ANODIZATION MECHANISM AND PROPERTIES OF BI-LAYER TANTALUM OXIDE FORMED IN PHOSPHORIC ACID

A Dissertation in
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By
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Abstract

The electrochemical growth of tantalum oxide thin films on tantalum anodes is a longstanding field of scientific inquiry. The process of anodic oxidation is of industrial importance because it is used to form the dielectric material of electrolytic capacitors. From an academic perspective, the study of anodic oxidation is of interest because it examines the ionic conduction of materials under an electric field. This work describes the formation of thin anodic films on tantalum when anodization is performed in dilute phosphoric acid. It has long been known that such materials exhibit a bi-layer structure, but studies on the formation and characteristics of the individual layers are lacking.

A quantitative description for the formation of the two individual layers is achieved by determining the kinetic rate constants and thermodynamic transfer coefficients of point defect reactions. The Faradaic impedance due to the formation of oxygen vacancies and tantalum interstitials is determined; the experimental impedance is described using an equivalent electrical analog, and the model is optimized to experimental electrochemical impedance spectra (EIS). Empirical investigations of the growth rates of the individual oxide layers were made using FT-IR reflectance spectroscopy, transmission electron microscopy (TEM), and spectroscopic ellipsometry (SE.). The empirical investigations of oxide growth rates provide verification for the parameters of the reported point defect model (PDM). The optical properties of the individual layers formed under a variety of formation conditions are determined using SE. It is demonstrated that the dielectric functions of the inner layer of pure oxide are significantly different than the dielectric functions of the outer layer, which contains incorporated phosphate. Comparisons of the optical properties are made to oxide materials formed without incorporated species.
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Chapter 1: Introduction

1.1. Relevant Fields of Science

The research contained in this dissertation is relevant to several scientific disciplines and is a scientific approach to studying a commonly used industrial technique. Anodic oxidation is generally studied in the realm of electrochemistry, which in and of itself is a multi-disciplinary field claimed by chemists, physicists, and engineers (chemical, mechanical, and electrical). The fundamental questions of how ionic conduction occurs and how it can be described by science are longstanding, yet they are of technological importance for both electronic and structural materials. It is expected that a dissertation in materials science and engineering will utilize theories and conventions from several scientific disciplines, and this work is no exception.

The material studied in this work is tantalum oxide (Ta$_2$O$_5$), which is used as the dielectric layer in electrolytic capacitors[1] and in dynamic random access memory (DRAM)[2] applications; therefore, its properties are of interest to the electrical engineering community. When tantalum oxide is formed electrochemically, it can have a high formation efficiency [3-5] and hence tantalum is a metal of choice for studying the kinetics of anodic oxidation[6-12]. Anodic tantalum oxide has been the source of fundamental studies on the mechanisms of anodic oxidation.[13-15] Tantalum oxide has also been used as a model material for describing conduction mechanisms in thin films.[16] Finally, the characterization techniques utilized in this work, Fourier-Transform infrared spectroscopy (FT-IR), spectroscopic ellipsometry (SE), and transmission electron microscopy (TEM) are relevant to physical and analytical chemistry, optical physics, microscopy, spectroscopy, and materials characterization.

These studies are undertaken with the belief that we humans can achieve an improved understanding of our natural world by the application of scientific methodology and are motivated by the belief that such an understanding can improve the condition of people and the earth. Visitors to the Materials Research Laboratory at Pennsylvania State University are greeted by the Albert Einstein quote: “The concern for man and his destiny
must always be the chief interest of all technical effort. Never forget it among your diagrams and equations.” This work is humbly submitted with the belief that it has created knowledge that contributes to a better understanding of electrochemically formed metal oxides.

1.1.1. Passivity

Metal exposed to the atmosphere has a strong propensity to form a metal oxide. In the case of iron, the oxidation of metal is evidenced by the appearance of rust; in electrochemical terms, the iron is corroded. Corrosion presents serious challenges to modern society. It is natural for metals to form oxides or other minerals by combining with elements in their vicinity. Humans have manipulated minerals of the earth to make metals and alloys, but these materials are thermodynamically unstable. Thus we are challenged to preserve these man-made materials in their unnatural state.

Several metals, such as aluminum, titanium, and tantalum, form a passive layer at the metal/atmosphere interface. This passive layer preserves the underlying metal by preventing atmospheric oxygen from reacting with the metal. This passive layer is often termed a “native oxide” and is typically on the scale of a few nanometers. Aluminum is the most reactive element on the periodic table; however, it is used for food containers and airplane bodies. The native oxide on aluminum is on the order of tens of atoms thick; it is this nano-scale thin film that allows for the extreme passivity of aluminum based materials. While corrosion represents the dark side of oxidation, passive layers of oxide are fundamental to many of the materials underpinning much of our technology.

Although the conversion of metal to thermodynamically stable oxide, such as the rusting of metals, has been a vexing problem for civilizations, scientists’ ability to harness this phenomenon and produce technologically useful materials is encouraging.
1.1.2 Capacitors

In addition to applications for maintaining structural integrity, metal oxides are extraordinarily useful as electronic materials. Tantalum oxide is an insulating material (dielectric) commonly used in commercially produced capacitors. A capacitor is a device that stores energy by separating electronic charge; the parallel plate capacitor is the simplest model of a capacitor and consists of an insulating material sandwiched between two conducting materials. Electrical charge builds up at the metal/oxide interface; the separation of charge is a form of potential energy. This energy can be released extremely rapidly when a large pulse of electrical energy is needed. Therefore, capacitors are indispensable devices in consumer electronics such as cellular telephones, televisions, and computers. Internally implanted heart defibrillators also rely on a capacitor to provide a quick, powerful burst of electric energy to a failing heart.

1.1.3 Anodic Oxidation (Anodization)

While a native oxide naturally forms on tantalum when it is exposed to air, electrochemical techniques can be used to grow oxides that range from nanometers to microns (1 micron = 1,000 nanometers; 10 atoms ≈ 1 nanometer) in thickness. The process of anodic oxidation, or anodizing, involves submerging two electrodes in a conducting electrolyte and applying a bias between the two electrodes. The positively charged electrode is the anode and the negatively charged electrode is the cathode. Oxidation reactions dominate at the anode while reduction reactions dominate at the cathode. When the anode is tantalum metal, the applied bias generates an intense electric field across the oxide and causes the oxide to grow as the tantalum and oxygen atoms migrate under the influence of the electric field. This process of ionic conduction in solids has been studied for many years, but it is still under debate.
1.1.4 Point Defect Model

The point defect model (PDM) was introduced in 1981 by Chao, Lin, and Macdonald [17, 18] as a means of describing the formation, steady state, and breakdown of passive films. The PDM is a mechanistic model that uses defect chemistry reactions to describe passive films; in this work a PDM is developed to describe the bi-layer oxide that forms when tantalum is anodized in phosphoric acid. Models are a scientist’s way of attempting to describe and predict reality, however, we are limited by what we are capable of perceiving. As we sit and contemplate the observations we make in our laboratory caves, our results are projected shadows on the walls (or computer screens) of our laboratory. Electrochemical impedance spectra (EIS) contain the information of how oxides form; the truth of ionic conduction mechanisms is contained in these spectra. However, from our perspective in our dank laboratory cave, all we can see is the shadow of the truth. In desperation we turn to mathematics with hopes that a mathematical model can be used to extract reality from our observations. In this work, a physical, mathematical model is developed to describe anodic tantalum oxide’s impedance response to a perturbing AC signal. This model provides a thermodynamic and kinetic description of how tantalum oxides form.

A ‘model’ is the scientist’s effort to take observations and interpret them in a way that is enlightening and a fair approximation of reality. By definition, a model can never describe reality. Rather, it is a tool for simplifying reality into terms and explanations that can be comprehended by humans. Anodic oxidation will continue to occur under natural laws regardless of whether we humans are capable of understanding the truth. There is no such thing as a perfect model because models by definition are simplifications of reality. This concept may seem daunting to the aspiring scientist, but it is possible to compare models and determine their relative merits and failures.

Albert Einstein described the objectives of theoretical physics with the statement: “…the supreme goal of all theory is to make the irreducible basic elements as simple and few as possible without having to surrender the adequate representation of a single datum of
This is often simplified to the maxim: “Everything should be made as simple as possible, but not simpler” and should be the motto of a good scientist.

1.2. Objectives

The objectives of this work are to present a model that describes how tantalum oxide forms during anodic oxidation and to better understand the growth and properties of the individual layers of bi-layer tantalum oxide. A physical, mechanistic model is described and then quantified using electrochemical impedance spectroscopy (EIS) and constraints set by empirical growth laws. The formation and properties of an entire anodic oxide is typically studied; the unique aspect of this work is its treatment of the anodic oxide as two distinct thin films.

1.3 Organization of Manuscript

Chapter 2 of this dissertation is a far-reaching literature review on the growth mechanisms and properties of anodic tantalum oxide. The review provided herein is expected to be a useful resource for assessing the development of anodic oxidation theory and for referencing the properties of tantalum oxide. It is recognized that reading the literature review in its entirety in one sitting may result in information saturation, thus it is suggested that the reader peruse sections of interest.

In order to effectively create a model of the oxidation process, experimental observations are imperative. The purpose of Chapter 3 is to assess the growth of tantalum oxide in 0.1 M phosphoric acid as functions of anodization time and voltage. Oxides formed in phosphoric acid have a bi-layer structure where the inner layer of oxide (adjacent to the metal) is pure tantalum oxide, but the outer layer of oxide (adjacent to the electrolyte) contains phosphate incorporated from the electrolyte. While the growth and characterization of the total oxide film has been well characterized, the growth and properties of the individual oxide layers have not been sufficiently studied. In particular, the evolution of the individual layers with respect to anodization time has not previously
been examined. A combination of Fourier-transform infrared reflectance spectroscopy (FT-IR reflectance spectroscopy), transmission electron microscopy (TEM), and wet electrochemistry are used to deduce the growth laws of bi-layer tantalum oxide.

Chapter 4 provides further characterization of the individual oxide layers. Experimentally, it is difficult to assess the electronic or optical properties of the individual layers due to the geometry of the system. Electrical measurements must be made across a stack of the two layers; thus the system behaves as two RC elements in series. It is not trivial to measure the properties of the two layers separately. Spectroscopic ellipsometry (SE) is used to determine the complex dielectric functions of the individual layers. The results are compared to anodic tantalum oxide formed without incorporated phosphorus. SE is used to characterize the structure of the oxide.

Chapter 5 is a necessary but comparatively uninteresting chapter which presents the collection and preliminary analysis of electrochemical experiments. The details of electrochemical impedance spectroscopy (EIS) experiments and determination of their adherence to linear systems theory (LST) are provided. Results of Mott-Schottky analysis are also presented.

Chapter 6 describes the point defect model (PDM) of tantalum oxide. This model is closely based on the models previously reported for platinum[20] and alloy 22.[21, 22] Optimization to the model in Chapter 6 was not constrained by the growth rates and ionic current of the oxide layers determined in Chapter 3; the effect of anodization time was not considered in defining the predicted thickness of the oxide.

Chapter 7 presents the derivation, parameterization, and assessment of a bi-layer point defect model. This model was created with the benefit of constraints determined by the growth laws and oxide properties determined in chapters 3 and 4. Prior to optimization, the thickness of the oxide was determined from the growth laws described in Chapter 3; the growth rates of the individual oxide layers provided estimates for the ionic currents due to the production of tantalum interstitials and oxygen vacancies.
Chapter 8 summarizes the conclusions for this dissertation, and Chapter 9 contains detailed recommendations for future work on tantalum anodization. The effect of curvature on the anodization process and on the properties of formed oxide has been discussed considerably amongst the author, Dr. Dickey, Dr. Macdonald, and Dr. Randall and by representatives of electrolytic capacitor companies at the Center for Dielectric Studies (CDS) meetings. Amorphous, anodic tantalum oxide is also an interesting material for study for its medium range order (MRO). The effect of variables such as growth rate, growth temperature, and electrolyte concentration would be expected to influence the MRO. Finally, solid state electrical characterization, such as current density vs. electric field and temperature, impedance spectroscopy, and thermally stimulated depolarization current (TSDC) may provide crucial information on how incorporated species effect the electrical and ionic transport properties of the oxide.
Chapter 2: Literature Review of Anodic Tantalum Oxide

2.1 Growth Laws

2.1.1 Introduction

The ionic transport mechanism responsible for growth of anodic oxide tantalum films has been studied for more than 50 years. Early postulations described the oxide as a stationary oxygen sub-lattice traversed by metal cations.[13] Amsel and Samuel doubted that the oxygen atoms move but conceded that oxygen movement could possibly occur by highly correlated vacancy diffusion.[13] Other early models also suggested that the motion of metal atoms is responsible for oxide growth.[23] Currently, there is consensus that both the metal and oxygen species are mobile and that oxide growth occurs simultaneously at the metal/oxide and oxide/solution interfaces.[24-29] This observation is at odds with fundamental theories of ionic conduction in solids. In concurring with other researchers, Young and Smith have noted “One of the most unexpected and least easy to explain facts is that both metal and oxygen atoms are shown by marker experiments to be mobile.”[30] Despite many years of research, a physical model capable of accounting for all of the phenomenological observations of anodic oxidation has not been universally accepted. One objective of this dissertation is to address the mechanism of anodic oxidation for tantalum oxide.

2.1.2 Oxygen Isotope Studies

Understanding the movement of oxygen atoms during the formation of anodic oxides is fundamental to developing a model of the anodization process. Anodization in enriched water, H$_2^{18}$O, is one method of studying the distribution of particular oxygen atoms. The order in which oxygen atoms are incorporated into the oxide was studied by analyzing alpha particles ($\alpha$) generated by the reaction $^{18}$O (p,$\alpha$)${}^{15}$N, which has a sharp resonance at proton energies of 1165 ± 1 keV;[31] however it can only be used to probe oxides less than 500 nm thick due to its low energy. Thicker oxides can be examined by measuring
alpha particles generated by the reaction $^{17}\text{O} \left( ^3\text{He},\alpha \right) ^{16}\text{O}$ at 16 MeV[31] the observed energy of the alpha particle depends on the depth of the reaction and can be used to sample oxides 5μm thick.[31]

Amsel and Samuel [31] used an isotopic tracer method to study the transport of oxygen atoms in anodic alumina. An initial galvanostatic anodization was performed to 40V (55nm of oxide) in electrolyte enriched to 90% $^{18}\text{O}$. A second anodization to 220V was carried out in electrolytes containing natural water (0.204% $^{18}\text{O}$). The second anodization step would add an additional 250 nm of oxide.

**Figure 2-1:** After [13]. Schematic of the distribution of oxygen isotopes in alumina after anodizing aluminum to 55nm of oxide in $\text{H}_2^{18}\text{O}$ electrolyte followed by anodizing an additional 250nm in $\text{H}_2^{16}\text{O}$ electrolyte.

Alpha particles produced from the reaction $^{18}\text{O} \left( \text{p, } \alpha \right) ^{15}\text{N}$ were detected and used to trace the location of $^{18}\text{O}$ atoms.[13] As shown in Figure 2-1, the order of oxygen atoms was conserved during the anodization of aluminum. The $^{16}\text{O}$ isotopes from the second anodization did not diffuse through to the metal/oxide interface. Likewise, the $^{18}\text{O}$ isotope
was not observed in the outer region of the film. The oxide film was stripped from its aluminum support so that the isotopic content of the film at the metal/oxide interface could be measured; there was a 9nm region adjacent to the metal composed of $^{16}\text{O}$.\cite{13}

In the case of chemically polished tantalum, this native oxide layer was measured to be 3.5nm.\cite{32} This suggests that the oxygen atoms comprising the native oxide remain at the metal interface during anodization. Due to energy straggling of the emitted alpha particles, it is not possible from the data to definitively determine if there is isotopic mixing near the $^{16}\text{O}$ oxide and $^{18}\text{O}$ oxide interface. \cite{13}

Pringle\cite{33} designed similar experiments for tantalum that measured both the gross features of oxygen transport and the finer details at the $^{18}\text{O}/^{16}\text{O}$ interface.\cite{33} Tantalum was anodized first to 88nm in $^{16}\text{O}$ electrolyte and then to more than 300 nm in $^{18}\text{O}$ electrolyte. The oxide was then etched, as shown in Figure 2-2, so that the isotopic concentration of $^{18}\text{O}$ could be determined as a function of depth in the oxide. In order to measure the isotopic concentration near the $^{16}\text{O}/^{18}\text{O}$ boundary, the oxide was etched to thicknesses centered within a few nm of $h_i$, the thickness after the initial anodization.
Figure 2-2: After [33]. Schematic showing how the depth profile of $^{18}$O was determined in a film that was anodized to an initial thickness, $h_i$, in $H_2^{16}$O electrolyte and then to a final thickness, $h_f$, in $H_2^{18}$O electrolyte.

In terms of the gross features of the $^{18}$O distribution profile, Amsel & Samuel’s[13] and Pringle’s[33] results are in agreement. However, Pringle’s more precise depth profile indicates that the order of oxygen atoms is largely conserved, but there is some mixing of the order of O atoms.[33] It is suggested that the O atoms migrate, probably by a mechanism where all O atoms migrate in succession as vacancies are produced.[33]

The movement of oxygen appears to be statistical in nature and based on a large number of O atoms that make a series of small jumps. Figure 2-3 shows the distribution of $^{18}$O after the two step anodization if it is assumed that oxygen moves by a series of single, successive jumps. As shown in Figure 2-4, mixing of the $^{16}$O and $^{18}$O populations is analyzed as forced diffusion from a constant source into a semi-infinite medium.[33] The diffusion model is described using the error function,
and is shown in the top cartoon of Figure 2-4; the bottom cartoon of Figure 2-4 shows the $^{18}$O profile measured from the formed anodic oxide. Pringle’s experiment[33] indicates that it is quite clear that oxygen migrates under the electric field applied during anodic oxidation.

**Figure 2-3:** After [33]. Top diagram: Distribution of oxygen isotopes for a film initially anodized in $\text{H}_2^{16}\text{O}$ electrolyte to a thickness of $h_i$ and successively in $\text{H}_2^{18}\text{O}$ electrolyte to a thickness of $h_f$ where oxygen atoms move by single, successive jumps. Bottom diagram: Neutron count profile corresponding to the $^{18}\text{O}$ distribution shown above.
Figure 2-4: After [33] The top cartoon is a plot of Equation 2-1 which describes a forced diffusion profile. The bottom plot demonstrates the distribution of $^{18}$O isotopes in the anodic oxide.
Figure 2-5: After[34]. Distribution of $^{18}$O in Samples A and B. Sample A was anodized in dilute citric electrolyte prepared in $^{18}$O enriched water to 45 nm (30V). Sample B was formed with the same procedure and then further anodized to 90 nm (60V) in concentrated $\text{H}_3\text{PO}_4$ in natural water.

The distribution of $^{18}$O atoms (with an accuracy of $\pm 3\%$) in films anodized in concentrated phosphoric acid has been examined by Montero, et.al.[34] The electrolytes employed were 14.7 M $\text{H}_3\text{PO}_4$ in water of natural isotopic concentration and 0.1 M citric acid or 0.5wt % ammonium citrate prepared in 70% $^{18}$O enriched water. The incorporation of phosphorus in the outer layer of oxide is well known[28, 35, 36] and will be discussed in section 2.1.5 of this review. When dilute electrolyte was used in the first anodization and followed by anodization in concentrated $\text{H}_3\text{PO}_4$, the order of oxygen
atoms was largely conserved. However, when the first anodization was done to 30V (45nm) in concentrated \( \text{H}_3\text{PO}_4 \) and the second anodization was done in dilute citric electrolyte, some inversion of the order of oxygen atoms was observed, as shown by the bottom cartoon in Figure 2-5. The number of \(^{18}\text{O} \) atoms detected by nuclear analysis is shown in Figure 2-6 and the SIMS (secondary ion mass spectroscopy) results for \(^{16}\text{O}, ^{18}\text{O}, \text{P}, \) and \(^{18}\text{O}/(^{16}\text{O}+^{18}\text{O}) \) are shown in Figure 2-7.

![Diagram](image)

**Figure 2-6:** After [34] Normalized \(^{18}\text{O} \) depth profiles determined by the reaction \(^{18}\text{O}(p, \alpha)^{15}\text{N} \) anodized to 45 nm in concentrated \( \text{H}_3\text{PO}_4 /\text{H}^{16}\text{O} \) electrolyte and then in \(^{18}\text{O} \) dilute electrolyte.[34]

**Figure 2-7:** After [34] SIMS results showing the varying concentrations of \(^{18}\text{O}, ^{16}\text{O}, \) and \( \text{P}. \) The dashed line is the relative amount of \(^{18}\text{O}, ^{18}\text{O}/(^{16}\text{O}+^{18}\text{O}) \). The time is SIMS sputtering time. [34]

In the outer layer, the isotope is purely \(^{18}\text{O} \), which indicates that the order of oxygen is conserved in the outer layer. After the “pure \(^{18}\text{O} \)” layer, the concentration decreases and goes through a minimum and then increases back to the concentration of the outer layer:
This demonstrates that the order of oxygen atoms is partially inverted in this region of oxide. However, the $^{18}\text{O}$ atoms never accumulate at the metal/film interface, so in the innermost depths of the inner layer, oxygen order is always conserved. It is imperative to stress that inversion of the $^{18}\text{O}$ and $^{16}\text{O}$ isotopes only occurs when high concentrations of phosphoric acid are used. This implies that the ionic conductivity of the films is greatly affected by the high concentration of phosphorus. The SIMS results indicate that $^{18}\text{O}$ atoms are present throughout the thickness of the oxide, almost to the metal/oxide interface.

The location of the phosphorus maximum coincides with a local minimum in the $^{18}\text{O}$ concentration, which has been interpreted to mean that phosphorus is incorporated in the form of phosphate ions ($\text{(PO}_4\text{)}^{3-}$), rather than as interstitials. Regardless of the formation voltage during the second anodization, the region where the oxygen atoms reverse order is in the P-rich oxide formed during the first anodization. i.e., the outer layer of the P-rich oxide is prone to not conserve the order of O atoms upon the second anodization.

The incorporation of phosphorus will likely have a significant effect on the ionic conductivity of the film. Thus, caution must be used when trying to extrapolate these results to films formed in the dilute electrolytes commonly used in the electrolytic capacitor industry. The inversion of oxygen order may occur due to differences in the energy and local bonding of each atomic species. If phosphorus atoms are incorporated as phosphate anions, then the oxygen atoms in the oxyanion will have a decreased mobility. Studies have shown[37, 38] that incorporated phosphorus inhibits oxygen mobility and oxygen permeation rates through the oxide during thermal treatments.

Anodization in electrolytes made from enriched oxygen has also been demonstrated as a way of determining whether the source of oxygen is from H$_2$O or from other species in the electrolyte. Using ammonia citrate enriched to 70% in $^{18}\text{O}$, it was determined that at least 98% of the oxygen in the film comes from the water in the solution.[39] Anodization in organic solvents with $^{18}\text{O}$ labeled KNO$_3$ and small amounts of water
produced oxides where 80% of the oxygen originated from water and 20% from the KNO$_3$. [40]

2.1.3 Cation Isotope Studies

While isotopic studies have been used to describe the role of oxygen in the growth of anodic films, comparable experiments on the role of cations are more difficult due to half-lives and expenses, i.e., death and taxes limit what a scientist can achieve. However, one experiment using radioactive tantalum has been reported[14]. Deuteron bombardment was used to form a layer of radioactive $^{182}$Ta on the surface of the metal via the reaction $^{181}$Ta (d, p) $^{182}$Ta. In reference to Figure 2-8, disk P1 was not oxidized while P2 was anodized to 120V. The oxide on P2 was then dissolved in HF. The distribution of $^{182}$Ta on the non-oxidized substrate (P1) was a pure diffusion profile while it is evident that reversal of the $^{182}$Ta and $^{181}$Ta isotopes took place in the substrate that had been anodized. This demonstrates that tantalum cations are mobile and do not strictly conserve nor reverse their order. This suggests that the behavior of tantalum cations is more complex than oxygen species.
Figure 2-8: After [14]. A layer of $^{182}\text{Ta}$ was formed on substrates P1 and P2. Substrate P2 was anodized and then the oxide was stripped. The $^{182}\text{Ta}$ profile of P2 is indicative of a diffusion profile. This indicates that during anodization, tantalum atoms are mobile.

While not as straightforward of an experiment, the movement of metal cations was also studied by making tantalum/aluminum layered structures and then performing anodization.[13] The location of aluminum was determined by detecting gamma particles from the reaction $^{27}\text{Al} (p, \gamma)^{28}\text{Si}$. [13] It was found that there is some mixing of the tantalum and aluminum atoms, which suggests that the metal atoms are mobile. The amount of tantalum in the oxide was found to depend on the formation voltage as shown in Figure 2-9 and Figure 2-10.[13] An abrupt change in the concentration of aluminum, $C_{\text{Al}}$, (as shown for the 60V specimen) indicates that there is no mixing of the Ta and Al atoms in the oxide. The fact that the concentration profile is not a step function for the other samples indicates that the Ta and Al atoms do not strictly conserve their order during anodization. The concentration of Ta atoms relative to Al atoms versus the formation voltage is shown in Figure 2-10 where the concentration is normalized so that $C_{\text{Al}} = 1$ for $\text{Al}_2\text{O}_3$. 
Figure 2-9: After [13] The relative concentration of aluminum atoms is plotted as a function of depth in the oxide for varying formation voltages.

Figure 2-10: After [13] The percentage of Ta to Al atoms versus the formation voltage.

Care must be taken in extrapolating conclusions from these layered structures to films having single cation species. This observation suggests that Ta and Al atoms migrate relative to each other, but it does not follow that particular Ta atoms must migrate with respect to neighboring Ta atoms. Furthermore, the implications of either a potential drop or a change in the electric field at the Al/Ta or Al₂O₃/Ta₂O₅ interface could significantly change the system’s behavior.

2.1.4 Kirkendall Marker Experiments

Numerous studies have used supposedly inert, uncharged markers to study the mechanism of anodic oxidation. The Kirkendall marker method has been widely used to measure the contribution of each lattice species to the growth of the oxide. In this technique, a small concentration of an inert, radioactive element is deposited just beneath the surface of a metal. After anodic oxidation, an energy loss spectrum is measured to determine the location of the marker layer. The ideal marker is uncharged and does not
migrate under the influence of an electric field, has a large radius to minimize diffusion into the lattice, is used in a trace amount so as not to disturb the chemistry of the system, and can be located in-situ without damaging the oxide.[41] The noble gas isotopes $^{125}\text{Xe}$ and $^{222}\text{Rn}$ are commonly used.

High fluences of implanted species can have a significant effect on the properties of the oxide film. The presence of noble gas markers increases the rate of dissolution of oxide in HF-NH$_4$F stripping solution, and also affects the optical properties of the film as measured by ellipsometry.[42] Therefore, interpretations from inert marker experiments must be made with caution. However, Pringle asserts that inert markers do not affect the kinetics of anodization; by comparing the behavior of different markers, he concluded that the markers are inert and only very slightly mobile.[43]

The determination of to what extent the oxide forms by cation egress or oxygen ingress is made by measuring the depth of the marker layer. If metal ion migration is responsible for oxide growth, fresh oxide forms at the solution interface and the oxide will grow on top of the marked layer. If growth occurs via inward motion of oxygen, the oxide forms at the metal/film interface and will be buried beneath the marker layer. If oxide growth is an interfacial process, then marker atoms will form a row of atoms at the same depth, however, if oxide growth occurs in the bulk of the oxide, the row of marker atoms will broaden into a diffuse band.

The transport number of the metal, $t_m$, is defined as

$$t_m = \frac{d_{\text{Marker}}}{d_{\text{total}}} \quad [2-2]$$

where $d_{\text{total}}$ is the total thickness of the oxide and $d_{\text{Marker}}$ is the distance between the marker layer and the oxide/electrolyte interface.

The transport number of the oxygen is

$$t_O = 1 - t_m \quad [2-3]$$
The transport number represents the fraction of the film formed by movement of the ion. While it has been shown that the noble gas tracers do not move in the formed oxide,[41] it may not follow that such tracers are immobile during the growth of the oxide film.

Table 2-1 is an ambitious, if incomplete, attempt to compare \( t_m \) values reported by various authors; it is important to note that the methodology, and hence the assumptions and errors, vary widely between different sources. Depending on the electrolyte used for anodization, electrolyte species may incorporate in the outer portion of the film. The result is a distinct bi-layer structure where the inner layer is chemically pure metal oxide and the outer layer has a chemistry distinctive of the electrolyte. It is crucial to note that many authors use the boundary between the inner and outer layer of oxide to determine the transport number. It has since argued that some incorporated species may be more mobile than oxygen atoms, hence the inner/outer layer boundary may be a poor determinant of the transport number.[28, 44] In such an analysis, the migration rate of incorporated species relative to O atoms is given by the ratio of the thickness of the ‘contaminated’ layer below the marker to the thickness of the layer between the marker and the metal. Figure 2-11 is a schematic showing this definition. Efforts to correlate the relative mobility of an incorporated anion to charge or ionic radii have not been effective; thus, relative mobility rates have been reported, but there is not a clear explanation for their values. Furthermore, the interface between the “pure” and “contaminated” oxides is sharp. If the incorporated species are truly mobile, a distribution of the concentration of the atoms, similar to a diffusion profile, would be expected.
Figure 2-11: Schematic for defining the mobility of incorporated anions relative to oxygen.
Table 2-1: Summary of transport numbers for tantalum in anodic tantalum oxide. The key for surface preparation is: C: chemically polished; E: Electropolished; S: Sputtered Ta; VA: Vacuum annealed, and HF: Dip in HF.

<table>
<thead>
<tr>
<th>Surface Preparation</th>
<th>Current Density mA/cm²</th>
<th>Electrolyte</th>
<th>Tracer Method</th>
<th>Metal Transport #</th>
<th>Temp °C</th>
<th>Formation Voltage</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>0.1M H₂SO₄</td>
<td>¹²⁵Xe, ²²₂Rn, ⁷⁹Kr, ⁴¹Ar</td>
<td>0.243 +/- 0.003</td>
<td>25</td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td>0.1M H₂SO₄</td>
<td>Incorp. Si</td>
<td>0.24</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>E</td>
<td>5</td>
<td>0.1M H₃PO₄</td>
<td>Incorp. Si</td>
<td>0.24</td>
<td></td>
<td></td>
<td>[45]</td>
</tr>
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<td></td>
<td>0.26</td>
<td></td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.18</td>
<td>20</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.26</td>
<td>20</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.28</td>
<td>20</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>S</td>
<td>10</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.32</td>
<td>20</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>S</td>
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<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.14</td>
<td>85</td>
<td></td>
<td>[48]</td>
</tr>
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<td>S</td>
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<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.18</td>
<td>85</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.20</td>
<td>85</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>0.06% H₃PO₄</td>
<td>Xe</td>
<td>0.29</td>
<td>85</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
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<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>C, E, VA</td>
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<td>14.7M H₃PO₄</td>
<td>^3²P</td>
<td>0.35</td>
<td></td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>C, E, VA</td>
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<td>1.0M H₃PO₄</td>
<td>^3²P</td>
<td>0.46</td>
<td></td>
<td>[49]</td>
<td></td>
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<td>C, E, VA</td>
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<td>0.1M H₃PO₄</td>
<td>^3²P</td>
<td>0.48</td>
<td></td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>C, E, VA</td>
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<td>0.01M H₃PO₄</td>
<td>^3²P</td>
<td>0.47</td>
<td></td>
<td>[49]</td>
<td></td>
</tr>
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<td>0.001M H₃PO₄</td>
<td>^3²P</td>
<td>0.49</td>
<td></td>
<td>[49]</td>
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</tr>
<tr>
<td>C, E, VA</td>
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<td>0.1M H₂SO₄</td>
<td>^3⁵S</td>
<td>0.52</td>
<td></td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.26</td>
<td>25</td>
<td>10</td>
<td>[41]</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.26</td>
<td>25</td>
<td>60</td>
<td>[41]</td>
</tr>
<tr>
<td>C</td>
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<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.31</td>
<td>25</td>
<td>10</td>
<td>[41]</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.31</td>
<td>25</td>
<td>60</td>
<td>[41]</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.29</td>
<td>25</td>
<td>10</td>
<td>[41]</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>0.1M Na₂SO₄</td>
<td>^1²⁸Xe</td>
<td>0.29</td>
<td>25</td>
<td>125</td>
<td>[41]</td>
</tr>
<tr>
<td>E, HF</td>
<td>1.0</td>
<td>0.1M Na₂SiO₄</td>
<td>SIMS</td>
<td>0.24</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td>E, HF</td>
<td>1.0</td>
<td>0.1M H₃PO₄</td>
<td>SIMS</td>
<td>0.51</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td>E, HF</td>
<td>1.0</td>
<td>0.1M H₂SO₄</td>
<td>SIMS</td>
<td>0.48</td>
<td>25</td>
<td>100</td>
<td>[45, 47]</td>
</tr>
<tr>
<td>E, HF</td>
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<td>0.1M NH₄B₅O₈</td>
<td>SIMS</td>
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<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td>E, HF</td>
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<td>0.1M Na₂WO₄</td>
<td>XPS</td>
<td>&lt;0.02</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
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<td>0.1M Na₂MoO₄</td>
<td>XPS</td>
<td>&lt;0.02</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td>E, HF</td>
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<td>0.1M Na₂CrO₄</td>
<td>XPS</td>
<td>&lt;0.02</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
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<td>E, HF</td>
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<td>0.1M Na$_3$VO$_4$</td>
<td>XPS</td>
<td>None detected</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
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<td>---------------</td>
<td>----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>E, HF</td>
<td>1.0</td>
<td>1.0M KCl/KBr/KI</td>
<td>XPS</td>
<td>None Detected</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td>E, HF</td>
<td>1.0</td>
<td>1.0M NH$_4$F</td>
<td>XPS</td>
<td>[F] higher at m/o interface</td>
<td>25</td>
<td>100</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.044M NH$_4$H$_2$BO$_7$</td>
<td>$^{222}$Rn</td>
<td>0.28±0.01</td>
<td>25</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>0.044M NH$_4$H$_2$BO$_7$</td>
<td>$^{222}$Rn</td>
<td>0.34±0.01</td>
<td>25</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3% Ammonium Citrate</td>
<td>$^{125}$Xe</td>
<td>0.71</td>
<td>10</td>
<td></td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3% Ammonium Citrate</td>
<td>$^{125}$Xe</td>
<td>0.40</td>
<td>40</td>
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<td>[50]</td>
</tr>
<tr>
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<td>$^{125}$Xe</td>
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<td>200</td>
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<td>[50]</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3% Dibasic ammonium citrate</td>
<td>$^{125}$Xe</td>
<td>0.32±0.09</td>
<td>280</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>3% Dibasic ammonium citrate</td>
<td>$^{222}$Rn</td>
<td>0.26±0.02</td>
<td>280</td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.23 N H$_3$PO$_4$</td>
<td>Ellipsometry, Incorporated P</td>
<td>0.51-0.52</td>
<td>25</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.23 N H$_3$PO$_4$</td>
<td>Ellipsometry, Incorporated P</td>
<td>0.56</td>
<td>25</td>
<td></td>
<td>[52]</td>
</tr>
</tbody>
</table>
2.1.5 Incorporated Species

When anodization is completed in certain electrolytes, the formed oxide will contain species from the electrolyte. When incorporated species are present in anodic oxide, a bilayer structure forms where the inner oxide, at the metal/oxide interface, is free from incorporated species. The outer layer at the oxide/electrolyte interface contains incorporated species. There is typically a sharp dividing line between the two oxides and the chemistry of the outer layer is continuous, i.e., there is not a concentration gradient of the incorporated species. Tracing of radioactive $^{32}$P has been used to determine that the concentration of phosphorus in the outer layer is uniform.[53] Likewise, ellipsometry of anodic tantala indicates that the oxide is better described by a distinct two layer model than by a model where the outer layer has a graded concentration of phosphorus.[52]

From a practical perspective, the incorporated species often result in the oxide having advantageous dielectric characteristics. The incorporated species can decrease the permittivity and the ionic conductivity of the oxide[35]. It has been demonstrated that the inner layer of oxide, which does not contain phosphorus, crystallizes before the outer layer of oxide when they are examined under a focused electron beam of a transmission electron microscope.[29]. It is probable that the phosphorus acts as a glass former and inhibits crystallization of the amorphous oxide. At temperatures $> 200^\circ$C, oxygen diffuses readily through anodic tantala, and the metal will uptake oxygen from the oxide; this results in an oxygen concentration gradient. Pawel has concluded that incorporated phosphorus inhibits the diffusion of oxygen through the oxide.[37]

Montero, et.al., have demonstrated that incorporated phosphorus is in the form of non-dissociated phosphate anions. A tri-layer oxide was made by performing an initial anodization in 14.7 M $\text{H}_3\text{PO}_4$ followed by a second anodization in $^{18}$O enriched water of 0.5% ammonium citrate. The location of the phosphorus maximum corresponded to the position of $^{18}$O minimum, but not to the position of the maximum in the $^{16}$O depth distribution; this is shown in Figure 2-7 and indicates that phosphate is not disassociated.[34]
Assuming that the transport number of Ta is independent of formation current density, Arifuki, et.al., concluded that phosphorus is a mobile species and the depth of its migration depends on the current density. This study used incorporated phosphorus as a marker. As shown in Figure 2-12, the degree of P migration is linear with the log of the formation current. However, it has more recently been demonstrated that transport numbers are probably functions of the current density. Therefore, the mobility of phosphorus relative to oxygen as reported by Arifuku, et.al., is not valid.

**Figure 2-12:** Arifuku, et.al., have claimed that the degree of phosphorus migration relative to oxygen is linear with the log of the current density used during anodization. However, this analysis falsely assumes that transport numbers are independent of the formation current density. [44]

Nitrogen is not typically incorporated when nitric acid is the electrolyte; and is only observed when concentrated (93%) HNO₃ is the electrolyte. Using organic solvents and KNO₃, the concentration of nitrogen is determined by analysis of the nuclear reaction: \( N^{14} (d, \alpha) C^{12} \). The concentration of nitrogen is reported to be < 0.8% N atoms per oxygen when the formation electrolyte is N-methylacetamide (NMA) with 0.4wt% KNO₃ and 0.4 wt% H₂O; when glycol is substituted for NMA, there are up to 2.5% N
atoms relative to O atoms.[40] Over a wide range of growth conditions, it is determined that more than 80% of the oxygen in the oxide originated from water while the remainder originated from the salt.[40] These experiments use electrolyte solutions with very low water contents, otherwise the source of oxygen would be primarily from water rather than other oxygenated species.

Nuclear analysis of films anodized in 95% H$_2$SO$_4$ demonstrates that the SO$_4^{2-}$ : Ta ratio in the outer layer is about 0.75:1.[54] Fluorine is the only species that has demonstrated the ability to migrate through the entire thickness of anodic tantala. For anodization in 0.09 M KF, the concentration of fluorine is constant through most of the film but increases abruptly at the oxide/metal interface.[34]

The migration rate of phosphorus relative to oxygen gradually increases with the electric field. According to the high-field conduction equation, current varies exponentially with electric field.

\[
J = J_0 \exp\left(-\frac{Q - q\lambda\tilde{E}}{k_BT}\right)
\]  \hspace{1cm} [2-4]

Where \(J\) is the current density, \(J_0\) and \(Q\) are constants, \(q\) is the charge of the moving ion, \(E\) is the electric field, and \(\lambda\) is a distance on the order of a few Å.[55] It has been noted that the presence of incorporated species, phosphorus included, is associated with an increase in the electric field as evidenced by the measured current.[49] There are potential pitfalls to this conclusion. The increased current could be due to a change in the properties of the oxide rather than an increase in the field. Incorporated phosphate may provide trap sites that encourage some type of conduction. The electric field is typically defined as the applied voltage divided by the oxide thickness. This definition of the electric field is conventional in solid state science, however, it is noted that the electric field is not a directly measured entity. Rather, it is defined using a measured (or assumed) dielectric thickness; this thickness can be altered by the application of the electric field due to electrostriction. The point being that there are theoretical limits to
assuming that the electric field is a monolithic variable defined simply by a thickness and an applied voltage.

A rather exhaustive study was carried out by Shimizu, et.al, in determining the mobility of various species incorporated from the electrolyte.[47] Films were anodized on electropolished tantalum substrates at 1mA/cm$^2$ to 100V at 25°C in the following electrolytes: 0.1M ammonium pentaborate, 0.1M phosphoric acid, 0.1M sulphuric acid, 0.1M sodium tungstate, 0.1M sodium orthosilicate, 0.1M sodium molybdate, 0.1M sodium chromate, 0.1M sodium orthovanadate, 1.0M ammonium fluoride, 1.0M potassium chloride, 1.0M potassium bromide, and 1.0M potassium iodide.

For samples anodized in sodium orthosilicate, a bi-layer is observed as well as an approximately 4nm layer between the metal substrate and pure oxide. This is in agreement with Maurel [56] who determined that the surface preparation leaves a 4.5nm layer containing $1.5 \times 10^{14}$ F atoms/cm$^2$.

Incorporated species are not observed for anodization in KCl, KBr, or KI; only surface contamination at the oxide/electrolyte interface is observed for anodization in sodium tungstate, sodium molybdate, sodium chromate, and sodium orthovanadate.[47] Fluoride is detected throughout the oxide for anodization in ammonium fluoride.[47] The ratio of the outer layer to the total oxide thickness for the remaining electrolytes are summarized in Table 2-2. The depth of incorporated species (borate, phosphate, silicate, and sulfate) is variable, but the location of the marker is constant; this has been used to suggest that markers such as Xe or Rn are not significantly mobile.
Table 2-2: Ratio of the outer layer, i.e., the oxide containing incorporated species to the total oxide thickness. The oxides were formed to 100V at 1mA/cm² at 25°C.[47]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>d_{outer} / d_{total}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M Na₄SiO₄</td>
<td>0.24</td>
</tr>
<tr>
<td>0.1 M H₃PO₄</td>
<td>0.51</td>
</tr>
<tr>
<td>0.1M H₂SO₄</td>
<td>0.48</td>
</tr>
<tr>
<td>0.1M NH₄B₅O₈</td>
<td>0.11</td>
</tr>
</tbody>
</table>

For anodization in 0.1 M tungstate, molybdate, chromate, vanadate electrolytes, the data do not suggest a fluorine contaminated layer at the metal/film interface, nor is there incorporation of electrolyte species in the oxide film.[47] It is particularly interesting that a fluorine contaminated layer is observed on films anodized in acidic solutions but not for oxides formed in metal salts. Also, this observation raises questions concerning the native oxide-- it seems to suggest that atoms originally at the metal interface have somehow been removed after anodization in metal salt electrolytes.

For anodization in ammonium fluoride, the concentration of F increases slightly with depth and a 4nm thick layer rich in F (and consistent with TaF₅) is found at the metal/oxide interface.[47] This layer is not to be confused with the F containing layer attributed to the chemical polishing procedure.

In the case of anodization in phosphoric and sulfuric acid, the incorporated species are mobile under the electric field, however, Si is found to be stationary. An alternative explanation is that Si atoms are mobile but coincidentally have the same mobility of inert Xe and Rn markers. It is suggested that Si is incorporated as SiO₂ while P and S are incorporated as charged oxyanions, (PO₄)³⁻ and (SO₄)²⁻. Marker experiments were carried out assuming Si as an immobile tracer; an initial anodization was performed in 0.1 M sodium orthosilicate to 10V; this resulted in a 16 nm film with a 3.8 nm outer layer containing the immobile Si atoms. A second anodization to 100V was performed in the various electrolytes. This is a more accurate method of determining the transport number.
of metal and oxygen species because it accounts for the mobility of incorporated species. Using this method, it was determined that the metal transport number is between 0.24 and 0.25 for all of the electrolytes studied. The significant conclusion from this work is that the boundaries between the phosphorus containing layer and the layer does not contain phosphorus is NOT coincident with the boundary between oxides formed by tantalum interstitial or oxygen vacancy migration. A schematic of the proposed structure and growth from the two processes is shown in Figure 2-13. This structure and mechanism assumes that the depth of incorporated species id dependent on their mobility relative to oxygen. Such a mechanism would predict a graded concentration profile, similar to a diffusion profile, of the incorporated species. However, the interface is abrupt.[52, 53]

![Figure 2-13](image)

**Figure 2-13:** The phosphorus containing layer determined for anodization to 100V in 0.1M$\text{H}_3\text{PO}_4$ at 1mA/cm$^2$ at 25° C on electropolished tantalum is approximately one-half of the oxide. However, only one-quarter of the oxide forms by outward migration of tantalum. [28]

For the same amount of charge passed, the film thickness (as measured by the interference color) for films formed in 0.01 M$\text{H}_3\text{PO}_4$ was the same for films formed in
0.01M $\text{H}_2\text{SO}_4$, however, the phosphate containing films had 6-8% lower capacitance. Conversely, if same current density is used to achieve a particular formation voltage, the capacitance of the two oxides will be the same, but the thickness appears to be different. [49] The constant variable between oxides formed with the same passage of charge but in different electrolytes is the product of the capacitance and the forming voltage (CV). As is typical, the decrease in the dielectric constant was accompanied by an increase in the dielectric strength. It should be noted that phosphorus is incorporated into the film in higher concentrations than sulfur; this may account for the different properties of the films. [49]

Phosphoric acid electrolytes of concentrations 0.001M, 0.01 M, 0.1 M, 1.0 M, and 14.7M were used to study phosphorus incorporation as a function of electrolyte concentration.[53] Comparison was made to oxide formed in 0.01M $\text{H}_2\text{SO}_4$ [53]. As shown in Figure 2-14, the weight of incorporated phosphorus is proportional to the concentration of phosphoric acid. Figure 2—15 demonstrates that the amount of incorporated phosphate varies significantly with the current density employed during growth.[49] The temperature has a less influential but measurable effect, as shown in Figure 2-16.[49]

![Figure 2-14: After [53]. Weight of incorporated phosphorus versus reciprocal capacitance for various electrolyte concentrations.](image-url)
Figure 2-15: Weight of incorporated phosphorous vs. reciprocal capacitance for various current densities.[49]

Figure 2-16: Weight of incorporated phosphorus vs. reciprocal capacitance for various temperatures. Current density is 1.0mA/cm².[53]

For current densities of 0.1-10 mA/cm² and at 85 °C, the migration rate, as defined in Figure 2-11, of P species is in the range of 0.20-0.25[48]. For current densities less than 0.1 mA/cm², incorporation of P is very low and is only detected at the surface[48]. For a current density of 5mA/cm² and at 20°C, the relative migration rate is 0.30 while the P is present in 51% of the film thickness.[48]
For oxides formed to 150V in 0.06 wt% H₃PO₄ at 85°C on sputtered tantalum, the amount of incorporated phosphate was found to be linear with respect to the log of the current density.[57] This is shown in Figure 2-17 with the corresponding concentration values in Table 2—3.

