrams (SBD) are presented that indicate the variation in film composition with different surface treatment and polarization conditions. It is concluded that the passive film on pure aluminum in sulfate solution contains primarily AlOOH and not Al(OH)\(_3\) at all the pH values studied. The only exception being that at pH 2 in chloride free sulfate where a thick Al\(_2\)O\(_3\) layer forms between the metal and the oxyhydroxide layer. The equilibrium phase predicted by the Pourbaix diagram, however is Al(OH)\(_3\). It is stated that AlOOH could be a metastable intermediate film. The film thickness is shown to increase with anodic polarization as evidenced by the diminishing metallic Al peak in the XPS spectrum.

Thompson et al. (25) have described the relative contribution of O\(^2-\)/OH\(^-\) and Al\(^3+\) in the growth of the anodic film on aluminum. Both anions and cations are shown to be mobile in the anodic film. However the film growth takes place at the film/electrolyte interface only at current densities above a critical current density (\(i_{\text{crit}}\)) where the current efficiency for film
formation is high. The cations that are transported through the passive film at current densities below $i_{\text{crit}}$ are directly injected into the electrolyte and do not contribute to film growth. At lower current densities, the film growth takes place only at the metal/film interface due to the transport of $O^{2-}/OH^-$ ions. The value of $i_{\text{crit}}$ depends on the anion in the electrolyte and is reported to be $10A/m^2$ in chromate electrolyte.

A discussion of the possible passive film growth kinetics for Al is presented by Dignam (26). The kinetics observed are consistent with either Mott-Cabrera’s high field controlled growth, or according to a mechanism involving the homogeneous generation of defect pairs with both defects mobile. The latter is due to the intrinsic ionic defects (Schottky or Frenkel) caused by lattice dissociation at sufficiently high temperatures. These defects are generated with the aid of the electric field within the passive film, and their diffusion and migration under the field causes film growth.

Several studies have been conducted to gain a fundamental understanding of the pitting process in pure aluminum (27-29). Foley (28) has reviewed the literature pertaining to this subject. The author presupposes that the aggressive anions have to penetrate the oxide film either through migration or chemical dissolution or by an ion exchange process before they can attack the metal surface. The transport of chloride ions to the metal surface through defects in the passive film, with little impediment, is also a possibility (30-32). Several models have been proposed for the initiation and stability of pits, and these have been reviewed comprehensively (33). One of the more viable models is that due to Galvele (31), who has proposed a transport controlled localized corrosion model that requires the establishment of a critical pH in the occluded cell for pit stability. The acidic
solution inside pits is proposed to cause dissolution of the passive film. Assuming that local changes in the concentration of different species arises due to transport-limited processes, a quantitative prediction of such changes are made by employing diffusion equations for a unidirectional pit. According to Galvele (31), the minimum local current density for pit stability in a specific system is dependent on the dimensions of the defect in the metal surface that can serve as a pit nucleus. The product of this minimum local current density (i) and a characteristic defect dimension (x) causes the local pH within the occluded cell to attain the critical value that dissolves the passive film. The pitting potential is then the value at which the above minimum pit current density can be obtained. The above model assumes that the inherent defects in the passive film permit easy transport of the electrolyte and aggressive anions to the metal/film interface. Also, the defects in the passive film itself have been suggested to serve as diffusion paths causing agglomeration of the necessary ions. Frankel (34) has reported the occurrence of a transition from metastability to stability in pit growth at an 'x.i' value that is three orders of magnitude higher than that predicted by Galvele. Therefore the applicability of the critical acidification model for stainless steel has been questioned. Sato (35) has suggested that etch pitting occurs at low potentials by the lowering of the local pH below a critical value, and polished pits occur at high potentials by the local increase in the aggressive anion concentration above a critical value.

Some authors (34,36,37) believe that a necessary condition for stable pit growth is the presence of a salt film at the pit bottom. The salt film is argued to be necessary to account for the potential drop between the bulk solution in contact with the passive surface and the electrolyte in contact
with the active pit surface. A simple calculation of this potential drop (ohmic drop) based on the pit current density, the occluded cell dimension, and the solution conductivity inside the pit (36) suggests that the value is significantly lower than the difference between the critical pitting potential and the Flade potential for stainless steel. However, it seems to us that the presence of a salt film is the result of a high dissolution rate within the pit and the consequent acidification. The chloride salt films (for example FeCl$_2$, NiCl$_2$) are stable only in highly acidic solutions. Besides, from the shape of the pits grown against gravity, toward gravity and sideways on stainless steel specimens, it follows that the salt film present at the bottom of pits decreases the corrosion rate. Finally, although the presence of a salt film may be relevant to the stability of a polished pit, it is difficult to imagine its role in the growth of crystallographic pits in pure aluminum. Vetter and Strehblow (36), while responding to this question suggest that the epitaxially grown salt film will reflect the dissolution characteristics of the metal surface underneath, by a corresponding variation in its ionic diffusivity. Bargeron and Givens (38) have discussed the formation and rupture of hydrogen blisters on aluminum and have suggested that such ruptured blisters serve as precursors for pit initiation. A refinement of the events leading to the formation and rupture of blisters in ion-implanted aluminum has been reported by Natishan and McCafferty (39). A recent study that employed a stainless steel microelectrode to study the transient current behavior from individual pits, points out the necessity of an oxide film covering the pit surface to cause stable pit growth (40). Frankel (34) too has reported that the presence of an oxide film covering the pit is a necessary requirement for pit
stability, until a salt film can precipitate on the pit surface. The exception to this being the formation of a deep pit (100 to 200 μA) before film rupture.

2.3 PASSIVATION OF METASTABLE ALUMINUM ALLOYS

Several investigations have been carried out on the corrosion and passive film characteristics of sputtered alloys of aluminum with Cr, Cu, Mo, Si (2), and W (3) in 0.1 M KCl at pH 8. They report a significant (> 200mV) enhancement in the pitting potential with all alloying elements except Si (no improvement). The authors employed X-ray Photoelectron Spectroscopy (XPS) to study the composition of the passive film and to rationalize the cause for the ennoblement in the pitting potential. The study attributes the localized corrosion resistance of the Al-Cr (4) and Al-Mo (4) films to the presence of CrOOH and molybdate (Mo4+ and or Mo6+) respectively in the passive film that act as a barrier to the penetration of aggressive Cl- anions through the film. Ta2O5 and ZrO2 (2) in the passive film on Al-Ta and Al-Zr alloys, respectively, are suggested to impede Cl- penetration and thereby cause an ennoblement in the pitting potential compared to that for pure aluminum. Frankel et al. (5) have studied the influence of alloying element concentration (in the range of 5 to 40 atom %) on the pitting potential of sputter deposited aluminum alloys in 0.1 M NaCl. The elements used were Mo, Nb, Ta, Ti, and Cr. The pitting potential continuously increased with concentration of the alloying element for Mo, Nb, and Ta. Alloys containing Ti and Cr exhibit only a small increase in pitting potential at low solute concentrations (less than 20 at.% for Ti and 35
at.\% for Cr), but exhibit a steep increase at higher concentrations. However, all the alloying elements investigated show a significant increase (> 400 mV) in the pitting potential over that of pure aluminum even for the lowest alloying element concentration used. Szklarska-Smialowska has reported the enhanced pitting resistance of super-saturated Al-Cr and Al-Ta sputtered films (6). Yoshioko et al. have studied sputtered films of Al-Zr (7) and Al-W (8) and have attributed the enhanced corrosion resistance to the presence of oxidized Zr and W in the passive film respectively. The corrosion tendencies of sputtered alloys of aluminum with Ti, Zr, Nb, Ta, Mo, and W are presented in another study by the same investigators (9). Natishan et al. (10) have incorporated various elements (Mg, Al, Si, Cr, Zr, Nb, Mo, and Zn) on the surface of aluminum through ion implantation and studied their pitting resistance. A correlation was found between the pH of zero charge (pHzch) of the oxides of the implanted elements and the pitting potential of the samples. An oxide surface is negatively charged at pH values less than the pHzch and positively charged at pH values greater than the pHzch. The authors propose that the pitting potential increases with alloying if the pHzch of the oxide of the alloying element is lower than that of aluminum oxide. A lower pHzch implies that the alloyed electrode surface is negatively charged for a greater pH range than the unalloyed surface. This results in a negative residual charge on the electrode surface for a greater pH range that causes an electrostatic repulsion of the chloride ions and hence increases the pitting potential. This analysis breaks down while trying to explain the enhanced pitting potential of Al alloyed with W. This is because XPS studies fail to reveal any oxidized W in the passive film. A critical analysis of the various
hypotheses to rationalize the enhanced pitting resistance of the metastable aluminum alloys is presented by Szklarska-Smialowska (41).

2.4 ELLIPSOMETRY STUDIES ON PURE ALUMINUM

Several studies have been conducted to study the surface film on aluminum under vacuum and in the presence of electrolytes employing ellipsometry. The aim of these studies is to evaluate the refractive index and thickness of the oxide films for various applications. An introduction to the theoretical and practical aspects of ellipsometry is presented in Appendix A. Allen's study (42) on bulk aluminum and vapor-deposited thin films has resulted in values for the real (n) and complex (k) part of the refractive index for pure aluminum and also provided a quantitative insight into the reactivity of aluminum with oxygen at 10⁻⁹ torr vacuum. Any study that aims to directly quantify the optical constants of pure aluminum has to be conducted at high vacuum (<10⁻⁷ torr). Allen (42) employed a combination of Auger Electron Spectroscopy (AES), argon ion sputtering, and ellipsometry to conduct this study. The samples used were mechanically polished, and cleaned in organic solvents. They were placed in the multi-purpose chamber and evacuated to 10⁻⁹ torr. Subsequent AES analysis indicated an air formed (between polishing and evacuation) oxide film of 10 Å thickness. This oxide film was removed by argon ion sputtering. The sputtering was continued until the oxygen peak on the AES spectrum disappeared. Ellipsometric investigations were then conducted (at 10⁻⁹ torr) on pure bare Al and evaluation of the Δ (the relative phase change upon reflection) and ψ
(the relative intensity change upon reflection) values indicated $n$ and $k$ to be 1.566 and 7.938, respectively at $\lambda = 6328$ Å. Another valuable observation in this study is the rate of contamination of pure aluminum by oxygen at $10^{-9}$ torr. Allen reported the re-occurrence of the oxygen peak in the AES spectrum after only 15 minutes at $10^{-9}$ torr vacuum following completion of the in situ cleaning process. The oxide layer formed at this pressure saturates at 2.5 Å thickness. Allen (42) attributed the scatter in the optical constants of aluminum found in the literature to varying levels of oxygen contamination on the surface (as most of the studies were done at comparatively higher pressures of $10^{-4}$ to $10^{-6}$ torr). The effect of such contamination is to reduce the apparent values of the optical constants (Table 1).

Table 1: Variation in the apparent real and complex part of the refractive index with different levels of surface contamination with oxygen (42)

<table>
<thead>
<tr>
<th>Measured Film Thickness (Å)</th>
<th>Measured $\psi (°)$</th>
<th>Measured $\Delta (°)$</th>
<th>n</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.84</td>
<td>145.31</td>
<td>1.566</td>
<td></td>
</tr>
<tr>
<td>7.938</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>41.83</td>
<td>144.72</td>
<td>1.522</td>
<td></td>
</tr>
<tr>
<td>7.802</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>41.83</td>
<td>144.26</td>
<td>1.486</td>
<td></td>
</tr>
<tr>
<td>7.698</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From the magnitude of the change reported by Allen, however, it seems unlikely that such contamination can account for the relatively large scatter documented in literature.

Greef and Norman (43) have taken an air formed oxide covered aluminum as a reference state and studied the subsequent anodic film growth and dissolution kinetics. The $\Delta$ and $\psi$ signal from such a reference state was considered to be the bare surface signal for model development. The authors claim that such a procedure does not in any way affect the qualitative conclusions drawn. Although this study does not provide any quantitative data, it does provide valuable insights into the growth and dissolution kinetics of the oxide film on aluminum under the experimental conditions employed. Aluminum rods (99.999%) were mechanically polished to 0.05 $\mu$m and immersed in NaOH (0.1, 1.0, 4.0 M concentration). Ellipsometric studies were conducted at different anodic potentials in the passive range and for different electrolyte concentrations. The refractive index of the oxide film increased with increasing anodic potential and decreasing electrolyte concentration (Figures 11 and 12). As the refractive index of the oxide film is proportional to its density, the above observations yield qualitative information on the variation of compactness with polarization potential and electrolyte concentration. An experiment was conducted at a specific anodic potential in 0.1M NaOH and the results were fitted to a model. The oxide film was modeled as a composite film with an inner compact layer (higher refractive index) and an outer porous layer (lower refractive index), as illustrated in Figure 13. Greef and Norman (43) also studied the dissolution characteristics of the oxide film by polarizing the specimens either at an anodic potential in the active dissolution range or at open circuit. This was
done after a passive film had formed. Two distinct dissolution kinetics were observed depending on the electrode potential.

a) Upon exposure at open-circuit potential, the \( \Delta \) and \( \psi \) values returned to the reference state values (obtained before passivation). The path followed by the \( \Delta \) vs \( \psi \) curve during dissolution was, however, different from that followed during film growth (Figure 14). The authors fitted these data with a model that requires simultaneous dissolution of both the inner and outer layers of the oxide film. A graphic illustration of the growth and dissolution characteristics predicted by the model is presented in Figure 15.

b) When dissolution kinetics were studied by polarizing the passive specimen to potentials in the active dissolution range, the \( \Delta \) and \( \psi \) values traced a loop before returning to the reference point (Figure 16). The loop size was proportional to the steady state dissolution rate at that potential. At high anodic potentials, the loop size was small due to reduced steady state dissolution caused by film formation. At open circuit and at cathodic potentials, the loop size was either negligible or absent due to the low steady state dissolution potentials, in the active range, the loop size was the largest. The authors interpreted this loop formation as due to parallel dissolution of the metal substrate along with the film and the consequent surface roughening. They claimed that following such surface roughening, a preferential dissolution of the substrate again occurred that smoothened out the surface and returned the optical values to their reference state. The substrate surface roughening was associated with a drop in the \( k \) value. The variation in \( k \) is illustrated graphically in Figure 17.
Figure 11: Family of anodization curves at the indicated growth potentials. Al exposed to 0.1M NaOH. Each run was carried out with a freshly polished electrode (43).