**Table 2-3:** Phosphorus incorporation as a function of current density of formation in 0.06 wt% H₃PO₄.[57]

<table>
<thead>
<tr>
<th>Current Density, mA/cm²</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Ta₂O₅ 0.011Ta₃(PO₄)₅</td>
</tr>
<tr>
<td>1.0</td>
<td>Ta₂O₅ 0.022Ta₃(PO₄)₅</td>
</tr>
<tr>
<td>10.0</td>
<td>Ta₂O₅ 0.035Ta₃(PO₄)₅</td>
</tr>
<tr>
<td>100.0</td>
<td>Ta₂O₅ 0.045Ta₃(PO₄)₅</td>
</tr>
</tbody>
</table>

**Figure 2-17:** The concentration of incorporated phosphorus for anodization in dilute electrolyte is linear with the log of the formation current density. The composition of the outer layer is expressed as Ta₂O₅ xTa₃(PO₄)₅. The oxides are formed to 150V in 0.06 wt% H₃PO₄ at 85°C.
It is important to distinguish the total amount of phosphorus in the film from its concentration; both the boundary between the inner and outer layers and the concentration can vary with the experimental growth parameters. For films formed at the same current density but in different electrolyte concentrations, the depth of the outer layer is the same. However, for a given electrolyte and increasing current densities, the inner/outer boundary moves inward, i.e., toward the metal. Thus, for higher current densities, the outer layer is relatively thicker and also contains a higher concentration of phosphorous than for films formed at lower current densities.

For anodization in 0.01 M solution NaH$_2$PO$_4$, the amount of P is virtually the same as for anodization in the acid, but in 0.01 M solution of Na$_3$PO$_4$ there is 50% less incorporated P compared to films anodized in acidic electrolytes.[49] This suggests that pH of the electrolyte plays an important role in the formation of the outer layer of oxide.

Anodization temperature had no measurable effect on the local concentration of phosphorus in the film. The slopes of activity of phosphorus vs. 1/C for the dissolution do not change with anodization temperature. The increase of phosphorus observed with decreased anodization temperature is due to movement of the boundary inward at lower temperatures rather than a change in local concentration.[53]

Two step anodization experiments were performed to determine if the concentration and distribution of phosphorus in the outer layer were affected by a second anodization in a phosphoric acid electrolyte of different molarity[49]. Figure 2-18 demonstrates the structure of the resulting oxide; the outer two layers of oxide contain phosphorus in different concentrations; the outermost layer is characteristic of the final anodizing electrolyte. This observation provides further evidence that oxide growth occurs at the film/electrolyte interface and that once incorporated, the phosphate ions are not freely mobile.
While the effects of experimental growth parameters on the chemistry of anodic tantalum oxide is interesting, it is worthwhile to consider what effects the incorporated phosphorus has on the properties of the oxide. Oxides formed in 0.001M H₃PO₄ versus 0.01M H₂SO₄ respond differently when heated in air at 400°C. The capacitance for oxides formed in phosphoric acid increased 24% versus 17% for sulfuric acid, and it required longer times for the phosphorus containing films to attain a steady state capacitance. Oxygen uptake for films containing phosphate was 25% slower than for oxides formed in sulfuric acid when the oxide was heated to 400°C. This indicates that the oxygen mobility is lower in anodic oxide films that contain phosphorus.

Table 2-4 shows that the increase in capacitance upon annealing at 400°C increases with electrolyte concentration between 0.001 and 1 M H₃PO₄, however, this is likely due to a decrease in the apparent dielectric thickness; the conductivity of the oxide at the metal/oxide interface increases considerably so that it behaves as part of the electrode instead of a blocking dielectric. Such a diffuse transition from electrode to dielectric results in a structure having high dielectric loss and the capacitance will vary with bias, temperature, and frequency.
Table 2-4: The effect of phosphoric acid concentration in the forming electrolyte on the capacitance and series resistance of anodic oxides with either 0V or 10V DC bias applied. [38] The formation voltage is assumed to be 75V, which corresponds to approximately 140 nm of oxide.

<table>
<thead>
<tr>
<th>Concentration $\text{H}_3\text{PO}_4$, M</th>
<th>0V Bias</th>
<th>10 V Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capacitance, µF</td>
<td>Series Resistance, Ω</td>
</tr>
<tr>
<td>0.001</td>
<td>3.985</td>
<td>16.3</td>
</tr>
<tr>
<td>0.01</td>
<td>4.027</td>
<td>20.3</td>
</tr>
<tr>
<td>0.1</td>
<td>4.437</td>
<td>27.0</td>
</tr>
<tr>
<td>1</td>
<td>5.404</td>
<td>15.4</td>
</tr>
<tr>
<td>14.6</td>
<td>4.656</td>
<td>2.6</td>
</tr>
<tr>
<td>0.001 (unheated)</td>
<td>3.1930</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The conductivity profiles shown in Figure 2-19 and Figure 2-20 illustrate that the presence of phosphorus in the outer layer hinders the thermal diffusion of oxygen and hence the ionic conductivity. [38] The thermal diffusion in the inner layer is used as a reference for defining what is ‘normal’ conductivity. Figure 2-20 demonstrates that the decrease in ionic conductivity is stronger when higher concentrations of phosphorus are incorporated into the outer layer. The conductivity term, $\sigma_0$, is defined as the distinction between resistive and capacitive behavior and is on the order of $2*10^{-9} \Omega^{-1}\text{cm}^{-1}$. 
Figure 2-19: After [38]. Conductivity profile of anodic oxide overlayed on a schematic of the chemical profile of the oxide.

Figure 2-20: After [38]. Conductivity profile of anodic oxide formed in different concentrations (1M, 8M, and 14.6M) of phosphoric acid.
2.2 Ionic Conduction

2.2.1 Classic Theory of Ionic Conduction

Under the high electric field present during anodic oxidation, ionic conduction follows the relationship

\[ i = i_0 \exp \left[ -\frac{Q - q\lambda E}{kT} \right] \]  \[2-5\]

Where \( i \) is the ionic current, \( i_0 \) and \( Q \) are constants, \( q \) is the charge of the mobile ion, \( E \) is the electric field and \( \lambda \) is a jump distance.[55] The schematic in Figure 2-21 is Verwey’s description of the potential energy of a mobile species under an applied field.[58] cited in [55]. In this model the diffusion of \( Ta_i \) through the oxide is the rate limiting factor for oxide growth. The high field model (HFM), which is discussed in greater detail in section 2.3 is of the general form

\[ i = A^* \exp \left[ B^* \tilde{E} \right] \] \[2-6\]

For the Verwey type model shown in Figure 2—21, \( A \) and \( B \) are defined as

\[ A' = 2^* \lambda C_M \nu q \] \[2-7\]

and

\[ B'' = -\frac{Q' - zF\lambda' \tilde{E}}{RT} \] \[2-8\]

where \( \lambda \) is the half jump distance, \( C_M \) is the concentration of interstitials in oxide, \( \nu \) is the vibrational frequency of ions, and \( Q \) is the activation energy at zero field.

This formulation assumes that the concentration of mobile species is independent of the electric field, but it has been suggested that the concentration of mobile ions is strongly
dependent on the electric field.[55] A sharp change in the activation energy for the movement of a tantalum interstitial was observed at $6 \times 10^6$ V/cm.[55] It was suggested that the influence of electric field on the activation energy is twice as great at fields less than $6 \times 10^6$ V/cm.[55] The reasoning for this counterintuitive conclusion is that at low fields, both the concentration and mobility of the charge increase with increasing field; however at high fields, further increasing the electric field increases the mobility but not the concentration of carriers.[55]

![Potential Energy Diagram](image)

**Figure 2-21:** After [55]. Schematic of the potential energy of a charged species as it moves through an ionic solid under an applied electric field as described by the Verwey model.

The Mott-Cabrera description of the HFM assumes that the limiting factor for oxide growth is the formation of tantalum interstitials as the metal/oxide interface.[59] The subsequent movement of the metal through the oxide is a relatively facile. The potential energy diagram for this type of mechanism is shown in Figure 2-22. In this model, $A$ and $B$ of the HFM are defined as
\[ A'' = C'_M \nu'q \]  

and

\[ B'' = -\frac{Q' - zF\lambda'\hat{E}}{RT} \]  

Where \( C'_M \) is the concentration of metal atoms on the metal side of the m/f interface, \( \lambda' \) is the half barrier distance, \( \nu \) is the vibrational frequency, and \( Q' \) is the activation energy for interstitial injection at zero field.

**Figure 2-22:** Schematic of the potential energy of a charged species as it is produced at the metal/oxide interface and then moves through an ionic solid under an applied electric field as described by the Mott-Cabrera model.

During anodic oxidation, a high electric field is present and Coulomb’s law can be used to approximate the energy of formation of defect species[60]
\[ E_f = -\frac{\chi^2 e^2}{r_0 E \varepsilon_0} \]  

[2-11]

Where \( \chi \) is the charge of the formed species, \( e \) is the elementary charge, \( r_0 \) is the initial position of a species, \( E \) is the electric field and \( \varepsilon_0 \) is the permittivity of free space. The concentration of the defect is then

\[ C_{\text{defect}} \propto C_{\text{defect}}^0 \exp\left( -\frac{\chi^2 e^2}{E \varepsilon_0} \right) \]  

[2-12]

Thus the concentration of a defect species will depend on the exponential of the square of the defect’s charge.\[60\] First principle calculations have shown that the charge of an oxygen vacancy in amorphous Ta\textsubscript{2}O\textsubscript{5} is +2 \[61\], if we accept that a tantalum interstitial has a +5 charge, we would expect that the concentration of oxygen vacancies would be considerably higher.

The concentration of point defects in tantalum oxide is too low to determine the defect species by mass changes.\[62\] In the case of thermal oxides of tantalum, it is accepted that oxygen vacancies are the dominant species except under a high partial pressure of oxygen.\[62, 63\] It would be logical to posit that oxygen vacancies far outnumber tantalum interstitials in anodic tantalum oxide. If this was true, oxide growth would occur primarily at the metal/oxide interface. Despite the logic of this prediction, the experimental literature definitively shows that tantalum interstitials are indeed mobile during anodization.

Thin layers of anodic tantalum can be treated as an n-type semiconductor\[64\], which implies that the dominant defects will be oxygen vacancies and/or tantalum interstitials. The defect chemistry reactions for tantalum interstitials and oxygen vacancies (Equations 2—13 and 2--14) show that forming either species results in excess electrons.

\[ Ta \rightarrow Ta_i^{5+} + 5e^- + V_{Ta} \]  

[2-13]
\[ Ta \rightarrow \frac{\chi}{2} V_o^{*} + \chi e^- + T\alpha_{\text{ref}} \]  

where \( \chi \) is the oxidation state of the metal in the oxide.

### 2.2.2 Proposed Theories on the Mechanism of Anodic Oxidation

Typical theories of how charged particles move through an ionic solid when an electric field is applied fail to explain the transient ionic conductivity of previously formed oxides. When a constant voltage is applied to a formed oxide, a characteristic transient response is observed. Initially, the current will decay and then hold constant at a relatively low value, however, after the passage of a moderate amount of time (0.5 – 3 minutes), the ionic current will rapidly increase and finally reach a steady state value. A typical profile of this behavior is shown in Figure 2-23 [65] and has been the source of long standing debate concerning the growth mechanisms of anodic oxides.

The simple model of metal interstitials hopping over a series of field-mediated energy barriers is insufficient for explaining the observed transient behavior. Theory predicts that \( \frac{dJ}{dt} \) should decrease with time, however, under a constant applied field, \( \frac{dJ}{dt} \) is proportional to \( J^2 \). [30] Also, the Tafel slope (\( \frac{\partial E}{\partial \log i} \)) is independent of temperature[10], which conflicts with classical theories of ionic conduction. When a constant current growth is followed by a constant applied voltage, the transient Tafel slope decreases slightly with increasing temperature, which is counter to what theory predicts.
Several authors have postulated explanations for current transients of the form shown in Figure 2-23. Bean et al. [55] postulated that anodic oxides form as the applied electric field generates Frenkel defects; the resulting interstitial atoms are mobile, but the vacant lattice sites are immobile. They suggested that these stationary vacancies result in a negative space charge, which causes the transient behavior. The space charge changes sluggishly with electric field, and the concentration of mobile ions as the oxide grows just cancels the space charge effect. The question of space charge has also been a point of contention in developing a model of anodic oxidation. In the Cabrera and Mott model, the space charge is negligible and the metal interface controls the kinetics. [59] The concentration of mobile ions is free to alter without regard to electroneutrality. In contrast, Verwey’s theory posits that the space charge layer at the interface isolates the body of the film from interfacial effects. [66]

Dignam has sought to explain transients by assuming that the current drives ionic conduction. Young describes this current driven polarization mechanism: [67]
Ions are driven by an effective field, which includes a Debye type polarization of the oxide. The relaxation time is inversely related to the current density, thus a current driven component of dielectric polarization is identified.[67]

Young has interpreted transient behavior due to the concentration of mobile ions; the concentration changes with time, but there is a significant delay.[9] The classical approach to oxide growth by ionic conduction is to treat mobile ions as an independent linear harmonic oscillator. However, strain associated with a defect may favor the formation of a new defect in the immediate vicinity. Young assumes the need to have interaction of two defects where the process is triggered by the activation of one. The production of new defects is then proportional to $N$, the number of defects, and $J$, the current density. Young describes this as an autocatalytic cascade process and not due to the production and thermal motion of Frenkel defects.[10]

For a formed oxide, the ionic current at a given applied field depends on the history of the film[30]. Variables such as growth rate, anodization temperature, and gentle annealing of formed oxides have a strong effect on the ionic conductivity of the oxide. Some explanations for this observation are[30]:

1. Variation in the concentration of Frenkel defects
2. Variation in structure of glassy oxide
3. Blocking of channels
4. Dignam’s proposed current driven dielectric polarization
5. Diffusion of oxygen from the oxide into the metal substrate[68, 69]

### 2.2.3 Effects of Annealing Anodic Tantalum Oxide

The ionic conductivity of a formed anodic oxide is sensitive to annealing and to rapid changes in the applied voltage. Vermilyea suggests that a change in applied electric field changes the number of conducting ions and also the average local configuration of the atoms in the film.[70] Such a change in the medium range order may have a great effect on the mobility of the ions.
It is expected that annealing an amorphous oxide would cause the atoms to arrange in a more stable configuration. It may be that atomic movements induced by annealing are the same type of movements responsible for ionic conduction. [70] Thus, after a film has been annealed, the ionic conduction is decreased. Annealing has the effect of arranging the atoms in a configuration that is more stable under an applied electric field.

Gentle annealing at temperatures < 200°C has been shown to strongly affect the dielectric permittivity of the oxide. The formation conditions, such as rate of oxide growth are also important for determining the oxide permittivity. One explanation is that although all of the films are amorphous, the medium range order is an important structural determinant of the oxide properties.

If the oxide is heated to greater than 200°C, the capacitance and resistance increases. Smyth[68] maintains that this occurs due to the metal substrate taking oxygen from the adjacent oxide, which creates a gradient of oxygen vacancies across the oxide. The oxide at the interface is then a semiconductor due to the high concentration of oxygen vacancies. If the sample is then re-anodized, most of the dielectric properties will be restored to their values prior to annealing.[68] However, the dielectric constant is slightly increased due to the annealing step and remains heightened after re-anodization. The increase in the dielectric constant may be due to an increase in the crystalline order.[68]

Figure 2-24 shows the C-T curves for unheated oxide, oxide heated 30 minutes at 400°C in air, and oxide heated then re-anodized for four hours. Figure 2-25 shows that the length of re-anodization time is crucial for achieving recovery of the C vs. T profile.[71]

After annealing anodic tantala, the dependency of capacitance on temperature increases considerably above about -30°C, and the profile of the C vs. T curve changes.[71] Re-anodization does not affect the low temperature C vs. T relationship, which suggests that the oxygen vacancy profile at the metal/oxide interface does not change initially upon re-anodization. The complete removal of oxygen deficiency by re-anodization depends
upon the temperature of the heat treatment, but as Figure 2-25 demonstrates, the time scale is on the order of hours.[71]

**Figure 2-24:** After [71]. Capacitance vs. temperature plots of unheated (red line), heated 30 min at 400°C in air (blue circles and dashed line) and heated then re-anodized for four hours (green line) anodic oxides.

**Figure 2-25:** After [71]. Capacitance vs. temperature plots for anodized tantalum that was heated to 450°C and re-anodized for various times.
Electronic conductivity is attributed to the thermal equilibrium reactions:[71]

\[ V_o^{-••} \cdot 2e^- \Leftrightarrow V_o^{-\bullet} \cdot e^- + e^- \]  \hspace{1cm} \text{[2-15]}

\[ V_o^{-\bullet} \cdot e^- \Leftrightarrow V_o^{\bullet} + e^- \]

Considering first principle calculation results [61], the more correct reaction is:

\[ V_o^{-••} \cdot 2e^- \Leftrightarrow V_o^{••} + 2e^- \]  \hspace{1cm} \text{[2-16]}

As the temperature is reduced, the equilibria of the above reactions shifts to the left, which reduces the amount of conduction electrons. As shown in Figure 2-26, the thickness of the effective dielectric is determined by the temperature, and this accounts for the observed C vs. T behavior.[71] High concentrations of oxygen vacancies in the oxide near the metal interface cause that portion of the oxide to behave as a semiconductor rather than an insulator. This typically causes an increase in the measured permittivity because the dielectric thickness, L, is effectively thinner. \( C = \varepsilon \varepsilon_0 A/L \)
Schematic of the proposed conductivity profile of anodic tantalum oxide after heat treatment in air. The oxide near the metal/oxide interface is prone to behave as a semiconductor, which reduces the effective dielectric thickness. The conductivity that distinguishes the material as either an insulator or a semiconductor is noted as $\sigma_0$.

Smyth summarizes that, “The temperature and frequency dependences of capacitance indicate that the conductivity distribution is exponential with position in the oxide. The combination of these dependences yields an activation energy of 0.6 eV for the conduction process ……and, according to our hypothesis, this corresponds to one half of the ionization energy of the more weakly bound electron from an oxygen vacancy.”[69]
2.3 Kinetic Models of Anodic Oxidation

2.3.1 Models Based on the High Field Model
Anodic oxide films can be grown by either a galvanostatic (constant current) or a potentiodynamic method (stepped voltage.) The supplied current allows for the formation of oxide\[72]:

\[
2\text{Ta} + 5\text{H}_2\text{O} = \text{Ta}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^- \quad E_0 = -0.75 - 0.0591\text{pH} \quad [2-17]
\]

Where \(E_0\) is the equilibrium potential. Under an applied constant current, the oxide thickens and the potential difference between the anode and the cathode increases until a critical voltage is achieved. The change in voltage with anodization time is given by\[66]

\[
\frac{dV}{dt} = E_d \frac{dL}{dt} = i \frac{E_d M}{zF\rho} \quad [2-18]
\]

Where \(V\) is the potential difference between the anode and cathode, \(E_d\) is the electric field strength, \(L\) is the thickness of the oxide, \(i\) is the ionic current, \(z\) is the number of Faradays needed to form the molecular weight of the oxide, and \(M\) is the molecular weight of the oxide. When oxide forms at a constant voltage, (potentiostatic condition) its growth causes a continuous decrease in the field strength and the ionic current falls. Eventually the growth rate of the films becomes very small. This description of anodic oxidation is based on the High Field Model (HFM.)

In its simplest form, the HFM recognizes that the I-V relationship is not Ohmic, but is expressed in the form

\[
i = A* \text{Exp}[BE] \quad [2-19]
\]

where \(i\) is the ionic current, \(E\) is the electric field and \(A\) and \(B\) are constant fitting parameters. In 1934 Guntherschulze and Betz reported this model for tantalum oxide where \(A = 3.98 * 10^{-18}\) A/cm\(^2\) and \(B = 2.2 * 10^{-6}\) cm/V.\[66\] cited in \[52\]
In 1953, Vermilyea defined a model of oxide growth as a function of time as

\[
\frac{dL}{dt} = J \exp[(BE)] \exp\left[-\frac{W}{kT}\right]
\]

Where \(J = e^{-5.5} \text{ A/sec}\) is the current density, \(E\) is the electric field, \(B = 505 \text{ Å/V}\), and \(W = 0.71 \text{ eV}\) is the energy barrier for the movement of an interstitial.\([7, 52]\) cited in \([52]\)

The original HFM was modified by introducing a term \((qeE)\) to account for the field mediation of the energy barrier:

\[
i = i_0 \exp\left[-\frac{W - qaE}{kT}\right]
\]

However, this modification was not significant enough to describe experimental current vs. electric field observations, and the model was further modified by Young\([10]\) to take the form:

\[
i = i_0 \exp\left[-\frac{W - q(\alpha' + \beta E)E}{kT}\right]
\]

Where \(i_0 = 10^{8.24} \text{ Å/cm}^2\), \(W = 2.185 \text{ eV}\), \(\alpha = 6.995\text{Å}\), \(\beta = -3.35\text{Å/V/10}^7\text{V/cm}\), and \(q = 5e^-\). In studying the steady state kinetics of tantalum anodization, the steady state was defined by a constant ionic current. The field strength was defined as

\[
E = \frac{V - V_0}{L}
\]

Where \(V\) is the applied voltage and \(V_0\) is the interfacial potential drop, which is assumed to be constant with \(V\). The differential field strength, \(\left(\frac{\Delta V}{\Delta L}\right)_{i,T}\) is independent of oxide thickness and
\[
\frac{dV}{dt} = \frac{dV}{dL} \frac{dL}{dt} = \frac{EiM}{10F\rho}
\]

Young also interrogated the transient kinetics of the system by superimposing a small AC signal on the large DC bias.[10] The observed current upon the application of a high electric field approximates the form

\[
\frac{di}{dt} = k * i^2
\]

This is not what would be predicted if the electric field was directly related to the production of Frenkel defects. Rather, this “suggests mobile ions are produced by a cascade process in which moving ions eject ions from lattice sites into interstitial sites.”[10]

Young also suggests that a proper high field model must include the concentration of mobile species, N, in the ionic current.[10]

\[
i = 2a_2N\nu_2e^{-(w_2-q_2E)/kT}
\]

where \( a_2 = \alpha_2 - \beta_2E \)

This adjustment makes the activation distance a linear function of the field and the term \((W-q_2E)\) is the activation energy at a given field. For anodic tantala, \( a_2=2.23 \text{ Å, } \beta_2=0.106 \text{ Å (}10^6 \text{ V/cm}^{-1})\) and \( W_2= 1.28 \pm 0.1 \text{ eV}.\)[10]

The ionic admittivity, defined as the AC component of the ionic current divided by the electric field was measured by Young, et.al.[73] When the AC component is applied, the instantaneous value of the ionic current is lower when the field is increasing than when the field is decreasing, and this results in an inductive phase relation. It was suggested that at low frequencies, a “Faradaic capacitance” effect is measured where \( C_F = 1/(\tau*E_0) \) where \( \tau = MW/10F\rho \) is independent of oxide thickness. At moderate frequencies, the
The inductive effect is attributed to ionic conduction. At high frequencies, capacitive displacement dominates.[73]

The relaxation time, $\tau_m$, is given as

$$\tau_m = \chi / J_0 = \tau_0 \text{Exp}[(W - qE(a - bE))/kT]$$  \[2-28\]

where $\tau_0 = -24.49$ s, $a = -1.99 \times 10^{-7}$ q*cm, $W = 1.718$ eV, and $b = 3.328 \times 10^{-15}$ q*cm$^2$/V.[73]

The observation that history effects determine the ionic current is attributed to subtle structural changes of the oxide, and a term “S” is introduced to describe the effect a film’s history has on its ionic conduction properties.[67]

$$J = J_{ex} \text{Exp}[-(W_0 - \alpha E - bS)/kT]$$  \[2-29\]

$$J_{SS} = I_0 \text{Exp}[(W_0 - (\alpha + bf)E)/kT]$$  \[2-30\]

The activation energy, $W_0$, is a function of S, a vague quantity related to the history of the oxide and E, the electric field. While Young is frequently critical of Dignam’s model for its ad-hoc nature, the introduction of the “S” term seems to be itself an ad-hoc addition to the high field model. The physical origin of the “S” term is more nebulous than Dignam’s current-polarization explanation for the mechanism of anodization.

The average electrostatic (Maxwell) field is obtained by dividing the potential of the electrode by the oxide thickness. This type of kinetic model was first presented with the rate controlling step in oxide growth being the transport of ionic species through the oxide, where the mobile species must overcome a series of field-mediated energy barriers.[58] Mott and Cabrera postulated that the movement of charged species through the oxide is fast compared to the injection of metal ions from the metal into the oxide at the metal/film interface.[59] Thus, the rate limiting step for oxide growth is the formation of mobile ions at the metal/film interface.[59] Zhang, et.al., have outlined
some shortcomings of the HFM in its ability to explain the behavior of tantalum, niobium, tungsten, nickel, and zirconium and have shown that the Point Defect Model (PDM) is a more comprehensive description of oxide growth.[12]

### 2.3.2 Transients in the Electronic Current

The transient behavior of formed oxide can be studied to understand the growth kinetics of the oxide. Wilhelmsen[74] held formed oxides at the formation potential for 20 hours to achieve a quasi-steady state. Transients were then observed after the system was given a slight push by a change in the applied potential or current. The passive current was independent of potential or pH and was < 20 nA/cm².

### 2.3.3 Point Defect Model

The point defect model (PDM) is a mechanistic description of the formation and steady state of passive films and was first introduced by Chao, Lin, and Macdonald in 1981.[17] It was suggested that oxide growth occurs by the outward diffusion of oxygen vacancies, but the outward diffusion of metal species results in dissolution of the oxide.[17] The rate controlling step for metal and oxide vacancies was assumed to be the transport of species across the film, and defect species are assumed to be in equilibrium at the interfaces.[17] The model was simultaneously reported as a means of explaining chemical breakdown.[18] The framework for calculating an impedance response of a passive film[75] was published shortly after the initial publication of the PDM.

The original PDM implicitly assumes that the metal/film and film/solution interfaces are in electrochemical equilibrium, that the passive film contains a ‘high’ concentration of point defects, the electrical potential drop across the film / solution interface is a linear function of the applied voltage and the pH of the solution, and the electric field strength in the oxide is constant, regardless of the film thickness.[17, 76]
The general PDM has been modified to consider the bi-layer structure of metal oxides and also dissolution of the formed metal oxide into the solution.[76] By allowing for oxide dissolution, the steady state of the film exists when the rate of film growth is equal to the rate of film dissolution. A schematic showing the point defect reactions as first described by Macdonald and Urquid-Macdonald[76] is shown in Figure 2-27. Reactions (1), (3), and (4) are lattice conservative processes, while reactions (2) and (5) are not. Reaction (2) results in the metal/film interface moving inwards, i.e., toward the metal. Reaction (5) is the dissolution of the oxide, which results in the movement of the film/solution interface. Although Reactions (3) and (5) both result in ejection of metal into the electrolyte, they describe different processes. Reaction (5) describes the “concerted” removal of adjacent cation and anion sites, thus this constitutes the removal of a unit of oxide. However, Reaction (3) results in a vacancy which may submerge into the oxide lattice as cation species move outward. Cation interstitials are not considered in this model, but it is not difficult to make this extension. Analytical expressions are provided for the calculation of the steady state thickness of the barrier layer and current.[76, 77]

![Figure 2-27: Schematic of the 1990 PDM, which considers metal and oxygen vacancies in defining the passive oxide film.[76]](image-url)
The original PDM assumed that the interfaces were in electrochemical equilibrium, but the model has also been extended to “the case where kinetic effects control the generation and annihilation of metal and oxygen vacancies at the interfaces…”[78] Expressions are provided for determining whether the system has interfacial equilibrium or is controlled by kinetics, and also whether the film is a cation or anion conductor.[78] However, L vs. V, L vs. pH, L vs. C\textsubscript{M}δ\textsuperscript{+}, I vs. V, I vs. pH, and I vs. C\textsubscript{M}δ\textsuperscript{+} relationships must be known. Potentiostatic experiments on Ta, W, and Zr have demonstrated that the kinetic growths laws of the PDM are more satisfactory than the growth laws of the High Field Model (HFM.)[12] It was presented that Ta, W, and Zr are predominantly oxygen vacancy conductors.[12]

The PDM has been modified to include metal interstitials, as shown in Figure 2-28.[21] For p-type films, the dominant ionic species is metal vacancies, but for n-type films, the dominant defect can be oxygen vacancies, tantalum interstitials, or a combination of both species.

![Figure 2-28: Schematic of the general PDM that considers metal vacancies, oxygen vacancies, and metal interstitials in defining the passive oxide film.][21]
The PDM developed for platinum contains metal interstitials but not metal vacancies, and a schematic of the reactions is shown in Figure 2-29 [20, 79]. Because platinum has been shown to be an n-type semiconductor, it is assumed that the dominant defects are platinum interstitials, oxygen vacancies, or a combination of both.

![Figure 2-29: Schematic of the PDM reported for platinum.][20, 79]

The impedance response of a passive film can be measured experimentally using electrochemical impedance spectroscopy (EIS.) Experimental spectra have been used to quantitatively extract the physical parameters of the PDM for several passive films. This technique was first reported for iron by Lui[80], and the model was improved upon by Marx[81]. The technique has also been applied to platinum[20], Alloy 22[21, 22] and titanium[82]. A bi-layer model was developed for zirconium[83] where the outer layer was assumed to be a resistive layer having a porous structure.

### 2.3.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy provides a means of interrogating the kinetics of the anodization process. Impedance is the opposition of electrical current in an AC circuit and becomes an important property when Ohm’s Law does not apply. Ohm’s Law assumes that the resistance, R, does not depend on frequency, and that there is no phase
shift between the current and voltage. Impedance is expressed in the imaginary plane where the real component is analogous to the resistance and the imaginary component indicates the phase shift between the current and voltage. Impedance spectroscopy is carried out by applying a small, perturbing AC signal as a function of frequency. The input signal is a sinusoidal voltage function:

\[ V = V_0 \sin(\omega t) \quad [2-31] \]

And the response of the system to this signal is a sinusoidal current

\[ I = I_0 \sin(\omega t) \quad [2-32] \]

The impedance is then defined simply as the ratio of the applied voltage to the measured current:

\[ Z = \frac{V_i}{I_i} = \frac{V_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad [2-33] \]

The impedance is often expressed in the complex form

\[ Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) \quad [2-34] \]

Where the magnitude of the impedance is

\[ Z_0 = [Z(\text{Re})^2 + Z(\text{Im})^2]^{1/2} \quad [2-35] \]

and the phase angle is

\[ \phi = \tan^{-1}\left(\frac{Z(\text{Im})}{Z(\text{Re})}\right) \quad [2-36] \]

A schematic describing the measurement of the impedance is shown in Figure 2-30. An AC voltage is applied (as represented on the y-axis) and the resulting current shown on
the x-axis. The two-dimensional ellipse is termed a “Lissajous Figure” and is used to calculate the impedance, as shown in Figure 2-30.

\[
|Z| = \frac{AA'}{BB'}
\]

\[
\sin \varphi = \frac{DD'}{AA'}
\]

Figure 2-30: After [84]. Description of how the impedance and phase shift are determined from I-V Lissajous figure.

Impedance spectroscopy is used in different ways by various engineers and scientists. We approach the technique with our system, i.e., a ‘black box’, and we apply a perturbing signal and then observe its response. We know the input and the output, but interpreting what happens in between is difficult. The investigator

“finds that the box behaves as if it contained a combination of resistors and capacitors. The reaction of our investigator to the puzzle presented by the black box will differ according to whether he is a mathematician, electrical engineer, physicist or chemist. The mathematician will be satisfied by a description in terms of differential equations and the engineer by an equivalent circuit. However the physicist or chemist will want an interpretation in terms of the structure of the material whose response can be represented by the black box. The materials scientists will often be disappointed.”[85]
Invoking electrical analogs is the most common way of interpreting impedance spectra, but few authors have used electrochemical impedance spectroscopy as a means of studying electrochemical processes. For the application of EIS to electrochemical reaction kinetics, see for example [21, 86-88]

2.4 Electrochemistry of Tantalum Oxide

2.4.1 Electrochemical Thermodynamics of Tantalum Oxide

Tantalum forms a protective oxide layer when exposed to air or aqueous solutions. This oxide can be grown to a thickness of several hundred nanometers by the process of anodic oxidation. In this electrochemical technique, the base metal is submersed in an electrolyte and a positive voltage is applied. This causes an oxide to form where the thickness is typically a linear function of the applied voltage. Oxide formation occurs due to ionic conduction.

Tantalum oxide is the most noble oxide of the valve metals; the formation of the oxide suppresses oxygen evolution by the hydrolysis of water so that the current efficiency of formation can easily reach 100%.[5, 89] The oxide is also resistant to a wide variety of acidic and basic etchants; fluoride ions must be present in the etchant solution in order for the oxide to dissolve.

The Pourbaix diagram, as shown in Figure 2-31, demonstrates that only one stable oxidation exists for electrochemically produced tantalum oxide.
Figure 2-31: After [72]. Pourbaix’s potential vs. pH diagram for the tantalum-water system at 25°C.

The equilibrium potential, \( E_0 \), for the reaction

\[
2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10e^- \quad E_0 = -0.750 - 0.0591pH \quad [2-37]
\]

is impossible to measure directly due to the protective layer of oxide. According to Van Muyder and Pourbaix “tantalum pentoxide can be reduced to metallic tantalum; nevertheless, it does not seem possible to bring about this reduction by electrolytic means starting directly from the oxide.[72]” Young has hypothesized that “the same order of field strength would be required to reverse the film forming process as to make the ions
move during formation of the film, and the easy flow of electronic current during cathodic polarization makes such high fields difficult to obtain.”[89] Due to a lack of thermodynamic data, the solid hydrides (tantalic and pertantalic acid) and the soluble tantalates are marked as a mere guide. [72]

The overpotential for Reaction [2-32] is defined as the difference between the actual potential drop at the metal/solution interface and the equilibrium potential drop; thus this value is a measure of the driving force available for anodic oxidation.

The potential on the anode is given by

\[ V = \dot{E}_{Ox} * L + \partial \varphi \] \[\text{[2-38]}\]

where \( V \) is the applied potential, \( E_{ox} \) is the mean electrostatic field in the oxide, \( L \) is the oxide thickness and \( \partial \varphi \) is the sum of interfacial contributions to the overpotential.

Accepting that the point of zero charge is 2.9V[90], the oxide/electrolyte potential drop at pH=0 is +171 mV.[64]

The formation of anodic oxide begins at 0.2V vs. SHE in acidic solution and the dependency on pH is -60mV/pH.[64] The potential drop at the oxide/electrolyte interface is determined by the reaction[64]:

\[ H_2O \leftrightarrow OH^- (ox) + H^+ (aq) \] \[\text{[2-39]}\]

The capacitance of the oxide is given by the simple parallel plate model of a capacitor:

\[ C = \frac{A * \varepsilon * \varepsilon_0}{L} \] \[\text{[2-40]}\]

And substituting [35] into [33] gives

\[ V = \dot{E}_{Ox} * \frac{A \varepsilon_0}{C} + \partial \varphi \] \[\text{[2-41]}\]
This demonstrates how the electric field in the oxide can be measured by the plot of $1/C$ vs. $V$ and the intercept of the plot predicts the sum of the interfacial contributions to the overpotential.[89]

Young advises that when the applied voltage is 100 V or more, and the solution has high conductivity, the potential drop across the oxide will be within a few percent of the applied potential.[89] However, for thin films formed at lower formation voltages, it is not valid to assume that applied voltage equals the potential drop across the oxide.

### 2.4.2 Tantalum Anodization

#### 2.4.2.1 Growth Rates of Tantalum Oxide

The rate of oxide growth is a function of anodizing conditions such as electrolyte species and concentration, temperature, and applied current density. For a given applied constant current density, voltage is linear with time over a wide range, and the slope depends approximately linearly on the current density. The oxide thickness is linear with the applied voltage; although Young has shown the relationship is not perfectly linear[91], it is commonly assumed to be an operative truth.

The rate of oxide growth under galvanostatic conditions depends on the concentration of phosphoric acid electrolyte as shown in Table 2—5. The higher rate of oxidation in 0.1 M $\text{H}_3\text{PO}_4$ compared to 0.1M $\text{H}_2\text{SO}_4$ is related to the incorporation of phosphorus. This also accounts for why the rate is so high for anodization in concentrated phosphoric acid.
**Table 2-5:** Rate of film formation (V/s) during galvanostatic growth at 1.0mA/cm² for various electrolyte concentrations.[49]

<table>
<thead>
<tr>
<th>H₃PO₄ Concentration, M</th>
<th>Film Formation rate at 1.0 mA/cm², V/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>0.60</td>
</tr>
<tr>
<td>1.0</td>
<td>0.40</td>
</tr>
<tr>
<td>0.10</td>
<td>0.38</td>
</tr>
<tr>
<td>0.010</td>
<td>0.37</td>
</tr>
<tr>
<td>0.0010</td>
<td>0.38</td>
</tr>
<tr>
<td>0.001 + 0.001 M HCl</td>
<td>0.38</td>
</tr>
<tr>
<td>0.1M H₂SO₄</td>
<td>0.34</td>
</tr>
</tbody>
</table>

When oxide is grown at a fast rate, the heat produced by reaction does not dissipate and the temperature in the oxide can be significantly higher. The rate of galvanostatic oxide formation, i.e., dV/dt, depends on the applied current density; this dependence is attributed to temperature effects.[89]

The final thickness of a formed oxide to a particular voltage depends somewhat on the current density. As the current density increases, the amount of charge passed decreases.[92] This indicates that the final film thickness decreases as the current density is increased. The amount of charge passed for anodization in 0.06 wt% H₃PO₄ is shown for different current densities in Table 2-6.
Table 2-6: Amount of oxide formed for oxides grown at different rates to the same final voltage.[92] The charge passed is compared to the amount of oxide measured by RBS where the amount of oxide is converted to the charge needed to form the oxide.

<table>
<thead>
<tr>
<th>Current Density mA/cm²</th>
<th>Slope of V-t plot V/s</th>
<th>Charge (V*t) C/cm²</th>
<th>Charge (RBS) C/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>38</td>
<td>0.40</td>
<td>0.45</td>
</tr>
<tr>
<td>10</td>
<td>3.7</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>1</td>
<td>0.32</td>
<td>0.46</td>
<td>0.48</td>
</tr>
<tr>
<td>0.1</td>
<td>0.027</td>
<td>0.56</td>
<td>0.51</td>
</tr>
</tbody>
</table>

2.4.2.2 Anodization Constants

The anodization constant is defined as the thickness of oxide formed per applied volt; the value will vary with anodization temperature, electrolyte type and concentration, growth rate, and length of time held at formation voltage. Therefore, the anodization constant is only a constant value for a well specified anodization procedure. The units are typically given as nm/V, and this value is sometimes termed the inverse field strength of the oxide. The anodization constant increases with increasing temperature; this observation is explained by realizing that an increase in the temperature decreases the electric field. Some anodization constants, along with the experimental growth conditions are shown in Table 2—7.
Table 2-7: Anodization constants for anodic tantalum oxide formed under various conditions.

<table>
<thead>
<tr>
<th>Anodization Constant, nm/V</th>
<th>Forming Electrolyte</th>
<th>Growth</th>
<th>Temp</th>
<th>Thickness Determination</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.76</td>
<td>Various</td>
<td></td>
<td>25</td>
<td></td>
<td>[64]</td>
</tr>
<tr>
<td>1.84</td>
<td>Held 20 hours, corrected for surface roughness</td>
<td></td>
<td></td>
<td></td>
<td>[74]</td>
</tr>
<tr>
<td>1.87</td>
<td></td>
<td></td>
<td>85</td>
<td></td>
<td>[92, 93]</td>
</tr>
<tr>
<td>1.62</td>
<td>1mA/cm²</td>
<td></td>
<td>25</td>
<td></td>
<td>[92]</td>
</tr>
<tr>
<td>1.73 ± 0.03</td>
<td>0.06 wt% H₃PO₄</td>
<td>45 μA/cm²</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[93]</td>
</tr>
<tr>
<td>2.02 ± 0.10</td>
<td>0.06 wt% H₃PO₄</td>
<td>45 μA/cm²</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[93]</td>
</tr>
<tr>
<td>1.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[64]</td>
</tr>
<tr>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[89]</td>
</tr>
<tr>
<td>1.78</td>
<td>0.06 wt% H₃PO₄</td>
<td>100 mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.76</td>
<td>0.06 wt% H₃PO₄</td>
<td>10 mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.87</td>
<td>0.06 wt% H₃PO₄</td>
<td>1 mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.91</td>
<td>0.06 wt% H₃PO₄</td>
<td>0.1 mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>2.21</td>
<td>0.06 wt% H₃PO₄</td>
<td>45μA/cm² to 100V</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>2.45</td>
<td>0.06 wt% H₃PO₄</td>
<td>45μA/cm² to 100V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.67</td>
<td>0.06 wt% H₃PO₄</td>
<td>5mA/cm² to 150V</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.84</td>
<td>0.06 wt% H₃PO₄</td>
<td>5mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[92]</td>
</tr>
<tr>
<td>1.29</td>
<td>0.5M H₂SO₄</td>
<td>0.7 mA/cm²</td>
<td>25</td>
<td>Impedance</td>
<td>[5]</td>
</tr>
<tr>
<td>2.17</td>
<td>0.06 wt% H₃PO₄</td>
<td>0.01 mA/cm² to 100V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[48]</td>
</tr>
</tbody>
</table>
2.4.3 Surface Preparation of Tantalum

The properties of formed anodic oxide, such as DC leakage current and ionic conductivity, are dependent on the surface preparation of the tantalum substrate. Tantalum is often chemically polished by submersing the metal in a corrosive solution for a given time. The standard chemical bath frequently used is a 5:2:1.5 to 2 by volume mixture of 98% H₂SO₄:70% HNO₃: 49% HF. This treatment shifts the intercept of 1/C vs. V plots, which indicates a shift in the overpotential at the interface. Chemical polishing leaves a film that is chemically different from the native thermal oxide. It seems that this can be avoided by boiling the substrate in deionized water immediately after the chemical polish. This step is termed “leaching.” The unleached pre-existing film either has a) a higher conductivity or b) a lower dielectric constant than the leached film or c) both a & b. Without leaching, perhaps F⁻ ions are left on the surface. Unleached, chemically polished oxides are poorly adhered to the metal substrate.

Traditional mechanical polishing is also employed in some studies; the ASM standard recommends polishing with 15μ levigated alumina on a wax wheel followed by polishing with 1μ and 0.3μ alumina on Buehler microcloth. As with other refractory metals, tantalum is notoriously difficult to mechanically polish and is subject to gulling (metal pull out) and to embedment of the polishing media. Whether prepared by mechanical or chemical polishing, the resulting surface is not specularly smooth when observed in a light microscope. Vacuum annealing tantalum substrates prior to anodizing markedly improves the dielectric properties of the subsequently formed anodic oxide.

Electrochemical polishing involves applying a bias to an anode immersed in an acidic solution; in order to achieve a smooth surface, the electrode is rotated so that the process is mass transport limited by the movement of metal cations from the anode to the electrolyte. Using methanol and sulfuric acid in the absence of water, tantalum can be produced with a rms roughness of 3 nm. The thickness of the native oxide has been
measured using several different techniques and processing conditions, some results are summarized in Table 2-8.

**Table 2-8:** Thickness of native tantalum oxide measured by several different investigators and methods.

<table>
<thead>
<tr>
<th>Thickness of Native Oxide, nm</th>
<th>Method of Determination</th>
<th>Surface Preparation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>$^{18}$O, α spectroscopy</td>
<td>Chemical polish</td>
<td>[32]</td>
</tr>
<tr>
<td>2.0</td>
<td>Wet capacitance</td>
<td>Polished w/ Jeweler’s Rouge</td>
<td>[4]</td>
</tr>
<tr>
<td>1.8</td>
<td>Extrapolation of I/C vs. V plot</td>
<td>Chemical polish</td>
<td>[64]</td>
</tr>
<tr>
<td>1.5</td>
<td>XPS</td>
<td></td>
<td>[99] cited in [5]</td>
</tr>
</tbody>
</table>

### 2.4.4 Native Oxide and its Effect on Electronic Properties

The chemical purity of tantalum anodes is important in determining the direct leakage current of formed oxides. Nuclear microanalysis of oxygen has been used to show that a shift in overpotential at the metal/oxide interface is correlated with reduced oxygen content in the metal oxide. [39] The shift toward negative potentials in the overpotential indicates an initial layer of high ionic conductivity in the metal oxide.[39] For the case of tantalum, the N$_{16}$O curve is translated to a more negative potential for an unpolished substrate, which indicates the presence of a layer of increased conductivity. [39] This suggests that chemical polishing reduces the deleterious effect of the native oxide on the as-received tantalum.

To elucidate the role of the initial oxide, a thermal oxide was produced by heating an aluminum substrate in air for three hours at 520 °C and then anodizing it.[39] The x-axis intercept from a plot of oxygen activity vs. voltage did not translate to more negative potentials. It can then be concluded that the observed shift in the N$_{16}$O = $f$ (V$_{ox}$) does not “depend on the oxygen content of the initial layer but on its nature.”[39] It was
concluded that this thick thermal oxide behaves like a barrier layer and does not influence the growth law or undergo isotopic exchange during anodization.[39]

It has been suggested that substrates that are mechanically polished contain a TaO layer at the metal/oxide interface. After anodization, the deleterious effects of this “initial” oxide remain.[100] Thus, for oxides anodized to low voltages so that the film is less than 20 nm thick, the oxide behaves differently than thicker films. For thick films, the TaO at the interface comprises a relatively small percentage of the total oxide and contributes less to the properties of the entire oxide.

Kerrec et al. have suggested that the dielectric properties of thin oxides (formation voltages less than 15.2V) are significantly different than thick oxides (formation voltages greater than 15.2V). Impedance spectroscopy in the 1MHz to 5Hz range was used in conjunction with an electrical analog to calculate the dielectric constant to be 18.5 for thin films and 27.5 for thick films.[5] Figure 2-32 is a plot of the reciprocal capacitance as function of charge passed; the change in slope is evidence of a change in the dielectric constant.[5] In considering this data, it is important to remember that the initial oxide comprises a higher percentage of the total oxide on thinner films.

![Figure 2-32: After [5]. Reciprocal capacitance versus charge passed for a tantalum substrate.](image-url)
The role of phosphorus doping of tantalum has been investigated;[101] this type of doping is significantly different from incorporating phosphorus atoms during anodization in phosphoric acid. Doping allows for phosphorus atoms to occur at the metal/oxide interface, whereas phosphorus incorporated from the electrolyte is only present in the outer layer of the oxide. Thus, the repercussions of the presence of phosphorus are significantly different. If the surface concentration of phosphorus is less than 30 ppm on the anode surface prior to anodization, no effects on the wet leakage current are observed. However, at 50 ppm phosphorus, the leakage current and the profile of the current-time plot change significantly. The leakage behavior is shown for different doping levels in Figure 2-33. The direct leakage current is also sensitive to the formation temperature when the anodes are doped with 50 ppm phosphorus and sintered at 1600°C; this is demonstrated in Figure 2-34.

![Graph showing leakage current vs. time for tantalum doped with various amounts of phosphorus.](Image)

**Figure 2-33:** After [101] Leakage current plotted versus time for tantalum doped with various amounts of phosphorus, sintered at 1600°C and anodized at 60°C.
Figure 2-34: After [101]. Leakage current plotted versus time for tantalum doped 50ppm phosphorus, sintered at 1600°C and anodized at various temperatures.

2.4.5 Electronic Conductivity

The electronic current at the oxide/electrolyte interface has been studied by using the Fe$^{+2}$/Fe$^{+3}$ reduction-oxidation couple. This prevents the reduction-oxidation reaction of O$^2-/OH^-$. [54, 102] The limiting current density in 0.001 M Fe$^{+2}$ is reported to be 500 $\mu$A/cm$^2$ on agitation and 50 $\mu$A/cm$^2$ without agitation.[54, 102]

2.4.6 Electronic Structure of Formed Oxide

Macagno and Schultze report electrochemical properties of anodic tantala formed up to 10V at pH = 0, 0.3, 7, 14. [64] The response of the oxide to a 305 $\mu$V AC signal was measured from 50 Hz to 10 kHz; at frequencies greater than 1000 Hz, the ohmic drop and phase shift of the electrode were significant.[64] The capacitance of the oxide was
typically constant between 100 – 1,000 Hz, thus the C-V relationship was typically studied at 1000 Hz.[64]

Figure 2-35. After [64]. Dependence of the electrode capacity at 1,000 Hz on the negative electrode potential for various film thicknesses. The electrolyte is 0.5 M H₂SO₄ at 25°C, and the scanning rate is 25 mV/sec

As shown in Figure 2-35, the capacitance is independent of the applied voltage only for oxides thicker than 12-15 nm; these films can be considered insulators, but for films ≤ 10.5 nm the capacitance increases as the potential is lowered, thus indicating n-type semiconducting behavior.

The Mott-Schottky technique is used to determine the concentration of electronic donors or acceptors. The defect structure of thin anodic oxides can be analyzed by Mott-Schottky analysis. By collecting impedance data at a fixed high frequency (the kHz range), the capacitance of the space charge region can be calculated from
\[ C = \frac{1}{Z'' \omega} \]  

where \( Z'' \) is the imaginary component of the impedance and \( \omega \) is the angular frequency.

The donor density, \( N_d \), can be determined by sweeping the applied DC voltage while superimposing a small amplitude, high frequency AC voltage. The donor density is determined from:

\[ \frac{1}{C^2} = \frac{2}{e \varepsilon_r \varepsilon_0 N_d A^2} \left( V - V_{fb} - \frac{kT}{e} \right) \]  

\[ [2-43] \]

\[ N_d = \frac{2}{e \varepsilon_r \varepsilon_0 A^2} \frac{1}{dC^2/dV} \]  

\[ [2-44] \]

where \( e \) is the charge of an electron, \( \varepsilon_r \) is the dielectric permittivity, \( \varepsilon_0 \) is the permittivity of free space, \( A \) is the electrode area, \( V \) is the applied voltage, \( V_{fb} \) is the flatband voltage, \( C(0) \) is the capacity of free space, \( V_m \) is the potential in the metal, \( k \) is the Boltzmann constant, and \( T \) is the temperature[103].

The flatband potential, \( V_{fb} \), is determined by rearranging equation [2-43]:

\[ V_{fb} = V_m - \left( e N_d \varepsilon_r \varepsilon_0 A^2 \frac{KT}{2 C(0)^2} + e \right) \]  

\[ [2-45] \]

The Mott-Schottky plots obtained by Schultze and Macagno are shown in Figure 2-36.
Knowing the concentration of donors allows for the calculation of $L_D$, the Debye length. This value represents the distance over which mobile charge carriers screen out the electric field. It is the distance over which significant charge separation can occur and is expressed as [64]

$$L_D = \sqrt{\frac{L_0 L^* kT}{e^2 N}}$$  \[2-46\]

where $L_0$ is the initial oxide thickness, $L$ is the thickness of the formed oxide, and $N$ is the donor density. The space charge layer thickness is[64]

$$d_{sc} = L_D \sqrt{\frac{2e}{kT}} \sqrt{V - V_{fb}}$$  \[2-47\]
where $L_D$ is the Debye length.

**Figure 2-37**: After [64]. The dependence of the Debye length and donor concentration on oxide thickness. The electrolyte was 0.5 M H$_2$SO$_4$ at 25°C.

**Figure 2-38**: After [64]. The dependence of experimental ($E'_{fb}$) and corrected ($E_{fb}$) flat band potentials on film thickness. The electrolyte was 0.5 M H$_2$SO$_4$ at 25°C. The ‘true’
flat band potential, $E_{fb}$, was obtained by correcting the experimental value, $E'_{fb}$, for the potential drop in the Helmholtz layer.

As shown in Figure 2-37, the Debye length increases linearly with oxide thickness, and the donor density decrease is proportional to $1/\text{thickness}^2$. The overvoltages are very small; it is estimated that the sum of the metal and Helmholtz overpotentials is less than 300 mV. The flat band potential is reported at -850 mV; which is close to the equilibrium potential of the oxide. As shown in Figure 2-38 the flat band potential does not vary with oxide thickness.

For films thinner than 10 nm, the space charge within the oxide must be accounted for, however, for thicker films the space charge can be neglected, and the potential drop in the oxide is assumed to be linear; this implies that the electric field in the oxide is constant. The calculated potential drop for a 6 nm oxide is shown in Figure 2-39. A sample band diagram for a 6 nm tantalum oxide film is shown in Figure 2-40.

![Diagram](image)

**Figure 2-39:** After [64]: The calculated potential drop at the metal/oxide electrolyte interface for a 6nm oxide.
**Figure 2-40**: After [64]. The calculated band structure for a 6nm oxide when no bias is applied (dotted blue lines) and a 1V bias is applied (dashed red lines)

### 2.4.7 Impedance Spectroscopy of Formed Tantalum Oxide

Impedance spectroscopy has been used to characterize formed tantalum oxide films. It is imperative to distinguish between experiments that attempt to capture the electrode kinetics from experiments principally designed to characterize the dielectric properties of the formed oxide. The latter experiments are reviewed here. A summary of the impedance spectroscopy studies reported for anodized tantalum is shown in Table 2-9.
<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Formation Electrolyte</th>
<th>Testing Electrolyte</th>
<th>AC mV</th>
<th>Formation Voltage</th>
<th>Surface Preparation</th>
<th>DC during EIS, V</th>
<th>Growth Condition</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 -10⁵</td>
<td>0.33 M H₃PO₄</td>
<td>1 M HNO₃</td>
<td>10</td>
<td>10</td>
<td>Emery, 1μm Diamond</td>
<td>1 mA/cm²</td>
<td></td>
<td>[104]</td>
</tr>
<tr>
<td>0.1 -10⁵</td>
<td>0.5M H₂SO₄</td>
<td></td>
<td>20</td>
<td>8</td>
<td>400 emery → Chemical</td>
<td>0.1</td>
<td>Cyclic Pot Sweep</td>
<td>[105]</td>
</tr>
<tr>
<td>0.1 -10⁵</td>
<td>1 M HNO₃</td>
<td>20</td>
<td>8</td>
<td>400 emery → Chemical</td>
<td>0.1</td>
<td></td>
<td>Cyclic Pot Sweep</td>
<td>[105]</td>
</tr>
<tr>
<td>0.1 -10⁵</td>
<td>1 M H₃PO₄</td>
<td>20</td>
<td>8</td>
<td>400 emery → Chemical</td>
<td>0.1</td>
<td></td>
<td>Cyclic Pot Sweep</td>
<td>[105]</td>
</tr>
<tr>
<td>0.1 -10⁵</td>
<td>1 M NaOH</td>
<td>20</td>
<td>8</td>
<td>400 emery → Chemical</td>
<td>0.1</td>
<td></td>
<td>Cyclic Pot Sweep</td>
<td>[105]</td>
</tr>
<tr>
<td>5 - 10⁶</td>
<td>0.5M H₂SO₄</td>
<td>0.5M H₂SO₄</td>
<td>5 -20</td>
<td>2-70</td>
<td>SiC → 3μm Alumina →0.3μm</td>
<td>0.7 mA/cm²</td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td>5 -20,000</td>
<td>0.06 wt% H₃PO₄</td>
<td>1 M H₃PO₄</td>
<td>20</td>
<td>15 -100</td>
<td>Sputtered Ta</td>
<td></td>
<td>45μA/cm²</td>
<td>[93]</td>
</tr>
<tr>
<td>0.05 -10⁵</td>
<td>0.15 M NaCl</td>
<td></td>
<td></td>
<td></td>
<td>De-Greased</td>
<td></td>
<td>OCP, 0.95 1.65, 2.45</td>
<td>[106]</td>
</tr>
</tbody>
</table>
Electrochemical impedance spectroscopy (EIS) has been used to demonstrate that the behavior of anodic tantalum approximates a capacitor well. The equivalent circuit shown in Figure 2-41A provided a fair fit to EIS data. The solution resistance is labeled $R_s$, the resistivity of the oxide, $R_p$, the capacitance of the oxide, $C$, and the constant phase element (CPE), which represents a capacitor with distributed time constants, the inductance of the experimental system is $L$.

![Figure A](image.png)  
**Figure A:** Equivalent circuit consisting of solution resistance in series with the oxide, which is represented by a capacitor and resistor. [104]

![Figure B](image.png)  
**Figure B:** Equivalent circuit consisting of solution resistance in series with the oxide, which is represented by a constant phase element and a resistor. [93, 105]

![Figure C](image.png)  
**Figure C:** Equivalent circuit consisting of solution resistance in series with the oxide, which is represented by a constant phase element and a resistor. An inductor is also included. [5]

**Figure 2-41:** Equivalent circuits used by different authors to describe the impedance response of anodic tantalum oxide.

As shown in Figure 2-41B, a constant phase element (CPE) has been used in place of a simple capacitor element in the analysis of Lu, et al.[93]. It has been suggested, ad-hoc, that the CPE behavior is due to incorporated phosphorus species.[93] The equivalent circuit used by Kerrec [5] includes an inductor in series with the oxide and the solution resistance. Kerrec justifies that the CPE is due to TaO resulting from the surface preparation and from impurities incorporated from the electrolyte. The Nyquist plots show depressed semicircles where the center of the circle is below the real axis.[93] The leakage resistance in ohm*cm$^2$ and the CPE parameters obtained are shown for various formation voltages in Table 2-10.[93] While the values reported in the literature are given in resistance, the more relative value is the resistivity, $\rho$. Using the appropriate
anodization constants, the data in Table 2-10 is used to calculate the resistivity shown in Table 2-11.

**Table 2-10:** After [93]. Resistance and constant phase element (CPE) parameter from the optimization of impedance spectra to the equivalent circuit shown in Figure 2-41B. A CPE parameter value of 1 indicates purely capacitive behavior. The dielectric was formed in 0.06% $\text{H}_3\text{PO}_4$ at 45 $\mu\text{A/cm}^2$ to various formation voltages at 20°C or 85°C.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Resistance (20°C) $10^6$ Ω*cm$^2$</th>
<th>Resistance (85°C) $10^6$ Ω*cm$^2$</th>
<th>CPE Parameter (20°C)</th>
<th>CPE Parameter (85°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3.21</td>
<td>0.131</td>
<td>0.9913</td>
<td>0.9746</td>
</tr>
<tr>
<td>30</td>
<td>7.58</td>
<td>0.703</td>
<td>0.9910</td>
<td>0.989</td>
</tr>
<tr>
<td>50</td>
<td>17.6</td>
<td>0.811</td>
<td>0.9921</td>
<td>0.985</td>
</tr>
<tr>
<td>100</td>
<td>33.9</td>
<td>1.16</td>
<td>0.9950</td>
<td>0.9914</td>
</tr>
<tr>
<td>150</td>
<td>2.77</td>
<td>0.212</td>
<td>0.992</td>
<td>0.9824</td>
</tr>
</tbody>
</table>

**Table 2-11:** Resistivity of tantalum oxide calculated from the values in Table 2-10 and $\rho=RA/L$.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Resistivity (20°C) $10^{12}$ Ω*cm</th>
<th>Resistivity (85°C) $10^{10}$ Ω*cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.15</td>
<td>4.09</td>
</tr>
<tr>
<td>30</td>
<td>1.40</td>
<td>11.1</td>
</tr>
<tr>
<td>50</td>
<td>1.98</td>
<td>7.87</td>
</tr>
<tr>
<td>100</td>
<td>1.94</td>
<td>5.69</td>
</tr>
<tr>
<td>150</td>
<td>0.106</td>
<td>6.95</td>
</tr>
</tbody>
</table>

The effect of the anodizing electrolyte on the oxide properties was examined by Cavigliasso, *et.al.*, and the results are summarized in Table 2-12. The effect of formation voltage on the properties of tantalum oxide formed at 1mA/cm$^2$ in 1 M $\text{Na}_2\text{SO}_4$ and held
at the formation voltage for 48 hours is reported in Table 2-13. A bridge method was used to measure the impedance in the frequency range 250 Hz-25 kHz with no DC bias applied.[107] The measured low frequency resistivity of the oxide is summarized for several formation voltages in Table 2-13.

**Table 2-12:** Resistivity, dielectric constant, anodization constant, and phase angle of anodic oxides formed in different electrolytes as determined by impedance spectroscopy. The anodization constant was calculated from the current measured during potentiodynamic growth of the oxides.[105]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Resistivity $10^{12}$ Ω•cm</th>
<th>Dielectric Constant</th>
<th>Anodization Constant, nm/V</th>
<th>Phase Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>17 ± 2</td>
<td>26 ± 1</td>
<td>1.54 ± 0.04</td>
<td>88.6 ± 0.3</td>
</tr>
<tr>
<td>1 M HNO$_3$</td>
<td>10 ± 2</td>
<td>27 ± 1</td>
<td>1.50 ± 0.04</td>
<td>88.7 ± 0.4</td>
</tr>
<tr>
<td>1 M H$_3$PO$_4$</td>
<td>12 ± 3</td>
<td>25 ± 1</td>
<td>1.42 ± 0.04</td>
<td>88.5 ± 0.3</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>--</td>
<td>29 ± 2</td>
<td>1.65 ± 0.06</td>
<td>87.3 ± 0.4</td>
</tr>
</tbody>
</table>

**Table 2-13:** Oxide resistivity for oxides formed to different formation voltages; oxides were formed at 1mA/cm$^2$ in 1M Na$_2$SO$_4$ for 48 hours.[107]

<table>
<thead>
<tr>
<th>Formation Voltage, V</th>
<th>Resistivity (Ω•cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.42*10$^{14}$</td>
</tr>
<tr>
<td>20</td>
<td>1.79*10$^{13}$</td>
</tr>
<tr>
<td>40</td>
<td>2.15*10$^{11}$</td>
</tr>
<tr>
<td>60</td>
<td>3.73*10$^{10}$</td>
</tr>
<tr>
<td>80</td>
<td>3.11*10$^{10}$</td>
</tr>
</tbody>
</table>
2.4.8 Permittivity of Anodic Tantalum Oxide

Permittivity of anodic tantalum oxide depends on formation conditions [9] and is strongly affected by gentle annealing [10]. It would be misleading to simply cite a number for the dielectric constant of anodic tantalum oxide, as shown in Table 2-14, values from 18-28 have been reported using various characterization methods and varying growth conditions.

Randall [35] has made a thorough investigation on the relationship between permittivity and phosphorus incorporation. It has been noted that the product of the capacitance and formation voltage is constant over a wide range of electrolytes [53]; this observation has led to the conclusion that there is an inverse relationship between ionic conductivity and permittivity. Therefore, if one type of tantalum oxide has a lower dielectric constant, it would be expected to anodize faster. It follows that oxides formed at the highest rates would be predicted to have the lowest dielectric constants.

Table 2-15 shows the effect of incorporated phosphorus on the dielectric constant. The dielectric constants are inferred from wet measurements of the capacitance where the inner layer of oxide is assumed to have a constant dielectric constant of 27.6 [35]. It is noted that it is not physically possible to separate the true thicknesses and dielectric constants of the individual inner and outer layer of oxides using this measurement. An optical technique, such as spectroscopic ellipsometry, is better suited to determining the permittivities of the inner and outer layers of oxide.
Table 2-14: Some dielectric constants reported for anodic tantalum oxide and their methods of oxide growth and permittivity determination.

<table>
<thead>
<tr>
<th>Dielectric Constant</th>
<th>Method of Determination</th>
<th>Anodizing Electrolyte</th>
<th>Notes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.6</td>
<td></td>
<td>Dilute H₃PO₄</td>
<td></td>
<td>Cited in [93]</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>14.7 M H₃PO₄</td>
<td></td>
<td>Cited in [93]</td>
</tr>
<tr>
<td>18.5</td>
<td>Impedance Spectroscopy</td>
<td>0.5 M H₂SO₄ at 0.7 mA/cm²</td>
<td>25°C Thickness &lt; 18.5 nm</td>
<td>[5]</td>
</tr>
<tr>
<td>27.5</td>
<td>Impedance Spectroscopy</td>
<td>0.5 M H₂SO₄ at 0.7 mA/cm²</td>
<td>25°C Thickness &gt; 18.5 nm</td>
<td>[5]</td>
</tr>
<tr>
<td>25</td>
<td>Impedance Spectroscopy</td>
<td>1mA/cm² in 1 M H₃PO₄</td>
<td></td>
<td>Kerrec cited in[93]</td>
</tr>
<tr>
<td>28.2 ±0.9</td>
<td>Impedance Spectroscopy</td>
<td>0.06 wt% H₃PO₄</td>
<td>20°C</td>
<td>[93]</td>
</tr>
<tr>
<td>30.2 ±2.1</td>
<td>Impedance Spectroscopy</td>
<td>0.06 wt% H₃PO₄</td>
<td>85°C</td>
<td>[93]</td>
</tr>
<tr>
<td>26.7</td>
<td>Ellipsometry +</td>
<td></td>
<td>@ 1kHz</td>
<td>[109]</td>
</tr>
<tr>
<td>24.7</td>
<td>Rutherford Backscattering Spec +</td>
<td>0.01 % citric acid, 1.5 mA/cm²</td>
<td></td>
<td>[110]</td>
</tr>
<tr>
<td>25.3</td>
<td>Wet electrochemistry</td>
<td>Various</td>
<td></td>
<td>[64]</td>
</tr>
<tr>
<td>23 ± 3</td>
<td>I-V, Ellipsometry</td>
<td></td>
<td></td>
<td>[111]</td>
</tr>
<tr>
<td>21.2 ± 0.7</td>
<td>C vs. 1/V, Optical measurement of thickness</td>
<td>0.01% citric acid, 1mA/cm², hold 1 hour</td>
<td>@ 1kHz, Sputtered Ta, Solid State, Au electrodes</td>
<td>[112]</td>
</tr>
</tbody>
</table>
Table 2-15: After [35]. Effect of incorporated phosphorus on the dielectric constant of anodic tantalum oxide.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Fraction of Film Containing P</th>
<th>( \varepsilon ) of P containing layer</th>
<th>( \varepsilon ) of non-P containing layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H(_2)SO(_4)</td>
<td>--</td>
<td>--</td>
<td>27.6</td>
</tr>
<tr>
<td>0.001M H(_3)PO(_4)</td>
<td>0.48</td>
<td>25.9</td>
<td>26.7</td>
</tr>
<tr>
<td>0.01 M H(_3)PO(_4)</td>
<td>0.50</td>
<td>24.2</td>
<td>26.0</td>
</tr>
<tr>
<td>0.1 M H(_3)PO(_4)</td>
<td>0.49</td>
<td>21.3</td>
<td>24.0</td>
</tr>
<tr>
<td>1 M H(_3)PO(_4)</td>
<td>0.51</td>
<td>20.3</td>
<td>23.8</td>
</tr>
<tr>
<td>10 M H(_3)PO(_4)</td>
<td>--</td>
<td>--</td>
<td>20.8</td>
</tr>
<tr>
<td>14.7 M H(_3)PO(_4)</td>
<td>0.63</td>
<td>12.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

2.4.9 Tantalum Oxide Dissolution

2.4.9.1 Dissolution in solutions without fluorine

In the case of anodized alumina, the electrochemical dissolution of the oxide at the solution interface can be appreciable, thus the layer boundaries are constantly moving with reference to a laboratory frame of reference. However, the dissolution of tantala is generally negligible[39] except in fluorine containing electrolytes. In one particular experiment, the dissolution current of tantala was less than the detection limit of 0.003 \( \mu \)A/cm\(^2\). For comparison, the electrochemical dissolution for aluminum under similar conditions was 0.3 \( \mu \)A/cm\(^2\).[39] This indicates that the mobility of tantalum atoms is low at the oxide/solution interface.

Isotopic experiments have also indicated that the diffusion coefficient of oxygen atoms in anodic tantala is very low.[39] After submersing an anodic film originally formed in \( \text{H}_2^{16}\text{O} \) into a \( \text{H}_2^{18}\text{O} \) solution, the rate of isotopic exchange was measured. For tantalum oxide, the exchange saturated at about six hours, indicating that the exchange was
confined to the first (or first few) molecular layers at the oxide/solution interface. It should be noted that this experiment was not performed with the formation voltage applied, thus there was no external electric field.

### 2.4.9.2 Dissolution in solutions with fluorine

Tantalum oxide will dissolve uniformly in 48% HF, but the acid changes concentration during use. Vermilyea addressed this by stripping a standard sample along with the test sample and then referencing the dissolution rate to the standard.[113] Thus, the dissolution rates after annealing the oxides, shown in Figure 2-42, are *relative* rates where the standard reference is assumed to dissolve at 2 nm/sec.[113] It seems that subsequent authors addressed this experimental complication by using a buffered solution.

![Figure 2-42](image)

**Figure 2-42:** After [113]. Relative Dissolution rate in Å/seconds versus the annealing time at various temperatures.
Randall used a 14 wt% HF solution to strip the oxide and monitored the thickness by measuring the capacitance in 40% H$_2$SO$_4$.[53] At room temperature, Vermilyea reported an approximate rate of 120 nm/min[23] for dissolution in 48% HF. Amsel, citing a personal communication of J.P.S. Pringle, chose to use a 300 g NH$_4$F/ L solution in HF[54]. The buffered solution suggested by Pringle dissolves at 6.2 ± 0.3 nm/min at 27.5°C.[54] Stripping of the oxide was done in concentrated HF nearly saturated with NH$_4$F; the exact concentration of NH$_4$F has a significant effect on the stripping rate, which can be controlled between 2.5-15.0 nm /min.[114] A solution of 200 mL of 48% HF and 80 g of NH$_4$F stripped the oxide at a rate of 6.0 nm /min, and adding 20mL of 48% HF increased the rate to 14.0 nm/min.[114] The stripping rate increases with increasing temperature and increasing HF concentration; the uniformity increase with increasing fluoride concentration. [114] Freshly prepared solutions dissolved the oxide more rapidly, but after about one week, the rate falls to a constant value.[114] Using this method, layers as thin as 0.5 nm have been reproducibly removed; “a molecule of Ta$_2$O$_5$ occupies a cube of side 0.45 nm”[114] This is remarkable considering that a molecule of Ta$_2$O$_5$ would have a depth of this length.

The stripping may not be uniform if [114]

- The stripping rate is greater than 15.0 nm/min
- Specimens are held stationary in the stripping bath
- The same specimen is stripped repeatedly
- Oxide is formed beyond the breakdown voltage, i.e., crystalline structures do not strip easily or uniformly

Apiezon N vacuum grease is ideal for masking areas of the oxide. It is soluble in trichloroethylene and insoluble in acetone. It can be used up to 200V during anodizing and for any stripping conditions.[114]

The discussion above assumes anodization is in a dilute electrolyte. Dissolution rates for oxides formed in 95% H$_2$SO$_4$ and 80% H$_2$SO$_4$ are 50 and 12 nm/min, respectively.[54]
The dissolution rate of tantalum anodized in 0.01 N H\textsubscript{3}PO\textsubscript{4} was measured in 7 M NH\textsubscript{4}HF\textsubscript{2} via reflectance infrared spectroscopy. The authors suggested three regions of oxide, and the dissolution rates are shown in Table 2-16.[115] It is noted that this reported tri-layer structure is not in agreement with the majority of the tantalum oxide literature and it may be due to an artifact associated with the IR technique.

**Table 2-16:** Dissolution rates of the three oxide layers formed to 50, 100, or 300V.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Outer Diss. Rate nm/sec</th>
<th>Middle Diss. Rate nm/sec</th>
<th>Inner Diss. Rate nm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>4.0\texttimes10^{-2}</td>
<td>3.73\texttimes10^{-2}</td>
<td>3.60\texttimes10^{-2}</td>
</tr>
<tr>
<td>100</td>
<td>3.5\texttimes10^{-2}</td>
<td>3.76\texttimes10^{-2}</td>
<td>3.62\texttimes10^{-2}</td>
</tr>
<tr>
<td>300</td>
<td>3.3\texttimes10^{-2}</td>
<td>3.82\texttimes10^{-2}</td>
<td>3.68\texttimes10^{-2}</td>
</tr>
</tbody>
</table>

The dissolution rate of the outer layer oxide increases when the anodization is performed in concentrated H\textsubscript{2}SO\textsubscript{4}[23, 54], and Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}[23] in ethylene glycol. Montero used a stripping solution of NH\textsubscript{4}F/HF solution (40 g per 100 ml) and dipped the oxides into the solution at 30 second intervals; following each interval, the capacitance at 100 Hz was measured in 10% H\textsubscript{3}PO\textsubscript{4} solution.[116] If the oxide is perfectly uniform, the inverse capacitance would be a direct measurement of the oxide thickness, however the dielectric constant of the inner and outer layers is not the same. The change in dielectric constant manifests itself by an abrupt change of the slope of a plot of reciprocal capacitance vs. dissolution time; this is depicted in Figure 2-43. Interpretation of these results requires one to recall that both the dielectric constant and the dissolution rate in fluorinated etchants depends on the composition of the outer layer.
Figure 2-43: After [116]. Inverse capacitance of anodic tantalum anodized in different concentrations of H₃PO₄ versus dissolution time.

The effect of phosphorus incorporation on the dissolution rate is less straightforward to determine. Randall, et.al., used reciprocal capacity measurements to infer the thickness of the oxide[53] and concluded that the dissolution rate of the outer layer of oxide formed in concentrated H₃PO₄ is accelerated, [35, 53] however, this method of measuring thickness neglects differences in the dielectric constant of phosphorus containing oxide. Pringle asserts[117] that when this is corrected for, the dissolution rate of oxide formed in 85% H₃PO₄ will only be 2/3 the rate of the stoichiometric inner layer. Therefore, the incorporation of phosphorus actually decelerates the rate of oxide dissolution.[117]

Figure 2-44 shows the nuclear microanalysis results from two step anodization experiments. The solid red line represents oxide that was first anodized in 0.01 M H₃PO₄ and subsequently anodized in 1.0 M H₃PO₄. The dashed blue line represents oxide that was first anodized in 1.0M H₃PO₄ and then anodized in 0.01 M H₃PO₄. Upon first inspection, this indicates that the dissolution rate of oxide, as measured by the activity of oxygen, is faster when a higher concentration of phosphorus is incorporated into the oxide. Pringle asserts[117] that this is a misinterpretation of the data; when the lower
dielectric constant of the outer layer is taken into account, the change in thickness with dissolution time is greater in the inner layer of oxide.

**Figure 2-44:** After [53]. Activity of oxygen versus reciprocal capacity as the oxide is dissolved in 14 wt% HF for oxides anodized using a two-step anodization process where the molarity of the phosphoric acid was varied for each anodization step.

An, *et al.*, used ellipsometry to measure the dissolution rate of MO-CVD deposited Ta$_2$O$_5$ in a buffered fluoride stripping solution of 46.5% HF : 40% NH$_4$F in the ratio of 3:17. The addition of ammonium fluoride slows the rate of dissolution and homogenous dissolution is maintained. The dissolution rates for oxides deposited at various temperatures are shown in Table 2-17.[118]
Table 2-17: Dissolution rate of MO-CVD Ta$_2$O$_5$ in 46.5% HF : 40% NH$_4$F in the ratio of 3:17. [118]

<table>
<thead>
<tr>
<th>Dissolution Rate, nm/s</th>
<th>Deposition Temp, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6*10^-3</td>
<td>473</td>
</tr>
<tr>
<td>2.0*10^-3</td>
<td>573</td>
</tr>
<tr>
<td>1.1*10^-3</td>
<td>673</td>
</tr>
<tr>
<td>0.37*10^-3</td>
<td>773</td>
</tr>
</tbody>
</table>

2.5 Solid State Conductivity

Fifty five years ago, pioneering work on the general conduction mechanisms in thin insulating films was reported using anodized tantalum as a model system.[16] Ionic conduction was shown to be an inadequate explanation for conduction because biasing the sample did not show evidence of material transport from one electrode to the other. Tunneling mechanisms were also dismissed because a large temperature dependence on the current was observed[119]. While certainly not an exhaustive tabulation of conduction studies performed on tantala, Table 2-18 demonstrates that a single conduction mechanism cannot be used to explain conduction in tantalum oxide.
Table 2-18: Conduction mechanisms reported for tantalum oxide. Various growth methods such as thermal oxidation of tantalum, anodic oxidation, and sputtering have been used to form the oxide.

<table>
<thead>
<tr>
<th>Oxide Thickness</th>
<th>Growth Method</th>
<th>Cited Conduction Mechanism</th>
<th>Source</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-9 nm</td>
<td>Anodized, 0.5% H$_2$SO$_4$, 100 μA/cm$^2$</td>
<td>Anodic Direction: Electron Tunneling, Fowler Nordheim</td>
<td>[120]</td>
<td></td>
</tr>
<tr>
<td>4-9 nm</td>
<td>Anodized, 0.5% H$_2$SO$_4$, 100 μA/cm$^2$</td>
<td>Cathodic Direction: (Reverse Bias) Schottky emission</td>
<td>[120]</td>
<td></td>
</tr>
<tr>
<td>22 nm</td>
<td>Anodized</td>
<td>Defect enhanced tunneling</td>
<td>[121]</td>
<td>30 s RTA of 650-800C. Annealed 30 min. at 350C in reducing atmosphere</td>
</tr>
<tr>
<td>&lt;85 nm</td>
<td>Plasma-enhanced CVD</td>
<td>Trap-limited Poole-Frenkel</td>
<td>[122]</td>
<td></td>
</tr>
<tr>
<td>130 nm</td>
<td>Anodized to 75V in 0.01M H$_2$SO$_4$</td>
<td>Associated w/ oxygen deficiency, measure thermal activation energy</td>
<td>[69]</td>
<td>Exponentially graded ionic conductivity profile</td>
</tr>
<tr>
<td>50 nm</td>
<td>Sputtered Ta, Thermal Oxide</td>
<td>Poole-Frenkel, internal field assisted</td>
<td>[123]</td>
<td></td>
</tr>
<tr>
<td>20-220 nm</td>
<td>rf sputtered</td>
<td>Modified Poole Frenkel (bulk limited)</td>
<td>[124]</td>
<td>No heating</td>
</tr>
<tr>
<td>20-220 nm</td>
<td>rf sputtered</td>
<td>Poole Frenkel</td>
<td>[124]</td>
<td>Heat to 200C in air for 20 minutes</td>
</tr>
<tr>
<td>60-1350</td>
<td>rf sputtered</td>
<td>High field condition: Bulk limited</td>
<td>[125]</td>
<td>Highly imperfect films, i.e., oxygen deficient</td>
</tr>
<tr>
<td>60-1350</td>
<td>rf sputtered</td>
<td>Low voltage condition: Electrode limited. Modified Field Emission</td>
<td>[125]</td>
<td>Highly imperfect films, i.e., oxygen deficient</td>
</tr>
<tr>
<td>10-30 nm</td>
<td>Reactive rf sputtered</td>
<td>Poole-Frenkel</td>
<td>[126]</td>
<td>High Field, high Temperature</td>
</tr>
<tr>
<td>10-30 nm</td>
<td>Reactive rf sputtered</td>
<td>Hopping.</td>
<td>[126]</td>
<td>Moderate Field and intermediate Temperature.</td>
</tr>
<tr>
<td>?</td>
<td>e-beam evaporated Ta then plasma oxidation</td>
<td>Schottky</td>
<td>[127]</td>
<td>Temperature and Voltage dependency follows Schottky. T range: 77K-300 K</td>
</tr>
<tr>
<td>?</td>
<td>e-beam evaporated Ta then plasma oxidation</td>
<td>Field emission, trapezoidal barrier</td>
<td>[127]</td>
<td>Low Temperature</td>
</tr>
<tr>
<td>10-20nm</td>
<td>Sputtered Ta, Oxide anodized in 1% Na₂SO₄. Electrical measurements identical for anodic and thermal oxides.</td>
<td>Schottky</td>
<td>[128]</td>
<td>Deviates from Schottky at low T and for thin oxides</td>
</tr>
</tbody>
</table>
Defining the conduction mechanism in tantalum pentoxide is not a straightforward task. The two conduction mechanisms most frequently alluded to are Schottky emission and Poole-Frenkel effect, which results from a lowering of the Coulombic potential barrier at the metal/oxide interface under an applied electric field.[129]

The current in Schottky emission is electrode limited and given by the Schottky-Richardson relation:

\[
J = AT^2 \exp\left(-\frac{q\phi_0}{kT}\right) \exp\left(\frac{\beta}{kT} E^{1/2}\right)
\]

where

\[
A = \frac{2qm^*k^2}{(2\pi)^2h^3}
\]

\[
\beta = \left(\frac{q^3}{4\pi\varepsilon_0K_T}\right)^{1/2}
\]

Where \(\phi_0\) is the barrier height, \(E\) is the applied electric field, \(k\) is the Boltzmann constant, \(h\) is Planck’s constant, \(q\) is the electronic charge, \(\varepsilon_0\) is the permittivity of free space and \(K_T\) is the high frequency dielectric constant of the insulator.[129]

The current in Poole-Frenkel conduction is bulk limited and is due to the field enhanced electron emission from donor centers

\[
J = CE \exp\left(-\frac{q\phi_0}{kT}\right) \exp\left(\frac{\beta_{PF}}{kT} E^{1/2}\right)
\]

where

\[
\beta_{PF} = \left(\frac{q^3}{\pi\varepsilon_0K_T}\right)^{1/2}
\]

and \(C\) is a constant proportional to the density of trapping centers.[129]
The conduction mechanism cannot always be described as an electrode-limited process (Schottky emission) nor as a bulk limited process (Poole-Frenkel effect.) The dominant conduction mechanism will be dependent on several variables including: the method of film growth or deposition, on the thickness of the film, and on the defect densities in the oxide.

The Poole-Frenkel model of conduction is typically cited in describing conduction via trap-dominated transport. In this model, the electric field lowers the thermal emission barrier for conduction; this assumes that a coulombic trap does not couple to the lattice. Also, the theory assumes that the traps act independently. In reality, the high density of defects suggests that Poole-Frenkel theory may not apply. Also, the depth of the traps is significant, which suggests that large lattice distortions occur along with the defect. Considering these factors, it has been suggested that polaron conduction is a more accurate description than Poole-Frenkel conduction. [111]

Regardless of the correct conduction mechanism, there is consensus that defect states are important for defining the conductivity of Ta₂O₅ films. Thus, a review of defect state characterization is provided. Oxygen vacancies are frequently cited as being the most relevant defect species. Wu et.al. have used the relationship between electric field and leakage current to calculate the activation energy corresponding to the Poole-Frenkel barrier height. For DC-diode sputtered films, they observed a barrier height of 0.57 eV for films with a dielectric constant of 20 and a height of 0.46 eV for films with a dielectric constant of 25[130]. Sawada and Kawakami used local density approximation (LDA) calculations to predict that oxygen vacancies would occur 0.8eV below the conduction band[131]

Trapping centers in tantala thin films have been studied using thermally stimulated current (TSC) spectroscopy. In this technique, traps are populated then the system is heated under an electrical bias, and the current is measured as the traps are depleted. Seve and Lassabatere identified three trapping centers, with activation energies of 0.13, 0.42, and 0.55 eV for a 500nm thermal oxide on sputtered β Ta[132]. Defect
characterization has also been reported using a variant of TSC, ZBTSC (zero-bias thermally stimulated current) separately by Lau[133] and Devine[122].

Films grown via low-pressure metal-organic chemical vapor deposition (LP-MOCVD) demonstrated three different trapping centers for Si-LPCVD Ta₂O₅/Al structures. A trap level at 0.3 eV was deemed to indicate an acceptor level due to Si atoms substituting for Ta atoms, another defect at 0.8 eV below the conduction band is assigned to oxygen vacancies. [133] A defect observed at 0.6eV below the conduction band was not well characterized. Silicon / plasma enhanced CVD deposited Ta₂O₅/ aluminum sandwiches show a trap level approximately 1 eV below the conduction band.[122]

Defect states have been measured on films that were anodized from sputter deposited β Ta, using UV-stimulated photocurrent spectroscopy. Trap levels at 1.5 eV and 2.1eV below the conduction band of the oxide were observed. The 2.1 eV level appeared to be due to electron trapping in a deep state in the forbidden gap of Ta₂O₅. [129]

Knowing that defects are crucial to defining the electrical properties suggests that the electronic properties would vary significantly with the film purity. In the case of high purity rf-sputtered Ta₂O₅ films, the conduction mechanism was found to approximate the Poole-Frenkel condition. [124] However, in the case of films with large oxygen deficits, different conduction mechanisms are formed in the high field and low voltage regions. In the high field region, the mechanism is bulk limited, but it is electrode limited at low voltages and follows a modified field-emission conduction behavior. [125]

\[
J = \frac{q^2}{kT} l^2 \Gamma n^* E \tag{2-50}
\]

Where \( \Gamma \) is the mean hopping frequency between two sites separated by a distance, l, and \( n^* \) is the density of free electrons in the insulator. It was concluded that the charge carriers are small polarons in the case of oxygen deficient films.
Although defect dominated conduction suggests that the electrical properties of Ta$_2$O$_5$ would depend strongly on the growth method, it has been shown that the properties can be remarkably similar for various Ta$_2$O$_5$ films. Anodic tantala was formed by anodizing 200 nm of sputter deposited tantalum in 0.01 M citric acid at 0.2 mA/cm$^2$. The electrical characteristics were compared to CVD and PVD films as a function of applied electric field, time, temperature (100K-500K), and incident light (photoconductivity).

For thick films (greater than 30 nm) formed via PVD and anodization, the magnitude of leakage currents are nearly identical in reverse bias and comparable in forward bias.[111]. Figure 2-45 shows the general I-V behavior of 10 nm PVD, 10 nm CVD, 11 nm anodized, and 20 nm commercial capacitor. Despite differences in oxide formation, the I-V curves share a similar diode-like asymmetric shape. This is an indication that the underlying physics of charge transport is the same regardless of method of oxidation.

![Figure 2-45: I-V curves for anodized, CVD, and PVD thin tantala films.](image)

The photocurrent, which varies inversely with oxide thickness, measures the below band-gap photocurrent. Thus, it represents the number of defects averaged over the thickness
of the film. The dependence with oxide thickness suggests that defects in Ta$_2$O$_5$ are located near the metal-oxide interfaces and have a much lower density of defects in the bulk[111]. It is estimated that defect density is $10^{17}$/cm$^3$ in the bulk and $10^{19}$ to $10^{20}$/cm$^3$ in a thin film[111].

The effect of defect density on photoconductivity was investigated by heating the bottom electrode. This causes oxygen to diffuse into the tantalum substrate and results in a band of defects across the oxide film.[111] This research indicates that some commonly measured electrical properties of Ta$_2$O$_5$ are independent of growth method.

### 2.6 Optical Properties of Tantalum Oxide

#### 2.6.1 Infrared Spectroscopy of Tantalum Oxide

#### 2.6.1.1 Assignment of IR Absorption Bands

Weltner and McLeod reported on the IR, visible, and near UV spectroscopy of TaO and TaO$_2$ molecules vaporized from tantalum oxide at 2270 K in Ar and Ne atmospheres at temperatures of 4K and 20K.[134] The observed IR peaks for TaO and TaO$_2$ are shown in Table 2-19.
Table 2-19: After [134]. Bonding frequencies for Ta-O measured in neon or argon atmospheres.

<table>
<thead>
<tr>
<th>Frequency cm⁻¹</th>
<th>Species</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>TaO</td>
<td>Argon</td>
</tr>
<tr>
<td>971</td>
<td>TaO₂</td>
<td>Argon</td>
</tr>
<tr>
<td>914</td>
<td>TaO₂</td>
<td>Argon</td>
</tr>
<tr>
<td>1028</td>
<td>TaO</td>
<td>Neon</td>
</tr>
<tr>
<td>988</td>
<td>TaO₂</td>
<td>Neon</td>
</tr>
<tr>
<td>927</td>
<td>TaO₂</td>
<td>Neon</td>
</tr>
<tr>
<td>995 (weak)</td>
<td>TaO₂</td>
<td>Neon</td>
</tr>
<tr>
<td>968 (medium)</td>
<td>TaO₂</td>
<td>Neon</td>
</tr>
</tbody>
</table>

When interpreting IR spectra as a function of processing conditions, authors typically use XRD (X-ray diffraction) to confirm phase changes in the oxide, thus providing strong evidence that changes in the IR absorption spectra are due to bonds specific to a crystalline structure. Vanadium forms several stoichiometric compounds with oxygen, each having a distinct crystal structure that can be identified using XRD. Therefore, it is possible to assign observed IR bands to different vanadium oxides. Tantalum only forms one stable oxide[135], Ta₂O₅, thus standards do not exist for other oxidation states of tantalum.