Figure 12: Family of growth curves at 2.5 V, for NaOH Concentrations of 0.1M (A), 1.0M (B), and 4.0M (c) (43).
Figure 13: Comparison of the duplex model for film growth (dashed line) superimposed upon the experimental curves (open circle) and the uniform film model curve (bold line). The inset shows the schematic of the duplex model (43).

Figure 14: Growth curves for 2.5V in 0.1M NaOH interrupted at different film thicknesses (G) and their resultant dissolution curves at open circuit (D) (43).
Figure 15: A three-dimensional plot indicating how the refractive index of the film varies from A (the initial anodic pulse) to D (the dissolution limit) with both time and film thickness (43).

Figure 16: A family of curves for growth at 2.5V (G) interrupted at different stages to show the dissolution signal at -0.5V (D) (43).
Dell'oca et al. (44) conducted a similar study on pure aluminum, and traced the variations in Δ and ψ with anodization at constant current density in 0.6M H₃PO₄. They quantitatively determined the film thickness at which porous film formation commenced. This thickness was determined from the point at which the Δ, ψ curve deviated from a reference curve which was obtained in 3% tartaric acid electrolyte which imparts a compact oxide film on aluminum. The authors were able to model the trends in the Δ and ψ values only by requiring both the porous layer and the compact layer to grow simultaneously. While Greef and Norman (43) propose that the compact layer stops growing after the formation of the porous layer, Dell'oca and Fleming (44) claim that after the formation of the porous film, the compact
layer contributes up to 20% of the total film growth rate. The study also reported the voltage at which pore initiation occurs (from voltage vs. thickness curves and from the thickness at which pore initiation occurs). For all current densities investigated, this voltage corresponds to about 80% of the peak voltage obtained at that particular density.

2.5 EIS STUDIES OF PASSIVATION AND PITTING:

Selected investigations have indicated the possible range of information pertinent to passivation that can be obtained by using EIS. Impedance studies on film-covered electrodes are done with one of 2 approaches. Most of the impedance studies are aimed at simulating the electrode surface by an electrically equivalent set of passive circuit elements. Quantitative values for the passive circuit elements are obtained from fitting the experimental frequency spectrum to that corresponding to the assumed circuit elements. These values are then used to derive the rates of electrochemical reactions (45, 46). The second set of studies, which is quite rare, uses the frequency dispersion of the impedance characteristics to obtain mechanistic information regarding processes occurring on the electrode surface (47). Macdonald has presented an instructional review of the various problems that can be addressed with EIS (48) and points out the merits of the second approach. One major limitation of the first approach is that it rarely provides any information on the physico-chemical processes taking place at the electrode surface (47,48). Also, there are instances where a negative real component has been experimentally observed in the impedance spectrum, e.g. in the active/passive transition region in iron (47). A negative resistance
can be interpreted through a mechanistic approach by taking into account the surface coverage of the electrode by an oxide layer (48). This causes a drop in current with increase in applied voltage and accounts for the negative real part of the resistance. However no passive circuit elements can be used to simulate such data. This review outlines studies that are typical in employing the above 2 approaches but only as applied to study passivity. Numerous studies have been conducted employing EIS to study dissolution rates, diffusional processes, porous films etc. that are not included here.

Azumi et al. (45) have conducted a detailed impedance study on the passivation of iron in borate and phosphate electrolytes. Experiments were conducted at various potentials in the passive range at frequencies from 0.01 Hz to 10 kHz. The electrolyte pH ranged from 3.1 to 10.5. The impedance spectrum was modeled by an equivalent circuit comprised of 2 parallel R-C elements connected in series to each other (Figure 18). The R and C values of one of the 2 R-C groups, defined as $R_H$ and $C_H$, varied with the anions in the electrolyte in a reversible fashion. This was attributed to the response from the Helmholtz double layer at the oxide/electrolyte interface. The other R-C group, defined as $R_L$ and $C_L$, (responsible for impedance response at frequencies lower than 100Hz) was attributed to the space charge layer in the passive film. The film thickness values were calculated from 3-parameter ellipsometry and were combined with the capacitance measurements to yield a value of 40 for the dielectric constant of the passive film. As the thickness calculated from the capacitance data is less than that calculated from 3-parameter ellipsometry, the authors conclude that an inner layer that is electron conductive is present as a part of the passive film. The capacitance and resistance of the Helmholtz layer remained constant with applied
potential up to the oxygen evolution potential. The resistance of the passive film on the other hand decreases with potential in spite of an increasing film thickness. Based on capacitance data plotted in the Mott-Schottky format and as $1/C$ vs. potential, the authors conclude that the passive film under the conditions studied behaves as a semiconductor whose space charge thickness is comparable to the film thickness.

Keddam et al. (47) have studied the passivity of iron in acidic media over a wide frequency range. The study reports the presence of three distinct regions; a high-frequency capacitive loop, an intermediate frequency inductive behavior and a low-frequency capacitive branch. The high frequency capacitance loop is attributed to ionic transport in the passive film

Figure 18: Frequency dependence of absolute value and phase angle of impedance of iron electrode passivated at 0.63V RHE in pH 6.5 borate solution. Solid line is a theoretical line calculated from the equivalent circuit shown (45).
according to the high field mechanism. The authors use the potential dependence of the high frequency resistance value to corroborate the high field ionic transport mechanism by Mott-Cabrera. The inductive response at intermediate frequencies is due to either the accumulation of a surface charge or the presence of an intermediate oxidation step in the film. One tenth of the current involved in the low frequency capacitance loop is associated with the film thickness variation, while the rest is attributed to modulations in the dissolution current density across the film.

Hitzig et al. (46) have conducted impedance experiments on anodized and sealed aluminum under freshly prepared conditions and under aged conditions in chloride solution and on atmospheric exposure. The study fits the experimental impedance spectrum to equivalent circuits that reflect the physical phenomena on the metal surface. As freshly prepared the samples exhibited 2 time constants which were attributed to the inner barrier layer and an outer porous layer, each with its resistance and capacitance values. The 2 RC circuits were assumed to be connected in series. The schematic of the oxide layer and the corresponding equivalent circuit are presented in Figure 19. Upon aging in non-aggressive solutions, the porous film was assumed to be removed in selected areas and replaced by 'passive pits'. This is modeled by a parallel combination of the circuit described earlier, and an RC segment due to the 'passive pit'. The area fraction of the unaffected region is assumed to be \( \theta \) and that of the region covered with passive pits is \( 1-\theta \). A schematic of the oxide layer and the equivalent circuit is presented in Figure 20. The effect of aging on the impedance spectrum is to gradually reduce and eventually remove the plateau due to the porous film resistance. The study also develops an equivalent circuit and a corresponding
impedance spectrum for aging in aggressive solutions. This results in the replacement of the passive pits mentioned earlier by active pits (Figure 21). The metal in these regions is assumed to be in direct contact with the electrolyte. Impedance spectra for increasing coverage of the metal surface with these active pits are presented. The modeling points out that the impedance spectrum is very sensitive to the presence of active pits as even a few pits cause a significant lowering of the low frequency impedance response. Predictions of the model are verified using anodized aluminum with artificial pits, and the model predictions are applied to interpret impedance response from actual exposure to different environments.

### 2.6 ELECTRONIC PROPERTIES OF PASSIVE FILMS:

Extensive work has been done to characterize the electronic properties of passive films by treating them as a semiconducting layer with a high charge carrier density. The charge carrier density and flat band potential are typically obtained from the slope and intercept, respectively, of the Mott-Schottky plot (49). Photo-electrochemical spectroscopy is another popular technique to probe the electronic properties of the passive films. A review on the subject has been written by Stimming (50). These studies yield information regarding the mobility gap in the passive film, nature and density of defect levels within the band gap of the passive film. The spectroscopic information, obtained in-situ, can be used to learn about the chemical and structural nature of the passive film. The review paper by Stimming (50) provides a theoretical background for photo-electrochemical experiments and addresses the electronic properties of passive films. The
Figure 19: Schematic representation of the oxide layers on aluminum (A) and the corresponding equivalent circuit (B). Index b denotes the barrier layer and p the porous layer (46).

Figure 20: Schematic representation of an inhomogeneous oxide layer on aluminum with a passive pit (A) and the corresponding electrical equivalent circuit (B)(46).
approximations for treating thin films, and differences between behavior of crystalline semiconductors and passive films are pointed out. A treatment on the theoretical and experimental dependence of the photocurrent on the wavelength of light and electrode potential is presented. Finally, a brief account of the photo-electrochemical responses of passive films on several materials are presented. This behavior was classified into noble metals, valve metals and transition metals.

Konig et al. (51) have discussed the influence of charge carriers and their energy distributions in the passive film on the capacitance behavior and
electron transfer rates. The differences in the behavior of n-type and p-type semiconducting passive films are pointed out by considering passive films on Fe in borate solution (n-type) and Ni in NaOH solution (p-type). The authors point out that the common assumption in most passive film models is a linear drop in potential across the passive film, giving rise to a constant electric field throughout the film. This requires that there is no space charge within the passive film according to the Poisson's equation:

$$\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} + \frac{d^2\phi}{dz^2} = -\rho/k\varepsilon_0$$

where $\phi$ is the electric potential, $\rho$ the charge density, $k$ the dielectric constant, and $\varepsilon_0$ the Permittivity of free space.

However, experiments indicate the presence of a space charge density of $10^{20}$ cm$^{-3}$ in the passive film on most materials. The relatively high charge carrier density in passive films in comparison to classical semiconductors indicates that the space charge layer extends for only a few nanometers (in classical semiconductors it extends to approximately 1000 Å). This implies that the space charge layer could be smaller than the passive film thickness and hence there may not be a constant electric field throughout the passive film. Also, the authors point out that the model of Mott-Cabrera that assumes the transport of ions in a high electric field requires a linear decrease in capacitance with log(time) during film formation. Experimental data do not indicate a linear drop in capacitance at any of the formation potentials studied for iron in pH 8.4 borate buffer. The capacitance decreases initially but remains constant subsequently even though the XPS data indicate film
growth. The implication is that film formation takes place at the metal/oxide interface without any electric field in it.

Di Quarto et al. (52) have studied the photo-electrochemical behavior of anodic films formed on aluminum. Anodization was done in ammonium tartrate solution at voltages ranging from 8 to 90 volts. The main observation is the evidence for interference effects, seen as peaks in the photocurrent response as a function of anodization voltage. This distance between the photocurrent peaks, the wavelength of light, and the refractive index of aluminum oxide are used to estimate the electric field in the anodized film. The study also arrives at the electronic band diagram for the oxide film along with its relation to the Fermi level on the metal surface. The band gap between the valence and conduction bands is estimated as 6.0 eV by determining the threshold energies for anodic and cathodic photo currents and correcting them for the influence of image forces on the Schottky barrier at the metal/film interface. The authors also hypothesize that the optical transitions causing both anodic and cathodic photo currents occur in the metal at the metal/film interface. The strong dependence of the photocurrent on the electric field, weak dependence on the film thickness, and the very low quantum yield are presented as evidence for the above hypothesis. The presence of anodic photo currents at low wavelengths and cathodic photo currents at high wavelengths at the same potential (potentials between -0.5 and -1.1 V (MSE) has been attributed to the trapping of electrons and holes in the passive film. In a later study, Di Quarto et al. (53) present photocurrent spectra from an anodized aluminum surface but in 2 different electrolytes with varying electrolyte compositions. Based on this study, the authors conclude that anodic photo currents are not caused by transitions at
the metal/film interface as suggested earlier by the same authors (52), because the threshold energy varies with the electrolyte composition, and because the metal/film interface behavior is not expected to vary with the nature of the electrolyte. The study concludes that anodic photo currents are caused by optical transitions from the valence band to defect states due to incorporated species from the electrolyte in the anodic film. Based on the exponential dependence of the anodic photocurrent on the electric field, the authors conclude that the photo-carriers are transported according to a mechanism controlled by a trap limited mobility in a band of defects formed by the incorporated species.