In FT-IR spectroscopy research, most peak positions are determined from transmission experiments. Features in a transmission spectrum will depend on the material’s absorption coefficient, but a reflectance spectrum will also depend on the refractive index of the film. The exact positions of absorption bands can also vary slightly as functions of the apparatus, such as the incident angle of the infrared beam. Therefore, direct comparisons cannot always be made between experimental reflectance spectra and literature transmission spectra.

The assignment of specific vibrational modes to absorption peaks of a Ta₂O₅ spectrum is a tricky endeavor. Ono, et.al., have drawn conclusions by comparing their transmission
Ta$_2$O$_5$ spectrum to vibrational modes assigned for the V$_2$O$_5$ system.[136] Therefore, their assignments given in Table 2-20 should be accepted with caution. It is noted that these assignments are cited and accepted by numerous other authors seeking to characterize TaO$_x$ films.

**Table 2-20:** After [136]. Assignment of transmission IR absorption peaks for Ta$_2$O$_5$ made by comparison to V$_2$O$_5$.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Assigned Vibrational Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>210</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>O$\equiv$3Ta, Ta$\text{—}O$—Ta Deformation Mode</td>
</tr>
<tr>
<td>510, 570</td>
<td>500-650</td>
</tr>
<tr>
<td></td>
<td>O$\equiv$3Ta Stretching Mode</td>
</tr>
<tr>
<td>810</td>
<td>800-900</td>
</tr>
<tr>
<td></td>
<td>Ta$\text{—}O$—Ta Stretching Mode</td>
</tr>
</tbody>
</table>

Surganov, et.al, assigned each absorption band frequency to an oxidation state and/or a structure of tantalum oxide; this is shown in Table 2-21; however, this assignment is dubious in some cases as back tracking the references was neither easy nor convincing. It is noted that for the sources cited[137, 138], one is a Russian book and the other is a journal article which does not seem to exist, i.e., no articles for the cited authors and year of publication could be located. Therefore, the validity of assigning structures to the absorption peaks could not be determined by this reviewer.

Citing [137, 138] Surganov, *et.al.*, conclude that the 1130 cm$^{-1}$ absorption band is due to the “internal transition layer of oxide with a reduced content of oxygen and a low coordination of Ta atoms (TaO).”[139] It is important to note that this absorption band is in close proximity to the 1110 cm$^{-1}$ band reportedly related phosphate groups present in anodic tantalum oxide.[115, 140] The band at 960 cm$^{-1}$ is due to the rutile phase, TaO$_2$. The band at 505 cm$^{-1}$ is attributed to the “external oxygen-saturated amorphous oxide with a high coordination number for Ta.”[139]
Table 2-21: After [141]. Assignment of absorption frequencies to structural phases of tantalum oxide

<table>
<thead>
<tr>
<th>Band Maximum, cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>Presumably Ta(_2)O(_3)</td>
</tr>
<tr>
<td>1130</td>
<td>TaO</td>
</tr>
<tr>
<td>1030</td>
<td>Presumably Ta(_2)O(_3)</td>
</tr>
<tr>
<td>960</td>
<td>TaO(_2) Rutile</td>
</tr>
<tr>
<td>900</td>
<td>(\alpha)-Ta(_2)O(_5)</td>
</tr>
<tr>
<td>780</td>
<td>High Temperature (\beta)-Ta(_2)O(_5)</td>
</tr>
<tr>
<td>760</td>
<td>Bonded Structures of rhombic (\beta)-Ta(_2)O(_5)</td>
</tr>
<tr>
<td>650</td>
<td>Rhombic (\beta)-Ta(_2)O(_5)</td>
</tr>
<tr>
<td>610</td>
<td>(\alpha)-Ta(_2)O(_5)</td>
</tr>
<tr>
<td>505</td>
<td>Amorphous Ta(_2)O(_5)</td>
</tr>
<tr>
<td>450</td>
<td>(\alpha)-Ta(_2)O(_5)</td>
</tr>
</tbody>
</table>

Using specular reflectance, multiple reflectance, and direct transmission IR, Vratny [142] studied adsorbed species on both thermal and anodic tantala films. Tantalum substrates were sputtered to a thickness of 500 nm and were anodized in a 1:2:3 solution of water, oxalic acid, and ethylene glycol at 105°C. Figure 2-46 compares the high energy portion of transmission spectra from thermal and anodic tantalum oxide. Considerable differences are observed between the two types of oxide, which indicates significant differences in the structures and/or chemistries of the oxides. The lower energy IR spectra of the thermal oxide indicates a large amount of adsorbed water (4000-3500 cm\(^{-1}\)) and carbon dioxide (2350 cm\(^{-1}\)); this is attributed to the porous nature of the thermal oxide.[142]
Figure 2-46: After [142]. Comparison of transmission spectra from thermal and anodic tantalum oxide. The relative transmission between the two spectra is arbitrary.

Spectra collected from thermal, anodic, wet anodic (held at 100% humidity for four hours), and dry anodic (held at 110°C for 24 hours) oxides were compared. Transmission spectra were compared to grazing incidence reflectance (10°) and oblique reflectance (30°) spectra. A summary of the adsorbed species for the different oxides and IR collection methods is shown in Table 2-22. Spectra for the various oxides can be seen in [142], but the spectra are not reproduced here. The form of the spectra varies considerably as a function of sample type and collection method, but as shown in Table 2-22, the assignments for the absorption peaks are similar.
Table 2-22: Data compiled from[142]. Absorption peaks and the assigned adsorbed chemical species for different types of tantalum oxide collected by various FT-IR spectroscopy techniques. Some peak positions are approximate as they were read by this reviewer from the spectra and were not always tabulated by the original author.

<table>
<thead>
<tr>
<th>Peak, cm$^{-1}$</th>
<th>Assignment</th>
<th>Oxide</th>
<th>Spectra Collection</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3950</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3950</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3900</td>
<td>Chemisorbed H$_2$O or CO$_2$</td>
<td>Dry Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3750</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Thermal</td>
<td>Transmission</td>
</tr>
<tr>
<td>3740</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Thermal</td>
<td>Transmission</td>
</tr>
<tr>
<td>3720</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Thermal</td>
<td>Transmission</td>
</tr>
<tr>
<td>3700</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Anodic</td>
<td>Transmission</td>
</tr>
<tr>
<td>3650</td>
<td>Chemisorbed H$_2$O or CO$_2$</td>
<td>Dry Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3630</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Anodic</td>
<td>Oblique Reflectance</td>
</tr>
<tr>
<td>3580</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Anodic</td>
<td>Oblique Reflectance</td>
</tr>
<tr>
<td>3600-3400</td>
<td>Physisorbed H$_2$O</td>
<td>Dry Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3500-3100</td>
<td>Physisorbed H$_2$O</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3500-3100</td>
<td>Physisorbed H$_2$O</td>
<td>Anodic</td>
<td>Transmission</td>
</tr>
<tr>
<td>3400</td>
<td>Chemisorbed H$_2$O (OH$^-$)</td>
<td>Dry Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>3400-3200</td>
<td>Physisorbed H$_2$O</td>
<td>Anodic</td>
<td>Oblique Reflectance</td>
</tr>
<tr>
<td>3300</td>
<td>Physisorbed H$_2$O</td>
<td>Thermal</td>
<td>Transmission</td>
</tr>
<tr>
<td>3300</td>
<td>Physisorbed H$_2$O</td>
<td>Anodic</td>
<td>Transmission</td>
</tr>
<tr>
<td>3000</td>
<td>C-H Residue</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>2950</td>
<td>C-H Residue</td>
<td>Anodic</td>
<td>Transmission</td>
</tr>
<tr>
<td>2800</td>
<td>C-H Residue</td>
<td>Thermal</td>
<td>Transmission</td>
</tr>
<tr>
<td>2800-2600</td>
<td>C-H or carboxalate OH</td>
<td>Anodic</td>
<td>Oblique Reflectance</td>
</tr>
<tr>
<td>2950</td>
<td>CO$_2$</td>
<td>Dry Anodic</td>
<td>Grazing Reflectance</td>
</tr>
<tr>
<td>2500-2350</td>
<td>CO$_2$</td>
<td>Anodic</td>
<td>Oblique Reflectance</td>
</tr>
<tr>
<td>2400</td>
<td>CO$_2$</td>
<td>Wet Anodic</td>
<td>Grazing Reflectance</td>
</tr>
</tbody>
</table>
The nature of chemisorbed versus physisorbed water has been demonstrated using tritiated electrolyte.[143] A sample anodized in tritiated electrolyte was compared to a sample anodized in typical electrolyte and then submerged in the tritiated electrolyte. The samples were then placed in an oven at 170°C and 50% relative humidity for one hour. “The results show that tritium occluded in the film during growth either existed in higher concentration within the film, or was more tightly bound within the film than the tritium which was adsorbed in the dipping experiment after anodization.”[143] This suggests that the water on the substrate that was merely submerged in tritiated electrolyte was physically adsorbed as opposed to chemically adsorbed. These experiments confirm the IR studies that attribute different absorption bands to chemi- and physi-sorbed water.

The IR bands attributed to water and carbon dioxide absorption from anodic oxide have been studied as a function of moderate annealing temperatures and pressure as shown in Figures 7 and 8 of Vratny’s report.[142] Upon heating the oxide to 200°C under vacuum, the 3300 cm\(^{-1}\) peak corresponding to physisorbed water decreased, however the 3700 cm\(^{-1}\) peak corresponding to chemisorbed water increased slightly due to a reduction in background “as a result of the decrease in hydrogen bonded surface water”[142]
A substantial portion of adsorbed water and carbon dioxide are removed under a weak vacuum ($10^{-2} - 10^{-3}$ Torr). When the sample is heated, more expulsion of adsorbed species occurs; CO$_2$ is removed at 100°C while H$_2$O is expelled at ~200°C.[142] This observation has interesting implications for defining the structure of tantalum oxide.

Transmission FT-IR measurements were performed on Ta$_2$O$_5$ films that were CVD deposited on silicon substrates.[144] A “newly observed peak” is reported at 2340 cm$^{-1}$ when the oxide is annealed in an O$_2$ atmosphere, but it is not present when annealed in an N$_2$ atmosphere. It is concluded that this peak is observed due to the formation of Ta=O double bonds.[144] The authors discuss why the peak is not attributable to CO$_2$, but this reviewer remains unconvinced. Inspection of other IR spectra in the literature shows that others have observed this peak, but have not made a chemical assignment. Apparently, they have taken the more orthodox opinion that it is due to CO$_2$ or carbonyl groups, which is consistent with the assignment given in 1965 by Vratny.[142] Some more recent citations have propagated the double tantalum-oxygen bond theory, but it is a questionable conclusion.

FT-IR reflectance spectra of a native oxide, a compact thermal oxide, and a compact anodic oxide are shown in Figure 2-47 where the substrate is sputtered tantalum. [141] The chemistries and/or structures of the thermal and native oxides are considerably different.

Anodization of sputtered Al/Ta layers was performed in 0.4 M oxalic acid at 20°C.[141] This resulted in an array of Ta$_2$O$_5$ pillars in an Al$_2$O$_3$ matrix when a sufficient amount of the outermost metal has been anodized. Using the band assignments shown in Table 2-21, it was concluded that the thermal oxide contains higher concentrations $\alpha$ and $\beta$ Ta$_2$O$_5$. The columnar tantalum oxide contains TaO, TaO$_2$, and Ta$_2$O$_5$, and it is also assumed that Ta$_2$O$_3$ is present. Also, the dense anodic film is more disordered than films of the columnar oxide [141]
Figure 2-47: Reflection spectra of thermal and anodic Ta$_2$O$_5$ and anodic Ta$_2$O$_5$ pillars in anodic Al$_2$O$_3$[141]

Similar experiments were also carried out by anodizing in 0.4M H$_2$SO$_4$ [139] Figure 2-48 shows IR reflectance spectra from 1500 – 400 cm$^{-1}$ for (1) native oxide, for (2) columnar Ta$_2$O$_5$ structures anodized to 23V, and for (3) columnar structures anodized to 250V and held for 15 minutes. The native oxide shows weak, broad absorbances at 1130, 960, and 505 cm$^{-1}$, the thin (23V) Ta$_2$O$_5$ pillars also show bands at 1250, 1100, and 760 cm$^{-1}$. In comparing the thick (250V) pillars to the thin pillars, a weak 580 cm$^{-1}$ band appears; the 760 cm$^{-1}$ band becomes more distinct, and the intensities of the 1250 and 1000 cm$^{-1}$ bands increase.[139]
Figure 2-48: Reflectance spectra of anodic tantala columns formed in sulfuric acid and of the native oxide.[139]

It is concluded that the columns of anodic tantala contain three oxide phases of the Ta-O system: TaO, TaO₂, and Ta₂O₅. By examining the localization of the bands at 760 and 505 cm⁻¹, it is concluded that the degree of ordering of the pentoxide and the fraction of crystalline β Ta₂O₅ and rutile TaO₂ inclusions increases when the formation voltage is increased from 23V (no hold time) to 250V (15 minutes hold time). The ‘behavior’ of the 1250 and 1000 cm⁻¹ absorption peaks “permits the assumption” that Ta₂O₅ forms at higher formation voltages.

2.6.1.2. IR of anodic tantalum oxide formed in H₃PO₄

Tantalum oxide formed in phosphoric acid exhibits a distinct absorption band attributed to incorporated phosphate in the oxide. As much of this dissertation studies oxides formed in H₃PO₄, a significant literature search is reported for anodization in this particular electrolyte.
Chemically polished tantalum was anodized in 0.002 M HNO$_3$ at 60°C at constant current of 500 μA/cm$^2$ and held at the formation voltage “about” two hours.[145] Spectra were collected at varying formation voltages (30-200V) and compared to the native oxide.

At formation voltages up to 100V, absorption peaks are observed at 1050 and 810cm$^{-1}$. Significant changes in the IR reflectance spectra are seen when the formation voltage exceeds 100 V; the width of the absorption band near 1100 cm$^{-1}$ narrows, and the 1050cm$^{-1}$ peak shifts to 950 cm$^{-1}$. The band at 810 cm$^{-1}$ also shifts to a lower frequency. [145] The implicit assumption in these measurements is that the infrared signal is not limited by the thickness of the oxide films, i.e., the theoretical sampling depth is significantly greater than the oxide thickness.

By considering the change in peak heights at different formation voltages (Figure 2-49), the authors conclude that when the formation voltage exceeds 100 V, only the growth of outer oxides can be observed. [145] This conclusion is not in agreement with the conventional growth models of anodic tantala; further investigation of this description is prescribed.
Figure 2-49: Optical density at different frequencies versus formation voltage.[145]

A more thorough investigation by the same authors was subsequently undertaken.[115, 140] As shown in Figure 2-50, a broad band in the FT-IR reflectance spectra is observed from 1000 – 700 cm\(^{-1}\) which corresponds to tantalum oxide. The authors resolve the broad Ta-O band into three components[140]; however, this procedure seems arbitrary and not based on chemical reasoning. A smaller absorption band occurs from 1200-1000 cm\(^{-1}\) when anodization is completed in phosphoric acid; thus the band is attributed to incorporated phosphate. It is noted that the authors plot the x-axis from low wavenumbers to high wavenumbers; this is opposite of conventional IR data presentation and is noted so as to reduce confusion when it is compared to other figures.
Figure 2-50: FT-IR spectra showing how the broad Ta-O band is deconvolved into three component bands. The phosphorus related band occurs at 1100 cm$^{-1}$.[140]

The spectra reported for oxide formed in dilute HNO$_3$ show absorption around 1100 cm$^{-1}$ [145]. However, in a subsequent paper the same authors report that the 1100 cm$^{-1}$ is only observed when the anodizing electrolyte contains phosphate, phosphonate, or phosphinate.[140] This author is aware that FT-IR reflectance is sensitive to low concentrations of phosphoric acid in the electrolyte; if the electrochemical cell is not sufficiently cleaned after anodization in dilute phosphoric acid, the PO$_4^{3-}$ band is observed for oxides formed in Na$_2$SO$_4$. If however, the small peak observed is characteristic of anodization in dilute HNO$_3$, it suggests that there could be a different explanation for the origin of the 1100 cm$^{-1}$ peak, i.e., it may not be related to (PO$_4$)$^{3-}$ vibrations but could possibly indicate a Ta-O mode that occurs when (PO$_4$)$^{3-}$ groups are present in the film. It is recognized that the 1100 cm$^{-1}$ peak is assumed to be related to
(PO₄)³⁻ vibrations, but it is conceivable that different bonding configurations could be responsible.

As seen in Figure 2-51, intensities of the two Ta-O bands, (925 and 800 cm⁻¹) increase with formation voltage. The rates of their increase, however, change in the 70-90V region where the rates become slower, and the rate of change for the phosphorus related peak increases at a faster rate.[140] Again, interpretation of these results are straightforward if it is assumed that all of the oxide is equally sampled; however, if the measured IR signal depends on the depth of the phonon-IR interaction, interpretation of the signal becomes complicated. Figure 2-52 shows a logarithmic dependence of the phosphorus concentration with oxide thickness; the dependence on electrolyte concentration is also shown.
Figure 2-51: Optical density of absorption bands versus oxide thickness and formation voltage. Data for the phosphorus related peak (1110 cm\(^{-1}\)) is shown for three different concentrations of electrolyte.[140]
Figure 2-52: Quadratic plot of the phosphorus related peak at different formation voltages.[140]

Further investigations of the multi-layer structure were made by successively stripping controlled thicknesses of oxide and taking reflectance IR spectra. Tantalum substrates were chemically polished and anodized at a constant current density of 1.0 mA/cm² in 0.01N H₃PO₄ at 20 °C. The applied formation voltage was removed as soon as the intended voltage was achieved; there was no hold time at the formation voltage. Films
were anodized to a given thickness and then chemically stripped using 7M NH₄HF₂ at 60°C.[115]

The authors conclude that the oxide contains three distinctive layers; the innermost layer is uniform regardless of the formation voltage, but phosphate ions are incorporated in the middle and outermost layers.[115] The three layers grow from the initial formation voltage, and the growth rate for the layers are “nearly equal.”[115] For formation voltages below 100V, the middle layer has a constant chemical structure, but above 100V “its chemical structure changes with voltage” The chemical structure of the thin, outermost layer varies at all formation voltages.[115] It is noted that the tri-layer description is unique to this group of researchers; generally a bi-layer description of the oxide is reported.

For sufficiently thin films the etching rate of the NH₄HF₂ solution was found to be constant so that the thickness stripped off was proportional to the immersion time, indicating that the film was uniform. For thicker films, however, the rate changed at two immersion times, which suggests that the film was composed of three layers with different chemical properties.[115] The profiles for films formed to 100V (165nm) and 300V (497 nm) are shown below in Figure 2-53 and Figure 2-54, respectively. Table 2-23 shows the thickness of each layer for anodization at 50V, 100V, and 300V. The refractive indices and dissolution rates in the etching solution are shown in Table 2-24.
Figure 2-53: Optical density quantified for Ta-O modes (925 and 800 cm$^{-1}$) and for the P-O mode (1110 cm$^{-1}$) using IR reflectance spectroscopy. The depth profiles of an oxide anodized to 100V was determined be successively etching the oxide and collecting IR spectra.[115]
Figure 2-54: Optical density quantified for Ta-O modes (925 and 800 cm\(^{-1}\)) and for the P-O mode (1110 cm\(^{-1}\)) using IR reflectance spectroscopy. The depth profiles of an oxide anodized to 300V was determined by successively etching the oxide and collecting IR spectra.[115]
Table 2-23: Summary of the layer thicknesses and (% of the total oxide thickness) for tri-layered oxide samples anodized to 50, 100, and 300V.[115]

<table>
<thead>
<tr>
<th>Formation Voltage, V</th>
<th>Total Thickness, nm</th>
<th>Outer Layer Thickness, nm</th>
<th>Middle Layer Thickness, nm</th>
<th>Inner Layer Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>83</td>
<td>8 (10%)</td>
<td>29 (35%)</td>
<td>46 (55%)</td>
</tr>
<tr>
<td>100</td>
<td>165</td>
<td>18 (11%)</td>
<td>59 (36%)</td>
<td>88 (53%)</td>
</tr>
<tr>
<td>300</td>
<td>497</td>
<td>32 (6.4%)</td>
<td>225 (45%)</td>
<td>240 (48%)</td>
</tr>
</tbody>
</table>

Table 2-24: Refractive indices (\(\eta\)) and dissolution rates of the layers of oxide formed in 0.01 N H\(_3\)PO\(_4\).[115]

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Inner</th>
<th>Middle</th>
<th>Outer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\eta)</td>
<td>Diss rate, nm/min</td>
<td>(\eta)</td>
</tr>
<tr>
<td>50</td>
<td>n/a</td>
<td>0.040</td>
<td>2.12</td>
</tr>
<tr>
<td>100</td>
<td>n/a</td>
<td>0.035</td>
<td>2.10</td>
</tr>
<tr>
<td>300</td>
<td>n/a</td>
<td>0.033</td>
<td>2.09</td>
</tr>
<tr>
<td>Average</td>
<td>0.036±0.004</td>
<td>2.10±0.02</td>
<td>0.0377±0.0005</td>
</tr>
</tbody>
</table>

2.6.1.3 Determination of crystal structure from IR spectra

The crystalline structure of metal oxides can be inferred by examining the low frequency region \((700-240 \text{ cm}^{-1})\) of the IR spectra.[146] The sensitivity of this measurement is illustrated by Figure 2-55, which compares spectra of the anatase and rutile phases of TiO\(_2\).[146] Descriptions of the peaks observed for \(\alpha\) and \(\beta\) phases of Ta\(_2\)O\(_5\) are given in Table 2-25 and Table 2-26, respectively; the peaks from the \(\alpha\) spectra are poorly defined. It should be noted that the IR signal drops rapidly with decreasing frequency. Thus,
sample requirements for these measurements are more stringent than for spectroscopy at higher frequencies.

**Figure 2-55:** Low frequency IR can be used to distinguish crystallographic phases of metal oxides. Spectra of rutile and anatase TiO$_2$ are shown as an example above.[146]

**Table 2-25:** Description of the absorption bands for $\alpha$ Ta$_2$O$_5$.[146]

<table>
<thead>
<tr>
<th>Peak, cm$^{-1}$</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>612</td>
<td>Strong, very broad</td>
</tr>
<tr>
<td>450</td>
<td>Broad shoulder</td>
</tr>
<tr>
<td>300</td>
<td>medium</td>
</tr>
</tbody>
</table>
Table 2-26: Description of the absorption bands for $\beta$ Ta$_2$O$_5$; the bands are poorly defined.[146]

<table>
<thead>
<tr>
<th>Peak, cm$^{-1}$</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>575</td>
<td></td>
</tr>
<tr>
<td>455</td>
<td>Shoulder</td>
</tr>
<tr>
<td>315</td>
<td></td>
</tr>
</tbody>
</table>

When interpreting IR spectra as a function of processing conditions, authors typically use XRD (X-ray diffraction) to confirm phase changes in the oxide, thus providing strong evidence that changes in the IR absorption spectra are due to bonds forming a particular crystalline structure. However, it is noted that deposition techniques, such as sol-gel, sputter depositing, or CVD, can result in impure oxide films. So, it is possible that some of the changes observed on annealing could also be attributed to the removal or chemical conversion of impurities.

Transmission IR spectra of MO-CVD films deposited at various temperatures were compared to reference spectra of polycrystalline $\beta$ Ta$_2$O$_5$ as shown in Figure 2-56[118]. Broad peaks from the reference oxide are observed at 595, 745, 830, and 885 cm$^{-1}$. The spectra are noticeably dependent on the deposition temperature, thus indicating that IR spectroscopy is sensitive to physical and/or chemical differences sensitive to MO-CVD deposition parameters. The onset of absorbance for the deposited films circa 1100 cm$^{-1}$ starts at a higher frequency with a more gradual onset when compared to the standard spectra. Although not discussed by these authors, similar observations have prompted others to speculate that this higher frequency absorption is due to the presence of sub-oxides. In a similar study, tantalum pentoxide was deposited by photo-induced CVD as a function of deposition temperature, and the effect of UV annealing at 400°C was examined. Absorption bands observed in the 800-400 cm$^{-1}$ region were attributed to Ta—O—Ta and Ta—O stretching modes. The weaker absorption bands observed at 1000-800 cm$^{-1}$ were attributed to the TaO and TaO$_2$ sub-oxides. This assumption was
made using Weltner & McLeod[134] experiments on gaseous TaO and TaO$_2$ molecules at temperatures approaching absolute zero.

**Figure 2-56:** After[118] Transmission spectra of $\beta$ Ta$_2$O$_5$ standard compared to spectra from MO-CVD oxides deposited at either 473K or 773K.[118] The relative scale for the different specimens is arbitrary.
Significant changes were observed in the transmission FT-IR spectra from 1100-100 cm\(^{-1}\) for 10 nm and 100 nm Ta\(_2\)O\(_5\) CVD films deposited on silicon substrates then annealed to 600°C (amorphous) and 800°C (crystalline) in an O\(_2\) ambient.[144] Zhang, et.al., also studied CVD films deposited on silicon wafers; a UV annealing step resulted in the formation of an interfacial SiO\(_2\) layer as measured by XPS and FT-IR.[147] UV annealing also reduces the amount of sub-oxide, oxygen vacancies, and the defect density in the films.[147] The effect of annealing the oxides is illustrated by Figure 2-57; several other authors have observed a similar change in the spectra from \(\approx1100\)-800 cm\(^{-1}\) upon annealing. This change is typically attributed to a reduction in sub-oxides, but it could also be related to the removal or conversion of impurities.

**Figure 2-57**: Infrared spectra of CVD oxide films on silicon. An interfacial SiO\(_2\) layer forms upon annealing and the sub-oxides of tantalum are oxidized. [147]
2.6.2 Ellipsometry of Tantalum Oxide

2.6.2.1 General Discussion of Ellipsometry and Optical Constants

Spectroscopic ellipsometry can be used to simultaneously determine the complex dielectric function and thickness of a material. A typical experimental ellipsometry setup is shown in Figure 2-58 the incident beam is defined by a p-wave, which oscillates parallel to the plane of incidence, and an s-wave, which oscillates perpendicular to the plane of incidence.

![Schematic of an ellipsometry experiment showing the orientation between the source, specimen, and detector.](image)

**Figure 2-58:** Schematic of an ellipsometry experiment showing the orientation between the source, specimen, and detector.

The phase difference between the incident s and p waves is termed \( \delta_1 \). After the beam interacts with the sample, the p and s components exhibit a different phase shift, \( \delta_2 \). The change in the phase shift, \( \Delta \), is a key ellipsometric parameter and is given by[148]:

\[
\Delta = \delta_1 - \delta_2
\]

[2-51]

The other key ellipsometric parameter describes how the intensity of the beam changes after interacting with a material. The reflection condition, \( r \), is defined as[148]
\[ r \equiv \frac{\text{Amplitude of the Outgoing Wave}}{\text{Amplitude of the Incoming Wave}} \]  

and the experimentally measured value is, \( \Psi \), which is given by [148]

\[ \tan \Psi = \frac{|r^p|}{|r^s|} \]  

[2-53]

where \( r^p \) and \( r^s \) are the reflection conditions for the \( p \) and \( s \) components.

The complex reflectance ratio is given as [148]

\[ \rho = \frac{R_p}{R_s} = \tan \Psi e^{j\Delta} \]  

[2-54]

Which is related to the pseudo dielectric \( \langle \varepsilon \rangle \) function using an ambient substrate model [149]

\[ \langle \varepsilon \rangle = \varepsilon_a \left( \frac{1-\rho}{1+\rho} \right)^2 \sin^2 \Phi + \cos^2 \Phi \tan^2 \Phi \]  

[2-55]

Where \( \varepsilon_a \) is the ambient dielectric function and is equal to one and \( \Phi \) is the incident angle used in the experiment. Thus the dielectric response of a system is easily determined from an ellipsometry spectrum. In order to extract a physical description of the material under study it is necessary to build a model and optimize it to a set of measured spectra. Spectra may be collected at several incident angles.

The relationship between the indices of refraction and dielectric functions are shown below [150]. The terms are defined in Table 2-27.
Table 2-27: Terms for relating the index of refraction and the complex dielectric function.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Complex index of refraction</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Real index of refraction</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>(\varepsilon_1)</td>
<td>Real component of dielectric function</td>
</tr>
<tr>
<td>(\varepsilon_2)</td>
<td>Imaginary component of dielectric function</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Complex dielectric function</td>
</tr>
<tr>
<td>(\sigma_r)</td>
<td>Real optical conductivity</td>
</tr>
<tr>
<td>(\omega)</td>
<td>Light wave frequency</td>
</tr>
</tbody>
</table>

The complex index of refraction, \(N\) is defined as

\[
N = \eta + i \kappa = \sqrt{\varepsilon_1 + i \frac{4\pi\sigma_r}{\omega}} \quad [2-56]
\]

which is related to the complex dielectric function,

\[
\varepsilon = N^2 = \varepsilon_1 + i \frac{4\pi\sigma_r}{\omega} \quad [2-57]
\]

where \(\sigma_r\) is the real optical conductivity, and \(\omega\) is the frequency of the light.

The real component of the dielectric function depends on the refractive index, \(\eta\), and the extinction coefficient, \(\kappa\):

\[
\varepsilon_1 = \eta^2 + \kappa^2 \quad [2-58]
\]
as does the imaginary component

$$\varepsilon_2 = \frac{4\pi\sigma_r}{\omega} = 2\eta\kappa \quad [2-59]$$

The refractive index and extinction coefficient can be expressed in terms of the dielectric function by rearranging the above equations.

$$\eta = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}} \quad [2-60]$$

$$\kappa = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}} \quad [2-61]$$

The polarization of a bulk solid, $P$, can be expressed as the sum of the polarizations due to all constituent atoms

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{\text{local}}(j) \quad [2-62]$$

Where $N_j$ is the concentration and $\alpha_j$ is the polarizability of the atoms, $j$, and $E_{\text{loc}}(j)$ is the local field at atom sites $j$. The Clausius-Mossotti relation allows one to infer the dielectric constant from the electronic polarizability and, in CGS units, is given by:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum N_j \alpha_j \quad [2-63]$$
Since the polarizability, $\alpha$, is an atomic parameter, the role of incorporated phosphorus in determining the bulk dielectric function can be determined if the volume fraction of phosphorus is known. The polarizabilities of atoms in oxides have been compiled by R.D. Shannon[151], and the values relevant for anodic tantala are shown in Table 2-28 below.

### Table 2-28: Polarizabilities of relevant species in oxides.[151]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Polarizability, $\alpha$, Å$^3$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^{2-}$</td>
<td>2.01</td>
<td>0.005</td>
</tr>
<tr>
<td>OH$^-$.</td>
<td>2.27</td>
<td>0.010</td>
</tr>
<tr>
<td>P$^{+5}$.</td>
<td>1.22</td>
<td>0.005</td>
</tr>
<tr>
<td>Ta$^{+5}$.</td>
<td>4.73</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Assuming that the frequency used for our IR and SE experiments is sufficiently high, we can neglect the dipolar and ionic contributions to the polarizability; under this condition, the dielectric constant depends only on the electronic polarizability, and the Clausius-Mossotti relation can be expressed as

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{4\pi}{3} \sum N_j \alpha_j$$  \[2-64\]

where $\eta$ is the refractive index.

The theory described above was developed for crystalline materials, and it is assumed that it can be extended to amorphous solids.
2.6.2.2 Optical Properties of Anodic Tantalum Oxide

The optical properties of tantalum oxide have been measured for oxides grown by a wide array of thin film deposition techniques, and the growth processing conditions invariably affect the properties of the oxide. The properties of oxides formed by anodic oxidation are discussed first. A summary of the refractive index measured by ellipsometry on anodized tantalum oxide is shown in Table 2-29 and the effect of anodizing electrolyte is shown in Table 2--30. The refractive index of the film varies with the growth rate, temperature, and electrolyte. Table 2-31 demonstrates the effects of temperature and formation current density on the refractive index of anodic tantala formed in dilute sulphuric acid.[152] Table 2—32 summarizes reported values for the complex refractive index of metallic tantalum.
**Table 2-29:** Summary of optical properties of anodic tantalum oxide prepared under different experimental conditions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Electrolyte</th>
<th>Formation V Thickness</th>
<th>Refractive index</th>
<th>Notes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChemPol → MechPol → Electropolish</td>
<td>0.2 N H₂SO₄</td>
<td></td>
<td>2.269; See next table</td>
<td>Thin outer absorbing layer</td>
<td>[152]</td>
</tr>
<tr>
<td>ChemPol → MechPol → Electropolish</td>
<td>Conc H₂SO₄</td>
<td></td>
<td>2.16 -0.024i</td>
<td></td>
<td>[152]</td>
</tr>
<tr>
<td>ChemPol → MechPol → Electropolish</td>
<td>0.2 N H₂SO₄ 25°C, 60°C</td>
<td>&gt;90V ; 10 mA/cm²</td>
<td>2.21 @ 5461Å</td>
<td>In-situ ellipsometry.</td>
<td>[153]</td>
</tr>
<tr>
<td>Sputtered Ta</td>
<td>0.01% Citric Acid</td>
<td>0.1 - 10 mA/cm²</td>
<td>2.22 ; ε = 26.7 @ 1kHz</td>
<td></td>
<td>[109]</td>
</tr>
<tr>
<td>Single Xstal Mech Polish, Electropolish</td>
<td>0.1M H₂SO₄ 25°C</td>
<td>48 μA/cm² to 250V</td>
<td>2.203 ± 0.005</td>
<td>Incorporated S, no effect on optical properties</td>
<td>[154]</td>
</tr>
<tr>
<td>Chem Polish</td>
<td>0.2N H₂SO₄ 25.8°C</td>
<td>10mA/cm²</td>
<td>2.14 + 0.292/λ/Å - 2.305</td>
<td></td>
<td>[155]</td>
</tr>
<tr>
<td>Chemically Polished</td>
<td>0.2 N H₂SO₄ 23°C</td>
<td></td>
<td></td>
<td>Uniform</td>
<td>[156]</td>
</tr>
<tr>
<td>Single Xstal Electropolish</td>
<td>0.2 N H₂SO₄</td>
<td></td>
<td>2.195 (no field)</td>
<td>Uniform</td>
<td>[157]</td>
</tr>
</tbody>
</table>
Table 2-30: Influence of the forming electrolyte on the refractive index of anodic tantalum oxide as measured by ellipsometry.[35] Films are grown to 0.1 C/cm² passed current at 25°C on substrates that were chemically polished, then electrochemically polished and then vacuum annealed.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>2.19</td>
</tr>
<tr>
<td>0.001M H₃PO₄</td>
<td>2.19</td>
</tr>
<tr>
<td>0.01 M H₃PO₄</td>
<td>2.22</td>
</tr>
<tr>
<td>0.1 M H₃PO₄</td>
<td>2.21</td>
</tr>
<tr>
<td>1 M H₃PO₄</td>
<td>2.21</td>
</tr>
<tr>
<td>10 M H₃PO₄</td>
<td>2.16</td>
</tr>
<tr>
<td>14.7 M H₃PO₄</td>
<td>2.11</td>
</tr>
</tbody>
</table>

Table 2-31: Refractive index as a function of temperature and growth rate for anodization in sulfuric acid. [152]

<table>
<thead>
<tr>
<th>Film Thickness</th>
<th>Electrolyte</th>
<th>Temperature</th>
<th>Growth Rate</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950 ± 10Å</td>
<td>0.2 N H₂SO₄</td>
<td>Room</td>
<td>25 mA/cm²</td>
<td>2.269 ± 0.001</td>
</tr>
<tr>
<td>1950 ± 10Å</td>
<td>0.2 N H₂SO₄</td>
<td>Room</td>
<td>0.025 mA/cm²</td>
<td>2.286 ± 0.003</td>
</tr>
<tr>
<td>1948 ± 3Å</td>
<td>0.2 N H₂SO₄</td>
<td>0° C</td>
<td>25 mA/cm²</td>
<td>2.264 ± 0.001</td>
</tr>
<tr>
<td>1948 ± 3Å</td>
<td>0.2 N H₂SO₄</td>
<td>94.5°C</td>
<td>25 mA/cm²</td>
<td>2.276 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Concentrated H₂SO₄</td>
<td></td>
<td></td>
<td>2.16 - 0.024i</td>
</tr>
</tbody>
</table>
Table 2-32: Complex index of refraction of various tantalum substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Complex index of refraction</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtered β (tetragonal)</td>
<td>3.43 – 3.66i</td>
<td>[109]</td>
</tr>
<tr>
<td>Sputtered α (BCC)</td>
<td>2.90 – 2.41i</td>
<td>[109]</td>
</tr>
<tr>
<td>Single Crystal, Mechanical &amp; Electropolished</td>
<td>2.47 – 2.573i</td>
<td>[154]</td>
</tr>
<tr>
<td>Chem → Mech → Electropolish</td>
<td>3.30 (±0.02) – 2.22 (±0.02)i</td>
<td>[153]</td>
</tr>
<tr>
<td>Single Crystal, Electropolished</td>
<td>2.46 – 2.573i</td>
<td>[157]</td>
</tr>
</tbody>
</table>

Although the refractive index is often reported as a constant, it is a function of the energy of the incident beam and has been reported as a function of wavelength by Young[155], Vermilyea[7], Charlesby[158], and Waber[159]. Young has given the empirical Hartmann equation for films anodized at 10 mA/cm² at 25°C as

\[
\eta = 2.14 + 0.292 \left[ \frac{\lambda}{10^3 A} - 2.305 \right] \tag{2-65}
\]

Oxides formed in dilute (0.2 N) sulfuric acid demonstrate a thin outer layer of absorbing oxide which may be only a few angstroms thick.[152] The bulk of the oxide is homogenous and non-absorbing.[152] For films formed in concentrated sulfuric acid, a large fraction of the film is absorbing and thick oxides are not homogenous. It has been well documented that a bi-layer oxide structure forms when anodization is completed in concentrated H₂SO₄.[54] The absorption index of oxides formed in such electrolytes is “about equal” to the index for the thin absorbing layer observed for anodization in dilute sulfuric acid.[152]

Smith and Young confirmed that films grown in dilute sulphuric acid do not indicate an optical bi-layer structure.[154] From their analysis, it seems that although SO₄⁻² species
are incorporated, they do not have a substantial effect on the optical properties at the 0.1 M H₂SO₄ electrolyte concentration considered.[154]

In contrast to anodization in dilute H₂SO₄, oxides formed in dilute H₃PO₄ show changes in the optical properties due to the incorporated phosphorus. Dell’Oca, et.al., attempted to fit ellipsometry data to a model with a graded phosphorus concentration profile, but it was determined that a distinct bi-layer structure simulated the experimental data more satisfactorily.[52] Substrates that were a.) mechanically polished and dipped in 48% HF, b.) electropolished or c.) mechanically polished and then electropolished exhibited the same effect.[52]

Oxide formed in 0.2N H₂SO₄ is isotropic and homogeneous at zero field but is optically anisotropic when a field is applied.[154, 157] In situ ellipsometric measurements during the galvanostatic oxidation of tantalum, niobium, and tungsten show that both the refractive index and the thickness of the oxide change suddenly on changing the current applied to the film.[89] For all three metals, the thickness increases linearly with the electric field, whereas both the refractive index and the dielectric constant at 1000Hz were found to decrease linearly with increasing field. It is concluded that these changes are due to the variation in the density of the film with the applied field.[156] Cornish, et.al., have confirmed that the thickness increases as the refractive index decreases and the oxide becomes birefringent under an applied electric field.[157] The ordinary and extraordinary refractive indices are reduced according to the square of the field.[157] Representative data of the effect of applied field on the oxide thickness and refractive index vs. time is shown in Figure 2-59.
Figure 2-59: After [157] Change in thickness (ΔD) and refractive index (Δη), vs. time for an oxide thickness of 236.5 nm to which a field of 5.07*10^2 MV/m was applied at t=0. An increase in oxide thickness is concurrent with a decrease in the refractive index when a field is applied to a formed oxide.

2.6.2.3 Optical Properties of Tantalum Oxide not Grown by Electrochemical Means

A fair amount of literature exists on the optical characterization of tantalum oxide deposited by various chemical and physical thin film deposition techniques. The properties of the oxide depend on parameters such as porosity, incorporated impurities, deposition temperature, non-stoichiometry, and annealing conditions. A correlation between reduced oxygen content and reduced refractive index has been observed for plasma enhanced-CVD oxide films.[160] Oxides formed by ion beam sputtering exhibit the opposite effect, where oxygen deficient (sub-oxides) had a higher refractive index and substantially greater extinction coefficients[161]. The refractive index and extinction coefficient of MO-CVD Ta\textsubscript{2}O\textsubscript{5} films was measured at different deposition temperatures.[118]

The optical properties, including the dielectric function, of reactive rf-magnetron sputtered tantalum oxide were studied over the energy range of 0.03-8.5 eV (40µm-145 nm). The matrix of samples studied and their properties is given in Table 2-33; the effect
of annealing is reported for several specimens. The density of the film was varied by adjusting the growth temperature, oxygen partial pressure, and total gas pressure.\[162\] The as-deposited tantalum oxide was amorphous. Absorption began near 4.5 eV, and the material was transparent below this transition.\[162\] Absorption in the IR region around 3600 cm\(^{-1}\) was attributed to adsorbed water in the pores of the sputtered oxide. The refractive index varied from 2.04 to 2.16 depending on the growth conditions.\[162\] The thicknesses of the oxides were 175-465 nm.

A two layer model was constructed to simulate the oxide; the outer layer contains the surface roughness and the inner layer describes the dielectric properties of the oxide where the oxide contains pores filled with adsorbed water.\[162\] An effective medium approach (EMA) was used to model the theoretical spectra. The effective dielectric function of the oxide, \(\varepsilon\), was determined from\[162\]

\[
0 = f_m \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon} + (1 - f_m) \frac{\varepsilon_{Ta} - \varepsilon}{\varepsilon_{Ta} + 2\varepsilon} \tag{2-66}
\]

Where \(f_m\) is the volume fraction of water and \(\varepsilon_m\) and \(\varepsilon_{Ta}\) are the dielectric functions of adsorbed water and tantalum oxide, respectively. Spectra for \(\varepsilon_{Ta}\) were determined by “using a generalized parametric dielectric function model.”\[162\] The volume percentage of adsorbed water, \(f_m\), is significant to the interpretation of the results.

The optical properties of amorphous as deposited and annealed orthorhombic \(\beta\) Ta\(_2\)O\(_5\) were compared for rf sputtered thin films.\[163\] Upon annealing, the thickness of the oxide decreased by approximately 50nm, presumably due to densification.\[163\] The reviewer notes that annealing will likely result in an interfacial SiO\(_2\) layer. In the IR region, the transverse optical phonons (TO) shifted from 630 cm\(^{-1}\) for the amorphous oxide to 510 cm\(^{-1}\) for the crystalline beta phase; likewise, the longitudinal phonons (LO) shifted from 790 cm\(^{-1}\) to a considerably lower frequency.\[163\] The real (\(\varepsilon_1\)) and imaginary (\(\varepsilon_2\)) components of the dielectric function are shown for the amorphous oxide and polycrystalline \(\beta\) oxide in Figure 2-60.
Table 2-33: Deposition conditions and properties of rf-magnetron sputter deposited tantalum oxide films. Analysis was performed on oxides before and after annealing one hour at 700°C. Values shown in *italics* are obtained from IR-SE data analysis, whereas the other values are determined from NIR-VUV-SE data and AFM analysis.[162, 163]

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Deposition Conditions</th>
<th>Pre-Annealing Properties</th>
<th>Post-Annealing Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp °C</td>
<td>O₂ flow sccm</td>
<td>Total Pressure, mTorr</td>
</tr>
<tr>
<td>Ta1</td>
<td>20</td>
<td>4.5</td>
<td>15</td>
</tr>
<tr>
<td>Ta2</td>
<td>20</td>
<td>8.0</td>
<td>15</td>
</tr>
<tr>
<td>Ta3</td>
<td>100</td>
<td>4.5</td>
<td>15</td>
</tr>
<tr>
<td>Ta4</td>
<td>200</td>
<td>4.5</td>
<td>15</td>
</tr>
<tr>
<td>Ta5</td>
<td>20</td>
<td>4.5</td>
<td>17</td>
</tr>
</tbody>
</table>
Figure 2-60: Real, $\varepsilon_1$, and imaginary, $\varepsilon_2$, components of the dielectric function for amorphous and polycrystalline tantalum oxide.[163]
Chapter 3: Growth Laws of Bi-Layer Tantalum Oxide Formed in Dilute Phosphoric Acid

3.1. Experimental Procedures

3.1.1. Sputter Deposition

Sputter deposited substrates were fabricated using a Kurt J. Lesker CMS-18 deposition chamber. The starting substrates were Si(100) p-type, boron doped prime wafers obtained from Silicon Quest International.