Shukla et al.(54) have studied the photo-electrochemical behavior of passive films on aluminum in 1M NaClO4 solution with and without chloride ions. The photo currents were found to be cathodic in the entire potential range investigated (-1.0 to -0.5 volts). The photocurrent observed was due to a sub-band gap absorption in the oxide film. The authors present a photo-electrochemical laser image of the metal surface in the absence (Figure 22) and presence (Figure 23) of the chloride ions and demonstrate the chloride induced pitting of the passive film in situ. The pit sizes are reported to be around 10 μ.
Figure 22: Photo-electrochemical laser image of passive aluminum in 1M NaClO4 at -0.8 V(MSE). The line width is 10μm in both the horizontal dimensions (54).

Figure 23: Photo-electrochemical laser image of a corroded passive film on aluminum recorded with an electrolyte which is 1M NaClO4 and 1.6M NaCl solution. Exposure time = 844 seconds. Line width in both the horizontal dimensions is 10μm (54).
CHAPTER III

EXPERIMENTAL PROCEDURE

The materials used in this study were pure bulk aluminum (99.999%) polished to a 0.3μ surface finish with an alumina suspension, sputtered pure aluminum film (from 99.999% pure target), sputtered Al-4 at.% Cr, Al-9at.% Cr and Al-10at.% Ta alloy films. The composition of alloy films were determined using Auger depth profiling through the entire film thickness and found to be uniform (6). The structures of the films were determined using diffraction patterns and bright and dark field images from the Transmission Electron Microscope (TEM) (6). All the Cr alloy films exhibit a single phase structure with no Cr rich phase. This implies that all the solute atoms are present in the Al matrix as super-saturated solid solutions. In the case of the Al-10at.%Ta film most of the Ta is contained in solid solution. However, a small amount of grain boundary second phase is observed in the Al-10at.%Ta film that is amorphous in nature.

The bulk aluminum was ultrasonically cleaned for 5 minutes and then rinsed in methanol and dried. The alloy films were cleaned with an argon jet to remove any dust particles present on the surface. All electrical contacts to the alloy films were made through silver epoxy contacts and a copper wire.
The films were masked to cover the edges and the silver epoxy contacts with a marine epoxy. Considerable care was taken to avoid crevice attack in the chloride solutions as the sputtered films pose severe adhesion problems with the masking agent. Most of the conventional coatings (lacquer etc.) do not adhere to the film surface well enough to prevent crevice attack as the sputtered film surface is not rough enough. The problems were particularly severe in this study as the samples had to stay exposed to the chloride solution for lengthy time intervals to facilitate the acquiring of impedance data as a function of anodic potential. Several experiments were conducted with different adhesives to determine the appropriate one. The marine epoxy remained adhered very well to the film surface even after prolonged exposure to the chloride solution. With an adherent coating, the current density should rise sharply with an anodic potential step and subsequently decrease exponentially with time and stabilize to a time-invariant value. The loss of adherence of the coating with the substrate surface resulted in a gradual increase in anodic current density as a function of time at a fixed potential. This was taken as a diagnostic criteria to evaluate the coating adherence to the substrate and experiments where the current density increased gradually with time at constant potential were ignored.

The samples were maintained at the open circuit potential (OCP) for around 2 hours. The duration at OCP was determined by the time taken for the potential to stabilize sufficiently for the Electrochemical Impedance Spectroscopy (EIS) experiments. The samples were first placed in the electrochemical cell without the electrolyte and exposed to an argon atmosphere for 7 hours. Subsequently the cell was filled with the electrolyte
from a reservoir that was independently deaerated with argon for 7 hours. The transfer of solution from the reservoir to the cell was done without exposure to air. The argon bubbling was continued during the duration of the experiment. The electrolytes used were 0.3 wt% NaCl (pH = 6.8) and a sodium sulfate solution at the same pH and conductivity. The solution resistance in all the experiments was 60-80 ohms*cm². A platinum counter electrode and a Saturated Calomel Reference Electrode (SCE) were used in the experiments. The planar surfaces of the counter and working electrodes, of nearly equal surface areas, were parallel and faced each other directly, ensuring minimal variation in current distribution with frequency. All potentials in this paper are referred to the SCE.

The impedance experiments were performed with a Solartron 1250 Frequency Response Analyzer (FRA) and an EG&G PAR 273 potentiostat. The FRA was controlled by a 386SX Personal Computer with a data acquisition software developed specifically for this study. The EIS equipment employed for the pure bulk aluminum consisted of a Solartron 1172 Frequency Response Analyzer (FRA), Wenking ST 72 potentiostat and an Apple IIE microcomputer. The impedance data were obtained from both systems under identical conditions and confirmed to be identical. Passive film resistance and capacitance were obtained by performing a non-linear least-square fit analysis of the impedance data to a simulated equivalent circuit using commercial software (92). The capacitance values for pure bulk aluminum alone were determined by a procedure detailed by Scully et al. (64). This involves plotting the imaginary component of admittance, after removing the solution resistance, vs. frequency. The slope of the resulting
straight line gives the capacitance of the passive film. The correlation coefficient for the straight lines used for calculating capacitance information was between 0.990 and 0.999. This procedure is rigorous only if the impedance data form a full semicircle in the complex plane at capacitive frequencies. However, the impedance data reported here exhibit a slight depression in the complex plane.

Experiments were conducted at constant potentials, in the passive range and at the pitting potential, as a function of exposure time. Potentiostatic anodic polarization experiments were conducted by changing the applied potential in 50 mV steps and holding the potential constant until the current stabilized. This amounted to an effective scan rate of 1 to 5 mV/min, depending on the duration of EIS experiments. Immediately after completion of the electrochemical experiments, the bulk aluminum samples were rinsed in double distilled de mineralized water and methanol and subsequently observed in a light microscope and a Scanning Electron Microscope (SEM). Some samples were ultrasonically cleaned before observation in the SEM.

Rudolf Research model RR 2000 automatic Ellipsometer was used to obtain the optical data. The wavelength of light used in this study was 546.1 nm. Modeling of the optical data was performed using the McCrackin program (93), modified to handle simultaneous growth of both constituents of a dual layered film. The refractive index of the pure aluminum substrate was taken as 1.05 - 5.5 i from the literature (84).
CHAPTER IV

RESULTS AND DISCUSSION

The anodic polarization curves for all the materials used in this study in a deaerated 0.1M sodium chloride solution are presented in Figure 24.(6) These are potentiodynamic scans that provide a background for the results reported in this study.

4.1 Pure Bulk Aluminum

4.1.1 EIS Results During Potentiostatic Anodic Polarization

The passive film resistance on pure bulk aluminum was found to be 12 kohm-cm\(^2\) after exposure at the open-circuit potential (-1070 mV SCE) for 5 hours. Upon potentiostatic anodic polarization, the passive film resistance increased to a maximum of 17.5 kohm-cm\(^2\) at -925 mV and decreased subsequently to 14.5 kohm-cm\(^2\) at the pitting potential. The variation of film resistance with potential is illustrated in Figure 25. In another experiment, pure bulk aluminum was exposed to the open circuit potential (OCP) for 24 hours. The passive film resistance for this sample at the end of the 1 day OCP exposure was 7.9 kohm-cm\(^2\). Subsequently, an
Figure 24: Anodic polarization curves for pure bulk Al, Al film, and Al alloy films in deaerated 0.1M NaCl solution.
Figure 25: Variation of passive film resistance and capacitance with anodic potential for pure bulk Al in NaCl solution

Anodic potential step was applied to the sample from OCP to -660 mV in 1 minute. The anodic current decayed from 11 $\mu$A/cm$^2$ to 4 $\mu$A/cm$^2$ in 9 minutes. EIS experiment was performed after holding the sample at this potential for 20 minutes. The passive film resistance was as high as 24 kohm-cm$^2$. The sample did not pit at this potential for more than 4 hours. In constant potential experiments, when the pure aluminum was polarized to -700 mV in the studied solution, the initial passive film resistance was between 60 and 110 kohm-cm$^2$, which indicates that the prior potential-time history, and not the applied potential alone, determines the protectiveness of the passive film on pure aluminum.
4.1.2 Constant Potential Experiments At The Passivation Potential

Impedance and optical data were obtained as a function of exposure time at a constant potential of -700mV (passivation potential) and -675 mV (pitting potential). The current at the passive potential is initially cathodic and less than 0.1μA/cm². The cathodic current continuously decreases with exposure time and after around 4 hours the current becomes anodic. The anodic current continuously increases to around 5μA/cm² in 11 hours (Figure 26). The current exhibits a noisy behavior superimposed on the uniform trend described above. The impedance data obtained at this potential exhibits capacitive behavior at high frequencies, and a Warburg-type diffusional behavior at low frequencies for the first 3 hours of exposure time. At longer exposure times, while the behavior at high frequencies is capacitive, the low frequency spectrum changes from the diffusional characteristic to that of a second time constant (Figures 27 a,b,c). The passive film resistance decreases continuously with exposure time from 66 kohm-cm² to 10.2 kohm-cm² in 60 hours (Figure 28), while the film capacitance increases from 7.1 to 9.7 μF/cm² in the same time (Figure 29). In two other constant potential experiments conducted at the passive potential (-700 mV SCE), the passive film capacitance was found to be 2.5 and 3.7 μF/cm² within the first hour of sample immersion in solution. However, both samples showed an increase in film capacitance by 2 μF/cm² during a 10 hour exposure at the passivation potential. Upon completion of the experiment the sample surface had a few shallow pits that had apparently repassivated. The oxide film on the sample surface at these regions was found to be removed (Figure 30). A similar observation of pits
at the passivation potential has been reported earlier (57). The sample surface was also found to contain a high density of bright circular or oval spots (Figure 31). These are very adherent features as they remained on the sample surface even after ultrasonic cleaning for 30 minutes in double distilled demineralized water, and in acetone.

4.1.3 Constant Potential Experiments At The Pitting Potential

Considerable effort was taken to arrive at the appropriate pitting potential (critical pitting potential) where the pit induction period was prolonged to as long as 5 hours. The objective in these experiments was to determine the variation in current density, polarization resistance, and film capacitance during the pit induction period. The dissolution current density at the pitting potential (-675 mV) remained at around 1 to 2 \( \mu \text{A/cm}^2 \) for 5 hours (induction time for pitting), and then increased.

The surface film at the pitting potential increases by about 1 \( \mu \text{F} \) (25%) during the duration of the experiment (Figure 34). The sample surface had one 50 \( \mu \) pit (size of the mean pit opening dimension) at the end of the experiment (Figure 35) and a few other pits that were smaller than 5\( \mu \) in dimension. The maximum current density in the experiment was less than 30\( \mu \text{A/cm}^2 \). However, in two other experiments conducted at the pitting potential, where the incubation period for pitting was 1 hour and 3 hours, there was very little variation in the film capacitance during this period. Also, the film capacitance for these samples after a 20 minute exposure time were 3.2 and 4.2 \( \mu \text{F/cm}^2 \), respectively. A 10 \( \mu \) sized crystallographic pit observed in another experiment that was terminated with the mean
Figure 26: Current behavior with exposure time at passivation potential for pure bulk Al in NaCl solution

Figure 27: Impedance data in the Nyquist format at the passivation potential for pure bulk aluminum in NaCl solution. a: Exposure time = 1 hour
Figure 27 (Cntd.)

b: Exposure time = 4 hours

c: Exposure time = 48 hours
Figure 28: Variation in passive film resistance with time at passivation potential for pure bulk Al in NaCl solution

Figure 29: Variation in passive film capacitance with exposure time at passivation potential for pure bulk aluminum in NaCl solution
Figure 30: Shallow repassivated pit on pure bulk aluminum with the surface film removed after constant potential experiment at the passivation potential (-700mV vs. SCE) in NaCl solution.

Figure 31: Bright spots on the pure bulk aluminum surface after constant potential experiment at the passivation potential in NaCl solution.
Also, the current behavior exhibits a significantly higher noise amplitude than at the passivation potential. The noise behavior is clearly evident throughout the induction period, commencing from immediately after sample immersion in solution. The current behavior during the incubation period is shown in Figure 32. The applicability of EIS to a system that exhibits noisy behavior can be called into question as the stability criterion could be violated. However, the important parameter here is the signal to noise ratio. The EIS data for the system studied here is considered to be useful as the data clearly fit a single semicircle in the complex plane. Also, the lowest frequency used was 0.1 Hz and hence the data collection time was less than 3 minutes. Polarization resistance (Rp) values obtained from EIS data show random fluctuations. This indicates that Rp values are sensitive to localized events. However, the general long time trend indicates a decrease in this parameter (Figure 33). The capacitance of the surface film at the pitting potential increases by about 1 μF (25%) during the duration of the experiment (Figure 34). The sample surface had one 50 μm pit (size of the mean pit opening dimension) at the end of the experiment (Figure 35) and a few other pits that were smaller than 5μ in dimension. The maximum current density in the experiment was less than 30μA/cm². However, in two other experiments conducted at the pitting potential, where the incubation period for pitting was 1 hour and 3 hours, there was very little variation in the film capacitance during this period. Also, the film capacitance for these samples after a 20 minute exposure time were 3.2 and 4.2 μF/cm², respectively. A 10 μ sized crystallographic pit observed in another experiment that was terminated with the mean current density at 1 μA/cm² is shown in Figure 36.
Figure 32: Current behavior during incubation period at critical pitting potential (-675 mV vs. SCE) for pure bulk Al in NaCl solution

Fluctuations in pol. resistance correspond to fluctuations in current density

Figure 33: Variation in polarization resistance with exposure time at critical pitting potential for pure bulk Al in NaCl solution
4.1.4 Optical Behavior

Information regarding the nature and growth kinetics of the surface film was obtained by modeling the optical data. Ellipsometry data obtained for pure aluminum indicates continuous film growth on the metal surface with time (Figure 37). Optical data also indicate the growth of an outer layer over an inner protective passive film. The optical behavior cannot distinguish between the film growth characteristics at passive and pitting potentials as these differences are very localized in nature and ellipsometry is a surface averaging technique.