3.1.1.1. Tantalum Substrates

In order to deposit tantalum on silicon substrates, it was necessary to first deposit a titanium (Ti) adhesion layer and platinum (Pt) and tantalum nitride (TaN) layers. The Ti, TaN, and Ta layers were deposited by rf-magnetron sputtering while the Pt layer was deposited using dc-magnetron sputtering. The target power, bias, and cathode current for Pt were 190W, 550V, and 298 mA. During the deposition of TaN the flow rate of N$_2$ was 2.3-2.5 sccm. Operating conditions during the depositions are summarized in Table 3-1 and Table 3-2. All deposition was done at room temperature, 19-22°C. The majority of anodization experiments were performed on substrates deposited as in Table 3-1 or Table 3—2, where the pressure during Ta deposition was 3 mTorr. The approximate tantalum thickness for the deposition conditions in Table 3-1 is 110 nm; in Table 3—2 it is 220 nm. A few Ta substrate layers were deposited at 5mTorr, as shown in Table 3-3. The pressure was reduced to 3mTorr for most depositions in hopes of increasing the achievable thickness. In reality, this likely led to a slower deposition rate and did not result in the achievement of a thicker tantalum film.
Table 3-1: Deposition conditions for fabricating ~110 nm tantalum substrates.

<table>
<thead>
<tr>
<th>Deposited Material</th>
<th>Pressure, mTorr</th>
<th>Ar Flow, sccm</th>
<th>Time, Sec</th>
<th>DC Bias, V</th>
<th>Forward Power, W</th>
<th>Reflected Power, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>5</td>
<td>16.5</td>
<td>300</td>
<td>303</td>
<td>288</td>
<td>10</td>
</tr>
<tr>
<td>Pt</td>
<td>2.5</td>
<td>7.5</td>
<td>600</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>TaN</td>
<td>5</td>
<td>15</td>
<td>1000</td>
<td>386</td>
<td>192</td>
<td>11</td>
</tr>
<tr>
<td>Ta</td>
<td>3</td>
<td>9</td>
<td>1500</td>
<td>370</td>
<td>192</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 3-2: Deposition conditions for fabricating ~220 nm tantalum substrates.

<table>
<thead>
<tr>
<th>Deposited Material</th>
<th>Pressure, mTorr</th>
<th>Ar Flow, sccm</th>
<th>Time, Sec</th>
<th>DC Bias, V</th>
<th>Forward Power, W</th>
<th>Reflected Power, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>5</td>
<td>18 ± 0.5</td>
<td>300</td>
<td>372 ± 3</td>
<td>285</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>Pt</td>
<td>2.5</td>
<td>9 ± 0.5</td>
<td>600</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>TaN</td>
<td>5</td>
<td>16 ± 0.5</td>
<td>1000</td>
<td>384 ± 3</td>
<td>190</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>Ta</td>
<td>3</td>
<td>10 ± 0.5</td>
<td>3000</td>
<td>367 ± 3</td>
<td>190</td>
<td>11 ± 1</td>
</tr>
</tbody>
</table>

Table 3-3: Alternate deposition conditions for fabricating substrates where the tantalum layer is thinner. The conditions for Pt were 195W, 561V, and 295 mA. The flow rate of N\textsubscript{2} was 2.3-2.5 sccm.

<table>
<thead>
<tr>
<th>Deposited Material</th>
<th>Pressure, mTorr</th>
<th>Ar Flow, sccm</th>
<th>Time, Sec</th>
<th>DC Bias, V</th>
<th>Forward Power, W</th>
<th>Reflected Power, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>5</td>
<td>18 ± 0.5</td>
<td>300</td>
<td>294 ± 2</td>
<td>290</td>
<td>11± 1</td>
</tr>
<tr>
<td>Pt</td>
<td>2.5</td>
<td>9 ± 0.5</td>
<td>600</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>TaN</td>
<td>5</td>
<td>17± 0.5</td>
<td>1000</td>
<td>390 ± 3</td>
<td>200</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>Ta</td>
<td>5</td>
<td>18 ± 0.5</td>
<td>1500</td>
<td>380 ± 3</td>
<td>200</td>
<td>11 ± 1</td>
</tr>
</tbody>
</table>

3.1.1.2 Gold Standard for IR
Infrared spectroscopy requires a reference spectrum in order to calculate the absorbance spectrum of a specimen. A gold standard was sputter deposited for this purpose, and the
deposition conditions are shown in Table 3-4. The Ti layer is deposited as an adhesive layer. The gold is expected to be 150 nm thick.

**Table 3-4:** Deposition conditions for sputtered Au standard.

<table>
<thead>
<tr>
<th>Deposited Material</th>
<th>Pressure, mTorr</th>
<th>Ar Flow, sccm</th>
<th>Time, Sec</th>
<th>DC Bias, V</th>
<th>Forward Power, W</th>
<th>Reflected Power, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>5</td>
<td>16.5 ± 0.5</td>
<td>320</td>
<td>312 ± 2</td>
<td>200</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>Au</td>
<td>2.5</td>
<td>16.5 ± 0.5</td>
<td>526</td>
<td>303</td>
<td>190</td>
<td>4 ± 1</td>
</tr>
</tbody>
</table>

### 3.1.2. Anodic Oxidation

#### 3.1.2.1. Formation in 0.1 M H₃PO₄

Anodic oxidation was performed in a model K0235 Princeton Applied Research flat cell. The counter electrode was a platinized mesh. A thin wire was used to make electrical contact to the front of the Ta substrate. A circular area of 1cm² was exposed to the electrolyte. The electrolyte was 0.1 M H₃PO₄. Oxides were formed using one of two different procedures:

1.) The voltage on a Hewlett Packard Model No. E3612A DC power supply was manually increased at a rate of 250 mV/seconds until the desired formation voltage was achieved. The current was not permitted to exceed 1mA/cm² during the voltage ramp. The formation voltage was maintained for 60 minutes

2.) The applied voltage was increased by automatically stepping the applied voltage 0.5V every 2 seconds using a Hewlett Packard 4140B pA/DC voltage source and then holding for 50 minutes at the formation voltage.

Samples were removed from the electrolyte and rinsed with deionized water. All experiments were done at room temperature unless otherwise noted.
3.1.2.2. Anodized Ta$_2$O$_5$ Standards

Tantalum oxide standards, which should be stoichiometric, free from incorporated electrolyte, and amorphous, were also made for comparison. They were anodized in either 0.1M Na$_2$SO$_4$ or 1.0M KCl to 70V and held at the formation voltage for two minutes; the samples were immediately rinsed and placed in boiling deionized water for eight minutes.

3.1.3. Transmission Electron Microscopy

3.1.3.1. Sample Preparation

Cross sectional TEM samples were prepared by bonding the faces of two oxide films together with G1 epoxy. The sandwich was then placed in a South Bay Technology clamp, placed on a hot plate, and heated to 150 $\pm$ 10° C for a minimum time of one hour. The samples were then mechanically thinned using a South Bay Technology Model 150C MC lapping and polishing fixture and 600 and 1200 grit SiC paper. A final polish was obtained using 1μm diamond paste on a sheet of standard photo copier paper. Each cross section sample was mechanically thinned to less than 20μm thick. A slotted copper grid was then affixed to the cross section using M-bond epoxy and placed on a hot plate at 150 $\pm$ 10°C for a minimum of one hour.

Samples were then loaded into a Fischione model 1010 dual gun ion mill such that the interface was perpendicular to the ion guns. A nitrogen cooled stage was used, and milling was never performed at stage temperatures greater than -90° C. It was necessary to use a cooling stage in order to prevent crystallization of the amorphous oxide.[164] The ion guns were initially set to 5kV and 5 mA, and the milling angle was 15°. The stage was rotated ± 15° about the sandwich interface. When it was judged that the specimen was nearing perforation at the interface, the ion guns were reduced to 3.5 kV.
and 3.0 mA with a milling angle of 8°. It is noted that the milling procedure was not strictly adhered to. The nature of TEM sample preparation requires the experimentalist to adjust conditions depending on the dimensions and milling behavior of each specimen.

### 3.1.3.2. Image Collection and Analysis

A JEOL 2010 transmission electron microscope (TEM) with a LaB$_6$ emitter was used for TEM imaging and for collecting electron diffraction patterns. Whenever possible, three separate regions of a cross sectioned oxide were examined for determining the thickness of the oxide layers. Due to the precarious uncertainty of TEM sample preparation, it was not possible always possible to find three electron transparent regions where the epoxy remained. For each area, five measurements of each layer’s thickness were made by drawing lines using Digital Micrograph version 1.81.78 software. The error bars for the thickness is the standard deviation of these measurements. The error is higher for samples that are less electron transparent. The standard deviation for the total oxide thickness is low; it is higher for the individual layers because the precise boundary between the inner and outer layers of oxide is difficult to define if the sample is not sufficiently electron transparent.

Digital Micrograph software is used to measure the transmitted intensity of the electron beam as a function of position. This intensity scales with the thickness of the prepared TEM specimen and also with the average atomic number, Z, of the material. The change in the average Z of the oxide due to phosphorus incorporation is noted by a change in the intensity of the transmitted electron beam.
3.1.4. Reflectance Fourier-Transform Infrared Spectroscopy

3.1.4.1. Spectra Collection

A Bruker IFS 66/S FT-IR spectrometer was used in conjunction with a Hyperion 3000 microscope to collect the infrared spectra. A 15X grazing angle objective having a numerical aperture of 0.4 and a working distance of 0.8 mm was used. The angle of incidence was approximately 80° with respect to the specimen’s normal direction, and the aperture was 150 μm X 150 μm. One thousand scans were collected at a resolution of 10 cm⁻¹. The reference spectrum was acquired using the sputtered gold substrate described in Table 3-4. For a few samples, the reference spectrum was taken from a CD₂(CD₂)₁₆S-Au self assembled mono-layer on gold. There was no significant change in the spectra for the two different reference substrates.

3.1.4.2. Spectra Processing

3.1.4.2.1. Evaluating Precision of Quantification Procedure

Quantitative processing of the infrared spectra was completed using OPUS 6.0 software published by Bruker Optik GmbH. It proved vital to develop a consistent method for subtracting the baseline prior to quantifying absorption bands. The experimental setup is capable of recording infrared spectra from 4000-600cm⁻¹, unfortunately the tail of absorption band attributed to Ta-O bonding frequencies extends beyond 600cm⁻¹, thus there is not any data to the right of the peak to use as a reference point for subtracting the baseline. In order to assess the precision and reproducibility of the procedure for quantifying data, three spectra were collected from three different areas of the same sample. The discussion below follows the analysis for an example specimen; this specimen was anodized to 70V at a rate of 250mV/sec in 0.1 M H₃PO₄ and held at 70V for 2 minutes. It was then boiled in deionized water for 8 minutes. The sample was
wiped with acetone, rinsed with ethanol, and blown dry with nitrogen prior to collecting
the spectra. The raw absorption spectra, prior to any manipulations, are shown in Figure
3-1.

![Figure 3-1: Three infrared spectra of a single tantalum oxide specimen. The oxide
thickness is approximately 120 nm.](image)

### 3.1.4.2.2. Background Subtraction

Initially, efforts were made to use a point circa 600 cm\(^{-1}\) in defining the baseline. This
procedure is termed “Baseline Subtraction Method I.” As shown in Figure 3-2, baseline
points were marked at 3750, 3500, 3000, 2500, 1600, and 1400 cm\(^{-1}\) and at the minimum
of the spectrum around 1200 cm\(^{-1}\) and at a point on the far right of the spectrum. A
second method of subtracting the baseline was termed “Baseline Subtraction Method II,”
and was defined using the points 3750, 3500, 3000, 2500, 1600, and 1400 cm\(^{-1}\) as shown
in Figure 3-3.
Figure 3-2: Demonstration of defining the baseline using a point to the right of the absorption band (top spectrum) and the resulting spectrum after baseline subtraction (bottom spectrum)
3.1.4.2.3. Quantification of IR Spectra

After baseline subtraction, the particulars of band quantification remain. Three methods of quantifying the data are explored: 1.) band height, 2.) band area, and 3.) curve fitting. Three spectra were acquired from different regions of the same specimen and used to calculate the average band height, band area, and the absolute standard deviation, σ, of these values. A curve fitting procedure was also explored as a method of quantification.

**Figure 3-3:** Demonstration of defining the baseline using Baseline Correction Method II (top spectrum) and the resulting spectrum after baseline subtraction (bottom spectrum).
3.1.4.2.3.1. Absorption Band Maxima

In calculating the error for the TaO/PO ratio, standard error propagation methods are used. The absolute standard deviation for a quotient is given by

\[
\sigma_y = y \sqrt{\left( \frac{\sigma_a}{a} \right)^2 + \left( \frac{\sigma_b}{b} \right)^2}
\]  

[3-1]

Where \( y \) is a function, ‘a’ and ‘b’ are the variables, and \( \sigma \) is the standard deviation.

The relative standard deviation is \( \sigma_y/y \). For ease of comparison, the relative standard deviation in percent is tabulated below and is defined as \( \sigma_y/y \times 100\% \). This value is labeled “Error, %” in the tables.

In determining the band height, the maximum of the 1000-750 cm\(^{-1}\) and 1200-1050 cm\(^{-1}\) are simply read from the baseline corrected spectra. The results are compiled in Table 3-5 for both methods of background subtraction.

<table>
<thead>
<tr>
<th>Table 3-5a: Peak height results using Baseline Subtraction Method I.</th>
<th>Table 3-5b: Peak height results using Baseline Subtraction Method II.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td>0.169</td>
</tr>
<tr>
<td><strong>( \sigma )</strong></td>
<td>0.001</td>
</tr>
<tr>
<td><strong>Error, %</strong></td>
<td>0.770</td>
</tr>
</tbody>
</table>

| **Average** | 0.0346 | 0.0353 |
| **\( \sigma \)** | 0.0003 | 0.0002 |
| **Error, %** | 0.928 | 0.68 |

| **Average** | 0.205 | 0.204 |
| **\( \sigma \)** | 0.002 | 0.001 |
| **Error, %** | 1.2 | 0.69 |
3.1.4.2.3.2. Integrated Area of Absorption Bands

In calculating the area of the absorption bands, two methods of defining the area were used. The two methods, ‘A’ and ‘B’ are defined in Table 3-6. Examples of the integrated areas for the two methods are shown in Figure 3-4 and the results are given in Table 3-7 (Baseline Subtraction Method I) and Table 3-8 (Baseline Subtraction Method II).

Table 3-6: Definitions for calculating the integrated area of the Ta-O and P-O absorption bands.

<table>
<thead>
<tr>
<th>Schematic Description</th>
<th>Method A</th>
<th>Method B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
<td>The frequency limits are defined and the integration is between the absorption band and the abscissa.</td>
<td>The frequency limits are defined, and a straight line is drawn between the limits. The integration is between the absorption band and the straight line.</td>
</tr>
<tr>
<td>Ta-O Frequencies</td>
<td>1060-690 cm⁻¹</td>
<td>1060-690 cm⁻¹</td>
</tr>
<tr>
<td>P-O Frequencies</td>
<td>1240-1070 cm⁻¹</td>
<td>1210-1070 cm⁻¹</td>
</tr>
</tbody>
</table>
Figure 3-4a: Depiction of the integrated area of the P-O and Ta-O absorption bands using Method A

Figure 3-4b: Depiction of the integrated area of the P-O and Ta-O absorption bands using Method B

Figure 3-4: Definition of absorption bands for calculating the integrated area.

Table 3-7: Integrated area of absorption bands using Baseline Subtraction Method I and either A or B type integration windows.

<table>
<thead>
<tr>
<th></th>
<th>Ta-O Area</th>
<th>P-O Area</th>
<th>TaO/P-O Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>38.8</td>
<td>3.46</td>
<td>0.089</td>
</tr>
<tr>
<td>σ</td>
<td>0.4</td>
<td>0.03</td>
<td>0.001</td>
</tr>
<tr>
<td>Error, %</td>
<td>0.932</td>
<td>0.991</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ta-O Area</th>
<th>P-O Area</th>
<th>TaO/P-O Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>31.5</td>
<td>0.910</td>
<td>0.0289</td>
</tr>
<tr>
<td>σ</td>
<td>0.1</td>
<td>0.005</td>
<td>0.0002</td>
</tr>
<tr>
<td>Error, %</td>
<td>0.34</td>
<td>0.56</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Table 3-8: Integrated area of absorption bands using Baseline Subtraction Method II and either A or B type integration windows.

Table 3-8a: Peak area results of integration method A and Baseline Subtraction Method II.

<table>
<thead>
<tr>
<th></th>
<th>Ta-O Area</th>
<th>P-O Area</th>
<th>TaO/P-O Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>40.7</td>
<td>3.47</td>
<td>0.0851</td>
</tr>
<tr>
<td>σ</td>
<td>0.1</td>
<td>0.02</td>
<td>0.0004</td>
</tr>
<tr>
<td>Error, %</td>
<td>0.26</td>
<td>0.44</td>
<td><strong>0.51</strong></td>
</tr>
</tbody>
</table>

Table 3-8b: Peak area results of integration method B and Baseline Subtraction Method II.

<table>
<thead>
<tr>
<th></th>
<th>Ta-O Area</th>
<th>P-O Area</th>
<th>TaO/P-O Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>31.5</td>
<td>0.895</td>
<td>0.0284</td>
</tr>
<tr>
<td>σ</td>
<td>0.1</td>
<td>0.007</td>
<td>0.0002</td>
</tr>
<tr>
<td>Error, %</td>
<td>0.35</td>
<td>0.78</td>
<td><strong>0.86</strong></td>
</tr>
</tbody>
</table>

3.1.4.2.3.3. Curve Fitting of Absorption Bands

Curve fitting was completed using the OPUS 6.0 software package published by Bruker Optik GmbH. An approximated spectrum was simulated by choosing appropriate peak positions, heights, and widths and then running a Levenberg Marquardt algorithm to optimize the model. The algorithm is capable of optimizing the Gaussian/Lorentian character of each component peak, however, allowing for the nature of the peaks to vary resulted in a greater deviation in the numerical descriptors of the peaks. Therefore, the peaks were set to be Gaussian. Figure 3-5 shows how one peak, “Peak 4” is used to define the P-O related band while the Ta-O band is comprised of three constituent absorption bands, labeled as “Peaks 1-3.” The average maximum, standard deviation, and percent error are reported for each individual peak and for ratios of peak 4 to each of the other three peaks in Table 3-9.
**Figure 3-5:** Depiction of the four component peaks used to simulate the experimental spectrum.

**Table 3-9:** Curve fitting results for spectra processed with two different baseline subtractions. Quantification results are given for the four peaks in Figure 3—5 and for the ratio of peak 4 to each of the other peaks.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Average</th>
<th>σ</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>0.01</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.01</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>0.157</td>
<td>0.004</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>0.0353</td>
<td>0.0006</td>
<td>1.6</td>
</tr>
<tr>
<td>4/1</td>
<td>0.30</td>
<td>0.03</td>
<td>10</td>
</tr>
<tr>
<td>4/2</td>
<td>0.35</td>
<td>0.5</td>
<td>14</td>
</tr>
<tr>
<td>4/3</td>
<td>0.225</td>
<td>0.006</td>
<td>2.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Average</th>
<th>σ</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.156</td>
<td>0.003</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>0.034</td>
<td>0.004</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>0.160</td>
<td>0.003</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>0.0363</td>
<td>0.0006</td>
<td>1.6</td>
</tr>
<tr>
<td>4/1</td>
<td>0.233</td>
<td>0.006</td>
<td>2.6</td>
</tr>
<tr>
<td>4/2</td>
<td>1.1</td>
<td>0.1</td>
<td>12</td>
</tr>
<tr>
<td>4/3</td>
<td>0.227</td>
<td>0.005</td>
<td>2.3</td>
</tr>
</tbody>
</table>

### 3.1.4.2.3.4. Summary of Quantification Methods

The most precise method of quantifying the amount of phosphorus relative to the amount of total oxide is to use Baseline Subtraction Method II and then manually note the maximum height of the broad absorption bands. However, there is less uncertainty in the phosphorus related peak for the procedures that use (Baseline Subtraction Method I and peak area B) or (Background Subtraction Method II and peak area A)
Quantification of IR is done using Baseline Subtraction Method II and then integrating the absorption bands as shown in Figure 3-4A or by reading maxima of the two broad absorption bands. The curve fitting procedure was attempted due to its use by Kihara-Morishitu[115] however; it is not considered sufficiently precise. Although the height of Peak 4, the region associated with phosphorus incorporation, is relatively consistent, peaks 1-3 compete against each other when the optimization algorithm is run. This leads to inconsistent numerical values. Perhaps if the peak positions were fixed the optimization procedure would be more consistent.

3.1.4.2.3.5. Verification of the Precision

The procedures for quantification by band area integration and band maxima were verified for three additional oxides formed to 70 V but held for different anodization times. Table 3-10 shows the precision of the band maxima procedure while Table 3-11 shows the precision of the integrated area procedure. The standard deviation is determined by collecting and separately processing three spectra from different areas of each specimen.

Table 3-10: Precision of the band maxima procedure for the quantification of the Ta-O and phosphorus related absorption bands and of the ratio of the two bands for oxides formed to 70V in 0.1 M H₃PO₄ and held for various formation times.

<table>
<thead>
<tr>
<th>Anodization Time, min</th>
<th>Ta-O Height</th>
<th>Error, %</th>
<th>P-O Height</th>
<th>Error, %</th>
<th>TaO/PO Height</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.169 ± 0.001</td>
<td>0.77</td>
<td>0.03460 ± 0.0003</td>
<td>0.93</td>
<td>0.205 ± 0.001</td>
<td>0.69</td>
</tr>
<tr>
<td>90</td>
<td>0.1963 ± 0.0004</td>
<td>0.19</td>
<td>0.03959 ± 0.0002</td>
<td>0.41</td>
<td>0.2016 ± 0.0009</td>
<td>0.45</td>
</tr>
<tr>
<td>120</td>
<td>0.1977 ± 0.0004</td>
<td>0.18</td>
<td>0.0397 ± 0.0002</td>
<td>0.44</td>
<td>0.2009 ± 0.001</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Table 3-11: Precision of the band area procedure for the quantification of the Ta-O and phosphorus related absorption bands and of the ratio of the two bands for oxides formed to 70V in 0.1 M H$_3$PO$_4$ and held for various formation times.

<table>
<thead>
<tr>
<th>Anodization Time, min</th>
<th>Ta-O Area</th>
<th>Error, %</th>
<th>P-O Area</th>
<th>Error, %</th>
<th>TaO/PO Area</th>
<th>Error, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>38.8 ± 0.4</td>
<td>0.93</td>
<td>3.46 ± 0.03</td>
<td>0.99</td>
<td>0.0891 ± 0.0004</td>
<td>0.51</td>
</tr>
<tr>
<td>90</td>
<td>42.26 ± 0.08</td>
<td>0.18</td>
<td>4.02 ± 0.03</td>
<td>0.80</td>
<td>0.0867 ± 0.0007</td>
<td>0.82</td>
</tr>
<tr>
<td>120</td>
<td>46.76 ± 0.09</td>
<td>0.20</td>
<td>4.03 ± 0.02</td>
<td>0.62</td>
<td>0.0868 ± 0.0006</td>
<td>0.65</td>
</tr>
</tbody>
</table>

In conclusion, the background is subtracted by marking baseline points at 3750, 3500, 3000, 2500, 1600, and 1400 cm$^{-1}$. The background subtracted spectra are then quantified using one of two methods:

1.) The area between the absorbance curve and the x-axis is integrated between 1060-690 cm$^{-1}$ for the Ta-O band and between 1240-1070 cm$^{-1}$ for the P-O band.

2.) The band maximums are recorded for the two absorbance bands

Quantification by two methods provides confirmation of the results and partially mitigates systematic errors associated with data processing. The uncertainty in the P-O: Ta-O ratio determined from different areas of the same sample is less than 1% for either method. The uncertainty in the measured absorbance of the P-O or Ta-O bands is also less than 1% for either method.
3.2. Results

3.2.1. Transmission Electron Microscopy

3.2.1.1. Structural Characterization of the Tantalum Substrate and Oxide

The diffraction patterns shown in this section were collected at a camera length of 30 cm with 200keV electrons. Figure 3-6 shows the indexed electron diffraction pattern of silicon, which was used as an internal reference. Figure 3-7 shows the diffraction pattern when the selected area aperture was centered around the tantalum substrate; however, the aperture was not sufficiently small to exclude the diffracted beam from the neighboring TaN. Table 3—12 shows interplanar spacings calculated from the literature lattice constant \(a_0=0.33013\text{nm}\) of BCC tantalum along with the interplanar spacings measured from the sputter deposited tantalum substrate. The close agreement between the interplanar spacings indicates that the tantalum substrate is consistent with BCC tantalum; however, the possibility of other phases has not been disproven. Interpretation of the diffraction pattern is complicated by the presences of the underlying sputtered TaNx layer, which could have a range of chemistry and hence lattice constants. Figure 3-8 shows the diffraction pattern from tantalum oxide; the diffuse rings are indicative of amorphous oxide. The selected area aperture was too large to exclude the diffracted intensity from the tantalum substrate, which explains why the Ta (110) reflection is observed.
Figure 3-6: Indexed electron diffraction pattern of silicon substrate along the [110] zone axis.

Figure 3-7: Selected area diffraction pattern of tantalum and TaN layers of the substrate. The indexed spots are for BCC tantalum.
Figure 3-8: Selected area diffraction pattern of amorphous tantalum oxide and polycrystalline BCC tantalum.

Table 3-12: Comparison of literature lattice spacings for BCC tantalum \( (a_0=0.33013 \text{nm}) \) to lattice spacings determined from the diffraction pattern in Figure 3-7.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Literature, nm</th>
<th>Measured, nm</th>
<th>Absolute difference, nm</th>
<th>Spot or Ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.2335</td>
<td>0.2297</td>
<td>0.0038</td>
<td>Spot</td>
</tr>
<tr>
<td>200</td>
<td>0.1651</td>
<td>0.1618</td>
<td>0.0033</td>
<td>Ring</td>
</tr>
</tbody>
</table>

3.2.1.2. Contrast Difference between Inner and Outer Layers of Oxide

Tantalum oxide formed in phosphoric acid has a bi-layer structure where the inner oxide (at the metal interface) is \( \text{Ta}_2\text{O}_5 \) while the outer layer contains incorporated phosphorus. Bright-field imaging of transmission electron microscopy (TEM) cross sectioned samples allows for thickness measurement of the two distinct oxide layers.[92] When phosphorus is incorporated into a portion of the oxide, that region scatters the electrons less because the
scattering cross section of phosphorus is significantly less than the cross section of tantalum. The contrast change indicative of a bi-layer structure is not observed when anodization is done in 0.1M Na$_2$SO$_4$. Figure 3-9 shows cross sectional bright field micrographs of tantalum anodized to 70V and held for one hour in 0.1 M Na$_2$SO$_4$ (A) and in 0.1 M H$_3$PO$_4$ (B). The thickness of the anodized oxide is approximately 130 nm for both samples.

**Figure 3-9:** Bright field TEM images of sputter deposited tantalum anodized in either 0.1 M Na$_2$SO$_4$ (left image) or 0.1M H$_3$PO$_4$ (right image).
3.2.1.3. Intensity Profiles of Bright Field Images

For clarity it is necessary to differentiate two different “thicknesses;” the thickness of the formed anodic oxide, which is directly proportional to the formation voltage, is termed the oxide thickness. The thickness of a thinned cross-sectional TEM specimen is termed the specimen thickness; the specimen thickness is the distance the electron beam traverses as it passes through the specimen and is not a controlled variable.

Digital Micrograph software is used to measure the transmitted intensity of the electron beam. A large area of the image is selected using a rectangle tool, and the intensity is measured as a function of position within the rectangle. This intensity scales with the specimen thickness of the prepared TEM specimen and also with the average atomic number of the material. Thus, if the specimen thickness is not uniform, the contrast profile may be dominated by the change in the specimen thickness, and the intensity change due to a change in average atomic number may be difficult to measure.

Figure 3-10 shows an intensity profile of 130 nm of Ta$_2$O$_5$ formed in Na$_2$SO$_4$; the sample is wedge-shaped and thinner at the oxide/epoxy interface than it is at the oxide/metal interface. The gradient in the intensity is attributed to a gradient in the specimen thickness.

Figure 3-11 shows the intensity profile when a bi-layer oxide is imaged. It has been published that the visual boundary, as noted by a change in contrast, is coincident with a chemical boundary.[92] Incorporated phosphate, which was measured by Rutherford backscattering spectroscopy (RBS), is found only in the outer portion of the oxide. The intensity profile exhibits a clear local maximum near the middle of the oxide layer that is indicative of the boundary between the inner and outer oxide layers.[92]

For the TEM specimen imaged in Figure 3-11, the specimen is thinner at the Si substrate/sputtered layers interface than it is at the oxide/epoxy interface. Figure 3-11 shows where the specimen was perforated by the ion beam during milling.
**Figure 3-10:** Cross section TEM intensity profile and accompanying image for a mono-layer oxide formed 0.1 M Na$_2$SO$_4$. The intensity profile demonstrates the effect of a gradient in specimen thickness.

**Figure 3-11:** Cross Section TEM intensity profile and accompanying image demonstrating the effect of a contrast change due to incorporated phosphorus.

When the grown anodic oxide is sufficiently thick, the change in contrast near the middle of the oxide is evident in the visual image and in the intensity profile. However, for thin oxides formed at low formation voltages, the majority of the intensity profile is dominated by the interfaces, i.e., the change in the intensities due to the metal/oxide and oxide/epoxy interfaces make it difficult to interpret intensity changes across the entire oxide. For this reason, it is necessary to calculate the intensity profile only near the middle of the oxide and to avoid integrating the transmitted intensity near the interfaces.
Figure 3-12 shows the intensity profile of such a selected region. When the bi-layer oxide is present, local minima and maxima are typically observed in the intensity profile. This feature in the intensity is not observed when the oxide is free of incorporated phosphorus; the corresponding measurement for oxide formed in 0.1 M Na$_2$SO$_4$ is shown in Figure 3-13.

**Figure 3-12:** Intensity profile and corresponding image for the middle region of a 130 nm bi-layer oxide film.

**Figure 3-13:** Intensity profile and corresponding image for the middle region of a 130 nm oxide formed in 0.1M Na$_2$SO$_4$. 
Figures 3-10 through 3-13 demonstrate that the intensity profile of the oxide can be used to determine the portions of oxide that contains incorporated phosphorus regardless of whether the TEM specimen is uniformly thinned in the z-direction. As shown in Figure 3-11 and Figure 3-12, the interface between two chemically distinct oxide layers is marked by a local maximum in the intensity near the middle of the oxide.

Figure 3-14 and Figure 3-15 show the intensity profiles and corresponding images for an oxide formed to 13 V vs. SCE, which corresponds to an oxide thickness of 26 nm. The intensity profiles are consistent with profiles from the bi-layer oxide formed to 70V (130nm), thus indicating a bi-layer structure.

Figure 3-14: TEM intensity profile and the corresponding image for oxide formed to 13V in 0.1 M H$_3$PO$_4$. The image is sampled on either end of the oxide so that both the Ta substrate and the epoxy are included in the intensity profile.
Figure 3-15: TEM intensity profile and the corresponding image for oxide formed to 13V in 0.1 M H₃PO₄. The image is sampled so as to exclude the Ta/oxide and oxide/epoxy interfaces.

Cross sectional TEM was also performed on a sample anodized to 6V in 0.1 M H₃PO₄. The thickness of the formed oxide is 14 nm, and the z-thickness of the prepared TEM specimen is relatively high. Therefore, it is difficult to make a definitive judgment on whether this thin oxide has a single layer or bi-layer structure. However, the profiles shown in Figures 3-16, 3-17, and 3-18 suggest that the oxide is bi-layer. Figure 3-16 samples the intensity across the metal, oxide, and epoxy; the gradient in intensity appears to be due to a gradient in the z-thickness of the specimen. However, if the interfaces are excluded when integrating the intensity, the profiles have a local minima near the middle of the oxide as shown in Figure 3-17 and Figure 3-18. This feature is consistent with profiles of a bi-layer oxide.
Figure 3-16: TEM intensity profile and the corresponding image for oxide formed to 6V in 0.1 M $\text{H}_3\text{PO}_4$. The image is sampled on either end of the oxide so that both the Ta substrate and the epoxy are included in the intensity profile.

Figure 3-17: TEM intensity profile and the corresponding image for oxide formed to 6V in 0.1 M $\text{H}_3\text{PO}_4$. The image is sampled so as to exclude the Ta/oxide and oxide/epoxy interfaces.
Figure 3-18: TEM intensity profile and the corresponding image for oxide formed to 6V in 0.1 M H$_3$PO$_4$. A section of the image shown in the above Figure 3-17 is sampled. The Ta/oxide and oxide/epoxy interfaces are excluded from the integration.

3.2.1.4. Anodization Constants for Particular Growth Conditions

The thickness of the inner layer, outer layer, total oxide, and the remaining metallic Ta for various formation voltages and times are shown in Table 3-13. The anodization constants (nm of oxide per applied volt) for this data is shown in Table 3-14. A native oxide of 2.6 nm was assumed when calculating the anodization constant of the inner layer and the total oxide.
**Table 3-13:** Thickness of the total oxide, inner and outer layers of oxide, and the Ta remaining after anodization as measured by TEM bright field imaging. The thickness of the initial Ta is estimated from the deposition conditions.

<table>
<thead>
<tr>
<th>Vf, V</th>
<th>Time at Vf, min</th>
<th>Inner Layer Thickness, nm</th>
<th>Outer Layer Thickness, nm</th>
<th>Total Oxide Thickness, nm</th>
<th>Initial Ta, nm</th>
<th>Remaining Ta, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>222 ± 2</td>
<td>n/a</td>
</tr>
<tr>
<td>6.24</td>
<td>60</td>
<td></td>
<td>14.6 ± 0.6</td>
<td>~110</td>
<td>100 ± 3</td>
<td></td>
</tr>
<tr>
<td>13.24</td>
<td>60</td>
<td></td>
<td>27.5 ± 0.9</td>
<td>222 ± 2</td>
<td>210.6 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>48 ± 1</td>
<td>47 ± 2</td>
<td>97 ± 1</td>
<td>~150</td>
<td>72 ± 2</td>
</tr>
<tr>
<td>70</td>
<td>2</td>
<td>53 ± 2</td>
<td>59 ± 2</td>
<td>115 ± 1</td>
<td>222 ± 2</td>
<td>n/a</td>
</tr>
<tr>
<td>70</td>
<td>60</td>
<td>68 ± 1</td>
<td>64 ± 2</td>
<td>131 ± 1</td>
<td>~150</td>
<td>66 ± 2</td>
</tr>
<tr>
<td>70</td>
<td>90</td>
<td>66.7 ± 0.6</td>
<td>66 ± 1</td>
<td>132 ± 1</td>
<td>222 ± 2</td>
<td>149 ± 2</td>
</tr>
<tr>
<td>70</td>
<td>6135</td>
<td>79 ± 1</td>
<td>74 ± 2</td>
<td>152 ± 2</td>
<td>222 ± 2</td>
<td>188 ± 5</td>
</tr>
<tr>
<td>70</td>
<td>2 (Na2SO4)</td>
<td>n/a</td>
<td>n/a</td>
<td>131 ± 1</td>
<td></td>
<td>68 ± 2</td>
</tr>
</tbody>
</table>

**Table 3-14:** Anodization constants for oxides formed to various voltages and held for various lengths of time.

<table>
<thead>
<tr>
<th>Vf (V)</th>
<th>Time at Vf (min)</th>
<th>Anodizing Electrolyte</th>
<th>Total Oxide Anodization Constant (nm/V)</th>
<th>Inner Layer Anodization Constant (nm/V)</th>
<th>Outer Layer Anodization Constant (nm/V)</th>
<th>Ta consumed, nm/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>2</td>
<td>0.1 M H3PO4</td>
<td>1.61 ± 0.01</td>
<td>0.72 ± 0.03</td>
<td>0.84 ± 0.03</td>
<td>1.53</td>
</tr>
<tr>
<td>70</td>
<td>60</td>
<td>0.1 M H3PO4</td>
<td>1.83 ± 0.01</td>
<td>0.93 ± 0.01</td>
<td>0.91 ± 0.03</td>
<td>1.20</td>
</tr>
<tr>
<td>70</td>
<td>90</td>
<td>0.1 M H3PO4</td>
<td>1.85 ± 0.01</td>
<td>0.92 ± 0.01</td>
<td>0.94 ± 0.01</td>
<td>1.04</td>
</tr>
<tr>
<td>70</td>
<td>6135</td>
<td>0.1 M H3PO4</td>
<td>2.13 ± 0.01</td>
<td>1.1 ± 0.03</td>
<td>1.06 ± 0.03</td>
<td>--</td>
</tr>
<tr>
<td>70</td>
<td>2</td>
<td>0.1 M Na2SO4</td>
<td>1.83 ± 0.01</td>
<td>Not applicable</td>
<td>Not Applicable</td>
<td>1.17</td>
</tr>
<tr>
<td>70</td>
<td>60</td>
<td>0.1 M H3PO4</td>
<td>1.90 ± 0.01</td>
<td>0.91 ± 0.02</td>
<td>0.94 ± 0.04</td>
<td>1.56</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>0.1 M H3PO4</td>
<td>1.88 ± 0.07</td>
<td>Not Resolved</td>
<td>Not Resolved</td>
<td>--</td>
</tr>
<tr>
<td>13.2</td>
<td>60</td>
<td>0.1 M H3PO4</td>
<td>1.9 ± 0.1</td>
<td>Not Resolved</td>
<td>Not Resolved</td>
<td>1.62</td>
</tr>
</tbody>
</table>
3.2.2. Infrared Spectroscopy

3.2.2.1. Effect of Incorporated Phosphorus

The effect of incorporated phosphorus on the infrared spectrum of tantalum oxide is observed by comparing spectra anodized in different electrolytes. The standard anodic Ta$_2$O$_5$ specimens described in section 3.1.2.2 which were anodized in either 0.1 M Na$_2$SO$_4$ or 1.0 M KCl are compared to oxides formed in 0.1 M H$_3$PO$_4$. As shown in Figure 3-19, all of the oxide specimens show a broad absorption band at 1000 – 800 cm$^{-1}$, however, only the oxide formed in H$_3$PO$_4$ shows an absorption band at 1200 – 1100 cm$^{-1}$. Thus, infrared spectroscopy provides a method for determining the relative amount of phosphorus in the oxide. The method for quantifying the relative amount of P-O from FT-IR reflectance spectroscopy is described in 3.1.4.2.3.5.

Figure 3-19: FT-IR reflectance spectra of oxides anodized to 70V in either 0.1 M H$_3$PO$_4$, 0.1 M Na$_2$SO$_4$, or 1.0 M KCl electrolyte.
3.2.2.2. Effect of Boiling Oxide

In preparing anodic tantalum oxide for use as a standard material, the specimens are sometimes boiled in deionized water. The samples examined by IR spectroscopy in Figure 3-20 were anodized to 70V at a rate of 250mV/sec and then held for two minutes at 70V. The electrolyte was either 0.1 M Na$_2$SO$_4$ or 0.1 M H$_3$PO$_4$. Boiling seems to have a minimal effect on oxides formed in H$_3$PO$_4$, examination of the peak intensities, suggests that the optical thickness of the oxide thickens slightly. For films formed in Na$_2$SO$_4$, however, there is a notable increase in the absorbance from 1150 – 1030 cm$^{-1}$ for the boiled sample. The larger, broad band at 1000 – 800 cm$^{-1}$ decreases slightly. This could indicate that while boiling does not increase the thickness of the oxide, it does cause a change in the chemistry of the film. This may indicate that hydroxide-like groups are present in films that are anodized in 0.1 M Na$_2$SO$_4$ and subsequently boiled.

![Graph showing IR spectroscopy results](image)

**Figure 3-20**: Effect of boiling on specimens anodized to 70 V in either 0.1M H$_3$PO$_4$ or 0.1M Na$_2$SO$_4$.

3.2.3. TEM Calibration of IR Oxide Thickness

Transmission electron microscopy is used to calibrate the thickness-absorbance relationship of the oxide. The absorbance is measured by micro-reflectance FT-IR as described in section 3.1.4.1 and the oxide thickness is measured by bright field TEM
imaging. TEM is used to define the inner, outer, and total oxide layer thicknesses for particular samples. A calibration curve is then made using the quantified absorbance measured by IR spectroscopy. This method allows for the oxide thickness to be measured with a quick and easy bulk technique (IR) rather than a time consuming, difficult and nano-scale technique (TEM).

Either the integrated area of the absorbance bands or the maximum peak heights provide suitable quantification for calibrating the total oxide thickness. In order to assess the consistency of the data analysis procedure, analysis is completed using both quantification methods, and the final results are compared. The sum of the integrated areas of the Ta-O and P-O absorbance bands is plotted versus the total oxide thickness measured in the TEM in Figure 3-21. The sum of the band maxima versus total oxide thickness is shown in Figure 3-22.

The thickness of the outer layer of oxide is calibrated in a similar way; the integrated area of the P-O absorbance band versus the thickness of the outer layer is shown in Figure 3-23; the P-O band maxima versus thickness is plotted in Figure 3-24.

Figure 3-21: Sum of the Ta-O and P-O band areas versus TEM thickness.
Figure 3-22: Sum of the Ta-O and P-O band maxima versus TEM thickness.

Figure 3-23: Area of the P-O absorbance band versus the thickness of the outer layer of oxide.
The thickness of the inner layer can be readily determined by subtracting the outer layer thickness from the total oxide thickness. The equations for calculating oxide thickness from IR absorbance are summarized in Table 3-15. It is noted that these calibration curves are valid for the IR spectroscopy setup described in section 3.1.4.1; the calibration of the total oxide will be generally true over most anodization constants. However, the calibration of the outer layer and inner layer thickness does not translate to oxides formed at different rates, temperatures, pH, electrolyte concentrations, or types of electrolyte.
Table 3-15: Calibration equations for calculating the thickness of the total oxide and inner and outer layers of oxide for anodic oxides formed at room temperature in 0.1 M H₃PO₄. The IR spectra was quantified using either the band areas or band maxima. \( A_{TaO} \) is the absorbance of the Ta-O band; \( A_{PO} \) is the absorbance of the P-O band.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Band Area Equations</th>
<th>Band Maxima Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Oxide</td>
<td>( L(nm) = \frac{A_{TaO} + A_{PO} - 0.7262}{0.3667} )</td>
<td>( L(nm) = \frac{A_{TaO} + A_{PO} - 2.55 \times 10^{-3}}{1.71 \times 10^{-3}} )</td>
</tr>
<tr>
<td>Outer Layer</td>
<td>( L(nm) = \frac{A_{PO} - 0.703}{0.049} )</td>
<td>( L(nm) = \frac{A_{PO} - 3.01 \times 10^{-3}}{5.29 \times 10^{-4}} )</td>
</tr>
<tr>
<td>Inner Layer</td>
<td>( L(nm) = \frac{A_{TaO} + A_{PO} - 0.7262}{0.3667} - \frac{A_{PO} - 0.703}{0.049} )</td>
<td>( L(nm) = \frac{A_{TaO} + A_{PO} - 2.55 \times 10^{-3}}{1.71 \times 10^{-3}} - \frac{A_{PO} - 3.01 \times 10^{-3}}{5.29 \times 10^{-4}} )</td>
</tr>
</tbody>
</table>

3.2.4. Beer-Lambert Law Analysis

The extent to which the intensity of the infrared signal decreases as it passes through a medium is determined by the absorbance coefficient, \( \alpha' \), of the medium and is described by the Beer-Lambert Law:

\[
I = I_0 e^{-\alpha'D}
\]  

[3-2]

Where \( I_0 \) is the incident intensity, \( I \) is the measured intensity, and \( D \) is the path length of the beam. This is equivalent to
\[
\log\left(\frac{I}{I_0}\right) = 2.2 \cdot \alpha \cdot D = \text{Absorbance}
\]

The ‘2.2’ multiplier arises from taking the \(\log_{10}\) of the exponential and should not be confused with any properties characteristic of the material or apparatus. In determining a reflectance absorbance spectrum from a test material, it must be reported with reference to a spectrum from a reference material. In this work, a sputter deposited gold substrate was used as the reference material. The Fourier-transform of an interferogram from the test material, \(T_m\), is referenced to the Fourier transform of an interferogram from the reference material, \(T_r\). The reported absorbance spectra are determined by the simple relationship:

\[
A = -\log \frac{T_m}{T_r}
\]

While the absorption coefficients have been reported for anodic Ta\(_2\)O\(_5\) using FT-IR reflectance spectroscopy [115], the reference substrate was not noted and the work reported herein is not a direct reproduction of the experiments reported by Kihara-Morishita. The optical properties, such as reflectivity and refractivity, of the reference substrates may influence the measured absorbance considerably. It is important to emphasize that the Beer-Lambert is an empirical relationship. Thus for a given experiment, the goal is to determine the relationship between two values: the intensity of the measured signal and a property of the test specimen (such as optical thickness or concentration). In this work, the oxide thickness (determined by TEM) was related to the measured absorbance, which does not require knowledge of the absorption coefficient.