4.1.5 Discussion of Results on Pure Bulk Aluminum

The steep increase in the passive film resistance with the application of a potential jump from OCP to -660 mV, and the high value for the film resistance in constant potential experiments, is due to the formation of a barrier film at the metal/preexisting oxide film (M/F) interface at a sufficiently fast rate that causes low levels of chloride penetration. This film is therefore thought to have a lesser amount of chloride anions incorporated in its defects. Evidence for the formation of anodic oxides on aluminum at the M/F interface has been presented by Thomson et al. (25). However, in anodic potentiostatic experiments done by a slow stepwise
Figure 34: Variation in interfacial capacitance with exposure time at the critical pitting potential for pure bulk Al in NaCl solution.

Figure 35: Pit formed at the end of the constant potential experiment at the pitting potential; maximum current density = 30μA/cm².
Figure 36: Pit formed at the end of the constant potential experiment at the critical pitting potential; maximum current density = 1 μA/cm²

Nature of surface film from modeling optical data:

**Open Circuit Potential:**
- Outer film refractive index = 1.45 - 0.03i
- Thickness = 40 nm
- Inner film refractive index = 1.45 - 0.00i
- Thickness = 20 nm
- Total exposure time = 27 hours

**Passivation Potential:**
- Outer film refractive index = 1.45-0.2i
- Thickness = 20 nm
- Inner film refractive index =1.45-0.0i
- Thickness = 12 nm
- Total exposure time = 35 hours
increase in potential (effective scan rate of 1 mV/min), the external current is always very low (< 3 μA/cm²), and hence the slow film growth could provide more time for the chlorides to migrate deeper into the film. The field assisted migration of phosphate anions toward the M/F interface has been shown earlier by Thompson et al. (25). The initial increase in film resistance results from the decreasing rate of the hydrogen evolution reaction (HER), because polarizing the sample in the anodic direction causes the potential to move closer to the equilibrium potential for the hydrogen evolution reaction. This causes a decrease in the (partial) cathodic current density arising from hydrogen reduction at the working electrode. Therefore, the applied anodic current density from the potentiostat keeps increasing until the equilibrium potential for the HER and than saturates. The decrease in resistance at higher potentials arises from potential-driven chloride ion incorporation in the passive film. The film capacitance decreases continuously with anodic potential indicating continuous passive film thickening. Experiments conducted in the sodium sulfate solution as a function of applied anodic potential do not show any decrease in resistance with potential at least up to -100mV (Figure 38). This provides evidence for the influence of chloride ions on the passive film resistance. The film resistance increases with potential from the open circuit potential in sodium sulfate solution, as in the chloride solution. This also arises from the decreasing rate of the HER. At potentials positive to the equilibrium potential for the HER (-660mV vs. SCE) the resistance remains constant within experimental error. The capacitance decreases continuously with potential, as observed in chloride solutions (Figure 38).
This is caused by the growth in film thickness with increasing anodic potential.

The initial cathodic current at the passivation potential that subsequently makes a smooth transition to an anodic current is equivalent to the corrosion potential drifting from potentials more noble than -700 mV to more active values. Such a drift in the open circuit potential and the associated noise has been clearly illustrated in terms of mixed potential diagrams and passive film breakdown at mechanical and residual defects in the passive film by Wood et al. (57). The noise in the current-time plot reported here at the passivation potential has been reported earlier (32, 58, 59). The continuous increase in the anodic current and the decrease in the passive film resistance with exposure time, in constant potential experiments at the passivation potential, is because of chloride incorporation in the passive film. Chloride incorporation must be occurring in a localized manner through defects in the passive film, as previous authors have failed to detect Cl\textsuperscript{-} in the bulk of the passive film as reviewed by Foley (27). The diffusional impedance spectrum at this potential (Figure 27), during initial exposure periods, is thought to result from ionic diffusion through an outer porous corrosion product film on top of the inner passive film.

Another possibility considered for this impedance behavior was ionic diffusion through the passive film. But this seems unlikely, because at longer exposure times the locus of the impedance data falls toward the real axis in the complex plane with the emergence of a second time constant (Figure 27 b,c). If ionic diffusion were responsible for the initial impedance behavior, this observation at longer exposure times can be
Figure 38. Variation of passive film resistance and capacitance with potential for pure bulk aluminum in sodium sulfate solution.

rationalized by a reduction in passive film thickness causing the diffusional boundary layer thickness to decrease. However, ellipsometry data indicate continuous film growth.

In addition, at the passivation potential for the exposure time at which the optical data indicates growth of an outer layer, the impedance data show the emergence of a second time constant. The second time constant in the impedance data is arises from the formation of an outer film, which makes the metal surface electrically equivalent to 2 capacitors connected in series, among other resistive components. Mansfeld and Shih (60) associate the observation of a transmission line-like impedance behavior at low frequencies at the open circuit potential to the formation of pits. A similar experimental observation was made in this study in the first
3 hours after sample exposure at the passivation potential, but there was no evidence of pitting for up to 3 days of exposure in solution. Also, the transmission line-like behavior disappears at longer exposure times and gives rise to a second time constant. If the initial transmission line-like behavior is because of pitting, there is no reason for the pitting process to terminate at longer exposure times. We therefore believe that such impedance behavior in our experiments is due to ionic diffusion in the outer corrosion product layer. The passive film resistance in experiments reported here (60 to 110 kohm-cm²) was 4 to 8 times the passive film resistance at open circuit potential (15 kohm-cm²). No meaningful information from the impedance spectrum at low frequencies at the pitting potential could be extracted owing to the noise at such frequencies. The observation of shallow repassivated pits with a ruptured oxide film suggests that blistering of the oxide film does not necessarily lead to rapid pit propagation as proposed by Natishan and McCafferty (39). The bright spots observed on the metal surface could be blisters containing hydrogen bubbles as suggested earlier (38, 39).

The noise in the external current at the pitting potential observed throughout the experiment from immediately after sample immersion in chloride solution is attributed to dynamic, localized passive film breakdown and repair processes, that are continuously taking place on the metal surface (61-64). Bertocci et al. (59), Uruchurtu and Dawson (32), and Uruchurtu (65) have performed spectral analysis of electrochemical noise for pure aluminum at passivation and pitting potentials. Uruchurtu and Dawson (65) attribute the noise behavior to the presence of localized activation and repassivation at the passivation potentials, with the
repassivation process hindered at the pitting potential. Therefore the
damage processes that give rise to pitting affect the metal surface
underneath the film immediately upon exposure. This means that
mechanisms that propose penetration of the oxide film by chloride ions
during the induction period are not applicable for pure aluminum.
Chloride ions are able to migrate through defects in the passive film on
aluminum, to the M/F interface, immediately after sample exposure to
solution at the pitting potential. Subsequently, the noise in current arises
from the hydrolysis reaction,

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \quad \text{---4.1}$$

taking place in both forward and reverse directions. This observation is
consistent with the localized corrosion model proposed by Galvele (31).
Also, the observation of pits smaller than 10 μ without an oxide cover
suggests that such a cover is not a necessary requirement for pit stability, as
has been suggested earlier (34, 40).

The polarization resistance values at the pitting potential are higher
than the polarization resistance values at the passive potential. This arises
from the fact that the resistance values are determined primarily by
defective regions on the metal surface and by conditions inside occluded
cells. The presence of hydrogen bubbles inside acidified occluded cells at
the pitting potential can cause a high resistance path to form. This will
cause the measured resistance to be higher at the pitting potential compared
to that at the passive potential.
The increase in capacitance with time at the passivation and pitting potential results from an increase in the film dielectric constant. This arises due to the incorporation of chloride ions in the passive film, causing the film to have a higher defect concentration. The increase in film capacitance cannot be attributed to the formation of pits \textit{per se}, as has been suggested by Scully et al while discussing the relative capacitance increase in their pure aluminum and Al-Cu alloy films (66). This is because capacitance is measured from the entire sample surface, in contrast to the passive film resistance that might arise predominantly from the low resistance paths through pits. The measured capacitance is the sum of the capacitance arising from the passive and pitted or defective regions of the sample surface, as these two capacitances are in effect connected in parallel. Therefore, if the measured 25% increase in capacitance in the pitting potential experiment described above is due to the formation of a pit whose fractional coverage of the sample surface is only about 10^-5 (for one 50 \mu\text{m} diameter pit observed in this experiment on a 1.16 cm^2 total surface area), the pit capacitance should be higher than 0.1 F/cm^2. This is an unreasonably high value because the double layer capacitance is usually of the order of 50 \mu\text{F/cm}^2. Also, in 2 other constant potential experiments above the pitting potential, the capacitance values remained constant while the pitting current density increased from 1\mu\text{A/cm}^2 to more than 30 \mu\text{A/cm}^2. Therefore the increase in capacitance is primarily because of a film conversion process on the entire sample surface. Therefore caution should be exercised while using the pitting corrosion model suggested by Mansfeld et al., (60) because the passive film dielectric constant and/or film thickness may vary as pitting occurs. In other words, the capacitance
increase cannot be attributed solely to the increasing area fraction of pits on the metal surface.

The results of modeling the optical data are presented in Figure 37. The difference in the film growth characteristics at exposure times greater than 5 hours, for the open circuit potential, passivation potential and pitting potential, is modeled by different film absorption coefficients at these potentials. This arises from different levels of chloride incorporation in the outer film. The optical behavior from the pitted sample after stable pit formation arises predominantly from the metal substrate rather than the surface film. A quantitative analysis of the data obtained at the pitting potential is not made because the sample was inhomogeneous at this potential. The illuminated area comprised of pitted and passive regions and hence the data presented is not exclusively from the pitted surface.

4.2 Sputtered Pure Aluminum Film

The impedance behavior of the passive film on sputtered pure aluminum in chloride solution is shown in Figure 39. The pitting potential for Al film is -350 mV (6). The initial increase in resistance with potential from the open circuit potential is due to the influence of the Hydrogen Evolution Reaction (HER) as indicated for the bulk aluminum data. The decrease in resistance observed for bulk aluminum at high anodic potentials is also observed in this case. The aluminum film in the sodium sulfate solution behaves similar to bulk aluminum in the same solution. As shown in Figure 40, the resistance increases initially at potentials below the equilibrium potential for the HER and then saturates. The passive film
capacitance for the sputtered aluminum film decreases continuously with anodic potential in both the chloride (Figure 39) and sulfate solutions (Figure 40) as is the case for pure bulk aluminum. The capacitance behavior will be discussed in greater detail later in this chapter. The similarity in the qualitative behavior (variation with potential) of the pure bulk aluminum and the sputtered film validates the applicability of the impedance technique to the sputtered films. The passive film resistance in sodium chloride solutions for the sputtered pure aluminum film is significantly higher than that for the bulk aluminum as presented in Figures 24 and 38. This could arise from two factors. The smooth surface of the sputtered film compared to the bulk aluminum sample will cause significant difference in the apparent surface area of the two surfaces. Secondly, a more uniform distribution of defects and a smaller mean defect size may be present in the sputtered film because of the sputtering of defects from the bulk sample. Such a defect nature can cause the passive film on the sputtered aluminum to be more uniform and hence result in higher values for the passive film resistance. Also, the quantitative values of the passive film resistance were not very reproducible, probably because of the sensitivity of the resistance values to defects in the passive film that are not uniform in all the samples. The pitting potential for the sputtered films were also 300 mV higher than that for the pure bulk aluminum samples. The sputtered film could contain oxygen picked up in the sputtering chamber although TEM results (6) do not indicate any detectable levels of oxygen. The incorporation of oxygen in the film is believed to influence the pitting potential. The pitting potential can also be influenced by the smaller defect size in the sputtered film. As pointed out later for the alloy
films, the pitting potential is hypothesized to be independent of the passive film resistance.

4.3 Aluminum-Tantalum (Al-Ta) Alloy Films

The variation in film resistance with anodic potential for the sputtered Al-Ta film in chloride solution is shown in Figure 42. The pitting potential for this sample is +400mV (6). The film resistance in the case of the Al-Ta film (Figure 42) increases initially from the Open Circuit Potential (OCP) because of the decreasing rate of the HER as explained earlier. The film resistance shows a peak between -400 and -300 mV, which is related to the enrichment of tantalum oxide in the passive film. Earlier studies conducted using XPS (67) reported the steep increase in enrichment in tantalum oxide in the passive film at an overvoltage of 800 mV in 0.1M KCl solution (Figure 43). The open circuit potential in that study was between -1250 and -1300 mV vs SCE. The potential corresponding to the sharp increase in enrichment was therefore between -450 and -500mV SCE. The similarity in the potential values corresponding to the peak in the passive film resistance and the peak in the enrichment behavior lends evidence to the argument that the film resistance is sensitive to the chemistry of the passive film. The decrease in the film resistance at a potential 100mV cathodic to the enrichment potential can be understood in terms of the increased current necessary to selectively oxidize tantalum to cause enrichment. A rearrangement in the structure of the passive film
Figure 39. Variation in passive film capacitance and resistance with potential for Al film in NaCl solution.

Figure 40: Variation in passive film resistance and capacitance with potential in sodium sulfate solution.
must take place prior to the enrichment of Ta in the passive film. Although enrichment effects on the passive film resistance are evident in the Al-Ta film in chloride solutions, the film resistance sharply drops with potential at -200mV even though the pitting potential for this sample is +400 mV. Therefore the enrichment in the oxide of the alloying element in the passive film may not have a significant effect on the pitting potential, contrary to earlier suggestions (67). The current density data as a function of potential are also presented in Figure 42. The slope of the current density curve can be seen to correlate with the resistance curve (Figure 42). This correlation arises because the resistance is inversely proportional to the slope in the current density curve at the potential where the
resistance is determined. However this argument must be employed with caution as the amplitude of the potential signal applied to determine the impedance is only 15 mV. Therefore the resistance is sensitive only to the slope in the current density curve in the immediate vicinity of the potential at which the resistance is determined. The behavior of Al-Ta in sodium sulfate also closely follows the enrichment profile of tantalum oxide in sulfate. The film resistance continuously increases and does not show any decrease prior to the enrichment peak as in the case of the chloride solution (Figure 44). This can be rationalized by considering the enrichment profile of tantalum oxide in the passive film in sodium sulfate (67) (Figure 43). Unlike the case in chloride solution, the enrichment in tantalum oxide in the passive film increases gradually and continuously with increasing potential in sulfate solution with no sharp discontinuity. Therefore, rearrangements in the passive film take place continuously with potential, and their effect on the film resistance is balanced by the effect of increasing amounts of tantalum oxide. The Mott-Schottky (M-S) plot exhibits linear behavior over most of the potential region for the tantalum film in both chloride and sulfate solution (Figures 45 and 46 respectively). The linearity in the M-S plot indicates that the measured capacitance is not from the helmholtz double layer, but possibly from the space charge double layer (Appendix B) in the semiconducting passive film. Another interpretation for the capacitance behavior is presented later.
Figure 42. Variation of passive film resistance and current density with potential for Al-10at.% Ta film in NaCl solution.

Figure 43: Ratio of oxidized alloying element to oxidized Al as a function of overpotential for Al-Cr and Al-Ta alloys in deaerated 0.1M KCl and for Al-Ta alloys in 0.1M Na2SO4 (67).

OCP for Al-Ta in KCl = -1280 mV
OCP for Al-Ta in Na2SO4 = -1315 mV
OCP for Al-Cr in KCl = -1126 mV
Figure 44. Variation in passive film resistance with potential for Al-10at.% Ta in sodium sulfate solution.

Figure 45. Mott-Schottky plot for Al-10at.% Ta in sodium chloride solution.
4.4 Aluminum-Chromium (Al-Cr) Alloy Films

Al-Cr films of two different compositions, 4 at.% Cr (Al-4Cr) and 9 at.% Cr (Al-9Cr), were studied. The pitting potential of the Al-4Cr film is +100mV and for the Al-9Cr film +300 mV (6). The resistance behavior of both samples shows the influence of oxidized Cr enrichment in the passive film, as was the case of the Al-Ta films. The film resistance exhibits a peak at around -400mV in both Al-4Cr and Al-9Cr samples (forward scan of Figure 47 and Figures 48). This peak is observed in both chloride and sulfate solutions (Figures 47-50). Based on earlier XPS studies (67), this peak can be attributed to the enrichment of oxidized chromium in the passive film (Figure 43). The fact that the increase in resistance observed in the forward scan for Al-4Cr is not lost in the reverse scan (Figure 47) indicates that the change in the passive film that causes the resistance increase is irreversible. As the oxidized Cr does not get reduced at lower potentials, the irreversibility of the passive film resistance further corroborates the enrichment argument.

As in the case of the Al-Ta film in chloride solutions, the film resistance for the Al-Cr films decreases with anodic potentials above -400mV. As the pitting potential is +100 and +300mV for the Al-5Cr and Al-9Cr films respectively, the decrease in film resistance is observed at potentials very cathodic to the pitting potential. These resistance trends also indicate that the enrichment in the oxide of the alloying element in the passive film does not have a significant effect on the ennoblement of the
Figure 46. Mott-Schottky plot for Al-10at.% Ta in sodium sulfate solution.

Figure 47: Variation in passive film resistance with electrode potential in the forward (anodic direction) and reverse scan for Al-4 at.% Cr in NaCl solution.
Figure 48. Variation in passive film resistance with potential for Al-9at.% Cr in sodium chloride solution.

Figure 49. Variation in passive film resistance with potential for Al-4at% Cr in sodium sulfate solution.
Figure 50. Variation in passive film resistance with potential for Al-9at.% Cr in sodium sulfate solution.

Pitting potential. The Mott-Schottky plots show a linear region for the Al-4Cr and Al-9Cr samples in both chloride and sulfate solutions (Figures 51-54), as in the case of the Al-Ta film.

The variation of capacitance with potential may also be determined by another important factor. If the passive film were to behave as a dielectric, any increase in passive film thickness with potential would cause the capacitance to decrease with potential as given by the expression for the capacitance of a dielectric;

\[ C = \kappa \varepsilon_0 A/d \]
where $C$ is the capacitance of the dielectric, $A$ the surface area, $\kappa$ the dielectric constant, $d$ the thickness of dielectric and $\varepsilon_0$ the permittivity of free space.

Previous investigators (17) have attempted to distinguish the influence of the space charge layer and the thickness of the dielectric layer on the passive film capacitance by plotting $1/C^2$ vs. $E$ (Mott-Schottky plot) and $1/C$ vs. $E$. In principle, if the former influence were to dominate, the $1/C^2$ vs. $E$ plot should yield a straight line, and if the latter influence dominates, $1/C$ vs. $E$ should yield a straight line. Unfortunately this method does not yield a valid conclusion in this study as the potential range employed was not large enough to mathematically isolate the two behaviors. In the potential range employed, both plots yielded straight lines with similar correlation coefficients.

A different technique was employed in this study in an attempt to distinguish the influence of the space charge layer from the dielectric thickness. If the capacitance variation is because of the influence of the space charge layer, all variations arise from varying levels of band bending in the semiconducting passive film (appendix B). Therefore such variations would be reversible with potential. However, if the capacitance variation with potential is because of the influence of the thickness of the dielectric, no reversibility of capacitance with potential should be observed because the oxides formed at higher potentials do not undergo thinning at lower potentials. Therefore experiments were conducted to check for the reversibility of the passive film capacitance. Impedance experiments were conducted on all the samples in sodium sulfate solution at various potentials during a potentiostatic anodic scan, and during a reverse scan to the open
circuit potential. It can be seen from figures 55 to 58 that the capacitance variation is mostly reversible with anodic potential. This indicates the predominant influence of the variation in the space charge layer thickness on the measured capacitance values. The capacitance behavior, however, is not completely reversible for all the samples, which indicates some influence of the film thickness variation on the capacitance values.

Calculations were made to determine the space charge densities and flat band potentials for the passive films on the sputtered alloys. These values were extracted from Mott-Schottky plots. The theory and equations upon which such calculations are based are detailed in Appendix B. The results of such calculations for experiments conducted in sodium sulfate solution are presented in Table 2. The values for the space charge densities of passive films on metals are of the order of $10^{26}$ m$^{-3}$ (50). The values in Table 2 are within this order of magnitude. All the values reported in Table 2 were calculated from the capacitance data obtained during the reverse scan of potentials. This is important as during the forward anodic scan of potentials, the passive film thickness continuously increases and this might significantly influence the calculated flat band potential. Also, during the forward scan the alloy films get progressively more enriched in the solute element and therefore the chemistry of the passive film does not remain constant during the scan.
Figure 51. Mott-Schottky plot for Al-4 at.\% Cr in sodium chloride solution

Figure 52. Mott-Schottky plot for Al-9 at.\% Cr in sodium chloride solution
Figure 53: Mott-Schottky plot for Al-4at.% Cr in sodium sulfate solution.

Figure 54: Mott-Schottky plot for Al-9at.% Cr in sodium sulfate solution.
Table 2: Space charge densities ($N_d$) and flat band potentials ($V_{fb}$) for sputtered Al-Cr and Al-Ta films

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample#</th>
<th>Electrolyte</th>
<th>$N_d$ ($#/m^3$) x10^26</th>
<th>$V_{fb}$ (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al Film</td>
<td>21193</td>
<td>Na2SO4</td>
<td>5.49</td>
<td>-1.491</td>
</tr>
<tr>
<td>Al-10Ta</td>
<td>011493</td>
<td>Na2SO4</td>
<td>8.643</td>
<td>-1.500</td>
</tr>
<tr>
<td>Al-4Cr</td>
<td>20193</td>
<td>Na2SO4</td>
<td>6.47</td>
<td>-1.480</td>
</tr>
<tr>
<td>Al-9Cr</td>
<td>10493</td>
<td>Na2SO4</td>
<td>7.97</td>
<td>-1.050</td>
</tr>
</tbody>
</table>

The dielectric constant was assumed to be 8 for all the calculations above.

The space charge density and flat band potential data are not presented for samples in the chloride solution as the aggressiveness of the electrolytes resulted in the films being damaged before the completion of the reverse scan.

Upon comparing the magnitudes of the passive film resistance for all the films and bulk aluminum investigated in this study, it is evident that there is no correlation between the film resistance and the pitting potential. Moreover, the impedance data presented here are representative of at least three different experiments under identical conditions. Although all the data obtained under identical conditions show very reproducible qualitative
trends, the magnitude of the resistance and capacitance do vary considerably. This can be attributed to the sensitivity of the impedance data to defects in the passive film.
Figure 55: Variation in passive film capacitance with potential during forward and reverse scans for Al film in sodium sulfate solution.

Figure 56: Variation of passive film capacitance with anodic potential during forward and reverse scan for Al-10at.% Ta in sodium sulfate solution.
Figure 57: Variation in passive film capacitance with anodic potential during forward and reverse scan for Al-4at.% Cr in sodium sulfate solution.

Figure 58: Variation in passive film capacitance with anodic potential during forward and reverse scan for Al-9at.% Cr in sodium sulfate solution.
CHAPTER V

CONCLUSIONS

1. Distinct difference in the amplitude of the noise behavior of the current data at the pitting and passive potentials for pure bulk aluminum was observed in chloride solution. This clearly indicates the presence of localized passive film breakdown/repair processes at the pitting potential. Such processes commence soon after sample immersion in the solution at the pitting potential. The aggressive anions that cause pitting are able to influence the bare metal surface almost instantaneously upon the immersion of pure aluminum in chloride solutions, at the pitting potential, even if the pit incubation period is as long as 5 hours.

2. The random fluctuations in the polarization resistance data obtained from pure bulk aluminum at the pitting potential indicate that Electrochemical Impedance Spectroscopy (EIS) is sensitive to localized processes.

3. Crystallographic pits with a 5µ mean dimension form on pure bulk aluminum at the pitting potential even when the anodic current density is only 1µA/cm²
4. The increase in capacitance with increased exposure time at the passivation and pitting potential, for pure bulk aluminum, is caused by a change in the entire surface film than by any localized effects as proposed earlier.

5. Differences in optical behavior of pure bulk aluminum with applied anodic potential are due to different absorption coefficients of the outer film formed on top of the inner passive film. Different levels of chloride induced defects in the outer film give rise to different absorption coefficients.

6. Impedance experiments done on bulk aluminum and sputtered aluminum films indicate that both behave in a qualitatively identical manner as a function of applied anodic potential.

7. Impedance experiments on sputtered alloy films are sensitive to passive film chemistry and can monitor the variation in film resistance with anodic potential. Film resistance data show peaks at potentials where prior studies using XPS (67) have indicated sharp increases in enrichment levels of the oxides of the alloying element. This is true for both Al-Ta and Al-Cr alloy films. Such peaks are not observed in the case of the pure Al films.

8. The passive film resistance of the Al-Cr and Al-Ta alloys decreases with anodic potential after the effects of enrichment are observed. The decrease in resistance is observed from potentials that are 500 mV (Al-4
at%Cr), and 800 mV (Al-10 at.% Ta and Al-9 at.% Cr) cathodic to the pitting potential. Therefore enrichment effects in the passive film do not play a significant role in determining the pitting potential.