As an exercise, the oxide thickness predicted using the reported absorption coefficient[115] is determined. Figure 3-25 shows the ray diagram of the experiment assuming that the refractive index of Ta\(_2\)O\(_5\) is 2.2[35] and that the angle of incidence is 80° with respect to the specimen normal.
Figure 3-25: Ray diagram showing the path of the infrared beam where the angle of incidence is 80° and the refractive index of Ta₂O₅ is 2.2.

In reference to the experimental ray diagram shown in Figure 3-25, the path length, D, is twice d and related to the oxide thickness, L:

\[ D = 2.237 \times L \] \hspace{1cm} [3-5]

Assuming specular reflectance, the expected absorbance, A, for our particular apparatus is given as

\[ A = 2.2 \times \alpha \times 2.237 \times L \] \hspace{1cm} [3-6]

\[ A = 4.92 \times \alpha \times L \] \hspace{1cm} [3-7]

Kihara-Morishita reported absorption coefficients for the inner and outer layers of tantalum oxide as determined by FT-IR reflectance spectroscopy for specimens anodized to 50V or 100V at 1.0 mA/cm² in 0.01 N H₃PO₄ at 20°C.[115] The FT-IR spectra were quantified by arbitrarily deconvolving the broad Ta-O absorption band into three
component bands, and the absorption coefficients are reported for the largest two deconvolved bands.[115] Their results are summarized in Table 3-16.

**Table 3-16:** After[115]. Absorption coefficients at different wavenumbers of two oxides formed to 50V or 100V at 1.0 mA/cm² in 0.01 N H₃PO₄ at 20°C.[115]

<table>
<thead>
<tr>
<th></th>
<th>Inner Layer</th>
<th>Outer Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>50V</td>
<td>2.55*10³</td>
<td>1.38*10³</td>
</tr>
<tr>
<td>100V</td>
<td>2.54*10³</td>
<td>1.35*10³</td>
</tr>
<tr>
<td>Average</td>
<td>2.54*10³</td>
<td>1.36*10³</td>
</tr>
</tbody>
</table>

The best agreement between TEM measured oxide thickness and the thickness predicted by FT-IR reflectance measurements is obtained when the total oxide thickness is assumed to have an absorption coefficient of 2.55*10³ cm⁻¹. Table 3-17 shows that the oxide thickness calculated directly from the absorbance is consistently greater than the thickness measured directly by TEM imaging.

This suggests that a greater fraction of the incident intensity is being reflected or scattered in our experiments than in Kihara-Morishita’s experiment. As discussed previously, the difference in materials used for collecting the reference spectrum is a source of discrepancy. The geometry of the different experiments may be another factor. The angle of incidence in Kihara-Morishita’s experiments was 45°, whereas 80° was used in our experiments. Therefore, the optical path length is greater in our experiments for a given oxide thickness. If scattering of the beam within the specimen is occurring, the attenuation of the beam would be greater for our experimental setup. The assumption of specular reflection may not be totally valid and some degree of diffuse reflectance may occur.
**Table 3-17**: Comparison of the oxide thickness measured using TEM imaging with the thickness calculated from FT-IR reflectance spectra and Kihara-Morishita’s absorbance coefficient.

<table>
<thead>
<tr>
<th>TEM Total Oxide Thickness, nm</th>
<th>IR Total Oxide Thickness, nm</th>
<th>Percent Difference, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>108</td>
<td>11</td>
</tr>
<tr>
<td>131</td>
<td>142</td>
<td>8.06</td>
</tr>
<tr>
<td>115</td>
<td>135</td>
<td>16.0</td>
</tr>
<tr>
<td>132</td>
<td>157</td>
<td>17.3</td>
</tr>
<tr>
<td>152</td>
<td>174</td>
<td>13.5</td>
</tr>
</tbody>
</table>

### 3.2.5. Oxides as a Function of Formation Voltage

#### 3.2.5.1. Spectra

Figure 3-26 shows IR spectra of samples that have been grown by manually ramping the voltage of a Hewlett Packard Model No. E3612A DC power supply at an approximate rate of 250 mV/sec and then held at the formation voltage for 60 minutes.
Figure 3-26: IR spectra of oxides anodized in 0.1 M H$_3$PO$_4$ at an approximate voltage increase rate of 250 mV/s and held at the formation voltage for 60 minutes.

It is well established that oxide thickness is linear with applied voltage[4], and it is reported here that absorbance is also linear with oxide thickness. As described in section 3.1.4.2 the absorbance is quantified by subtracting the baseline and then either reading the band maximum or integrating the area under the absorption band. Analysis is reported for the two methods of spectra quantification.

3.2.5.2. Quantified Band Maxima

Figure 3-27 demonstrates the absorbance of the band maxima vs. formation voltage for the Ta-O and the P-O band. The plot shows two data sets formed under two different experimental conditions. The oxides in the “60 min” data set were grown by manually increasing the applied potential at a rate of 250mV/sec and then maintaining the final voltage for 60 minutes. The oxides in “50 min” data set were formed by automatically
increasing the potential at 250mV/sec and then maintaining the final voltage for 50 minutes. Complete experimental details are described in section 3.1.2.1. Linear regression was performed for each plot, and the equations and $R^2$ values are reported in Table 3-18. The sum of the two peak maxima (absorbances at $\sim$915 cm$^{-1}$ and $\sim$1105 cm$^{-1}$) is useful for quantifying the total thickness of the oxide; this sum is plotted versus formation voltage in Figure 3-28 and the linear regression results are given in Table 3-19. The equations in Tables 3-18 through 3-21 provide the relationship between formation voltage and absorbance; it is elementary to show the relationship between formation voltage and oxide thickness by using the equations in Table 3-15.

**Figure 3-27:** Band maxima of the Ta-O and P-O absorption bands versus formation voltage for samples anodized by either, i.) manually ramping the formation voltage then holding for 60 minutes or ii.) automatically ramping the formation voltage and holding for 50 minutes.
Table 3-18: Linear regression results for the data plotted in Figure 3-27. The absorbance at the peak maximum, A, is a function of the formation voltage, V_f.

<table>
<thead>
<tr>
<th>Ta-O Peak Max Formula</th>
<th>P-O Peak Max Formula</th>
<th>Experimental Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A=2.61 \times 10^{-3} (V_f) + 8.95 \times 10^{-4}$</td>
<td>$A=5.58 \times 10^{-3} (V_f) + 4.6 \times 10^{-4}$</td>
<td>Automatic Ramp, 50 Minute Hold</td>
</tr>
<tr>
<td>$R^2=0.998$</td>
<td>$R^2=0.993$</td>
<td></td>
</tr>
<tr>
<td>$A=2.55 \times 10^{-3} (V_f) + 4.82 \times 10^{-4}$</td>
<td>$A=5.31 \times 10^{-3} (V_f) + 3.10 \times 10^{-5}$</td>
<td>Manual Ramp, 60 Minute Hold</td>
</tr>
<tr>
<td>$R^2=0.997$</td>
<td>$R^2=0.949$</td>
<td></td>
</tr>
<tr>
<td>$A=2.59 \times 10^{-3} (V_f) + 2.15 \times 10^{-3}$</td>
<td>$A=5.52 \times 10^{-4} (V_f) + 2.70 \times 10^{-5}$</td>
<td>Both Sets of Data</td>
</tr>
<tr>
<td>$R^2=0.997$</td>
<td>$R^2=0.978$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-28: Sum of the Ta-O and P-O band maxima versus formation voltage for two experimental data sets.
Table 3-19: Linear regression analysis of the data in Figure 3-28 showing the relationship between the sum of the Ta-O and P-O band maxima to the formation voltage.

<table>
<thead>
<tr>
<th>Sum of Ta-O and P-O Band Maxima vs. Formation Voltage</th>
<th>Experimental Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>A=3.17<em>10^{-3}</em>(V_f) + 1.099*10^{-3} R^2=0.998</td>
<td>Automatic Ramp, 50 Minute Hold</td>
</tr>
<tr>
<td>A=3.082<em>10^{-3}</em>(V_f) + 4.79*10^{-3} R^2=0.992</td>
<td>Manual Ramp, 60 Minute Hold</td>
</tr>
<tr>
<td>A=3.14<em>10^{-3}</em>(V_f) + 2.65*10^{-2} R^2=0.996</td>
<td>Both Sets of Data</td>
</tr>
</tbody>
</table>

3.2.5.3. Quantified Band Area

Figure 3-29 shows the integrated band area of the individual Ta-O and P-O absorbance bands versus the formation voltage. Regression results are shown in Table 3-20. Figure 3-30 shows the sum of the Ta-O and P-O band areas versus formation voltage for two data sets. Linear regressions for the plots in Figure 3-30 are given in Table 3-21.
Figure 3-29: Integrated area of the IR absorption bands vs. formation voltage for oxides grown by either, i.) manually ramping the formation voltage then holding for 60 minutes or ii.) automatically ramping the formation voltage and holding for 50 minutes.

Table 3-20: Linear regression results for the data plotted in Figure 3-29. The integrated area of the absorbance, $A$, is a function of the formation voltage, $V_f$.

<table>
<thead>
<tr>
<th>Ta-O Band Area Formula</th>
<th>P-O Band Area Formula</th>
<th>Experimental Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A=0.626*(V_f) - 0.558$</td>
<td>$A=0.0567*(V_f) + 0.0837$</td>
<td>Automatic Ramp, 50 Minute Hold</td>
</tr>
<tr>
<td>$R^2 = 0.998$</td>
<td>$R^2 = 0.992$</td>
<td></td>
</tr>
<tr>
<td>$A=0.610*(V_f) + 0.695$</td>
<td>$A=0.0501*(V_f) + 0.223$</td>
<td>Manual Ramp, 60 Minute Hold</td>
</tr>
<tr>
<td>$R^2 = 0.994$</td>
<td>$R^2 = 0.925$</td>
<td></td>
</tr>
<tr>
<td>$A=0.623*(V_f) - 0.157$</td>
<td>$A=0.055*(V_f) + 0.092$</td>
<td>Both Sets of Data</td>
</tr>
<tr>
<td>$R^2 = 0.996$</td>
<td>$R^2 = 0.970$</td>
<td></td>
</tr>
</tbody>
</table>
**Figure 3-30:** Sum of the area of the Ta-O and P-O absorption bands as a function of formation voltage.

**Table 3-21:** Linear regression results for the data plotted in Figure 3-31. The sum of the two absorption band’s integrated area, A, is a function of the formation voltage, V_f.

<table>
<thead>
<tr>
<th>Formula for Sum of Ta-O Band and P-O Band Area vs. Formation Voltage</th>
<th>Experimental Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>A=0.685*(V_f) – 0.472</td>
<td>Automatic Ramp, 50 Minute Hold</td>
</tr>
<tr>
<td>R²=0.998</td>
<td></td>
</tr>
<tr>
<td>A=0.660*(V_f) + 0.917</td>
<td>Manual Ramp, 60 Minute Hold</td>
</tr>
<tr>
<td>R²=0.991</td>
<td></td>
</tr>
<tr>
<td>A=0.678*(V_f) – 0.065</td>
<td>Both Sets of Data</td>
</tr>
<tr>
<td>R²=0.996</td>
<td></td>
</tr>
</tbody>
</table>
3.2.5.4. Anodization Constants

The anodization constants are determined from the equations in Table 3-15 and from Table 3-20 and Table 3-21. The average anodization constant for the total oxide for the two data sets and two methods of IR quantification is 1.83 ± 0.04 nm/V. The average anodization constant for the outer layer is 1.06 ± 0.07 nm/V. The anodization constants for each case are shown in Table 3-22 (total oxide) and Table 3-23 (outer layer only).

**Table 3-22**: Anodization constant of the total oxide for different sets of data and IR quantification method.

<table>
<thead>
<tr>
<th>Anodization Constant, nm/V</th>
<th>Data Set</th>
<th>IR Quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>60 min, Manual</td>
<td>Sum of Areas</td>
</tr>
<tr>
<td>1.83</td>
<td>50 min, Auto</td>
<td>Sum of Areas</td>
</tr>
<tr>
<td>1.85</td>
<td>Manual and Auto</td>
<td>Sum of Areas</td>
</tr>
<tr>
<td>1.80</td>
<td>60 min, Manual</td>
<td>Sum of Maxima</td>
</tr>
<tr>
<td>1.85</td>
<td>50 min, Auto</td>
<td>Sum of Maxima</td>
</tr>
<tr>
<td>1.84</td>
<td>Manual and Auto</td>
<td>Sum of Maxima</td>
</tr>
</tbody>
</table>

**Table 3-23**: Anodization constant of the outer layer of oxide for different sets of data and IR quantification method.

<table>
<thead>
<tr>
<th>Anodization Constant, nm/V</th>
<th>Data Set</th>
<th>IR Quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>60 min, Manual</td>
<td>P-O Band Area</td>
</tr>
<tr>
<td>1.16</td>
<td>50 min, Auto</td>
<td>P-O Band Area</td>
</tr>
<tr>
<td>1.12</td>
<td>Manual and Auto</td>
<td>P-O Band Area</td>
</tr>
<tr>
<td>1.06</td>
<td>60 min, Manual</td>
<td>P-O Band Maximum</td>
</tr>
<tr>
<td>1.00</td>
<td>50 min, Auto</td>
<td>P-O Band Maximum</td>
</tr>
<tr>
<td>1.04</td>
<td>Manual and Auto</td>
<td>P-O Band Maximum</td>
</tr>
</tbody>
</table>

The anodization constant has been determined for oxides formed from 20-100V for 50 minutes using the IR measured thickness of the oxide. The total oxide thickness vs.
formation voltage is shown in Figure 3-31. The anodization constant for 50 minute anodization in 0.1 M H$_3$PO$_4$ is 1.83 ± 0.06 nm/V and the initial oxide is 2.6 nm. Anodization constants are typically quoted for a particular electrolyte, temperature, and growth rate, but the length of anodization time is often not specified. Table 3-24 shows that the anodization constant reported here is in agreement with the existing literature. Table 3-25 demonstrates that the native oxide compares well with values measured on a variety of substrates and with various characterization techniques.

**Figure 3-31:** Total oxide thickness versus formation voltage for oxides formed at 250mV/sec in 0.1 M H$_3$PO$_4$. The anodization constant is 1.83 ± 0.06 nm/V and the native oxide thickness is 2.6 nm.
Table 3-24: Anodization constants reported for tantalum anodized at room temperature.

<table>
<thead>
<tr>
<th>Anodization Constant, nm/V</th>
<th>Forming Electrolyte</th>
<th>Growth</th>
<th>Thickness Determination</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.83 ± 0.06</td>
<td>0.01 M H₃PO₄</td>
<td>250 mV/sec +50 minutes</td>
<td>TEM / FT-IR</td>
<td>This work</td>
</tr>
<tr>
<td>1.76</td>
<td>Various</td>
<td>25 mV/sec</td>
<td>Wet electrochem</td>
<td>[64]</td>
</tr>
<tr>
<td>1.84</td>
<td>Various</td>
<td>8 µA/cm² +20 Hour Hold</td>
<td>Coulometry</td>
<td>[74]</td>
</tr>
<tr>
<td>1.73 ± 0.03</td>
<td>0.06 wt% H₃PO₄</td>
<td>45 µA/cm²</td>
<td>Micromotem TEM</td>
<td>[93]</td>
</tr>
<tr>
<td>1.60 ± 0.05</td>
<td>0.01% citric acid</td>
<td>1mA/cm² + 1 Hour Hold</td>
<td>Talysurf Measurement</td>
<td>[112]</td>
</tr>
</tbody>
</table>

Table 3-25: Reported thickness of the native oxide on tantalum for a variety of surface preparations and methods of measurement.

<table>
<thead>
<tr>
<th>Native Oxide Thickness, nm</th>
<th>Method</th>
<th>Substrate Preparation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>L vs. V intercept; TEM &amp; FT-IR</td>
<td>Sputtered</td>
<td>This work</td>
</tr>
<tr>
<td>2.3</td>
<td>L vs. V intercept; TEM</td>
<td>Sputtered</td>
<td>[93]</td>
</tr>
<tr>
<td>0.8</td>
<td>L vs. V intercept; TEM</td>
<td>Sputtered</td>
<td>[93]</td>
</tr>
<tr>
<td>3.5</td>
<td>¹⁸O, α spectroscopy</td>
<td>Chemically polished</td>
<td>[32]</td>
</tr>
<tr>
<td>2.0</td>
<td>Wet capacitance</td>
<td>Polished w/ jeweler’s rouge</td>
<td>[4]</td>
</tr>
<tr>
<td>1.8</td>
<td>Extrapolation of 1/C vs. V plot</td>
<td>Chemically polished</td>
<td>[64]</td>
</tr>
<tr>
<td>1.5</td>
<td>XPS</td>
<td></td>
<td>[99] cited in [5]</td>
</tr>
</tbody>
</table>

3.2.5.5. Relative thickness of the outer layer
Since it is known that the concentration of phosphorus is constant in the outer layer[52, 53, 92], the absorbance of the Ta-(PO₄)³⁻ band relative to the Ta-O band indicates the relative thickness of the outer layer to the total oxide thickness. This analysis is shown where the absorbance is quantified by band maxima (Figure 3-32) and by integrated area of the bands (Figure 3-33.) The thickness of the outer layer relative to the total oxide does not depend on the formation voltage for a given, constant anodization time. At low
formation voltage (thin oxides) it is difficult to accurately quantify the spectra because the background relevant to the absorbance of the oxide is large.
Figure 3-32: Band maxima of the P-O band relative to the Ta-O Band vs. formation voltage.

Figure 3-33: Ratio of the quantified P-O band to the Ta-O band for oxides grown by manually ramping the formation voltage vs. formation voltage.
3.2.5.6. Discussion of Results as a Function of Formation Voltage

Accepting the well established observation that oxide thickness is linear with applied formation voltage allows for the conclusion that the measured absorbance of the IR signal is linear with oxide thickness. The P-O to Ta-O ratio of the absorption bands does not follow a trend as a function of formation voltage. This could not be confirmed for thin oxides (\(V_f = 2-8\)V) because the background subtraction was not feasible. The error bars are a liberal estimation of the error involved in quantifying the IR spectra from a single spectra and thus do not include variation between different samples. The anodization constant for the total oxide 1.8 nm/V was calculated from the quantified IR absorbance; this value agrees well with the value determined by Lu, et.al. for formation in 0.06 wt% \(\text{H}_3\text{PO}_4\).[92, 93] The absorbance-oxide thickness relation was calibrated using TEM.

Equations are presented for the quick determination of outer oxide and total oxide thickness from micro-reflectance FT-IR spectra. The oxides were formed potentiodynamically at 250 mV/sec in 0.1 M \(\text{H}_3\text{PO}_4\) at room temperature.

3.2.6. Oxides Formed as a Function of Anodization Time

3.2.6.1. Literature Comparison of Logarithmic & Inverse Logarithmic Growth Laws

Zhang, et. al., have derived criteria for diagnosing whether the HFM or the PDM is the more physically realistic model for anodic oxidation.[12] Current transient measurements were used for the diagnosis because current can be directly measured with a high degree of accuracy. The relationship between the current, \(i\), and its time derivative, \(i' = \frac{di}{dt}\), according to the HFM is of the form[12]

\[
\sqrt{-\frac{i'}{i(i-\delta)}} = C^* \ln(i) - \frac{C^*}{\sqrt{V}} \ln(A^*)
\] [3-8]
Where $\delta$ is the steady state current, $V$ is the applied voltage, and $C^*$ and $A^*$ are constants.

The PDM predicts that

$$\sqrt{-\frac{-i'}{i(i-\delta)}} = D^*$$  \[3-9\]

where $D^*$ is a constant. [12]

Thus, the HFM predicts that a plot of $\sqrt{-\frac{-i'}{i(i-\delta)}}$ versus $\ln(i)$ should be linear with a positive slope, but the PDM predicts that this plot will be a horizontal line. [12]

As shown by Figure 3-34 and Figure 3-35, transient current measurements reported by Zhang, et al., [12] on anodic tantalum show behavior consistent with the PDM but not the HFM.

**Figure 3-34:** After [12] Left: Plot of the current transient on tantalum at 12V. Right: Plot of $\sqrt{i'/i}$ vs. $\ln(i)$. The PDM predicts a horizontal line, which is more consistent with experimental data.
Figure 3-35: Current transient for tantalum for the second, fast transient. The initial, slowly decaying transient is neglected. A.) Plot of the fast current transient on tantalum at 12V and B.) Plot of $\sqrt{i'/i}$ vs. ln(i).

The HFM predicts an inverse logarithmic growth law where the oxide thickness is related to time of anodization by [7, 59]

$$\frac{1}{L} = A - B \ln(t)$$

[3-10]

which is an approximate solution of the thickness-time relationship described by the High Field Model (HFM). The oxide thickness is L, t is time of anodization, and A and B are constants.

Derivation of the thickness-time relationship from the PDM results in a direct logarithmic growth law

$$L_{BL} = L_0 + \frac{1}{b} \ln(1 + a' b \exp(-bL_0) t)$$

[3-11]
Where $L_{BL}$ is the thickness of the barrier layer, $L_0$ is the initial oxide thickness,
\[
a' = k_2 e^{a \alpha (1-\alpha)} e^{-\alpha \beta \rho H}
\]
and $b = \alpha_2 \gamma \chi E$; $k_2$ and $\alpha_2$ are the standard rate constant and transfer coefficient for the production of oxygen vacancies, $\alpha$ is the polarizability of the film/solution interface, $\gamma$ is F/RT, $\beta$ is the pH dependence of the potential drop at the film/solution interface, $\chi$ is the oxidation state of the metal, E is the electric field in the oxide and $V$ is the applied potential.[77]

3.2.6.2. Growth Rates of Inner and Outer Layer Thickness Measured by TEM

The TEM thickness of the individual oxide layers formed at 70 V vs. anodization time has been measured for times from 2 – 6135 minutes. The results are shown in Figure 3-36. As a rough approximation, oxide growth is logarithmic with time as shown by the trendlines in Figure 3-36. These trendlines are provided as a guide to the eye, and a more detailed analysis of the growth rate is discussed in section 3.2.6.4. The equations and $R^2$ values for the trendlines are shown in Table 3-26.

![Figure 3-36: Thickness of the inner and outer layers of oxide versus formation time as measured by TEM imaging.](image-url)
Table 3-26: Oxide growth increases with the natural logarithm of time. The y-axis intercepts represent the oxide that is predicted to exist when the formation voltage is reached.

<table>
<thead>
<tr>
<th>Layer of Oxide</th>
<th>Growth Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Oxide</td>
<td>$L \text{ (nm)} = 4.605 \ln \text{ (time, min)} + 111.8$</td>
<td>0.9994</td>
</tr>
<tr>
<td>Inner Layer</td>
<td>$L \text{ (nm)} = 3.183 \ln \text{ (time, min)} + 52.3$</td>
<td>0.9692</td>
</tr>
<tr>
<td>Outer Layer</td>
<td>$L \text{ (nm)} = 1.885 \ln \text{ (time, min)} + 57.3$</td>
<td>0.9889</td>
</tr>
</tbody>
</table>

3.2.6.3. FT-IR Reflectance Spectra

Background corrected IR spectra for oxides formed to 70 V and held for various lengths of time are shown in Figure 3-37.

![FT-IR Reflectance Spectra](image)

**Figure 3-37:** Background corrected IR spectra for oxides formed to 70V and held for different times at the formation voltage.

The growth of anodic tantalum oxide is logarithmic with time. For the anodization of other valve metals, such as aluminum, a steady state thickness is attained when the rates...
of oxide growth and dissolution are equivalent. However, in the case of tantalum, the oxide is not prone to ready dissolution and the thickness of the oxide continues to grow after several days of anodization. The integrated area and peak heights are reported for films formed to 70V at 250 mV/sec and then held for various lengths of time.

Figure 3—38 and Figure 3-39 show the quantified band maxima and band areas as a function of anodization time.

**Figure 3-38:** Band maxima of the absorption bands for oxides anodized to 70V vs. hold time at the formation voltage.
**Figure 3-39:** Integrated band area of the absorption bands for oxides anodized to 70V vs. hold time at the formation voltage.

**Table 3-27:** Fitted logarithmic expressions and $R^2$ parameters for the curves shown in Figure 3—38 and Figure 3-39. These equations are provided to visually demonstrate adherence to a generic logarithmic growth rate, and do not provide particular insight otherwise.

<table>
<thead>
<tr>
<th>Band</th>
<th>Quant Method</th>
<th>Growth Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-O</td>
<td>Maximum</td>
<td>$A_{Max}^{Ta-O} = 5.83 \times 10^{-3} \ln(time, \text{min}) + 0.164$</td>
<td>0.9697</td>
</tr>
<tr>
<td>P-O</td>
<td>Maximum</td>
<td>$A_{Max}^{P-O} = 7.32 \times 10^{-4} \ln(time, \text{min}) + 0.0362$</td>
<td>0.7778</td>
</tr>
<tr>
<td>Ta-O</td>
<td>Area</td>
<td>$A_{Area}^{Ta-O} = 1.42 \ln(time, \text{min}) + 38.5$</td>
<td>0.9657</td>
</tr>
<tr>
<td>P-O</td>
<td>Area</td>
<td>$A_{Area}^{P-O} = 0.085 \ln(time, \text{min}) + 3.66$</td>
<td>0.6748</td>
</tr>
</tbody>
</table>

The equations given in Table 3-15 were used to calculate the thickness of the oxide from the quantified absorbance. Figure 3-40 shows the data and regression analysis for quantification by IR band maxima. Figure 3-41 shows the data and regression analysis for quantification by the integrated area of IR absorbance bands. The fitted curves in Figure 3-43 and Figure 3-44 are the inverse logarithmic functions given in Table 3-28.
Figure 3-40: Oxide thickness calculated from the IR absorption band maxima vs. time of anodization at 70V.

Figure 3-41: Oxide thickness calculated from IR absorption band area vs. time of anodization at 70V.
3.2.6.4. Optimization & Comparison of Simple Growth Laws

Non-linear regressions of the inverse logarithmic and direct logarithmic growths laws described by equations 3-10 and 3-11 were performed on the measured thickness vs. anodization time measurements. The oxide thickness of anodic tantalum oxide is measured by FT-IR reflectance spectroscopy or TEM imaging. In order to evaluate the consistency of the analysis, the IR spectra were quantified using two methods: 1.) by integrating the area of the absorbance band and 2.) by noting the maxima of the absorbance bands. The thickness measured directly by TEM constitutes a third data set, although it only contains four data points. The fitting parameters for the three sets of data should concur.

The total oxide thickness measured by TEM directly and by TEM calibrated FT-IR is fitted to the growth laws. Results from the TEM data set are shown in Figure 3-42. The fitting parameters for the two equations are shown in Table 3-28. The IR experimental oxide thickness and the fitted growth laws for the total oxide thickness are shown in Figure 3-43 (quantified by area) and Figure 3-44 (quantified by maximum.) The IR experimental thicknesses for the individual inner and outer layers are shown in Figure 3-45 along with the optimized growth laws. As shown by Figure 3-43 and Figure 3-44, both growth laws describe the total thickness of the oxide very well. The uncertainty of the measured thickness is much greater than the difference in thickness predicted by the logarithmic versus the inverse-logarithmic growth law. The outer layer does not adhere to either law particularly well; this is likely due to the large measurement errors in determining the thickness of the outer layer.

Table 3-28 shows the parameters of the growth laws (a', b, L_0 for the logarithmic law and A, B for the inverse logarithmic law). For a given oxide layer, the parameters determined from the two sets of IR data (band area or band maxima) and TEM should be in agreement. It was trivial to achieve consistent results for the three data sets when optimizing the parameters of the inverse growth law. However, optimization of the logarithmic growth law required reasonable values of a' and L_0 to be set as constants.
while $b$ was determined. The value of $b$ was then set constant while $L_0$ and $a'$ were simultaneously optimized. This resulted in consistent parameters for the logarithmic law; however, the uncertainty of the parameters is significant. The average parameters for the three data sets are shown in Table 3-29 (inverse logarithmic growth law) and Table 3-30 (logarithmic growth law.)

![Figure 3-42](image)

**Figure 3-42:** Optimization of the logarithmic and inverse logarithmic growth laws to the total oxide thickness as measured by TEM imaging.
Figure 3-43: Growth laws for the total oxide. The oxide thickness is quantified using the integrated area of absorbance bands.

Figure 3-44: Growth laws for the total oxide. The oxide thickness is quantified using the band maxima of the absorbance bands.
Figure 3-45: Growth laws for the inner layer of oxide (top figures) and outer layer of oxide (bottom figures) when the thickness is quantified by the area of IR absorbance bands (left figures) or the band maxima of IR absorbance bands (right figures).
Table 3-28: Fitting parameters for the logarithmic growth law and the inverse logarithmic growth law for the total oxide, inner layer, and outer layer of oxide. The IR spectra were quantified using two distinct methods: Area of absorption band and Maxima of absorption band. The growth laws were also optimized to the oxide thickness as measured by TEM, although this data set only included four points. The coefficient of multiple determination ($R^2$) is shown for each optimization.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>Quant Method</th>
<th>Logarithmic Growth Law</th>
<th>Inverse Logarithmic Growth Law</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a'$ (cm/s)</td>
<td>$b$ (1/cm)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>IR Area</td>
<td>235±500 (2.20±0.16)*10^6</td>
<td>(1.15±0.03)*10^{-5}</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>IR Max</td>
<td>257±36 ($^*$) (2.18±0.01)*10^6</td>
<td>(1.18±0.03)*10^{-5}</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>TEM</td>
<td>238±265 (2.16±0.08)*10^6</td>
<td>(0.99±0.36)*10^{-5}</td>
</tr>
<tr>
<td><strong>Inner</strong></td>
<td>IR Area</td>
<td>210±140 (4.67±0.09)*10^6</td>
<td>(5.7±3.4)*10^{-6}</td>
</tr>
<tr>
<td><strong>Inner</strong></td>
<td>IR Max</td>
<td>228±108 (4.63±0.64)*10^6</td>
<td>(5.6±4.3)*10^{-6}</td>
</tr>
<tr>
<td><strong>Inner</strong></td>
<td>TEM</td>
<td>220±200 (4.38±0.14)*10^6</td>
<td>5.6*10^{-6}</td>
</tr>
<tr>
<td><strong>Outer</strong></td>
<td>IR Area</td>
<td>265±133 (4.41±0.06)*10^6</td>
<td>(5.2±3.4)*10^{-6}</td>
</tr>
<tr>
<td><strong>Outer</strong></td>
<td>IR Max</td>
<td>261±113 (4.28±0.07)*10^6</td>
<td>(6.1±0.4)*10^{-6}</td>
</tr>
<tr>
<td><strong>Outer</strong></td>
<td>TEM</td>
<td>219±42 (4.50±0.03)*10^6</td>
<td>(5.8±0.1)*10^{-6}</td>
</tr>
</tbody>
</table>

($^*$) Value was set as a constant during the regression analysis.
($^*$) Value was constrained.
Table 3-29: Average parameters of the inverse logarithmic growth laws in Table 3-28.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>A (cm⁻¹)</th>
<th>B (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>9.64 ± 0.11*10⁴</td>
<td>2351 ± 120</td>
</tr>
<tr>
<td>Inner</td>
<td>2.10 ± 0.10*10⁵</td>
<td>6277 ± 980</td>
</tr>
<tr>
<td>Outer</td>
<td>1.80 ± 0.06*10⁵</td>
<td>3542 ± 570</td>
</tr>
</tbody>
</table>

Table 3-30: Average parameters of the direct logarithmic growth laws in Table 3-28.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>a' (cm⁻¹)</th>
<th>b (cm⁻¹)</th>
<th>L₀ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>243 ± 270</td>
<td>(2.18 ± 0.08)*10⁶</td>
<td>(11.1 ± 0.1)*10⁻⁶</td>
</tr>
<tr>
<td>Inner</td>
<td>219 ± 150</td>
<td>(4.56 ± 0.29)*10⁶</td>
<td>(5.6 ± 3.8)*10⁻⁶</td>
</tr>
<tr>
<td>Outer</td>
<td>248 ± 96</td>
<td>(4.40 ± 0.05)*10⁶</td>
<td>(5.7 ± 1.1)*10⁻⁶</td>
</tr>
</tbody>
</table>

3.2.6.5. Validity of the Optimized Parameters of the Logarithmic Growth Law

In order to evaluate the validity of the optimized parameters of the direct logarithmic growth law, the oxide resistivity and electric field that satisfy the optimized parameters are calculated. The parameters determined for the logarithmic growth law of the total oxide are taken as \( a' = 235 \pm 500 \) and \( b = (2.20 \pm 0.16)*10^6 \). As described above, \( b = \alpha_2 \chi E \) and \( a' = k_2 e^{\alpha_0 (1-\alpha) \chi} e^{-\alpha_2 \beta \phi} \). The assumed values are the values determined for the PDM in section 6.2.3 where the oxides were formed in 0.06 wt% \( \text{H}_3\text{PO}_4 \) and the formation voltage is 4.8V. Assuming that \( \alpha_2 = 0.29 \), \( \chi = 5 \), \( k_2 = 1.13 *10^{-11} \), \( \beta = -0.06 \) V/pH, \( \phi_0 = -0.1 \) V, and pH=2.47, the value of b from the optimization procedure predicts an electric field of \( (0.39 \pm 0.83) *10^6 \) V/cm. In order to analyze \( a' \), it is necessary to assume a significant potential drop occurs across the oxide. Accepting that \( a' = 235 \) cm⁻¹ requires the potential drop at the metal/oxide interface to be 5.2 V. However, this experimental data was collected with an applied voltage of 70 V. This indicates that 64.8 V must be dropped across the oxide layer; following the description given by Ai, et.al.,[83, 165] this drop is given by the ohmic relationship, \( V = I_{\text{Experimental}} R_{\text{Oxide}} \). The measured current for anodization at <12V in 0.06 wt% \( \text{H}_3\text{PO}_4 \) was \( \approx 110 \) nA/cm² and is
used here as an approximation. This would require the resistance of the oxide to be $5.89 \times 10^8$ Ohms. For a 152 nm thick oxide film, this would dictate that the resistivity of the oxide is $3.88 \times 10^{13}$ Ohm*cm, which is a reasonable value for tantalum oxide. The resistivity and electric field of the oxide determined from the optimized parameters, $a'$ and $b$, are reasonable values and are within an order of magnitude of literature values. This is an *ad-hoc* analysis at the potential drop at the oxide/metal interface was not measured but was calculated so as to achieve reasonable values.

3.2.6.6. Relative Thickness of the Outer Layer

After several hours of anodization the absorbance of the PO$_4^{3-}$ band may cease to increase as shown in Figure 3—38 and Figure 3-39. This suggests that the outer layer either ceases to grow or grows at a very slow rate after a few hours of anodization. The thickness of the outer oxide layer that contains incorporated phosphorus relative to the total oxide thickness is obtained by taking the ratio of the integrated area of the PO$_4^{3-}$ band to the area of the Ta-O band; this is shown in Figure 3-46. The ratio of the PO$_4^{3-}$ band maxima to the Ta-O band maxima is shown in Figure 3-47. Both Figure 3-46 and Figure 3-47 indicate that at very long anodization times, the relative thickness of the outer, phosphorus containing layer decreases. This observation is consistent with observations made using TEM imaging.
Figure 3-46: Ratio of the phosphorus related band maximum to the Ta-O band maximum vs. anodization time.

Figure 3-47: Ratio of the phosphorus related band area to the Ta-O band area vs. anodization time.
3.3. Electrochemical Measurement of Oxide Growth Rate

3.3.1. Experimental

3.3.1.1. Surface Preparation of Ta

A bulk tantalum substrate was prepared from high purity, capacitor grade tantalum sheet that was mechanically polished using 15 µm diamond paste and polishing oil on photographic printer paper and then polished with 1 µm and 0.3 µm alumina on a cloth wheel. The substrate was then vacuum annealed at 1780° C for 30 minutes.

3.3.1.2. Measurement of Wet capacitance

The thickness of a thin oxide (10V formation) was determined as a function of time of applied voltage on a bulk, mechanically polished tantalum substrate. The cell described in the anodization procedure was used; the electrolyte was 0.06 wt% H$_3$PO$_4$, and a saturated calomel electrode (SCE) was used as the reference electrode. A Solartron 1287 electrochemical interface and 1255B frequency-response analyzer were used to measure the impedance at 1000Hz, and the capacitance was calculated from the imaginary component of the impedance. The oxide was formed to 10V vs. SCE and the applied potential was maintained for 30 hours. The applied potential was then reduced to 5V vs. SCE and maintained for an additional 100 hours.

3.3.2. Results

The thickness of the oxide was calculated from the parallel-plate capacitor equation with an assumed dielectric constant of 18.5. The reported dielectric constant of anodic tantala varies considerably between different sources. Macagno and Schultz[64] reported a value of 25.3; Kerrec, et.al.,[5] have reported a value of 18.5 for oxides thinner than 19nm. For the purposes of this analysis, the true dielectric constant and surface area do
not need to be known with certainty, since we are mostly interested in rates of growth. It is assumed, however, that the dielectric constant and surface area remain constant.

Figure 3-48 shows the change in the thickness with time when the formation voltage is held at 10V for 30 hours and then stepped down to 5V and held for an additional 100 hours. The initial thickness is determined from the first impedance measurement for each voltage condition. It was anticipated that reducing the applied voltage from 10V to 5V would induce the oxide to thin towards the steady state thickness of a 5V oxide by dissolution and, hence, that a dissolution rate could be determined. Upon stepping the formation voltage from 10V to 5V, the measured capacitance continued to decrease over the next 100 hours, thus indicating that the oxide continued to grow, albeit at a very slow rate. The discontinuity of the capacitance \textit{circa} 75 hours is likely due to instability in the reference electrode, e.g., an air bubble may have formed in the Luggin capillary of the experimental cell. For formation at 10V, the growth rate is approximately 1nm/day (1x10^{-5}nm/s), and when the applied voltage was reduced to 5V, the rate slowed to 0.1 nm/day (1x10^{-6}nm/s). This implies that the thickness of the oxide does not reach a steady state as is reported for many other valve metals\cite{20, 82, 83}; rather the extremely low solubility product of tantalum oxide effectively prevents the tantalum from being injected into the electrolyte solution, unless a complexing agent is present (e.g., $F^-$ or oxalic acid.)
Figure 3-48: The change in oxide thickness with time (bottom plot) when the applied potential is stepped from 10V to 5V (top plot). The change in oxide thickness was calculated from the wet capacitance at 1000 Hz.

3.4. Conclusions

The use of sputter deposited tantalum substrates allows for reasonable throughput of experiments and greatly expands the available analysis techniques for studying the properties of anodic oxides. Surface science techniques such as FT-IR reflectance spectroscopy and spectroscopic ellipsometry are complicated on bulk tantalum because the surface roughness of mechanically or chemically polished refractory metals is
typically rough. Preparing specimens for transmission electron microscopy proved to be particularly challenging because it is difficult to mechanically polish refractory metal sufficiently thin; also, because the metal substrates are not perfectly flat, it is difficult to bond the two oxide interfaces together when preparing a cross sectional specimen. This causes the cross section to de-laminate when it is still too thick for ion milling. Even when thin cross sectional specimens can be prepared, ion milling presents a considerable challenge. Tantalum oxide mills much faster than tantalum. As a result, the area of interest, the tantalum oxide, mills away extremely easily. While sputter deposited tantalum is less pure than bulk tantalum, it allows for achievable experiments because silicon wafers provide a flat, uniform substrate that is ideal for preparing TEM cross sections and applying surface science techniques. It is posited that the results and conclusions drawn from sputter deposited tantalum can be transferred to the theory of anodization of bulk tantalum metal.

FT-IR reflectance spectroscopy is a useful method for determining the total oxide thickness and the relative thickness of the phosphate containing layer. TEM imaging can also be used to determine the thickness of the individual layers, but it is an expensive, time-consuming, and highly localized measurement. FT-IR requires minimal sample preparation, simpler apparatus, and a few minutes of instrument time per spectrum. These characteristics make FT-IR reflectance an excellent technique for studying processing-property-chemistry relationships of anodic oxide films. FT-IR reflectance is quantified using either the band maxima or the band area of the absorbances; the precision of the technique is better than 1% for analysis on a particular sample. The thickness of the oxide was also calculated using the absorption coefficients reported by Kihara-Morishita[115], but there was approximately a 10% discrepancy between this calculated thickness and the thickness measured in this work. Differences in the apparatus and reference substrate are likely the source of the discrepancy.

Table 3-15 contains useful expressions for calculating oxide thickness from absorbance spectra collected as described in Section 3.1.4.1. This relationship was determined by calibrating FT-IR spectra with measurements made by TEM imaging. Reflectance FT-IR
and TEM imaging demonstrate that the thickness of the outer layer relative to the total oxide is not a function of formation voltage. The anodization constant obtained in this work is $1.83 \pm 0.06$ nm/V for anodization in 0.1 M H$_3$PO$_4$ grown at a rate of 250 mV/sec. This value is in good agreement with the literature. In the formation voltage range studied, 20 -- 100 V, the relative thickness of the phosphate containing oxide does not depend on formation voltage.

Bright field TEM imaging is explored as a means of identifying the boundary between the inner and outer layer of anodic tantalum oxide formed in 0.1 M H$_3$PO$_4$. The transmitted intensity of the electron beam is integrated over a defined area of the image, when the outer layer is present, a local maxima in the intensity is observed near the boundary of the inner and outer oxide layers. Changes in transmitted intensity due to a gradient in specimen thickness can be differentiated from intensity changes due to incorporated phosphorus. The intensity profile of an oxide formed in 0.1 M Na$_2$SO$_4$ shows a marked departure from the profile of oxide formed in 0.1 M H$_3$PO$_4$. This supports the conclusion that the contrast change is due to incorporated phosphorus. The bi-layer oxide structure is observed by direct TEM imaging for anodization in 0.1 M H$_3$PO$_4$ for samples anodized to 6 V, 12 V, 50 V, 70 V, and 100 V.

The wet electrochemical capacitance decreases steadily as a function of time of applied voltage. This suggests that the oxide grows indefinitely when an applied bias is maintained. However, this experiment is not sufficient for drawing a definitive conclusion because it is an indirect measurement of thickness that assumes the permittivity of the oxide is constant. The measured capacitance is a ratio of the permittivity to the thickness, thus a continual decrease in the capacitance could be attributed to either an increase in oxide thickness or a decrease in the dielectric constant, or a combination of both. However, TEM imaging and FT-IR reflectance spectroscopy confirm that the change in capacitance is attributable to an increase in the oxide thickness.
To a first approximation, the total oxide thickness increases with the natural logarithm of time. The optical thickness of the outer layer follows this trend only at moderate anodization times, i.e., between 10 and 240 minutes. This is evidenced by the poor R² values when regression is performed on the data. FT-IR analysis shows that the outer layer of oxide grows is thicker than the inner layer in the first few hours of anodization. After 2--4 hours at the formation voltage, the outer layer becomes the thinner layer due to its slower growth rate. The growths laws determined for the separate oxide layers can be used as constraints in optimizing the point defect model (PDM) to experimental electrochemical impedance spectra (EIS). One purpose of this analysis is to approximate the growth rate and hence the Faradaic current of anodized tantalum.

Zhang, et al., have shown that the point defect model (PDM), which predicts a direct logarithmic growth law, is more realistic than the High Field Model (HFM), which predicts an inverse logarithmic growth law, when describing electrochemical oxide formation on tantalum. In the integrated form (equations 3--10 and 3--11) both laws provide equally good fits to the experimental data. The uncertainty in the measured measurements is much greater than the difference between the two fitted growth laws, thus the goodness of fit is not a suitable indicator for determining the more accurate growth model. Rather, the basis for evaluating the suitability of a model is its ability to explain the greatest amount of observed phenomena. The HFM posits that the oxide forms solely at the oxide/solution interface due to the force of the electric field; the PDM allows for simultaneous oxide formation at two distinct interfaces. Zhang, et al., show that the differential of the predicted current is in agreement with the PDM but not the HFM.[12] The fitting results for both the inverse logarithmic law and the direct logarithmic growth law are reported because the HFM has been widely used in the past and continues to be cited and employed in the literature despite its inferiority to the PDM.