9. The capacitance data obtained as a function of potential indicates that the passive films in all the materials studied exhibit semiconducting behavior with a high space charge density. Variations in the thickness of the space charge layer determines the capacitance variation with potential.

10. The results obtained in this study indicate that models for pitting corrosion that assume a correlation between the bulk characteristics of the passive film and the pitting potential may not be valid, at least in the case of the metastable Al-4at.% Cr, Al-9at.% Cr and Al-10at.% Ta alloy films.
APPENDIX A

ELLIPSOMETRY

A.1 Introduction to Ellipsometry:

The kinetics of most corrosion and oxidation phenomena in materials is determined by the nature of the reaction product film that forms on the interface between the reactive media involved. It is therefore essential to completely understand the characteristics of the film to exercise control over the corrosion or oxidation process. The nature of the reaction product film ranges from the compact protective passive film formed on chromium in aqueous neutral environment at room temperature, to the non-protective oxide film on pure zinc under similar exposure conditions. The dramatic influence of the surface film on the kinetics of metal dissolution initiated the quest for understanding the nature of these films in the early twentieth century.

Ellipsometry is an optical technique that was first applied to study surface films in 1935 (69). This technique has since been used extensively in corrosion studies, due to its high sensitivity and ability to be used in-situ. The fundamental theory behind ellipsometry for film free surfaces was developed by Fresnel in the early nineteenth century. Following this, in 1890,
Paul Drude expanded the theory to film covered surfaces. Since the first application of ellipsometry in 1935 (69) to characterize surface films, significant refinements on the ellipsometer have taken place and the progress in instrumentation is continuing even at this time. Simultaneously, computational techniques to analyze the ellipsometric data have also evolved since the early manual calculations that could only employ the approximate form of the equations proposed by Drude. With the advent of high speed digital computers, it has become possible to solve for the optical and thickness parameters of surface films by employing the exact form of the Drude equations. It has also become possible to do it in a dynamic manner as
the surface reactions proceed. This has been achieved by suitably combining advances in ellipsometer instrumentation, high speed data acquisition, and computational techniques.

A.2 Theory

In order to fully comprehend the principles of ellipsometry, it is essential to understand the wave nature of light. Visible light is an electromagnetic radiation composed of electric and magnetic field vectors oscillating perpendicular to the direction of light propagation. The electric and magnetic field vectors are perpendicular to each other at any instant of time and at any point in space, and lie on a plane whose normal lies along the direction of propagation of the light. Due to the mutual orthogonality of the electric and magnetic field oscillations, specifying the nature of any of the fields completely defines the light wave. Therefore, in all the discussions that follow, only the electric field vector (E) will be considered. To completely specify a light wave in vacuum, one has to specify the amplitude, phase, frequency, wavelength, and direction of propagation of the light wave. The illustration of the fundamental principles of ellipsometry is best done by considering applications that employ light of a single wavelength (monochromatic light). The ensuing discussion will therefore assume 'light' to mean 'monochromatic light'. The direction of oscillation of the E vector is the polarization direction. The light from a monochromator comprises of E vectors oscillating in all possible directions normal to the propagation
direction, in a totally random fashion. This is called randomly polarized or unpolarized light.

When light is incident on an interface between two media of different refractive indices, a part of it gets reflected and a part of it gets refracted. The relative intensities of the two light waves is determined by the nature of the particular interface that causes such reflection and refraction. Ellipsometry deals only with reflection, and only this process will be discussed in this article. The above interactions may result in a change in amplitude, phase, direction of propagation, polarization, and velocity of the light wave. All such changes can be quantitatively predicted (page 284, 71). Ellipsometry utilizes the correlation between the change in polarization of the E vector upon reflection, and the physical nature of the two media that make up the interface, in order to determine the interface characteristics. As it is impossible to detect changes in polarization if the incident light wave is randomly polarized, ellipsometry employs linearly polarized light. As the name implies, linearly polarized light is one whose E vector oscillates along a line at any point in space as a function of time. The tip of the E vector at different points in space at any particular time instant, lies in one single plane that also contains the direction of propagation of the light (Figure 59).

In order to understand the change in polarization upon reflection, the plane of incidence has to be introduced. This is the plane that is defined by the incident light wave propagation vector and the normal to the reflecting interface. The component of the E vector that lies in this plane is called the P component, and that which is normal to the plane of incidence is called the S component. Light that is linearly polarized in any direction can be resolved into the P and S components, and this is always done due to the following
fact. When light polarized in either the S or P direction is incident on an interface, it undergoes reflection without any change in polarization, although there could be change in the amplitude and/or phase of the wave. What is to be noted here, and which forms the basis of ellipsometry, is that the change in phase of the wave caused by reflection is invariably different for the S and P components. Therefore, if an incident monochromatic light wave has its S and P components in phase with each other (which is necessarily true for linearly polarized light), upon reflection, the S and P components will be out of phase. Whenever this happens, the resulting state in the most general case, is elliptically polarized. The name elliptical polarization arises due to the fact that, at any point in space the tip of the E vector traverses an ellipse as a function of time. The orientation of the ellipse and its ellipticity is related to the physical nature of the film from which the reflection took place. The theory that governs this relation has been rigorously developed (page 284, 71).

The material of interest will be referred to as the substrate and the medium surrounding it (electrolyte in a corrosion application) will be referred to as the ambient medium. Theoretical relations that are relevant to reflection from a film-free substrate will be discussed first, following which a filmed substrate will be considered. There are two basic relations that relate the reflected, refracted, and incident E vectors. These are the Snell's law and the Fresnel complex amplitude reflection co-efficients (page 284, 71).
**Fresnel complex amplitude refection co-efficients:**

\[
\frac{E_{\varphi}}{E_{\varphi}} = r_p = \frac{N_1 \cos \phi_0 - N_0 \cos \phi_1}{N_1 \cos \phi_0 + N_0 \cos \phi_1} \quad \text{A.1}
\]

\[
\frac{E_{\pi}}{E_{\pi}} = r_s = \frac{N_1 \cos \phi_0 - N_1 \cos \phi_1}{N_0 \cos \phi_0 + N_1 \cos \phi_1} \quad \text{A.2}
\]

**Snell's law:**

\[N_0 \sin \phi_0 = N_1 \sin \phi_1 \quad \text{A.3}\]

\(N_0\) and \(N_1\) are the complex refractive index of the ambient medium and the substrate respectively; each is written as

\[N = n - ik \quad \text{A.4}\]

where,

\(n = \text{index of refraction}\)

\(k = \text{extinction coefficient or the absorptivity of the film.}\)

\(\phi_0 = \text{angle of incidence (Figure 60).}\)

\(\phi_1 = \text{angle of refraction (Figure 60).}\)

\(E = \text{complex amplitude of the E vector.}\)
the subscripts s, p stand for S and P components, while the subscripts r, i stand for the reflected and incident wave, respectively.

The index of refraction of a medium is defined as the ratio of the velocity of light in vacuum to the velocity of light in the medium. The complex refractive index is also the square root of the dielectric constant of the medium.

The complex amplitude of the E vector carries information about the amplitude and the phase of the wave. For instance, the reflection co-efficient for the P component, \( r_p \), can be written as follows.

\[
r_p = \left| r_p \right| e^{i\delta_p}
\]

where,

\( \left| r_p \right| = \) ratio of the amplitude of the P component of the E vector in the reflected to that in the incident wave.

\( \delta_p = \) phase shift in the P component of the reflected wave relative to the incident wave, caused by the reflection process.

The experimentally determined parameter in ellipsometry is the ratio of the complex Fresnel amplitude reflection coefficients for the P and S components, \( \rho \).

\[
\rho = \frac{r_p}{r_s} = \left| \frac{r_p}{r_s} \right| e^{(i \delta_r - i \delta_s)}
\]

This is usually written as
\[ \rho = \tan \psi e^{i\Delta} \]  

where \( \psi \) and \( \Delta \) are the instrument output data. The above equations can be re-written in the form,

\[ N_1 = N_0 \sin \phi_0 \left[ 1 + \frac{(1 - e)^2}{(1 + e)^2} \tan^2 \phi_0 \right]^{1/2} \]

This equation can be used to determine the complex index of refraction of the substrate \( N_1 \) from that of the ambient medium \( N_0 \) after experimentally determining the value \( \rho \) at the angle of incidence \( \Phi_0 \).

Figure 60: Oblique reflection and transmission of a plane wave at the planar interface between two semi-infinite media 0 and 1. "P" and "S" are axes parallel and perpendicular to the plane of incidence respectively (p. 271, 71).
Figure 61: Oblique reflection and transmission of a plane wave by an ambient (0)-film (1)-substrate (2) system with parallel-plane boundaries. (p. 283, 71).

The above equations were developed by Fresnel for a bare substrate and later Drude used them to develop his relations for a film covered substrate. The complex amplitude reflection coefficient for reflection from a film covered substrate is given by

\[ R_p = \frac{r_{01p} + r_{12p} e^{-i2\theta}}{1 + r_{01p}^* r_{12p} e^{-i2\theta}} \]
where,

\[ \beta = 2\pi \frac{d}{\lambda} N_1 \cos \phi_1 \]

\[ R_s = \frac{r_{01s} + r_{12s} e^{-i2\beta}}{1 + r_{01s}r_{12s} e^{-i2\beta}} \]

\[ R_p = |R_p| e^{i\sigma_p} \]

\[ R_s = |R_s| e^{i\sigma_s} \]

The ratio of \( R_p \) to \( R_s \) is given by

\[ \rho = \frac{R_p}{R_s} = \frac{|R_p|}{|R_s|} e^{i(\sigma_p - \sigma_s)} \]

This is the experimentally determined parameter in ellipsometry. It can also
be written as

$$\rho = \tan \psi e^{i\lambda}$$  \hspace{1cm} \text{Equation A.15}$$

where

$$\tan \psi = \frac{|R_p|}{|R_s|} \quad \text{and} \quad \Delta = \Delta_p - \Delta_s$$  \hspace{1cm} \text{Equation A.16}$$

The functional dependence of $\Delta$ and $\Psi$ on the system parameters can be symbolically written as

$$\tan \psi e^{i\lambda} = \rho (N_0, N_1, N_2, d_1, \phi_0, \lambda)$$  \hspace{1cm} \text{Equation A.17}$$

where $\lambda = \text{wavelength of light}$.

In the most general case $N_0, N_1, N_2$, the index of refraction of the ambient medium, film, and substrate respectively, are all complex, and hence $\rho$ is a function of 9 variables. However, the ambient medium is usually transparent and hence $N_0$ is real. Also, in most studies the substrate refractive index is evaluated before any film formation. Moreover, the angle of incidence $\theta_0$ and the wavelength of light used, $\lambda$, are known parameters. So the system unknowns are the 2 parameters $(n,k)$ in the film refractive index $N_1$, and the film thickness $d_1$. The problem in most studies then boils down to evaluating 3 unknowns from 2 experimentally determined parameters $(\Delta, \Psi)$. Clearly this cannot be done with one observation of $\rho$. This is one of the major drawbacks of the technique and ways of
circumventing it are addressed in a later section.

During the time when Drude developed his rigorous equations, he was unable to solve them in an explicit manner due to the absence of powerful computational techniques and machinery. Therefore, Drude expanded the exponential terms in a series form and used only the first term to arrive at the following approximate equations (page 10, 72).

\[
\Delta - \Delta' = -A \left(1 - \frac{1}{N_1^2}\right) \frac{d_1}{\lambda} \quad \text{------------------} \quad \text{A.18}
\]

\[
2(\psi - \psi') = B(1 - C) \left(1 - \frac{1}{N_1^2}\right) \frac{d_1}{\lambda} \quad \text{--------} \quad \text{A.19}
\]

where \(\Delta', \psi'\) correspond to the film free values; \(A, B, \) and \(C\) are functions of the angle of incidence and index of refraction of the substrate. The above equations are valid only when the film thickness is very small compared to the wavelength of the light being used, i.e. when \(d/\lambda << 1\).

The approximate form of the Drude equations is now being used mainly to get a quick qualitative measure of film thickness and refractive index rather than for quantitative studies.

Although seldom applied to corrosion studies, the theoretical interpretation of ellipsometric measurements to obtain sub-monolayer surface coverage with reaction products will have to be mentioned here for completeness. Kruger has reviewed the various theoretical models (73) that have been developed to take advantage of the excellent sensitivity inherent to ellipsometry for the detection of sub-monolayer films. One of these
models, for example, relates the fractional coverage of the substrate with the film to an effective refractive index for the interface region, and subsequently employs the Drude equations presented above.