At extended anodization times, the relative thickness of the phosphate containing layer decreases. Growth of the outer layer, which forms by Ta⁺ migration, is either halted or significantly slowed at extended anodization times. Relative to the outer layer, the inner layer grows at a faster rate at extended anodization times. This suggests that once a
critical thickness has been reached, the production and/or migration of tantalum interstitials is reduced relative to the production and/or migration of oxygen vacancies. It is interesting to ponder what effect the incorporated phosphate in the outer layer may have on the point defect reactions at the metal/oxide interface. Incorporated phosphate inhibits oxidation of tantalum, but it may influence tantalum interstitials and oxygen vacancies differently.
Chapter 4: Investigation of the Structure and Optical Properties of Anodic Tantalum Oxide by Spectroscopic Ellipsometry

4.1. Introduction

4.1.1. Effect of Incorporated Phosphorus

Anodic oxide films are formed by exposing a metal anode to an electrolyte then applying a bias between the anode and a counter or reference electrode. The resulting oxide is typically amorphous, uniform, largely reproducible, and its thickness is linearly proportional to the applied voltage. During oxide formation, the incorporation of electrolyte species from the anodizing electrolyte is a well known phenomenon.[35, 47, 54] Anodization of tantalum in phosphoric acid electrolytes results in the incorporation of phosphorus in the outer portion of the oxide. The inner layer of anodic tantalum oxide formed in phosphoric acid consists of Ta$_2$O$_5$, which is considered to be pure Ta$_2$O$_5$. The composition of the outer layer is dependent on the anodizing conditions. For anodization in many halide salts, such as KCl, the outer layer is pure Ta$_2$O$_5$,[47] however species from the electrolyte can be incorporated into the oxide when formation is completed in phosphoric acid, concentrated sulfuric acid, boric acid, or fluorinated electrolytes.[47] The chemical composition of the outer layer is constant, with no observed gradient in composition; the interface between the inner and outer layers is abrupt.[52, 53, 92]

From a practical perspective, the incorporation of phosphorus in the oxide can result in superior properties when used as the dielectric material in electrolytic capacitors.[101] While incorporated phosphorus decreases the dielectric constant of the material,[35] it also increases the breakdown strength[35] and discourages crystallization of the amorphous oxide.[29] Incorporated phosphorus also has a significant impact on the ionic conductivity of the formed oxide, and has been shown to inhibit oxygen conductivity.[34, 35] Anodic oxide films having incorporated phosphorus show complex processing-property relationships.[38, 101] Because incorporated phosphorus can have a profound
effect on the electrical properties of tantalum oxide, it is worthwhile to determine how anodization conditions affect the composition of the formed oxides and the resultant material properties.

The dielectric constants of the individual oxide layers have been reported by Randall[35] as a function of phosphoric acid molarity of the electrolyte. The concentration of incorporated phosphorus is proportional to the electrolyte concentration, [53] and the dielectric constant of both the inner and outer layers decreases with increasing phosphorus incorporation.[35] The dielectric constants were determined by measuring the wet capacitance as a function of immersion time in an etchant solution, and these results [35] are summarized in Table 4-1; examination shows that the fraction of the film containing phosphorus does not vary when the electrolyte is between 0.001 M and 1 M H₃PO₄; however, the dielectric constants of both layers are reduced as the concentration of the electrolyte is increased.

Table 4-1: After [35] Fraction of film containing phosphorus and the dielectric constants for the inner and outer tantalum oxide layers as functions of the phosphoric acid molarity.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Fraction of Film Containing P</th>
<th>$\varepsilon$, Outer Layer</th>
<th>$\varepsilon$, Inner Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>--</td>
<td>--</td>
<td>27.6</td>
</tr>
<tr>
<td>0.001M H₃PO₄</td>
<td>0.48</td>
<td>25.9</td>
<td>26.7</td>
</tr>
<tr>
<td>0.01 M H₃PO₄</td>
<td>0.50</td>
<td>24.2</td>
<td>26.0</td>
</tr>
<tr>
<td>0.1 M H₃PO₄</td>
<td>0.49</td>
<td>21.3</td>
<td>24.0</td>
</tr>
<tr>
<td>1 M H₃PO₄</td>
<td>0.51</td>
<td>20.3</td>
<td>23.8</td>
</tr>
<tr>
<td>14.7 M H₃PO₄</td>
<td>0.63</td>
<td>12.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Capacitance measurements cannot simultaneously measure both the oxide thickness and the dielectric constant. Spectroscopic ellipsometry (SE) to simultaneously measures both the thicknesses and complex dielectric functions of individual layers in a stack of dielectric layers.[148] Ellipsometry has been used to measure the thickness and
refractive index of oxide layers and to show that the bi-layer oxide consists of two distinct layers where the outer layer has a constant concentration of phosphate.[52] It has also been used to measure the refractive index and oxide thickness in-situ as a field is applied.[157] Such experiments have been done at a single wavelength, but spectroscopic ellipsometry can provide significantly more information concerning the optical properties of the materials in bi-layer structures.

4.1.2. Barrier Layer/Outer Layer Structure of Anodic Oxides

Regardless of electrolyte incorporation, many valve metals form a bi-layer structure where the inner layer is compact and termed a barrier layer and the outer layer is a precipitated porous layer.[166, 167] This behavior is well documented for anodic alumina, and the properties of the oxide change considerably when the oxide is boiled in deionized water, a process known as hydrothermal sealing (HTS).[167-169] After hydrothermal sealing, anodic alumina becomes much more corrosion resistant, thus boiling “seals” the porous outer layer. The pores of the outer layer are partially filled by a the procedure.[168] It is emphasized that this type of bi-layer describes two oxides that are structurally very different. The barrier layer is compact, and the outer layer is porous and can range from nanometers to microns in thickness. This dissertation deals mostly with bi-layer oxides where the differences between the two layers are attributed to chemistry and both layers have a compact structure.

Transmission electron microscopy (TEM) imaging has been used to reveal nanoporosity in non-thickness limited (NTL) anodic oxides formed from niobium.[170] Likewise, porosity is clearly visible in the TEM for anodic NTL films formed on aluminum and tantalum where the porosity is approximately 5%.[171] Such porosity is not, however, observed in TEM images of tantalum formed in dilute phosphoric acid. [92, 172, 173] Such experimental observations suggest that tantalum does not adhere to a bi-layer model having a compact barrier layer and a porous outer layer. Rather, the entire oxide is compact even when two compositionally different layers are present.
4.2. Objectives

The objectives of these studies are to determine the complex dielectric functions of the two distinct oxide layers formed during anodization in 0.1M H$_3$PO$_4$ and compare them to the dielectric function of Ta$_2$O$_5$ formed in 0.1 M Na$_2$SO$_4$. Spectroscopic ellipsometry is used to measure thicknesses and complex dielectric functions of the inner and outer oxide layers formed by anodization in H$_3$PO$_4$ or Na$_2$SO$_4$. The thickness and properties are measured as a function of anodization time and at several formation voltages for anodization in 0.1M H$_3$PO$_4$.

Wet electrochemical studies have shown that the inner and outer layers have different dielectric constants. The propensity to crystallize, the rate of dissolution in fluorinated solutions, and the chemistry of the two layers are distinct. It is unknown whether the different properties of the outer layer should be attributed to the incorporated phosphorus (composition) or to the porosity (structure) of the outer layer. Spectroscopic ellipsometry is used here to explore the possibility of porosity in the outer layer, and the effect of hydrothermal sealing on the oxide dielectric functions is also examined. This work is an effort to clarify whether the differences in the properties of the bi-layers are compositional (due to incorporated phosphate) or structural (due to porosity).

Thin ( <15nm) anodic oxides may exhibit different properties compared to thick oxides, thus the dielectric functions of thin oxides are compared to the functions of thicker oxides.

4.3. Experimental

4.3.1. Anodization

Tantalum substrates described in Section 3.1.1 were used. A model K0235 Princeton Applied Research flat cell with a platinized counter electrode was used during
anodization. The area of the anode exposed to the electrolyte was a circle of 1cm$^2$. Electrical contact to the tantalum was generally made by tightly pressing a thin wire between the tantalum and the Teflon sample holder. Anodization was done at room temperature in 0.1 M H$_3$PO$_4$ or 0.1 M Na$_2$SO$_4$. Potentiodynamic growth was completed at a rate of 250 mV/second until the desired formation voltage was achieved.

**Sample Set of Anodized Oxides**

1.) Low formation voltage (2-13V with respect to a saturated calomel reference electrode) oxides were formed in 0.1M H$_3$PO$_4$. The applied voltage was controlled by a Solartron 1287 electrochemical interface. The formation voltage was applied for one hour.

2.) Oxides were formed to 70V in 0.1 M H$_3$PO$_4$ and held at the formation voltage for various times. The applied voltage was controlled using a Hewlett Packard 4140B pA/DC voltage source. The potential is with reference to the counter electrode.

3.) Oxides were formed to 70V in *either* 0.1 M H$_3$PO$_4$ or 0.1 M Na$_2$SO$_4$; the formation voltage was applied for 2 minutes then removed from the cell and hydrothermally sealed by boiling vigorously for 8 minutes in deionized water. The applied voltage was controlled using a Hewlett Packard 4140B pA/DC voltage source. The potential is with reference to the counter electrode.

**4.3.2. Ellipsometric Spectra Collection**

Ellipsometry spectra in Tan $\Psi$ and Cos $\Delta$ were collected using a Sopra model number GES 5 rotating polarizer, spectral scanning ellipsometer. Spectra were collected ex-situ at room temperature at four angles of incidence, $\Theta_i = 45^\circ$, 70°, 75°, and 85°, from 1.4-5.0 eV. Analysis of spectroscopic ellipsometry was completed in WVASE 32 version 3.650.[174]
4.3.3. Spectroscopic Ellipsometry Analysis

4.3.3.1 Complex Dielectric Function Parameterization

The dielectric function parameterization of each Ta$_2$O$_5$ material is represented by a Tauc-Lorentz oscillator[175, 176] and a constant additive term to $\varepsilon_1$ represented by $\varepsilon_\infty$. The Tauc-Lorentz oscillator is represented by:

$$
\varepsilon_2 = \begin{cases} 
\frac{AE_0\Gamma}{(E^2-E_0^2)^2+\Gamma^2E^2} & \text{E > E}_g \\
0 & \text{E \leq E}_g 
\end{cases},
$$

and

$$
\varepsilon_1 = \frac{2}{\pi} P \int_0^\infty \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi,
$$

where $A$ is the amplitude, $\Gamma$ is the broadening, $E_0$ is the resonance energy, and $E_g$ represents a band gap determined from a parabolic band, constant momentum matrix element. The band gap, $E_g$, can also simply be considered to represent the onset of absorption in this model.

The optical response of a surface roughness layer incorporated into some models is represented by a Bruggemman effective medium approximation (EMA)[177] consisting of a 0.50 bulk film / 0.50 void mixture. Similarly, the optical response of a porous layer of oxide is represented by a Bruggeman EMA [177] consisting of a mixture of voids and the bulk.[174] The percentage of voids is analogous to porosity in this formalism.

In the ellipsometry analysis presented in this work, the underlying tantalum substrate was $\geq 140$ nm, and it is assumed that the penetration depth of the incident radiation in tantalum is short enough that the tantalum substrate has a semi-infinite thickness. Therefore, the optical model ignores the TaN, Pt, Ti, and Si layers of the substrate.
4.3.3.2. Native Oxide

The optical properties are extracted in the form of the dielectric function spectra ($\varepsilon_1$, $\varepsilon_2$), for sputtered tantalum. A least squares regression analysis with an unweighted error function\[178\], $\sigma$, is used to fit the experimental ellipsometric spectra in the high energy region (3.5-5.0 eV) to an optical model consisting of a semi-infinite tantalum layer / native Ta$_2$O$_5$ / air ambient structure. Reference dielectric function spectra were used for Ta\[179\] and Ta$_2$O$_5$ \[180\] to obtain the Ta$_2$O$_5$ thickness ($8.47 \pm 0.817 \text{ Å}$). At high energy ($> \sim 2.0—3.5 \text{ eV}$), dielectric functions of metals have been observed to exhibit small variation with respect to specific film processing conditions as opposed to behavior at low energy ($< 2.0 \text{eV}$), which has been observed to exhibit strong variations with the mean free path of electrons in the material.\[181\]

By fitting experimental spectra at high energy, the oxide thickness can be extracted while using reference optical properties. Once the native Ta$_2$O$_5$ thickness is determined, numerical inversion can be used to extract the dielectric function spectra specific to this sputtered Ta material over the complete spectral range. The results of this approach are shown in Figure 4-1 and compared to the reference dielectric functions for bulk Ta. From this comparison, it is observed that the low energy amplitude of $\varepsilon_2$ is higher for the sputtered Ta compared to the bulk Ta, which corresponds to a reduced mean free path length of electrons (i.e. increased disorder) as is expected for a sputtered Ta film.
Figure 4-1: Dielectric function spectra ($\varepsilon_1$, $\varepsilon_2$) for sputtered Ta determined from numerical inversion of spectra in ($\Delta$, $\psi$) at three angles of incidence ($\Theta_i = 45^\circ$, $70^\circ$, $75^\circ$, and $85^\circ$) (solid red line) compared to reference bulk Ta material (dashed black line).

4.3.3.3. Structural Models

Several candidate models were fabricated and attempts to optimize each model to the collected spectra were made. All models assume that the tantalum substrate thickness is
semi-infinite (≥ 150 nm) and that the outermost interface is in contact with the ambient atmosphere. The best fitting models are characterized by a low error function, σ, between the experimental and optimized spectra and by small error bars on the fitted parameters. Also, the model must return reasonable values for the optical parameters and for the thickness of the oxide.

The optical property and compositional models described above were combined to form structural models to describe the anodized tantalum oxide samples. Structural models for the tantalum oxide layers tested were:

1.) Single layer oxide
2.) Single layer oxide with surface roughness layer
3.) Bi-layer oxide
4.) Bi-layer oxide with surface roughness layer
5.) Compact barrier layer of oxide with an outer porous layer

**Single Layer Models**
Schematics of the single layer models, with and without surface roughness layers, are shown in Figure 4-2. The variable parameters in the SE models are the dielectric function parameters and the thickness of the oxide layer. The model that includes surface roughness adds the thickness of that layer as a parameter.
Figure 4-2: Schematics of the single layer oxide model with and without surface roughness. The oxide layer is described by a Tauc-Lorentz oscillator with a constant additive term to $\varepsilon_1$ while the surface roughness layer is modeled by a Bruggeman effective medium approximation (EMA)\cite{177} consisting of a 0.50 bulk film / 0.50 void mixture.

Bi-Layer Models
Each individual layer of the bi-layer model is described using a separate dielectric function parameterization. The variable parameters are the dielectric function parameters for each layer, the thickness of each layer, and the thickness of the surface roughness when applicable. Schematics of the bi-layer models are shown in Figure 4-3.

Figure 4-3: Schematics of the bi-layer oxide models with and without surface roughness. Each oxide layers is described by a Tauc-Lorentz oscillator with a constant additive term to $\varepsilon_1$ while the surface roughness layer is modeled by a Bruggeman effective medium approximation (EMA)\cite{177} consisting of a 0.50 bulk film / 0.50 void mixture.
Porous Outer Layer Model

The variable parameters in the model shown in Figure 4-4 are the thicknesses of the compact and porous layers, the porosity of the outer layer, and the dielectric function parameters describing the inner, compact layer of oxide.

**Figure 4-4:** Schematic of a bi-layer model having a compact inner layer and a porous outer layer. The porous oxide is modeled by an effective medium approximation (EMA) where the film is represented by fractions of bulk material and void. The inner layer of oxide is described by a Tauc-Lorentz oscillator with a constant additive term.

### 4.3.3.3. Evaluation of Models

The complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and microstructure for anodic Ta$_2$O$_5$ films were determined using a least squares regression analysis and an unweighted error function,[178] $\sigma$, to evaluate the optical structural models against the experimental ellipsometry spectra. This procedure allows for the determination of the thicknesses of the surface roughness and Ta$_2$O$_5$ layers as well as a parameterization of the respective Ta$_2$O$_5$ dielectric function.

The oxide thickness can be predicted to a fair degree of accuracy from the formation voltage and length of time that the voltage is applied. Transmission electron microscopy (TEM) and FT-IR reflectance spectroscopy have been used to determine the thickness as
a function of anodization time for formed oxides as described in 3.2.6.4. The thickness of anodic oxide as a function of formation voltage for an anodization time of fifty minutes is given by equation [4-2], and the thickness of oxide formed to 70 V is given as a function of formation time in equation [4-3] where the parameters are defined in Table 4-2.

\[ L_{nm}(V) = 1.8 \, nm \times V_f + 2.6 \, nm \] \hspace{1cm} [4-2]

\[ L = L_0 + \frac{1}{b} \ln(1 + a'b \exp(-bL_0)t) \] \hspace{1cm} [4-3]

**Table 4-2:** Average parameters of the direct logarithmic growth laws as reported in 3.2.6.4. Anodization time, \( t \), is in seconds and oxide thickness, \( L \), is in cm.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>( a' (\text{cm}^{-1}) )</th>
<th>( b (\text{cm}^{-1}) )</th>
<th>( L_0 (\text{cm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>243</td>
<td>( 2.18 \times 10^6 )</td>
<td>( 11.1 \times 10^{-6} )</td>
</tr>
<tr>
<td>Inner</td>
<td>219</td>
<td>( 4.56 \times 10^6 )</td>
<td>( 5.6 \times 10^{-6} )</td>
</tr>
<tr>
<td>Outer</td>
<td>248</td>
<td>( 4.40 \times 10^6 )</td>
<td>( 5.7 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

For all samples, spectra were collected at four different incidence angles: \( \Theta = 45^\circ, 70^\circ, 75^\circ, \) and \( 85^\circ \) from 1.4 to 5.0 eV. In order to maintain the highest sensitivity to film structure, optimization was completed using spectra from 3.0 to 5.0 eV. Optimization to different sets of spectra were completed:

1.) \( 45^\circ, 70^\circ, 75^\circ, 85^\circ \)
2.) \( 70^\circ \)

The unweighted error function, \( \sigma \), is used to evaluate the quality of the fit using the various models. In the tables that follow, *red italics* are used to note optimizations that failed to converge; such optimizations would result in one or more of the parameters...
going to an unphysical value with egregious error bars. **Bold green** is used to demonstrate which optimizations have the lowest average error.

4.4. Results and Discussion

4.4.1. Effect of Phosphorus Incorporation

The effect of incorporated phosphorus is examined by comparing oxides formed in either 0.1 M H$_3$PO$_4$ or 0.1 M Na$_2$SO$_4$. Phosphate incorporates in approximately the outer half of the oxide for the growth conditions employed here, but no species are incorporated from Na$_2$SO$_4$. Table 4-3 shows $\sigma$ for the optimizations to the candidate models. Different groups of spectra were separately analyzed. The best fits are indicated by the lowest average $\sigma$.

Table 4-3: Unweighted error functions, $\sigma$, for optimization to the candidate models. Spectra were analyzed for $\Theta=70^\circ$ and simultaneously for $\Theta=45^\circ, 70^\circ, 75^\circ, \text{ and } 85^\circ$.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Model→</th>
<th>Angles Analyzed</th>
<th>Monolayer</th>
<th>Mono w/ Rough</th>
<th>Bilayer</th>
<th>Bilayer w/ Rough</th>
<th>Porous Outer Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$PO$_4$</td>
<td>70</td>
<td>0.1751</td>
<td>0.05285</td>
<td><strong>0.04953</strong></td>
<td>0.04991</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
<td>45,70,75,85</td>
<td><strong>0.1388</strong></td>
<td><strong>0.1308</strong></td>
<td>0.04764</td>
<td><strong>0.04643</strong></td>
<td>0.0579</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>70</td>
<td>0.04266</td>
<td><strong>0.01822</strong></td>
<td>0.02691</td>
<td>0.02349</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>45,70,75,85</td>
<td>0.05167</td>
<td><strong>0.03972</strong></td>
<td>0.04189</td>
<td>0.04169</td>
<td>0.04573</td>
<td></td>
</tr>
</tbody>
</table>

For oxides formed in H$_3$PO$_4$, the bi-layer structural model gives lower $\sigma$ values than the mono-layer model. For the bi-layer model, including surface roughness considerably
increased the uncertainty in the optimized parameters but did not reduce $\sigma$; the thickness
of the roughness layer often converged to zero. These observations indicate that it is not
necessary to include a roughness layer in the bi-layer model.

For oxides formed in $\text{Na}_2\text{SO}_4$, the mono-layer model with a roughness term yields a
slightly better fit than for either bi-layer model.

Experimental spectra with fit results of the appropriate models are shown in Figure 4-5
for anodization in 0.1 M $\text{H}_3\text{PO}_4$ (bi-layer model). The superiority of the bi-layer model
in describing oxides formed in 0.1 M $\text{H}_3\text{PO}_4$ is demonstrated by Figure 4-6 and Figure
4-7 , where the best fit optimizations for both models are shown with the experimental
spectra collected at 70° and 75° incidence, respectively. The experimental spectra and
mono-layer model optimization are shown in Figure 4-8 for an oxide formed in 0.1 M
$\text{Na}_2\text{SO}_4$. 
Figure 4-5: Data and optimization results for specimen formed in 0.1 M H$_3$PO$_4$ and subsequently hydrothermally sealed. The bi-layer model without roughness best describes oxides formed to 70V in 0.1 M H$_3$PO$_4$. The solid lines represent the optimized model.
Figure 4-6: Comparison of the optimized mono-layer (black dashed line) and bi-layer (solid red line) models for spectra collected at 70° incidence for an oxide formed to 70V in 0.1 M H₃PO₄.
Figure 4-7: Comparison of the optimized monolayer (black dashed line) and bi-layer (solid red line) models for spectra collected at 75° incidence for an oxide formed to 70V ion 0.1 M H₃PO₄.
Figure 4-8: Data and optimization results for specimen formed in 0.1 M Na$_2$SO$_4$ and subsequently hydrothermally sealed. The mono-layer model with a thin (2-5 nm) surface roughness layer best describes oxides formed in 0.1 M Na$_2$SO$_4$. The solid lines represent the optimized model.

The oxide thickness determined from ellipsometry spectra for the Na$_2$SO$_4$ sample is shown in Table 4-4 when the mono-layer models are used and in Table 4-5 when a bi-
layer model is used. The mono-layer with surface roughness model gives the best agreement with oxide thickness measured by FT-IR reflectance spectroscopy. If the model with surface roughness is used for analyzing Na$_2$SO$_4$ specimens, the sum of the oxide layer thickness and the roughness layer thickness is in close agreement with the IR thickness. The bi-layer model consistently overestimates the thickness of the oxide. This observation, along with lowest $\sigma$ suggests that the mono-layer model with roughness is a better fit than the bi-layer model for samples formed in Na$_2$SO$_4$.

**Table 4-4:** Oxide thickness determined by SE for a sample anodized in 0.1 M Na$_2$SO$_4$ for two minutes. Results of two models are shown: 1.) Mono-layer and 2.) Mono-layer with surface roughness. The thickness of the oxide was measured to be 118.4 nm by FT-IR reflectance spectroscopy.

<table>
<thead>
<tr>
<th>Angles Analyzed</th>
<th>Mono-layer, No Roughness</th>
<th>Mono-layer, with Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Oxide Layer</td>
</tr>
<tr>
<td>70</td>
<td>118 ± 1</td>
<td>118.3 ± 0.6</td>
</tr>
<tr>
<td>45, 70, 75, 85</td>
<td>116.2 ± 0.3</td>
<td>117.7 ± 0.4</td>
</tr>
</tbody>
</table>

**Table 4-5:** Oxide thickness determined by SE using a bi-layer model for a specimen anodized in 0.1 M Na$_2$SO$_4$ for two minutes. The thickness of the oxide was measured to be 118.4 nm by FT-IR reflectance spectroscopy.

<table>
<thead>
<tr>
<th>Angles Analyzed</th>
<th>Bi-layer Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>70</td>
<td>123.3 ± 0.6</td>
</tr>
<tr>
<td>45, 70, 75, 85</td>
<td>121.6 ± 0.4</td>
</tr>
</tbody>
</table>
The thicknesses of the inner and outer layers of the sample anodized in 0.1 M \( \text{H}_3\text{PO}_4 \) as determined by SE are shown in Table 4—6 and compared to the thickness measured by TEM bright field imaging. SE measures the total oxide thickness accurately but does not measure the thickness of the individual layers precisely.

**Table 4-6:** Comparison of the inner layer, outer layer, and total oxide thicknesses measured by TEM imaging and SE.

<table>
<thead>
<tr>
<th>Method</th>
<th>Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Oxide</strong></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>117±7</td>
</tr>
<tr>
<td>TEM</td>
<td>115±1</td>
</tr>
<tr>
<td>FT-IR</td>
<td>117.2</td>
</tr>
<tr>
<td><strong>Inner Layer</strong></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>61±5</td>
</tr>
<tr>
<td>TEM</td>
<td>53±2</td>
</tr>
<tr>
<td><strong>Outer Layer</strong></td>
<td></td>
</tr>
<tr>
<td>SE</td>
<td>56±5</td>
</tr>
<tr>
<td>TEM</td>
<td>59±2</td>
</tr>
</tbody>
</table>

The complex dielectric function of the mono-layer oxide (\( \text{Na}_2\text{SO}_4 \)) is compared to the dielectric functions of the inner and outer layers of the bi-layer oxide (\( \text{H}_3\text{PO}_4 \)) in Figure 4-9. The onset of absorption, or band gap, for the mono-layer oxide is 4.00 ± 0.02 eV. The band gaps for the bi-layer oxide are 4.467 ± 0.002 eV (inner layer) and 3.86 ± 0.06 eV (outer layer). The onset of absorption of the inner layer of oxide is shifted to a higher energy while the onset for the outer, phosphorus containing layer is shifted to a lower energy. It is logical that the onset of absorption is lower for oxides having incorporated phosphate; the phosphorus may act as a dopant and likely provides additional allowed energy levels near the band edges, thus it is expected that phosphorus incorporation
would narrow the band gap and shift the absorption edge to a lower energy. The $E_g$ of the mono-layer oxide is intermediate between the individual layers of the bi-layer oxide.

![Graph of complex dielectric functions](image)

**Figure 4-9:** The complex dielectric functions of a mono-layer oxide formed in $\text{Na}_2\text{SO}_4$ and of the inner and outer layers of a bi-layer oxide formed in 0.1 M $\text{H}_3\text{PO}_4$. The total thickness of both specimens is ~118nm.

Tantalum oxide formed in $\text{H}_3\text{PO}_4$ shows markedly different optical properties from tantalum oxide formed in $\text{Na}_2\text{SO}_4$. This difference can be attributed to incorporated phosphate species. The samples anodized in $\text{Na}_2\text{SO}_4$ are best described by a mono-layer
model, while the samples anodized in H$_3$PO$_4$ to formation voltages ≥ 13V are best described using a bi-layer model. The total oxide thickness determined by SE is in agreement with the thickness measured by TEM and FT-IR reflectance spectroscopy. Although the SE analysis clearly discerns two distinct Ta$_2$O$_5$ layers in the structure, the error bars on the thickness values indicate that SE may only be sensitive to measuring the thickness of the individual layers within 10% due to the remaining similarities between the optical properties of each layer.

### 4.4.2. Effect of Hydrothermal Sealing

The matrix of samples for assessing the effect of hydrothermal sealing on mono-layer and bi-layer oxides is given in Table 4—7. The thickness of the total oxide has been calculated from the FT-IR reflectance absorbance of each specimen as described in Section 3.2.3.

**Table 4-7**: Sample set for determining the effect of hydrothermal sealing on formed mono-layer and bi-layer oxides. HTS = hydrothermal sealing

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Anodization Electrolyte</th>
<th>Formation Voltage and Time of Anodization</th>
<th>Hydrothermal Sealing</th>
<th>IR Total Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.1 M H$_3$PO$_4$</td>
<td>70V, 2min</td>
<td>No</td>
<td>117.2</td>
</tr>
<tr>
<td>P, HTS</td>
<td>0.1 M H$_3$PO$_4$</td>
<td>70V, 2 min</td>
<td>Yes</td>
<td>118.4</td>
</tr>
<tr>
<td>S</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>70V, 2 min</td>
<td>No</td>
<td>118.1</td>
</tr>
<tr>
<td>S, HTS</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>70V, 2 min</td>
<td>Yes</td>
<td>117.7</td>
</tr>
</tbody>
</table>

The error bars on the fitted parameters, (layer thickness and Tauc-Lorentz oscillator terms) are large when only spectra collected at 70° incidence are used for optimization. When optimization is done for “45°, 70°, 75°, 85°” data sets, the error bars are much smaller.
The oxide thicknesses determined by SE are compared to the thicknesses measured by FT-IR reflectance spectroscopy as shown in Table 4-8. The high uncertainty in the thickness of the bi-layer samples is attributed to difficulty in determining the precise boundary between the two layers. Thus the uncertainty in the total thickness is likely overestimated.

**Table 4-8:** Oxide thickness measured by SE where spectra at 45°, 70°, 75°, and 85° incidence are simultaneously analyzed compared to thickness measured by FT-IR reflectance spectroscopy. The samples containing phosphorus (P) are optimized to the bi-layer model while the samples formed in Na₂SO₄ (S) are optimized to a mono-layer model having a thin layer of surface roughness. HTS=hydrothermal sealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FT-IR L_{Total}, nm</th>
<th>SE L_{Total}, nm</th>
<th>SE L_{Inner}, nm</th>
<th>SE L_{Outer}, nm</th>
<th>SE L_{Oxide, nm}</th>
<th>SE L_{Rough, nm}</th>
<th>SE σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>117.2</td>
<td>117 ± 7</td>
<td>61 ± 5</td>
<td>56 ± 5</td>
<td></td>
<td></td>
<td>0.0605</td>
</tr>
<tr>
<td>P, HTS</td>
<td>118.4</td>
<td>115 ± 6</td>
<td>58 ± 4</td>
<td>57 ± 4</td>
<td></td>
<td></td>
<td>0.0534</td>
</tr>
<tr>
<td>S</td>
<td>118.1</td>
<td>117 ± 2</td>
<td></td>
<td>115.2 ± 0.3</td>
<td>2 ± 2</td>
<td></td>
<td>0.0397</td>
</tr>
<tr>
<td>S, HTS</td>
<td>117.7</td>
<td>118 ± 2</td>
<td></td>
<td>114.9 ± 0.2</td>
<td>3 ± 2</td>
<td></td>
<td>0.0304</td>
</tr>
</tbody>
</table>

The complex dielectric functions of the inner and outer layers of the bi-layer oxide are compared for the sealed and unsealed samples in Figure 4-10 (outer layer) and Figure 4-11 (inner layer). The complex dielectric functions of the mono-layer oxide formed in Na₂SO₄ are compared for the sealed and unsealed samples in Figure 4-12. The band gaps for the oxide layers are shown in Table 4-9.
Figure 4-10: The effect of hydrothermal sealing on the complex dielectric function of the outer layer of oxide formed in 0.1 M H₃PO₄.
Figure 4-11: The effect of hydrothermal sealing on the complex dielectric function of the inner layer of oxide formed in 0.1 M H₃PO₄.
Figure 4-12: The effect of hydrothermal sealing on the complex dielectric function of oxide formed in 0.1 M Na$_2$SO$_4$ where a mono-layer oxide model is used. The dielectric functions for an as anodized and a hydrothermally sealed oxide are remarkably similar.
Table 4-9: Band gaps determined for bi-layer oxides formed in H$_3$PO$_4$ and mono-layer oxides formed in Na$_2$SO$_4$. Hydrothermal sealing has little effect on the band gaps of the mono-layer oxide or the outer layer of the bi-layer oxide. However, the band gap of the inner layer of the bi-layer oxide is reduced when the oxide is hydrothermally sealed. HTS = hydrothermally sealed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ Total, eV</th>
<th>$E_g$ Inner Layer, eV</th>
<th>$E_g$ Outer Layer, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>n/a</td>
<td>4.467 ± 0.002</td>
<td>3.86 ± 0.06</td>
</tr>
<tr>
<td>P, HTS</td>
<td>n/a</td>
<td>4.327 ± 0.007</td>
<td>3.83 ± 0.04</td>
</tr>
<tr>
<td>S</td>
<td>4.00 ± 0.02</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>S, HTS</td>
<td>4.01 ± 0.01</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

As shown in Figure 4-12, hydrothermal processing of formed oxides had a minimal effect on the mono-layer oxides formed in Na$_2$SO$_4$, however, the onset of absorption was reduced by 0.14 eV and the magnitude of the imaginary component of $\varepsilon$ decreases above the band gap for the inner layer of the oxide formed in H$_3$PO$_4$ as shown in Figure 4-11. The absorption of $\varepsilon_2$ in the outer layer decreases upon hydrothermal sealing. Given the apparatus used in these experiments, the accuracy of $\varepsilon_2$ measured at higher energies may be questionable as the optics of the apparatus does not have good sensitivity at higher photon energies ($> \sim 5$ eV). As shown in Figure 4-11, the absorption of $\varepsilon_2$ for the inner layer is very low. Measurements at higher photon energies are needed to confirm this result.

4.4.3. Evaluating Porosity

As an exercise of thoroughness, oxide formed in 0.1 M Na$_2$SO$_4$ was also analyzed using an optical model having a porous outer layer. Table 4-10 shows the thickness, and band gap of an anodized film and a film that has been hydrothermally sealed. The dielectric functions of the oxides are shown in Figure 4-13.
Figure 4-13: The effect of hydrothermal sealing on the complex dielectric function for a mono-layer oxide formed to 70V in 0.1 M Na$_2$SO$_4$ when the porous model is used during optimization.

Table 4-10: Effect of hydrothermal sealing on a mono-layer oxide formed to 70 V in 0.1 M Na$_2$SO$_4$ when the porous model is used during optimization. HTS = hydrothermally sealed.

<table>
<thead>
<tr>
<th></th>
<th>Total, IR</th>
<th>Total, SE</th>
<th>Inner, SE</th>
<th>Outer, SE</th>
<th>$E_g$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>No HTS</td>
<td>118</td>
<td>113 ± 10</td>
<td>61 ± 6</td>
<td>52 ± 8</td>
<td>3.97 ± 0.02</td>
</tr>
<tr>
<td>HTS</td>
<td>118</td>
<td>114 ± 10</td>
<td>64 ± 6</td>
<td>50 ± 8</td>
<td>4.01 ± 0.02</td>
</tr>
</tbody>
</table>
One way of assessing the porosity of the outer layer is to compare freshly anodized oxides to oxides that have been hydrothermally sealed (HTS.) Upon HTS treatment, the pores in the oxide commonly become filled; this would have a significant influence on the dielectric properties of the oxide. As shown in Figure 4-12, the dielectric functions of HTS mono-layer oxide and a freshly anodized HTS oxide are remarkably similar. Figure 4-13 shows that the dielectric functions of the two specimens are extremely similar. Regardless of whether porous outer layer or the mono-layer model is used, the similarities of the dielectric functions indicate that HTS treatment has little or no effect on the structure or chemistry of the oxide for oxides formed in Na₂SO₄.

4.4.4. Effect of Formation Voltage

The effect of anodization voltage on the optical properties of tantalum oxide is examined for formation in 0.1 M H₃PO₄. Low formation voltage oxides are of particular interest because the percentage of the native oxide relative to the anodic oxide is greater at lower formation voltages. Also, interfacial effects are more likely to be observable when the oxide is thinner.

The optical properties of low formation voltage oxides (2 V-13 V) are explored and the results compared to the optical properties of higher formation voltage oxides. When spectra at all angles of incidence are considered, all of the models provide equally low σ. When only 70° incidence is considered, the thicker oxides (6 V, 13 V) slightly favor the bi-layer model, but the bi-layer model fails to converge completely for the thinner oxide (2 V). Although the σ values are slightly better for the bi-layer model, the error bars on the fitted parameters are significantly larger when a bi-layer model is employed. It is concluded that the mono-layer model, without surface roughness, is the best model for spectra collected from “thin” oxides (2 - 6 V) formed in 0.1 M H₃PO₄.

An example of the quality of fit typically achieved for a mono-layer model optimized to ellipsometry spectra collected from a thin oxide is shown in Figure 4-14. The σ values for simultaneous optimization of spectra collected at 45°, 70°, 75°, and 85° incidence are
shown in Table 4-11. The complex dielectric functions for oxides formed to 2 V, 4 V, or 6 V are shown in Figure 4-15. The thickness predicted from Equation [4-2] is compared with the thickness and band gap in Table 4-12. The oxide thickness versus formation voltage data is shown in Figure 4-16. Dielectric functions are compared for a 4V (11 nm) mono-layer oxide, a 13V (28nm) bi-layer oxide, and a 70V (118 nm) bi-layer oxide in Figure 4-17. The band gaps are shown as a function of formation voltage in Figure 4-18.
Figure 4-14: Example of experimental spectra (symbols) and the spectra fits using the optimized mono-layer model (solid lines) for a sample anodized to 4 V. Spectra were collected at four angles of incidence (45°, 70°, 75°, and 85°) and the model was simultaneously optimized to fit all of the spectra.
Figure 4-15: Complex dielectric functions ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for thin oxides formed at low formation voltages (2-6V) determined from a mono-layer model.

Table 4-11: Unweighted error function values for simultaneous optimization of spectra collected at 45°, 70°, 75°, 85° incidence.

<table>
<thead>
<tr>
<th>Sample/ Form V</th>
<th>Mono, No Rough</th>
<th>Mono, Rough</th>
<th>Bi, No Rough</th>
<th>Bi, Rough</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.05354</td>
<td>0.05363</td>
<td>0.05373</td>
<td>0.0538</td>
</tr>
<tr>
<td>4</td>
<td>0.01533</td>
<td>0.01536</td>
<td>0.01542</td>
<td>0.01537</td>
</tr>
<tr>
<td>4</td>
<td>0.008722</td>
<td>0.008653</td>
<td>0.008684</td>
<td>0.008698</td>
</tr>
<tr>
<td>6</td>
<td>0.05128</td>
<td>0.05128</td>
<td>0.05132</td>
<td>0.0513</td>
</tr>
<tr>
<td>13</td>
<td>0.03502</td>
<td>0.02705</td>
<td>0.0162</td>
<td>0.02832</td>
</tr>
</tbody>
</table>
Table 4-12: Optimization results when spectra collected at 45°, 70°, 75°, and 85° incidence are simultaneously analyzed. The thickness predicted from the anodization constant is shown along with the thickness and band gap calculated using spectroscopic ellipsometry analysis. The σ values are also shown for each optimization. The formation voltage is with reference to the saturated calomel electrode (SCE).

<table>
<thead>
<tr>
<th>Formation vs. SCE, V</th>
<th>Anodization Constant Thickness, nm</th>
<th>Ellipsometry Thickness, nm</th>
<th>Band Gap, E_g eV</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.9</td>
<td>3.5 ± 2</td>
<td>n/a</td>
<td>0.0535</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>9.1 ± 0.2</td>
<td>4.01 ± 0.01</td>
<td>0.0153</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>10.8 ± 0.1</td>
<td>3.81 ± 0.07</td>
<td>0.00870</td>
</tr>
<tr>
<td>6</td>
<td>14</td>
<td>13.1 ± 0.7</td>
<td>4.06 ± 0.18</td>
<td>0.0513</td>
</tr>
</tbody>
</table>

Figure 4-16: Oxide thickness of the total oxide and inner and outer layers of oxide as determined by spectroscopic ellipsometry analysis. The solid line is calculated from the anodization constant for tantalum oxide in 0.1 M H_3PO_4.
Figure 4-17: Complex dielectric functions for a thin, 4 V (11 nm) oxide with a mono-layer structure (dotted line); a thin 13 V (27 nm) oxide with a bi-layer structure (dashed lines); and a thick 70 V (118 nm) oxide with a bi-layer structure (symbols).
Figure 4-18: Dependence of the band gap on formation voltage and oxide structure. Oxides formed in phosphoric acid to 4V and 6V exhibit a mono-layer structure but a bi-layer structure at formation voltages >13V. The band gap of a mono-layer oxide formed to 70 V in 0.1 M Na$_2$SO$_4$ is also shown. The trendlines are the average band gaps for the inner and outer layers of bi-layer oxide formed in 0.1 M H$_3$PO$_4$.

Oxides formed to low formation voltages ( <13 V) are best described using a mono-layer oxide model. The average band gap for oxides formed from 4 V to 6 V (Table 4-12) is 3.96 ± 0.06 eV; this band gap is similar to the gap of the outer layer of the bi-layer oxide. As shown in Figure 4-18, oxide having a higher energy band gap only occurs when a bi-layer structure is formed. The absorption ($\varepsilon_2$) of the 2 V oxide is high and could be due to residual surface roughness of the tantalum substrate. When oxide is formed to a higher formation voltage, the surface roughness decreases.

4.4.5. Effect of Formation Time

It has been demonstrated in sections 3.3.2 and 3.2.6 that anodic tantalum oxide thickens continuously under a constant, applied voltage. It is worthwhile to examine the evolution of the dielectric functions with anodization time. Figure 4-19 compares the oxide thickness measured by SE (solid symbols) and TEM (open symbols) to the growth law reported in section 3.2.6.4 (solid line).
Figure 4-19: Thickness of the inner layer, outer layer, and total oxide as a function of anodization time. Oxide thicknesses are measured by SE (solid symbols) and TEM (open symbols). The solid line is the growth law determined in section 3.2.6.4.

The band gap of the inner and outer layers is shown vs. the time held at 70 V formation in Figure 4-20. The band gaps of the inner and outer layers decrease with anodization time. Equations for the regression lines shown in Figure 4-20 are given in Table 4-13. The average (mean) band gaps, defined as the onset of absorption, for oxides anodized to 70V in 0.1 M H₃PO₄ for various lengths of time are 4.4 ± 0.2 and 3.9 ± 0.1 for the inner and outer layers of oxide respectively.
Figure 4-20: Onset of absorption of the inner and outer layers of oxide versus anodization time for formation in 0.1 M $\text{H}_3\text{PO}_4$ to 70V.

Table 4-13: Regression results for the curves shown in Figure 4-20.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Curve Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>$4.40 - 0.020 \ln (\text{time, min})$</td>
</tr>
<tr>
<td>Outer</td>
<td>$3.87 - 0.012 \ln (\text{time, min})$</td>
</tr>
</tbody>
</table>

The thickness of the oxide as a function of anodization time as measured by ellipsometry is in agreement with the thickness measured by TEM and FT-IR reflectance spectroscopy. SE has the advantage of not requiring any such calibration and provides simultaneous optical, and hence electronic, characterization.
4.5 Conclusions

After optimization of the various models to spectra from anodic oxides formed under different conditions, the samples were grouped into three categories:

1.) Thin Oxides: samples anodized in 0.1 M H₃PO₄ to 2 -6 V. This category fit the mono-layer model without a roughness layer best.

2.) Thick Oxides: Samples anodized in 0.1 M H₃PO₄ to 13 -100 V. This category fit the bi-layer model best.

3.) Phosphorus free: Samples anodized to 70 V in 0.1 M Na₂SO₄. This category fit the mono-layer model best.

Whereas anodic oxide films commonly have a porous outer layer, anodic tantalum oxide formed in this study (0.1 M H₃PO₄ or 0.1 M Na₂SO₄ electrolyte) is compact throughout the thickness of the oxide. Using spectroscopic ellipsometry, it was determined that oxides formed in 0.1 M Na₂SO₄ are best described using a mono-layer, compact model of the oxide. Further evidence for the lack of a porous outer layer is given by comparing the dielectric functions of oxide freshly anodized and oxide that had been hydrothermally sealed; there was no difference between the ε of the as-anodized and the hydrothermally sealed films. The dielectric functions of the freshly anodized and hydrothermally sealed oxides are nearly identical for the mono-layer oxide. The conclusion that the outer layer is compact (and not porous) is in agreement with previous observations [92, 172, 173] of anodic tantalum oxide formed in dilute phosphoric acid.

The onset of absorption, which can be thought of as the band gap, is considerably different for oxides formed in different electrolytes and for the individual layers of the bi-layer oxide. For thin (2 - 6 V) oxides formed in H₃PO₄, where a mono-layer oxide model was employed, the onset of absorption occurred at an average value of 3.96 ± 0.06 eV. The mono-layer oxide formed in 0.1 M Na₂SO₄ exhibited an onset of absorption at 4.00 ± 0.02 eV regardless of whether the oxide was hydrothermally sealed. The band gaps for oxide formed in 0.1 M H₃PO₄ to 70V and held for different formation times were considerably different for the individual layers of the oxide. The band gap for the outer layer, which contained incorporated phosphorus, was 3.9 ± 0.1 eV while the band gap for
the inner layer was 4.4 ± 0.2 eV. It is interesting to note that the oxide only has an elevated onset of absorption when the outer layer of phosphate containing oxide is present, indicating that other defects may be present in the outer layer of oxides formed in H₃PO₄ or in the oxide formed in Na₂SO₄. The band gaps of the inner and outer layers of oxide shift to lower energy onset as the time of anodization is increased.
Chapter 5: Electrochemistry: Experimental Methods and Preliminary Analysis

This chapter contains a description of wet electrochemical experiments performed on bulk tantalum metal. First, metallic tantalum is oxidized using either a galvanostatic method (Section 5.1) or a potentiodynamic method (Section 5.2). The formation voltage is maintained for 24 hours and then electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis are performed on the oxides. The two data sets (Section 5.1 and 5.2) are independent of each other. The data reported in this chapter is analyzed by optimizing a point defect model (PDM) to the electrochemical impedance spectroscopy as shown in Chapters 6 and 7.