A.3 Experimental Procedure and Instrumentation

A brief discussion of the experimental techniques used to measure the $\Delta$ and $\psi$ values will now be presented. It is appropriate at this point to define ellipsometry. Rothen (page 7, 72) defines it as the art of measuring and analyzing the elliptical polarization of light. The basic experimental method that has been historically employed to accomplish this is the null-detection method. In the simplest sense, this involves placing a compensator and an analyzer in the path of the elliptically polarized light. The compensator introduces a known phase difference between the S and P components of the reflected wave. This phase difference is varied by the investigator until the wave that emerges from the compensator is linearly polarized. In other words, the compensator eliminates the phase difference between the S and P components, by imposing a phase change that exactly compensates for such a change caused by the reflecting surface. As the phase difference imposed by the compensator is a known quantity, the $\Delta$ due to reflection can be determined. The direction of polarization of the resulting linearly polarized light is determined by an analyzer. In order to achieve this, the analyzer is capable of continuous rotation, and at any particular angle transmits only the components of light that is polarized at that angle. Therefore, when the analyzer's transmission axis is normal to the polarization direction, no light passes through; this is called the null point (Figure 62). Once the
polarization direction is determined, the tangent of the angle that the polarization direction makes with the plane of incidence is the \( \tan \psi \) that appears in the equation for \( \rho \). This assumes that the incident light is linearly polarized at 45° to the plane of incidence. Clearly, the procedure just outlined is time consuming (typically requires a few minutes) and tedious. Moreover, visual detection of the null point is subject to error. It is therefore nearly impossible to conduct accurate dynamic measurements of a continuously changing surface film. In order to obviate these difficulties, automatic ellipsometers have been developed that facilitate accurate tracking of dynamic surface phenomena \textit{in-situ}, as they occur. An extensive account of all the automatic ellipsometers and their principle of operation is provided in the text by Azzam and Bashara (page 405, 71). A brief description of one, the rotating analyzer ellipsometer, will be outlined here. An illustration of its operation is presented in Figure 63. In this instrument, an angular encoder keeps track of the instantaneous angle (azimuth) of the analyzer as it continuously rotates at about 50 revolutions per second. Corresponding to each of these angles a photodetector determines the light intensity in that direction. By correlating information from the angular encoder and the photodetector, the light intensity as a function of angular position around the direction of light propagation is determined. This completely defines the ellipse of the reflected wave polarization, from which the \( \Delta \) and \( \Psi \) information can then be extracted. This procedure for collecting a set of data points takes about twenty milliseconds and the instrumentation is being improved to achieve higher accuracy and speed.
A.4 Advantages of Ellipsometry

Two important characteristics of ellipsometry make it an extremely valuable technique for surface analytical studies. These are its high sensitivity and its *in-situ* applicability.

Ellipsometry can be employed to detect sub-monolayer film coverage of the substrate surface due to its high sensitivity which arises from two factors(74):

a. Measurements in ellipsometry involves the determination of the ratio of the amplitude of the P-component of the E vector to that of the S-component, and the relative phase difference between the 2 components. Since these are relative measurements, any errors introduced by fluctuation of the light source (or other sources of amplitude modulation that have an identical effect on both s and p components) cancel out.

b. The other reason for the sensitivity arises from the fact that the measurements involve angular quantities. The rotating analyzer ellipsometer, for example, measures the light intensity in the reflected wave as a function of the angle from the plane of incidence. This, when combined with the fact that angular measurements can be made with high resolution, contributes to the sensitivity of the technique.

The other valuable characteristic of the technique is its *in-situ* applicability. Due to the fact that visible light is not absorbed by the ambient medium in a corrosion or oxidation situation, all ellipsometric studies can be conducted *in-situ*. This is unlike other surface analytical techniques such as Auger Electron Microscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS), etc. These
Figure 62: Illustration of the null-point, by having the analyzer transmission direction normal to the polarization direction of the incident light. (P. 1151, 70).

Figure 63: Schematic illustration of the operation of an automatic rotating-analyzer ellipsometer. (Page 413, Reference 71).
techniques suffer from the drawback that the sample must be placed in a high vacuum before the study can be conducted. This is thought to alter the nature of passive films, especially when they are hydrated (76).

Raman spectroscopy and Mossbauer spectroscopy are two other in-situ techniques that are currently being employed. These two techniques however, have a much lower sensitivity than ellipsometry. For instance in Mossbauer spectroscopy, the sampling depth is 3000 Å (76); Raman spectroscopy (77) requires at least 10 monolayers of film material for detection. Differential Reflectometry, Extended X-ray Absorption Fine Structure (EXAFS), Internal Reflection Infra-red Spectroscopy (IRIS), and Electron Spin Resonance (ESR) are other in-situ techniques that are currently being employed for surface analytical studies.

A.5 Limitations of Ellipsometry

The extensive application of ellipsometry to precisely determine the thickness, and to identify the structural and physical nature of surface films has been tempered by a few inherent problems associated with the technique.

a. The theoretical equation of Fresnel & Drude that model the reflection process is only applicable to a planar isotropic 3-dimensional film formed on a substrate. There are two common experimental conditions that violate this assumption. 1) Surface roughness in the substrate or at the substrate-film interface. 2) The situation where the surface film formed has a gradient in its refractive index or is a film of two or more uniform layers, each having a different refractive index. The variations in refractive index along the film thickness can arise due to either compositional or structural
variation. The real part of the refractive index of a surface film increases with the density of the film.

Several techniques have been employed by investigators to circumvent such non-ideal conditions. The presence of surface roughness can be modeled by replacing the roughened layer by an optically equivalent, homogeneous hypothetical film with sharp boundaries (72). The refractive index of such a film can be determined by an effective medium approximation. This uses the refractive indices of the substrate and the film and the volume fraction of the two phases to arrive at an effective refractive index for an optically equivalent film. The equations of reflection can then be applied and subsequent analysis carried out in a manner identical to that for a smooth interface. The problem of a gradient in the optical constant along the film thickness can be modeled by subdividing the film into several discrete homogeneous layers, each of which has a different (but smoothly varying) optical constant (73, 74).

b. Another significant problem associated with ellipsometry is the indeterminate set of equations in the case of an absorbing film (non-zero \( k \)). There are 3 unknown parameters for such a film (ie, the real and complex part of the refractive index of the film and the film thickness) and only 2 experimentally determined parameters (\( \Delta \) and \( \Psi \)), thus rendering a unique solution impossible. This problem has invoked a rather extensive array of solutions. Three popular ones are;

(i) Independent film thickness calculation by employing other techniques like coulometry.
(ii) Assumption of a non-absorbing film (\( k=0 \)).
(iii) Obtaining \( \Delta \) and \( \Psi \) values as the film grows, for continuously increasing
thickness. This set of data is compared to a model that assumes the uniform growth of a homogeneous film (73).

Cahan (78) has discussed the limitations of the above techniques and a few others. A discussion of the utilization of the intensity information in the reflected light wave, to narrow down the possible solutions for the film properties, is also presented. The widespread usage of this 3-parameter ellipsometry is primarily limited at present by the instability of the common light sources.

c. The uncertainty in the optical constants of different materials poses another problem in the precise identification of surface films. Variations in the refractive index of materials with grain size, sample size, surface contamination, surface stress and strain have been documented in literature (page 418, 71). A good example of the manifestation of such variations is the scatter in the literature data for the refractive index of pure aluminum.

These problems make it imperative to use a supporting experimental technique to corroborate the conclusions drawn from ellipsometry. Coulometry is sometimes employed for this purpose (page 252, 73). Differences between coulometry and ellipsometry results, however, could arise due to the following factors:
1. Surface roughness
2. Film hydration
3. Incorrect values for the cation oxidation state in the film and/or density of the film.
4. Film dissolution or metal dissolution through the film.

Other techniques that are employed include x-ray specular reflectivity (79), impedance spectroscopy (80), electron-optical techniques (86) etc. It
should be pointed out that most of the problems mentioned are not serious when ellipsometry is employed only to provide qualitative trends during film formation and growth. Hence ellipsometry is a very handy tool to study film growth kinetics.

A.6 Data Interpretation

Investigators have employed ellipsometry to study corrosion processes both as a qualitative and quantitative tool. Qualitative studies identify trends in the experimental parameters with the kinetics of film formation or dissolution. Such studies detect the occurrence of a film conversion process or provide insights into the growth mechanisms. For instance, the field assisted growth mechanism of oxide films can be detected by a linear variation in $\Delta$ with potential, since $\Delta$ is linearly proportional to film thickness at small values of the film thickness. Quantitative studies, under ideal conditions, can help identify the composition of the film and to determine the thickness of the film with precision. This latter procedure is employed extensively by the semiconductor industry to obtain accurate information about the effect of process variables on the thickness of oxide overlayers.

Qualitative techniques do not require an exact knowledge of the optical constants of the substrate. However, such techniques cannot make use of the excellent resolution provided by ellipsometry and the possibility of film identification \textit{in-situ}. Quantitative techniques suffer from all the drawbacks associated with the uncertainty in the values of the relevant optical constants. When calibrated with a complementary technique,
however, they provide valuable quantitative information.

It is worthwhile to document the qualitative conclusions drawn by various investigators from the trends in $\Delta$ and $\Psi$ values observed during the oxidation or dissolution of surface films. It should be pointed out that although these conclusions provide a good physical feel for the experimental parameters, they are not universally valid, and should be understood in the context of the particular experimental conditions.

(a) A decrease in $\Psi$ at a constant $\Delta$ has been observed (81) upon potential cycling of Cr in 85% $H_3PO_4$. This is attributed to a film conversion process where a film with a high absorptivity ($k$) is formed at a nearly constant thickness ($\Psi$ is inversely related to absorptivity).

(b) A simultaneous decrease in both $\Delta$ and $\Psi$ is attributed to the development of surface roughness in the metal/film interface with simultaneous growth of a transparent surface layer in an aluminum-NaCl solution (0.1N) system (82).

(c) A reduction in $\Psi$ (while $\Delta$ decreases continuously) is attributed to a change in the oxidation state of the film in an Ni-0.1MKOH system (83).

(d) If the $\Psi$ and intensity variations are very small during passivation (with a decrease in $\Delta$), it is likely that the film formed is transparent (82).

(e) The $\Delta$ vs $\Psi$ curve during film growth will lie in a closed loop if the film is transparent ($k=0$), and if the film is homogeneous with a constant refractive index (71).

The larger the size of the loop formed, the higher is the corresponding refractive index of the film and the greater its density.

(f) The higher the conductivity of a material, the higher is the concentration and mobility of charge carriers that can absorb the energy
contained in the light wave, and hence higher is the 'k' value (85).

(g) Large microcrystals and a rough substrate exhibit an apparent increase in 'k' for aluminum with respect to a very fine structure (86). This could be due to the free electrons in the grain boundaries that cause a reduction in conductivity. Since larger microcrystals have lesser grain boundary area per unit surface area, they might have a higher 'k' compared to smaller crystals.

(h) At small values of film thicknesses, a linear $\Delta$ vs $\Psi$ curve (decreasing $\Delta$ and increasing $\Psi$) obtained during film growth could mean that an oxide film with a constant refractive index is growing (83).

Review papers on ellipsometric studies as relevant to corrosion have been written by Kruger (72, 73), Paik (87), and Greef (88). A list of references on ellipsometry, as applied to corrosion and electrochemistry has been compiled by Hayfield (89). Notable contributions to instrumentation and data analysis pertaining to ellipsometry have been made in the recent past. Cohn et al. (90) have presented a technique (Dynamic Imaging Microellipsometry) to rapidly scan the sample to obtain a two-dimensional image of the surface by employing several optical detectors. This technique was developed to gain further insights into the nature of changes taking place in passive films associated with localized corrosion. Unfortunately the limited spatial resolution (not less than 1µ) prevents any significant fundamental insights into the localized corrosion phenomenon. De Smet and Ord (91) have reported the application of the simplex algorithm for an efficient calculation of the film refractive index. Starting with a reasonable 'guess' for the refractive index, the algorithm progressively determines 'better' values that minimize the difference between the calculated and
experimental optical parameters. A procedure for quantitative estimation of the goodness of fit is also presented. Gottesfeld (92) has written a comprehensive review of the principles and applications of ellipsometry to electrochemistry.
APPENDIX B

ELECTRONIC PROPERTIES OF PASSIVE FILMS

A detailed description of the charge distribution in semiconducting passive films and in the interface between the film and the electrolyte along with its variation with potential will be presented here. This involves the charge and potential distribution in the space charge layer of the passive film, surface states, and the Helmholtz (HZ) double layer. This description is essential to understand the variation in capacitance with electrode potential during anodic polarization of a metal covered with a semiconducting passive film. All the information presented in this chapter are condensed from the appropriate sections in reference 93.

The potential distribution at a semiconducting film/electrolyte interface is illustrated in Figure 64.

B.1 THE SPACE CHARGE LAYER

When electrons are transferred into or out of a semiconductor, a charged region is formed on its surface. This region is commonly referred to as the "space charge" layer and is assumed to have a uniform charge
density. The amount of charge in the space charge region depends on several processes. A semiconductor in vacuum will almost inevitably develop a space charge near the surface simply because some of the bulk carriers near the surface will be captured by surface states. When the semiconductor is dipped into a solution, the charge in the space charge region may change further because (a) the surface states will be affected by their interaction with the solution and the charge in the surface states will therefore change.
and/or (b) ions in solution with appropriate energy levels will inject or extract electrons from the semiconductor. The above will occur with an open circuit condition. Further variation in the space charge will occur if (c) a second electrode is dipped into the solution and an external voltage applied between the two electrodes different from the open circuit voltage. Then the space charge capacitor (capacitance, C) will charge up in accordance with;

\[ C = \frac{dQ}{dV} = \frac{Ake_0}{d} \]

where,

- \( k = \) dielectric constant
- \( \varepsilon_0 = \) permittivity of free space
- \( d = \) thickness of the space charge layer
- \( A = \) exposed area of the electrode surface

The charging will result in the addition (or subtraction) of a charge \( Q \) from the open-circuit case.

The ability to intentionally change the voltage in the semiconductor space charge region by controlling the applied voltage - changing it by an amount equal to the change of the imposed external voltage - is one of the key characteristics used in semiconductor electrochemistry. The voltage across the space charge will not always change by an amount equal to a change in the external voltage, because some of the change in voltage can appear across the other double layers in the circuit. In most cases of interest the semiconductor space charge dominates - most of any change in applied voltage does appear across the semiconductor space charge region.
The three forms of space charge layers that can be obtained on a semiconductor are illustrated in Figure 65. The depletion layer, shown in Figure 65a, sometimes also termed an exhaustion layer, forms if majority carriers are extracted in moderate amounts. The surface region is "depleted" of majority carriers, and minority carriers are not present, so the surface region is depleted (exhausted) of both forms of mobile carriers. Unless the electron potential (negative of the electric potential) at the semiconductor surface relative to the potential at the semiconductor bulk ($V_s$) is made very small, the surface region is essentially insulating. The space charge to insert into Poisson's equation is due only to ions or trapped charges in the depleted region. The accumulation layer, shown in Figure 65b, results when majority carriers are injected into the semiconductor from the surface, and these excess majority carriers form the space charge. The inversion layer, illustrated in Figure 65c results when majority carriers are extracted but the number extracted is excessive, so much that the majority carrier band (the impurities near the surface) cannot supply all the majority carriers required without resulting in excessive band bending. Carriers have to come from the minority carrier band. Thus, in the example of Figure 65c, where an $n$-type semiconductor is used for illustration, the majority carriers, electrons, are not only extracted from the conduction band, but also from the valence band (hole injection). The term "inversion" describes the fact that the semiconductor type has changed because of the process; in the case illustrated, the $n$-type semiconductor has actually been "inverted" to $p$ type at the surface.

Any of the surface layers in Figure 65 can be produced by varying the electrode potential. If a voltage is applied to make the semiconductor very
negative relative to the solution, the bands bend down at the surface: with an $n$-type semiconductor an accumulation layer (Figure 65b) is induced; with a $p$-type semiconductor, an inversion layer. As the voltage applied makes the semiconductor less negative and possibly slightly positive, the band picture moves to the depletion form, shown for $n$-type material in Figure 65a. With
an extremely high positive voltage on the semiconductor, relative to the solution, the bands bend up at the surface, becoming an inversion layer (Figure 65c) for $n$-type, or an accumulation layer for $p$-type.

As far as current flow is concerned, the electrode of Figure 65 will, in general, have diode characteristics. If the band bending is such as to move majority carriers to the surface, the diode is in the forward direction and, if energy levels are available in the solution to accept them, high currents can and will flow. Thus for the $n$-type example of Figure 65, the accumulation layer of Figure 65b and probably a modest depletion layer as in Figure 65a, will permit copious cathodic current flow with electrons flowing out of the semiconductor. When the voltage is lowered and reversed, such that majority carriers are drawn away from the surface, the barrier height is increased. In general, states are not available to inject electrons into the majority carrier band of the semiconductor, and the minority carrier density is too low to carry appreciable current. Therefore not only is there no electron flow out of the semiconductor, there is negligible current flow into it too. Thus negligible current flows. This becomes the reverse direction of the diode. The terms "forward direction" and "reverse direction" of the applied voltage thus describe both important characteristics of the barrier layer at the surface (large or small barrier) and the expected flow of current.

The counter change for the space change in the semiconducting passive layer is located at the film surface. These charges give rise to the space charge double layer.

To illustrate the potential distribution in the space charge region and the magnitude of the electron potential ($V_s$) on the semiconductor surface
relative to its bulk, a mathematical analysis is presented for a depletion layer. A similar analysis can be done for an accumulation layer.

Potential Distribution in the Depletion Layer:

As described above, the space charge in the depletion layer is the immobile charge on traps or on ionized donors or acceptors. As is usually done, the density of such charge is assumed as constant in the space charge region. Then Poisson's equation in one dimension (perpendicular to the electrode surface),

\[
d^2V/dx^2 = \rho/k\varepsilon_0
\]

(\(V\) refers to the electron potential and not the electric potential. This is used to facilitate direct application to the band model), becomes

\[
d^2V/dx^2 = qN_{sc}/k\varepsilon_0
\]

where \(N_{sc}\) is the density of positive charge in the space charge layer. (with \(p\)-type material \(N_{sc}\) is a negative number.) and \(q\) is the charge per ion. Upon integrating twice, this becomes

\[
V = (qN_{sc}/2k\varepsilon_0)(x - x_0)^2
\]

The boundary conditions, namely, \(X_0\) is the point where the field, \(dV/dx\), becomes zero, (Figure 65a) and the equation
\[ V(x) = \phi_b - \phi(x) , \]  

B.5

and \( V = 0 \) in the bulk semiconductor at \( x = 0 \) and at \( x > 0 \) are than applied. If it is specified, as is normally done, that \( x = 0 \) at the surface, then the surface barrier, \( V_s \), is given by

\[ V_s = \frac{qN_s x_0^2}{2\epsilon_0} \]  

B.6

This is the Schottky barrier.

In Figure 65a is shown the band model for a depletion layer using an n-type material as an example. The donor ions are indicated as being of constant density throughout the sample, including the space charge region. In the bulk of the sample they are neutralized by their electrons, but near the surface the available conduction band electrons have moved to the surface to create the double layer. We indicate the net charge at the surface as \( Q \), which, of course, equals the charge in the space charge region, \( +Q_{sc} \), i.e.,

\[ -Q = Q_s = qN_s x_0 = -qN_s \]  

B.7

where \( N_s \) is the density of electronic charges captured at the surface. Equation \( (B.7) \) can be inserted into Equation \( (B.6) \) to give another useful form of the Schottky relation:

\[ V_s = \frac{qN_s^2}{2\epsilon_0 N_s} \]  

B.8
It is of interest to estimate the value of \( x_0 \), the thickness of the insulating depletion layer. If a reasonable impurity density, say \( 10^{23} \text{ m}^{-3} \), a dielectric constant of 8, and a value of 1V for \( V_S \) are assumed, then \( x_0 = 10^{-7} \text{ m} \), \( m = 1000 \text{Å} \). As \( x_0 \) is insensitive to \( V_S \) and \( N_{SC} \), varying as the square root, it is seen that \( x_0 \) usually does not increase much above this order of magnitude. And compared to the Helmholtz double layer, around \( 3 \text{Å} \) thick, the semiconductor double layer is much thicker. It is also to be noted that these typical values yield, by Equation (B.7), an excess charge \( N_S \) of \( 10^{16} \text{ m}^{-2} \). This is a much lesser surface charge density than typically found on the Helmholtz planes (\( \sim 10^{18} \text{ m}^{-2} \)). The charges on the space charge layer cannot therefore account for the charges on the HZ layer as pointed out earlier.

Information regarding the charge carrier density in the space charge layer and the applied potential at which the valence and conduction bands do not undergo bending (flat band potential \( V_{fb} \)) can be obtained from the Mott-Schottky (M-S) plot. This is a plot of \( 1/(\text{capacitance})^2 \) vs. the electrode potential. The slope gives the charge carrier density in the space charge layer and the intercept gives \( V_{fb} \). The derivation of the equation on which the M-S plot is based will be presented here. The relation between the capacitance of the space charge layer and the applied potential is obtained by solving the Poisson's equation. From the Poisson's equation,

\[
d^2V/dx^2 = -(N_{SC}q/k\varepsilon_o)[\exp(-qV/kT) - 1] \quad \text{----------------} \quad \text{B.9}
\]

where

\( N_{SC} = \) density of charge carriers in the space charge region
\( V = \) electron potential (negative of the electric potential)
\[ N_{\text{sc}} \exp(-eV/kT) = \text{number of electrons in the conduction band}. \]

Upon integrating with the boundary condition \( \frac{dV}{dx} = 0 \) when \( V = 0 \),

\[ (\frac{dV}{dx})^2 = (2qN_{\infty}/k\varepsilon_0)\{V + (kT/q)[\exp(-qV/kT) - 1]\} \quad \text{B.10} \]

At the surface \( V = V_s \), and the factor \( \exp(-eV/kT) \) is negligible for reasonable value of \( V_s \). From Gauss's law,

\[ (\frac{dV}{dx})_{v_{-\infty}} = Q_{\infty} / k\varepsilon_0 A \quad \text{------------------------} \quad \text{B.11} \]

where \( Q_{\infty} \) is the total charge in the space charge layer and \( A \) the sample area.

Using the equation,

\[ C_{\infty} = \frac{dQ_{\infty}}{dV_s} \quad \text{--------------------------} \quad \text{B.12} \]

where \( C_{\infty} \) is the capacity of the space charge layer, and by differentiating the combination of equations B.10 and B.11 with respect to voltage \( V_s \), the capacitance of the space charge is obtained as,

\[ C_{\infty}^{-2} = (2/qN_{\infty}k\varepsilon_0 A^2)(V_s - kT/q) \quad \text{----------} \quad \text{B.13} \]

This is the often-used equation that relates the space charge capacity to the applied potential. The above equation is used in this study to determine the charge carrier density in the space charge layer and the flat band potential. A plot of \( 1/C_{\infty} \) vs applied voltage is referred to as the Mott-Shottky plot. The
$V_s$ in equation B.13 is related to the flatband potential ($V_{fb}$). For a non-degenerate semiconductor, all changes in the electrode potential appears across $V_s$. Therefore the electrode potential is given by:

$$V_m = V_s + V_{fb}$$

\textbf{B.2 THE HELMHOLTZ (HZ) LAYER:}

On the solution side of the HZ double layer, the charge originates by the accumulation of ions at the Outer Helmholtz Plane (OHP). On the solid side of the HZ double layer, the charge can arise in 3 forms; a) an accumulation of free charge, b) free charge trapped from the solid onto surface states, or c) adsorbed ions. The form that dominates varies with the solid. With these mechanisms of charging, concentrations of the order of $10^{17}$ to $10^{18}$ ions/m$^2$ can easily be reached. Concentrations of excess charge in this magnitude almost never appear in the space charge region of a nondegenerate semiconductor.

If the solid is an insulator, the charge on the solid surface cannot stem from free charges, and must be due solely to adsorbed ions or dipoles. Of particular importance is the adsorption of protons or hydroxyl ions. If the solid is a metal, the voltage of the HZ double layer is determined by electron exchange between ions in solution and the metal. Most of the charge on the metal is due to a change in occupancy of electronic levels near the Fermi energy at the surface. If the solid is a semiconductor, there is the possibility that either adsorption/desorption or electron transfer could control the Helmholtz potential. It turns out that for nondegenerate semiconductors, the
potential drop at the HZ layer \((V_H)\) is dominated by adsorption/desorption processes. Electron transfer processes contribute to \(10^{16} \text{ ions/cm}^2\) as will be shown later in the section on potential variation in the depletion layer of a semiconductor. This is very low compared to \(10^{18} \text{ ions/cm}^2\) present at the surface. If the solid is a degenerate semiconductor it behaves as an intermediate case between metal and semiconductor. \(V_H\) is more associated with electron transfer as more charges can be accommodated in the bands of the semiconductor near the surface.

The electrochemical potential of electrons inside the metal surface is taken to be the same as the Fermi energy in the metal. This is why the Fermi level of the metal and electron energy level of the relevant redox couple in the electrolyte are assumed to be the same at equilibrium.

The charged planes on 2 sides of the HZ region form the HZ double layer. The potential variation within the HZ region can be determined by solving the Possion's equation in one dimension.

\[
\frac{d^2\phi}{dx^2} = -\frac{\rho}{k\varepsilon_0}
\]

B.14

where

\(\phi = \) electrostatic potential

\(\rho = \) charge density

\(k = \) dielectric constant

\(\varepsilon_0 = \) permittivity of free space

\(x = \) distance coordinate in the dimension considered
As the HZ region is between the 2 charged layers, the region itself has zero charge density \( \rho \). So;

\[
\frac{d^2 \phi}{dx^2} = 0 \quad \text{------------------------} \quad \text{B.15}
\]

which results in;

\[
\phi = ax + b \quad \text{------------------------} \quad \text{B.16}
\]

where \( a \) and \( b \) are constants. Therefore, the potential variation within the HZ layer is linear: The electric field in the HZ layer is given by Gauss's law,

\[
E = \frac{Q}{kt_o} \quad \text{------------------------} \quad \text{B.17}
\]

where,

\( E = \) electric field in the HZ layer.
\( Q = \) change on either side of the HZ layer.

The Guoy Chapman region, together with the counter change in the HZ region and in the solid, form the Guoy double layer.
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