As shown in Figure 5-1, the voltage at the onset of oxide growth ($t = 0$) for the 4 V experiment is approximately 3.5 V although the previous experiment ended with 2 V applied. It was thought that this was due to current overshoot during the 2 V anodization, and a potentiodynamic set of experiments was performed to circumvent this problem. In hindsight, this problem is likely due to the lack of dissolution and continuous growth of tantalum oxide when the formation voltage is applied. It is not expected that the method of formation (potentiostatic or galvanostatic) will have a significant effect on the properties of the oxide. A vacuum annealed substrate was used in the potentiodynamic studies because the results are expected to be more reproducible[53] and the system to have a reduced electronic leakage current.[182]

5.1. Galvanostatic Data Set

5.1.1. Electrochemical Cell Design

Undoped high purity, capacitor grade tantalum sheet was obtained from H.C. Starck. Sputter deposited tantalum, as discussed in Chapters 3 and 4, is inferior to bulk metal for these experiments. The quality, density, and impurities of sputter deposited materials are
highly variable according to the sputtering chamber and the specific deposition conditions, which makes the experiments less reproducible by other authors. A stout copper wire was soldered to the backside of the tantalum sheet and the assembly was mounted in MetLab Corporation’s two-component epoxy resin and mechanically polished to 0.05 μm Al₂O₃. The exposed area of the working electrode was 1.7 cm². The glass three-electrode cell previously described[81] was fitted with a saturated calomel electrode (SCE) reference electrode and a platinum wire counter electrode. The cell was purged with ultra high purity argon 24 hours prior to anodization and during all measurements. The electrolyte was 0.06 wt% H₃PO₄; all experiments were completed at room temperature. The pH of the electrolyte was 2.47. Electrochemical experiments were performed using a Solartron 1268 electrochemical interface and a Solartron 1250 frequency response analyzer.

5.1.2 Summary of Experimental Sequence

The procedure for growing and characterizing the oxide at each voltage is as follows:

1.) Galvanostatic growth to desired formation voltage
2.) Potentiostatic hold at formation voltage for 24 hours
3.) Collect an impedance spectra from high frequency to low frequency
4.) Collect an impedance spectra from low frequency to high frequency
5.) Potentiostatic hold at the formation voltage for one hour
6.) Mott-Schottky Measurement
7.) Potentiostatic hold at the formation voltage for one hour

Upon completing this sequence, the apparatus was undisturbed as experiments were performed at the subsequent formation voltage.

i.) Metlab hardener (D.E.H. *24 Epoxy Curing Agent) was mixed with Metlab epoxy resin (D.E.R. *324) according to the package directions and allowed to harden for a minimum of 24 hours before proceeding.
5.1.3. **Oxide Formation**

Anodic tantalum oxide was formed galvanostatically with a current density of 45 \( \mu \)A/cm\(^2\) until the desired voltage was reached, then the potential was held at the formation voltage for 24 hours. The galvanostatic and potentiostatic growth profiles are shown in Figure 5-1 and Figure 5-2, respectively. All voltages are versus the SCE. Experiments at each formation voltage are done consecutively on the same specimen from low formation voltage to high formation voltage. The voltage across the sample at time = 0 for the intended 8 V anodization was greater than 8 V, which is why the “to 9.15 V” growth profile has so few data points. The current versus times relationship upon the continued application of the formation voltage (Figure 5-2) is characteristic of anodized films. The current has a roughly inverse logarithmic relationship with time.
Figure 5-1: Voltage versus time during 45 μA/cm² galvanostatic growth to 2.0, 4.0, 6.0, 9.15V and 12V vs. SCE.

Figure 5-2: Current density during potentiostatic hold at various formation voltages.
5.1.4. Impedance Collection

Impedance spectra were collected using a 20mV root-mean-square excitation voltage. The DC formation voltage was maintained during the impedance measurements. The frequency was scanned from 60 kHz to 0.01 Hz and then immediately scanned from 0.01 Hz to 60 kHz in order to ascertain if the system had shifted from steady state during the experiment. The real and imaginary components of the impedance that were measured as the frequency was scanned down are plotted for varying anodization voltages in Figure 5-3. Figure 5-4 depicts the familiar Bode representation of the impedance spectra. The spectra are characteristic of capacitive behavior.

**Figure 5-3:** Real and imaginary components of the impedance for oxides formed to various voltages where the frequency was scanned from high to low.
Figure 5-4: Bode plots of the impedance collected by scanning the frequency from high to low for oxides anodized to various formation voltages.

5.1.5 Assessment of Steady State

Throughout this dissertation, the imaginary component of the impedance is typically plotted along with the real component on the positive y-axis (Quadrant I in the complex plane). The experimental imaginary impedance was always a negative value; thus what is technically plotted is the negative of imaginary component. The real and imaginary components of the impedance are plotted when the frequency was scanned from 60 kHz to 0.01 Hz (Scanned Down) and from 0.01 to 60 kHz (Scanned Up). The “Scanned Up” and “Scanned Down” spectra are in close agreements as shown in Figure 5-5 (formed to 2V), Figure 5-6 (formed to 4.0V), Figure 5-7 (formed to 6.0V) and Figure 5-8 (formed to 8.0V). The agreement between the two sets of spectra is indicative of steady state.
Figure 5-5: Real and imaginary components of the impedance for anodization to 2V. The frequency was scanned from high to low (Down) and then immediately scanned from low to high frequency (Up.)

Figure 5-6: Real and imaginary components of the impedance for anodization to 4V. The frequency was scanned from high to low (Down) and then immediately scanned from low to high frequency (Up.)
Figure 5-7: Real and imaginary components of the impedance for anodization to 6.0V. The frequency was scanned from high to low (Down) and then immediately scanned from low to high frequency (Up.)

Figure 5-8: Real and imaginary components of the impedance for anodization to 8.0V. The frequency was scanned from high to low (Down) and then immediately scanned from low to high frequency (Up.)
In order to analyze the impedance spectra, the system under study must conform to linear systems theory, i.e., the system must be linear, exhibit causality, have a finite value, and be at steady state throughout the experiment. The Kramers-Kronig (K-K) transform can be used to evaluate whether or not a system is at steady state. The method of Urquidi-Macdonald, Real, and Macdonald [183, 184] is employed in applying the K-K transforms to the experimental impedance. The K-K transforms are used as a purely mathematical check on the data. The transforms are given as[183]:

\[
Z'(w) - Z'({\infty}) = \left(\frac{2}{\pi}\right) \int_{0}^{\infty} \frac{xZ''(x) - wZ''(w)}{x^2 - w^2} \, dx
\]

[5-1]

\[
Z'(w) - Z'(0) = \left(\frac{2\omega}{\pi}\right) \int_{0}^{\infty} \left[\frac{w}{x}Z''(x) - Z''(w)\right] \frac{1}{x^2 - w^2} \, dx
\]

[5-2]

\[
Z''(w) = - \left(\frac{2w}{\pi}\right) \int_{0}^{\infty} \frac{Z'(x) - Z'(w)}{x^2 - w^2} \, dx
\]

[5-3]

It is assumed that \(x \rightarrow x_{\text{min}} \rightarrow 0\) and that \(x \rightarrow x_{\text{max}} \rightarrow \infty\) in this derivation; a more complete derivation and discussion are presented elsewhere. [183, 184] In this study, the imaginary component (\(Z''\)) of the experimental impedance was used to calculate the real component (\(Z'\)) of the impedance. Likewise, the real component of the experimental impedance was used to calculate the imaginary component. The experimental and calculated components of the impedance for each formation voltage are compared in Figure 5-9 (2 V), Figure 5-10 (4 V), Figure 5-11 (6 V), and Figure 5-12 (8 V). The agreement between the experimental and calculated components is judged to be satisfactory.
Figure 5-9: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 2V.

Figure 5-10: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 4V.
Figure 5-11: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 6.0V.

Figure 5-12: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 8.0V.
5.2 Potentiodynamic Data Set

5.2.1 Substrate Preparation

Undoped high purity, capacitor grade tantalum sheet was obtained from H.C. Starck. It was mechanically polished by hand using 15 μm diamond paste and polishing oil on photographic printer paper. It was then polished using 1 μm and 0.3 μm alumina on a polishing wheel at slow speeds for many hours while being manually held against the wheel with very light pressure. The substrate was then vacuum annealed at 1780°C for 30 minutes courtesy of AVX corporation. It has been reported that vacuum annealed substrates provide more reproducible results, and the potentiodynamic growth method was used to avoid current overshoot during galvanostatic growth.

5.2.2 Substrate Characterization

Figure 5-13 shows a differential interference contrast (DIC) light micrograph of the substrate after polishing and annealing. This technique is sensitive to very small height changes in the topography, and the morphology reported here is typical of mechanically polished refractory metals. Figure 5-14 shows a bright field light micrograph of the same substrate after polishing and annealing. Figure 5-15 shows a montage of DIC micrographs, which captures the finish of the entire substrate; while this figure is no more enlightening than Figure 5-14, it demonstrates that the surface was free of scratches and is relatively homogeneous. This achievement may seem trivial, but it was the source of much suffering and grief for the author.
Figure 5-13: Differential interference contrast (DIC) light micrograph of polished and annealed tantalum substrate.

Figure 5-14: Bright field light micrograph of polished and annealed tantalum substrate.
Figure 5-15: DIC light micrograph montage of the entire tantalum substrate after it was polished and annealed.

X-ray photoelectron spectra (XPS) were collected from the tantalum substrate in order to assess the purity of the tantalum. Figure 5-16 shows a spectra that was taken of the as-received vacuum annealed substrate along with a spectra taken after a mild 30 second sputtering of the surface. Sputtering was performed to remove the surface contaminants. Quantification of the detectable contaminants is shown in Table 5-1. No major contaminants were detected by XPS, and the decrease in the concentration of the contaminants after a gentle sputter indicates that the contaminants are adsorbed on the
surface and not at higher concentrations in the bulk. Optical profilometry of the
substrate, as shown in Figure 5-17 indicated a rms roughness of 75-100 nm.

Figure 5-16: X-ray photoelectron spectra of a polished and vacuum annealed tantalum
substrate and a spectra after the surface contaminants have been removed by thirty
seconds of sputtering.
Table 5-1: Surface contaminants of the vacuum annealed tantalum substrate before and after a 30 second sputter. Atomic percent is determined from the XPS spectra shown in Figure 5-16.

<table>
<thead>
<tr>
<th>Element</th>
<th>As prepared, Atomic %</th>
<th>After 30 Sec Sputter, Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Zn</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Na</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 5-17: Optical profilometry of polished and vacuum annealed tantalum substrate.
5.2.3 Oxide Formation

A K0235 Princeton Applied Research flat cell electrochemical cell was used for electrochemical experiments along with a Solartron 1287 electrochemical interface and a Solartron 1255B Solartron frequency response analyzer. A saturated calomel electrode (SCE) and a platinized counter electrode were used. The oxide was formed potentiodynamically at a rate of 250 mV/sec until the formation voltage was reached. The Potentiodynamic scans for each formation voltage are shown in Figure 5-18 (current density vs. applied voltage) and in Figure 5-19 (applied voltage vs. current density). Figure 5-18 and Figure 5-19 are redundant, but both representations of the data are used in the literature. These plots indicate the current in the cell as the voltage is stepped. Most of the current is due to oxide formation. The current as a function of time during the potentiodynamic ramps is shown in Figure 5-20. The current for the 1V anodization is significantly higher because there was not a pre-existing anodic oxide on the substrate at the onset of the potentiodynamic scan.

![Figure 5-18](image-url): Current density vs. applied voltage as the voltage was potentiodynamically ramped at 250 mV/sec.
Figure 5-19: Applied voltage vs. current density as the voltage was potentiodynamically ramped at 250 mV/sec. The same data is shown in Figure 5-18 with the axes swapped.

Figure 5-20: Current density versus time at each formation voltage where the onset of each voltage sweep is time = 0 for the potentiodynamic sweeps shown in Figure 5-18 and Figure 5-19
5.2.4 Assessment of Steady State

In order to assess whether the system had reached a steady state, the frequency was scanned from high to low frequency (scan down) and then immediately scanned from low to high frequency (scan up). The real and imaginary components of the impedance for these two scans are shown in Figure 5-21 (1 V), Figure 5-22 (2 V), Figure 5-23 (4 V), and Figure 5-24 (6 V) and Figure 5-25 (8 V).

**Figure 5-21**: Real and imaginary components of the impedance for anodization to 1 V vs. SCE. The frequency was scanned from high to low (down) and then from low to high frequency (up).
Figure 5-22: Real and imaginary components of the impedance for anodization to 2V vs. SCE. The frequency was scanned from high to low (down) and then from low to high frequency (up).

Figure 5-23: Real and imaginary components of the impedance for anodization to 4V vs. SCE. The frequency was scanned from high to low (down) and then from low to high frequency (up).
Figure 5-24: Real and imaginary components of the impedance for anodization to 6V vs. SCE. The frequency was scanned from high to low (Scan Down).

Figure 5-25: Real and imaginary components of the impedance for anodization to 8V vs. SCE. The frequency was scanned from high to low (Scan Down).
**Kramers-Kronig Transformation Results**

Kramers-Kronig transformation of the experimental data was also used to assess the linearity, stability, steady-state, finiteness, and causality of the system. The experimental and transformed components of the complex impedance are shown in Figure 5-26 (1V) Figure 5-27 (2V), Figure 5--28(4V), Figure 5—29 (6V), and Figure 5—30 (8V).

![Graph](image)

**Figure 5-26:** Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 1V vs. SCE.
**Figure 5-27:** Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 2V vs. SCE.

**Figure 5-28:** Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 4V vs. SCE.
Figure 5-29: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 6V vs. SCE.

Figure 5-30: Real and imaginary components of the impedance obtained experimentally and calculated using the K-K transformation. The oxide was formed to 8V vs. SCE.
The real and imaginary components for each formation voltage are shown in Figure 5-31; the Bode representation of the spectra is shown in Figure 5-32, and the Nyquist representation in Figure 5-33. These representations of the data indicate that the spectra are consistent with highly capacitive behavior.

**Figure 5-31:** Real and imaginary components of the impedance when the frequency is scanned from high to low frequency at different formation voltages.
Figure 5-32: Bode plots from vacuum annealed tantalum substrate formed to various voltages; the impedance spectra are collected with the formation voltage applied.

Figure 5-33: Nyquist plot from vacuum annealed tantalum substrate formed to various voltages; the impedance spectra are collected with the formation voltage applied.
5.3 Mott Schottky Analysis

The impedance was measured at 1,000 Hz as the potential was swept in the negative direction; this technique is known as Mott-Schottky analysis and is discussed in more detail in Section 2.4.6.

When applied to the characterization of semiconducting electrodes, Mott-Schottky analysis allows for the determination of the flat band potential, $V_{fb}$, and the donor density, $N_d$. The relationship between the measured capacitance and the properties of the oxide is given by:

$$\frac{1}{C^2} = \frac{2}{qN_d\varepsilon_0\varepsilon A^2} (V_m - V_{fb} - \frac{KT}{q})$$

where $q$ is the elementary charge, $N_d$ is the donor density, $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ is the permittivity of the oxide, $A$ is the electrode area, $V_m$ is the band level of the metal, $V_{fb}$ is the flat band potential, $K$ is the Boltzmann constant, and $T$ is the temperature. The capacitance $C$, is calculated from the imaginary component of the impedance and the frequency:

$$C = \frac{1}{2\pi f \cdot Z^*}$$

The potential was swept from the formation voltage to -0.5V at a rate of 25mV/sec as the impedance was measured at 1,000 Hz. The potential was then immediately stepped in the positive direction from -0.5V to the formation voltage. The agreement of the two sweeps suggests that the act of sweeping the voltage at this rate has little effect on the semiconducting properties of the film.

Figure 5-34 shows the Mott-Schottky plots ($1/C^2$ vs. $V$) for the data set described in Section 5.1 and Figure 5-35 for the data set described in Section 5.2. The slopes, intercepts, and $R^2$ values are given in Table 5-2.
Figure 5-34: Mott Schottky plot obtained on oxides formed as described in Section 5.1.

Figure 5-35: Mott Schottky plot obtained on oxides formed as described in Section 5.2.
Table 5-2: Slope, intercept, and $R^2$ value for the $C^{-2}$ vs. $V$ plots measured at several formation voltages.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Data Set</th>
<th>Slope of $1/C^2$ vs. $V$</th>
<th>Intercept</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Section 5.1</td>
<td>8.31*10^9</td>
<td>1.54*10^{11}</td>
<td>0.986</td>
</tr>
<tr>
<td>4</td>
<td>Section 5.1</td>
<td>9.56*10^9</td>
<td>2.48*10^{11}</td>
<td>0.980</td>
</tr>
<tr>
<td>6</td>
<td>Section 5.1</td>
<td>3.1*10^{10}</td>
<td>1.1*10^{12}</td>
<td>0.431</td>
</tr>
<tr>
<td>12</td>
<td>Section 5.1</td>
<td>3.16*10^{10}</td>
<td>2.32*10^{12}</td>
<td>0.612</td>
</tr>
<tr>
<td>1</td>
<td>Section 5.2</td>
<td>6.60*10^9</td>
<td>5.35*10^{10}</td>
<td>0.904</td>
</tr>
<tr>
<td>2</td>
<td>Section 5.2</td>
<td>8.40*10^9</td>
<td>1.66*10^{11}</td>
<td>0.912</td>
</tr>
<tr>
<td>4</td>
<td>Section 5.2</td>
<td>1.33*10^{10}</td>
<td>2.94*10^{11}</td>
<td>0.901</td>
</tr>
<tr>
<td>6</td>
<td>Section 5.2</td>
<td>1.57*10^{10}</td>
<td>5.63*10^{11}</td>
<td>0.925</td>
</tr>
</tbody>
</table>

The calculated donor densities for the varying formation voltages are shown in Table 5-3 and plotted in Figure 5-36. Values are also shown for two separate experiments where one sample was mechanically polished then vacuum annealed (Section 5.2) and the other substrate was mechanically polished (Section 5.1); the two substrates were studied using a different experimental setup and slightly different formation conditions.

Table 5-3: Donor density calculated from Mott-Schottky analysis for oxide formed on two different substrates

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Mechanically Pol. Substrate Donor Density, $N_d$, cm$^{-3}$</th>
<th>Vacuum Annealed Substrate Donor Density, $N_d$, cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>8.54 * 10^{16}</td>
</tr>
<tr>
<td>2</td>
<td>3.95 * 10^{16}</td>
<td>6.71 * 10^{16}</td>
</tr>
<tr>
<td>4</td>
<td>3.32 * 10^{16}</td>
<td>4.24 * 10^{16}</td>
</tr>
<tr>
<td>6</td>
<td>1.04 * 10^{16}</td>
<td>3.59 * 10^{16}</td>
</tr>
<tr>
<td>12</td>
<td>1.44 * 10^{16}</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 5-36: Donor density as measured by Mott-Schottky analysis of tantalum oxide versus the formation voltage.

Rearranging, the flatband potential is calculated from:

\[ V_{fb} = V_m - \left( \frac{qN_d \varepsilon_0 \varepsilon A^2}{2 \ast C(0)^2} + \frac{KT}{q} \right) \]  

[5-6]

The potential of the metal is assumed to be 4.0 eV.\cite{64} The flat band potentials determined by Mott-Schottky analysis are shown in Table 5-4.

Table 5-4: Flat band potentials measured by the Mott-Schottky technique for oxide formed mechanically polished tantalum and vacuum annealed tantalum.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Mechanically Pol. Substrate Flat Band Voltage, V</th>
<th>Vacuum Annealed Substrate Flat Band Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>3.34</td>
</tr>
<tr>
<td>2</td>
<td>3.41</td>
<td>3.02</td>
</tr>
<tr>
<td>4</td>
<td>2.84</td>
<td>2.52</td>
</tr>
<tr>
<td>6</td>
<td>3.32</td>
<td>1.71</td>
</tr>
<tr>
<td>12</td>
<td>1.06</td>
<td>--</td>
</tr>
</tbody>
</table>
Discussion

Mott-Schottky analysis is applicable to ideal p-n junctions and contains four implicit assumptions which may not be characteristic of anodic tantalum oxide. It is assumed that:

1.) the dopant concentration is independent of the applied voltage. In the case of anodic films, increasing the voltage can cause the formation of point defects at the metal oxide interface.
2.) the dopant atoms are fully ionized. This may be true for point defects in tantalum oxide.
3.) the dimensions of the oxide are infinite. Specifically, the change in potential with respect to position goes to zero as the position goes to infinity ($d\phi/dx \to 0$ as $x \to \infty$).
4.) the dopant concentration is uniform. This is certainly disputable for anodic tantalum oxide. It is expected that the concentration of point defects is greatest at the metal/oxide interface for anodized thin films. This explains why the donor concentration is highest for the thinnest (lowest formation voltage) oxides.

It has been suggested that the potential drop due to the Helmholtz layer should be accounted for when interpreting Mott-Schottky plots measured in semiconductor/electrolyte systems.[186] The slope of the $C^{-2}$ vs. $V$ plot is not affected, thus the donor density is not altered, however, the intersection of the plot will shift by 

$$\frac{\varepsilon \epsilon_0 N_D}{8\pi C_H^2}$$

such that:
\[ V_{fb} = V_m - \left( \frac{qN_d \varepsilon_0 \varepsilon A^2}{2 * C(0)^2} + \frac{KT}{q} \right) + \frac{\varepsilon qN_d}{8\pi C_H} \]  

De Gryse, et.al.[186] quote that for titanium oxide, \( \varepsilon = 173 \), \( N_d = 10^{19} \text{ cm}^{-3} \), and \( C_H = 10^{-5} \) F/cm\(^2\), the shift in voltage \( (\varepsilon qN_d/8\pi C_H^2) \) is -0.12V. It seems that this should be a straightforward calculation, however, upon examination; this author cannot determine that the units of the term are “V” using this expression. If the term is modified to include the permittivity of free space, i.e., \( (\varepsilon_0 \varepsilon qN_d/8\pi C_H^2) \), this author calculates a shift of -0.0098V, which is still an order of magnitude greater than the value reported. The capacitance of the Helmholtz capacity is assumed to be 20 \( \mu \)F/cm\(^2\) for the tantalum oxide/electrolyte interface. [64]

5.4 Equivalent Electrical Circuit Analogs

Equivalent electrical circuit analogs are a common way of interpreting impedance spectroscopy. As discussed in Section 2.4.7, this technique treats the system under study as a combination of resistors, capacitors and inductors that mimics the measured impedance. In this study, the equivalent circuit shown in Figure 5-37 was used; tantalum oxide is described using a constant phase element (CPE1) and a resistor \( (R_e) \). The oxide is in parallel with the solution resistance \( (R_S) \). Regression results for the impedance collected from i.) mechanically polished substrates and ii.) mechanically polished and vacuum annealed substrates are shown in Table 5-5. It is demonstrated that the resistivity of the annealed substrate is higher but the dielectric constant is lower. Resistivity is directly proportional to surface area \( (\rho = R_e \frac{A}{L}) \) while the dielectric constant

\[ (\varepsilon = \frac{C}{\varepsilon_0} \frac{L}{A}) \] is inversely proportional to area. Therefore, the differences for the two substrates reported in Table 5-5 can be reasonably attributed to differences in the real surface area.
Figure 5-37: Equivalent circuit diagram used for approximating the capacitance and resistance of the tantalum oxide layer.

Table 5-5: The resistivity and dielectric constant of tantalum oxide formed on a substrate that was either mechanically polished or mechanically polished and then vacuum annealed. The oxide thickness is assumed to follow the relation $L(\text{nm}) = 1.83 * V$ [92].

<table>
<thead>
<tr>
<th>Formation Voltage, SHE Scale</th>
<th>Assumed Oxide Thickness, nm</th>
<th>Resistivity, $10^{13} , \Omega \cdot \text{cm}$</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Polished</td>
<td>Annealed</td>
</tr>
<tr>
<td>1.24</td>
<td>4.03</td>
<td>---</td>
<td>10</td>
</tr>
<tr>
<td>2.24</td>
<td>5.76</td>
<td>5.2</td>
<td>6.1</td>
</tr>
<tr>
<td>4.24</td>
<td>9.22</td>
<td>1.2</td>
<td>7.3</td>
</tr>
<tr>
<td>6.24</td>
<td>12.68</td>
<td>1.7</td>
<td>3.2</td>
</tr>
<tr>
<td>8.24</td>
<td>16.5</td>
<td>1.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>

5.5 Conclusions

Electrochemical impedance spectra are reported; the stability and steady state of the system has been demonstrated by:

1.) Scanning the frequency from high to low frequency and then immediately scanning the frequency from low to high frequency

and

2.) Applying Kramers-Kronig transformations to calculate the real component of the impedance from the experimental imaginary component and to calculate the imaginary component from experimental real component.
Therefore, the spectra reported here can be analyzed to characterize the growth kinetics of anodic tantalum oxide. In Chapters 6 and 7, point defect models are derived and optimized to the spectra collected in section 5.1 of this chapter.

Tantalum is characterized by a very large passive range when an external, positive voltage is applied. The equilibrium potential for oxide formation is -0.75 V on the hydrogen scale (see section 2.4.1). Application of a positive voltage results in the growth of tantalum oxide, which passivates the metal. The oxide layer continues to thicken and passivate the metal even when the applied voltage is greater than 100V. In this study, several formation voltages within the passive region are chosen for analysis. The maximum voltage is limited by the apparatus; applied voltages in the range of 1 – 8 V vs. SCE are reported here. Although the equipment will allow a maximum output voltage of 13.5V, EIS spectra collected at V ≥ 9 V were not of sufficient quality for analysis.

Mott-Schottky analysis demonstrates that thin oxide layers can be treated as semiconductors having donors at a concentration of $10^{16}$/cm$^3$; the concentration of donors in the oxide is greater for thinner oxides. This suggests that the oxide at the metal/oxide interface may be especially rich in defects such as oxygen vacancies. The measured defect concentration may not be constant over the depth of the oxide; rather, it is likely that the interface dominates the measurement for thin films. The trend of increasing conductivity with decreasing oxide thickness for anodic Ta$_2$O$_5$ was also reported by Macagno and Schulze [64], however, they report defect levels of $10^{20}$/cm$^3$ for oxides less than 8 nm thick [64]. As determined by the empirical growth laws of Chapter 3, the oxides formed in this work are expected to be significantly thicker; this is likely the explanation for why the defect concentration in this work is low. Macagno and Schulze reported that oxides thicker than about 8 nm exhibited insulator properties as opposed to semiconductor properties. [64] Equivalent circuit analysis indicates that the properties formed on mechanically polished and vacuum annealed substrates are very similar. Given the unknown discrepancies between the real surface areas of the two substrates, the properties are effectively the same.
Chapter 6: Unconstrained Point Defect Model of Anodic Tantalum Oxide

6.1 Introduction

The electrochemical formation of oxides from metallic anodes is an enduring field of scientific inquiry.[7, 9, 15, 17, 33, 58, 67, 76, 77, 87, 187-190] Explanations of oxide growth by ionic conduction mechanisms were reported in the 1930’s and have been continually elaborated on and disputed through the present day. A more thorough discussion of theories of anodic oxidation has been presented in Chapter 2 of this work. The point defect model (PDM) is a mechanistic description describing the formation of passive films in terms of point defect reactions. In this work, a PDM is developed for tantalum oxide. The model discussed below describes the formation and steady state of a mono-layer oxide. As shown in Section 3.2.1.2, tantalum oxide formed in phosphoric acid develops a distinct bi-layer structure, thus it is questionable whether the model described here is a sufficient description of reality. As discussed in Chapter 1, models are abstract representations of reality, and no model can achieve a perfect description of reality. A model should be made as simple as possible but not simpler, in other words it must describe observations but should not contain extraneous, ad-hoc parameters that unnaturally force the model to agree with observations.

In this work, the Faradaic impedance generated by point defect reactions is derived; an equivalent circuit is used to calculate the total impedance of the system. Electrochemical impedance spectra (EIS) experiments (as described in Section 5.1) are used to experimentally measure the impedance of the system. Non-linear regression is used to refine the parameters of the PDM to achieve the best fit between experimental impedance and the impedance calculated by the PDM. Table 6-1 defines the symbolism used in Chapter 6 and 7.
Table 6-1: Symbols and their respective definitions and units used in this report.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i$</td>
<td>Defined in Table 7-2</td>
<td>$V^{-1}$</td>
</tr>
<tr>
<td>$b_i$</td>
<td>Defined in Table 7-2</td>
<td>$cm^{-1}$</td>
</tr>
<tr>
<td>$a'$</td>
<td>Fitting parameter of logarithmic growth law</td>
<td>$cm^{-1}$</td>
</tr>
<tr>
<td>$b'$</td>
<td>Fitting parameter of logarithmic growth law</td>
<td>$cm^{-1}$</td>
</tr>
<tr>
<td>$j$</td>
<td>The imaginary number</td>
<td>n/a</td>
</tr>
<tr>
<td>$k_{1}^{00}$</td>
<td>Standard rate constant for reaction 1</td>
<td>mol/(cm$^2$*s)</td>
</tr>
<tr>
<td>$k_{2}^{00}$</td>
<td>Standard rate constant for reaction 2</td>
<td>mol/(cm$^2$*s)</td>
</tr>
<tr>
<td>$k_{3}^{00}$</td>
<td>Standard rate constant for reaction 3</td>
<td>mol/(cm$^2$*s)</td>
</tr>
<tr>
<td>$k_{4}^{00}$</td>
<td>Standard rate constant for reaction 4</td>
<td>cm/s</td>
</tr>
<tr>
<td>$k_{5}^{00}$</td>
<td>Standard rate constant for reaction 5</td>
<td>mol/(cm$^2$*s)</td>
</tr>
<tr>
<td>$n$</td>
<td>Kinetic order, pH dependence of the dissolution of oxide</td>
<td>n/a</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>seconds</td>
</tr>
<tr>
<td>A</td>
<td>Fitting parameter of inverse logarithmic growth law</td>
<td>$cm^{-1}$</td>
</tr>
<tr>
<td>B</td>
<td>Fitting parameter of inverse logarithmic growth law</td>
<td>$cm^{-1}$</td>
</tr>
<tr>
<td>$C_{IL}$</td>
<td>Geometric capacitance of the inner layer</td>
<td>F/cm$^2$</td>
</tr>
<tr>
<td>$C_{OL}$</td>
<td>Geometric capacitance of the outer layer, includes capacitance of the double layer</td>
<td>F/cm$^2$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusivity of Ta interstitial in the oxide</td>
<td>cm$^2$/s</td>
</tr>
<tr>
<td>$D_o$</td>
<td>Diffusivity of O Vacancy in the oxide</td>
<td>cm$^2$/s</td>
</tr>
<tr>
<td>E</td>
<td>Electric field in the oxide</td>
<td>V/cm</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
<td>96487 C/unit charge</td>
</tr>
<tr>
<td>$I_{ss}$</td>
<td>Steady state current density</td>
<td>Amps/cm$^2$</td>
</tr>
<tr>
<td>$I_i$</td>
<td>Current density due to Ta interstitial production</td>
<td>Amps/cm$^2$</td>
</tr>
<tr>
<td>$I_O$</td>
<td>Current density due to O vacancy production</td>
<td>Amps/cm$^2$</td>
</tr>
<tr>
<td>$J_O$</td>
<td>Flux of oxygen vacancies</td>
<td>mol/(cm$^2$*s)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$J_i$</td>
<td>Flux of tantalum interstitials</td>
<td>mol/(cm$^2$·s)</td>
</tr>
<tr>
<td>$K$</td>
<td>EF/RT</td>
<td>1/cm</td>
</tr>
<tr>
<td>$L$</td>
<td>Total oxide thickness</td>
<td>cm</td>
</tr>
<tr>
<td>$M$</td>
<td>Modulus</td>
<td></td>
</tr>
<tr>
<td>$L_{OL}$</td>
<td>Thickness of outer layer</td>
<td>cm</td>
</tr>
<tr>
<td>$L_{IL}$</td>
<td>Thickness of inner layer</td>
<td>cm</td>
</tr>
<tr>
<td>$L_0$</td>
<td>Thickness of oxide when formation voltage is reached</td>
<td>cm</td>
</tr>
<tr>
<td>$L_{ss}$</td>
<td>Steady state oxide thickness</td>
<td>cm</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant</td>
<td>8.314 J/(mol K)</td>
</tr>
<tr>
<td>$R_{IL}$</td>
<td>Electronic resistance in the inner layer</td>
<td>Ω</td>
</tr>
<tr>
<td>$R_{OL}$</td>
<td>Electronic resistance of the outer layer</td>
<td>Ω</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Solution resistance</td>
<td>Ω</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$V$</td>
<td>Applied formation voltage</td>
<td>V vs SHE</td>
</tr>
<tr>
<td>$Y'$</td>
<td>Real component of the admittance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Y''$</td>
<td>Imaginary component of the admittance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Z'$</td>
<td>Real component of the impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Z''$</td>
<td>Imaginary component of the impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Z_{Total}$</td>
<td>Experimental impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Polarizability of metal/solution interface</td>
<td>n/a</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Transfer coefficient for the $i^{th}$ process</td>
<td>n/a</td>
</tr>
<tr>
<td>$\beta$</td>
<td>pH dependence of potential drop</td>
<td>V</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>F/RT</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Permittivity of oxide</td>
<td>n/a</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space</td>
<td>8.854*10^{-14} F/cm</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Oxidation state of tantalum in the film</td>
<td>+5</td>
</tr>
<tr>
<td>$\chi'$</td>
<td>Chi-Squared</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>$\phi^0_{Es}$</td>
<td>Potential drop at the film/electrolyte interface</td>
<td>V</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
<td>radians</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Molar volume of oxide per cation</td>
<td>26.9 cm$^3$/mol</td>
</tr>
</tbody>
</table>
6.2 Point Defect Model

6.2.1 Description for Tantalum Pentoxide

The work described below is closely related to the model developed by Sun et.al. for the characterization of the passive film on platinum[20]. Only slight modifications were made to adapt the model to the anodized tantalum system. Constants such as the oxidation state of the metal, the molar volume of the oxide, and the pH of the system were set appropriately. The oxidation state of tantalum in both the electrolyte and oxide was +5, the molar volume of the oxide per tantalum atom was 26.9 cm$^3$/mol, and the pH was 2.47.

The Faradaic impedance of the tantalum/tantala system is generated by point defect reactions occurring at the metal/film interface. It is assumed that the rate determining step for oxide formation is the kinetic reactions that occur at the interfaces. A schematic of the PDM for anodic tantala is shown in Figure 6—1 Reaction (1) represents the movement of a tantalum atom from the metal to an interstitial position in the oxide network. Reaction (2) is the production of an oxygen vacancy at the metal/oxide interface; the simultaneous production of a tantalum atom on a tantalum site of the oxide results in oxide growth. Reaction (3) is the ejection of tantalum interstitials directly into the electrolyte; this process does not represent film dissolution because an oxygen site (either an oxygen atom or vacancy) is not removed from the oxide; it is assumed that the charge on the tantalum interstitial is the same as the charge of the aqueous ion. Reaction (5) is the dissolution of oxide. In order for the position of an interface to move with respect to a laboratory frame of reference, both an oxygen site and a metal site must be produced or consumed. Therefore, reactions (2) and (5) are not lattice conservative. Reactions (1), (3), and (4) are lattice conservative.
Figure 6-1: Schematic showing the point defect reactions at the metal/film and film/solution interfaces.

A simplified derivation of the Faradaic impedance follows. A more detailed derivation can be found elsewhere;[20] in this presentation, the assumption that \( \Gamma = \chi \) is made early in the derivation. In the derivation given by Sun[20], et.al., this assumption may not have been explicitly stated, but it was made in the final expression for the impedance, i.e., prior to optimization of the PDM to the experimental spectra.

The Faradaic current is the sum of the currents due to the formation of oxygen vacancies and tantalum interstitials

\[
I = F \left[ \chi k_1^0 e^{a_V} e^{L} + \chi k_2^0 e^{a_V} e^{L} \right] \quad [6-1]
\]

Where F is Faraday’s constant, \( \chi \) is the oxidation state of tantalum (5), \( V \) is the applied voltage, \( L \) is the oxide thickness, and the other terms are defined as:

\[
a_1 = \alpha_1 (1 - \alpha) \chi \gamma \quad [6-2]
\]

\[
b_1 = \alpha_1 \chi \gamma \tilde{E} \quad [6-3]
\]

\[
a_2 = \alpha_2 (1 - \alpha) \chi \gamma \quad [6-4]
\]

\[
b_2 = \alpha_2 \chi \gamma \tilde{E} \quad [6-5]
\]

\[
k_1^0 = k_1^{00} e^{-a_1 \beta \exp H} e^{-a_1 \beta \exp H} \quad [6-6]
\]

\[
k_2^0 = k_2^{00} e^{-a_2 \beta \exp H} e^{-a_2 \beta \exp H} \quad [6-7]
\]

\[
k_5^0 = k_5^{00} \quad [6-8]
\]
Where $\alpha$ is the polarizability of the barrier layer/solution interface, $\alpha_i$ is the transfer coefficient of the $i^{th}$ reaction, $k_i^{00}$ is the standard rate constant of the $i^{th}$ reaction, $\gamma$ is $F/RT$, $E$ is the electric field in the oxide, $\beta$ is the pH dependence of potential drop across the barrier layer/solution interface, and $\phi_{f,i}^0$ is the standard potential drop across the film/solution interface.

The Faradaic admittance due to the sinusoidal voltage applied during impedance spectroscopy is

$$Y_f = \frac{\partial I}{\partial V} = \left( \frac{\partial I}{\partial V} \right)_L + \left( \frac{\partial I}{\partial V} \right)_V \frac{\Delta L}{\Delta V}$$ \[6-9\]

### 6.2.2 Electrical Analog

Although the Faradaic impedance is the most interesting impedance element of the system, the experimental impedance of the electrochemical cell contains contributions from several processes. In order to separate the different impedance producing processes in the cell, the electrical analog shown in Figure 6-2 was used. The corresponding expression for the total, measured impedance is thus:

$$Z_{Measured} = \frac{1}{(Z_f + Z_w)^{-1} + R_{e,h}^{-1} + j\omega C_g^{-1}} + \frac{1}{j\omega C_{dl}^{-1}} + R_S$$ \[6-10\]

Where $Z_w$ is the Warburg impedance due to the transport of ionic defects, $R_{e,h}$ is the electronic resistance of the oxide, $C_g$ is the geometric capacitance of the oxide calculated from the parallel plate model of a capacitor, $Z_{OL}$ is the impedance of the outer layer, $C_{dl}$ is
the double layer capacitance, and $R_S$ is the solution resistance. This expression was then optimized to the experimental EIS data via a non-linear regression procedure. The commercial software package *DataFit Version 8.0.32* from Oakdale Engineering was used for the regression procedure. The formalism for expressing the experimental admittance during the regression procedure is given in Appendix A.

**Figure 6-2:** Electrical analog of the impedance producing components of the tantalum/tantala/electrolyte system.

### 6.2.3 Optimization Procedure

A summary of the optimization parameters and their definitions is shown in Table 6-2. The flowchart in Figure 6-3 diagrams the methodology used in optimizing the PDM parameters to the EIS data. First, a simple electrical analog was used to assign $R_{eh}$, $R_s$, and $\varepsilon$, defined respectively as: the resistance in the oxide due to electrons and holes, the solution resistance, and the dielectric constant.
Following the methodology used by Sun, et.al.[20], reasonable values for $n$, $\beta$, $\phi_{fs}^0$, were determined in a first stage optimization and then set constant. The kinetic order of the reaction with respect to $H^+$ for reaction (5), $n$, was maintained at 0.5. The dependency of the potential drop on the pH, $\beta$, was set to -0.010V, and the standard potential drop at the film/solution interface, $\phi_{fs}^0$, was set at -0.10 V. A second optimization of the model was performed using the real component of the impedance where the parameters were: $E$, the electric field in the oxide, $\alpha$, the polarizability of the oxide/solution interface, $k_i^{00}$, the standard rate constants for reactions 1, 2, 5 and the thermodynamic transfer coefficients, $\alpha_i$, for reactions 1 and 2. Thus, these seven parameters were set to arbitrary, albeit physically reasonable, values and a non-linear regression was performed on the real component of the impedance. In practice, all seven variables could not be optimized in a single step and copious iterations were completed until the parameters converged to the same value. It was particularly difficult to optimize the rate constant and transfer coefficient for reaction 1, which corresponds to the formation of tantalum interstitials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{e,h}$</td>
<td>Resistance of electrons and holes in the film</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Solution Resistance</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric Constant</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric Field in the film</td>
</tr>
<tr>
<td>$k_i^{00}$</td>
<td>Rate Constants: $i = 1, 2, 5$</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Transfer Coefficient $i=1,2$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Polarizability of the oxide/solution interface</td>
</tr>
<tr>
<td>$n$</td>
<td>Kinetic order of Reaction 5 wrt $[H+]$</td>
</tr>
<tr>
<td>$\phi_{fs}^0$</td>
<td>Standard potential drop at the f/s interface</td>
</tr>
<tr>
<td>$\beta$</td>
<td>pH dependence of voltage drop at f/s</td>
</tr>
</tbody>
</table>
During the regression procedure, the physical constants that describe the anodic film are the variables. Once the regression is complete, these variables can be used to calculate a steady state current density due to the Faradaic current, $I_{SS}$, and oxide thickness, $L_{SS}$, via equations [6-11] and [6-12]:

$$I_{SS} = \chi F[k'_{1}^{0}] \cdot \exp\left(-\frac{\alpha_{1}zF\beta \cdot pH}{RT}\right) \cdot \exp\left(-\frac{\alpha_{1}zF\phi_{f/s}^{0}}{RT}\right) \cdot \exp\left(\frac{\alpha_{1}(1 - \alpha)zFV}{RT}\right) \cdot \exp\left(-\frac{\alpha_{1}zFEFL_{SS}}{RT}\right) +$$

$$+ k'_{2}^{0} \cdot \exp\left(-\frac{\alpha_{2}zF\beta \cdot pH}{RT}\right) \cdot \exp\left(-\frac{\alpha_{2}zF\phi_{f/s}^{0}}{RT}\right) \cdot \exp\left(\frac{\alpha_{2}(1 - \alpha)zFV}{RT}\right) \cdot \exp\left(-\frac{\alpha_{2}zFEFL_{SS}}{RT}\right)$$

[6-11]

And

$$L_{SS} = \left(\frac{1 - \alpha}{E}\right) \cdot V - \frac{RT}{\alpha_{2}zEF} \cdot \ln\left(k_{2}^{0}\right) - \frac{\beta \cdot pH}{E} - \frac{\phi_{f/s}^{0}}{E} + \frac{2.303nRT \cdot pH}{\alpha_{2}zEF} + \frac{6.909nRT}{\alpha_{2}zEF}$$

[6-12]
The definition of each term, along with its method of determination, is shown in Table 6-3.

**Table 6-3:** Definition and origin of terms used in calculating oxide thickness and steady state current.

<table>
<thead>
<tr>
<th>Term</th>
<th>Physical Meaning</th>
<th>Method of Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_s$</td>
<td>Steady state current</td>
<td>Calculated from regression parameters</td>
</tr>
<tr>
<td>$L_{ss}$</td>
<td>Steady state oxide thickness</td>
<td>Calculated from regression parameters</td>
</tr>
<tr>
<td>$\chi, n$</td>
<td>Number of electrons transferred, 5</td>
<td>Constant</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
<td>Constant</td>
</tr>
<tr>
<td>$k_i^{00}$</td>
<td>Rate constant for the $i^{th}$ process</td>
<td>PDM Regression</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Polarizability</td>
<td>PDM Regression</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>Transfer coefficient for the $i^{th}$ process</td>
<td>PDM Regression</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field in the oxide</td>
<td>PDM Regression</td>
</tr>
<tr>
<td>$\phi_{0f/s}^0$</td>
<td>Potential drop at the film/solution interface</td>
<td>Initial PDM Regression. Constant for all formation voltages</td>
</tr>
<tr>
<td>$\beta$</td>
<td>pH dependence of potential drop</td>
<td>Initial PDM Regression. Constant for all formation voltages</td>
</tr>
<tr>
<td>$V$</td>
<td>Applied Formation Voltage</td>
<td>Experimental Variable</td>
</tr>
</tbody>
</table>

If the calculated current and thickness were not satisfactory, the seven parameters from the second stage optimization were adjusted and then a subsequent regression analysis was run. This arduous process was repeated until the thickness and current calculated from the PDM parameters were in agreement with the experimental values. Next, the parameters were used as initial values for optimization of the imaginary component of the impedance. The methodology was repeated for the imaginary component of the impedance. Finally, the real and imaginary components of the impedance were calculated from the PDM parameters and compared to the experimental impedance.

This procedure was completed for oxide anodized at 4V, 6V, and 8V. The parameters determined from each optimization procedure are shown in Table 6-4. The averages and standard deviations were obtained from optimization to the real and imaginary components at each formation voltage.
Table 6-4: Results obtained from the optimization procedure. The reported uncertainty is the standard deviation of the six optimizations. (The six optimizations are optimizations to the real and imaginary impedance components for formation voltages of 4V, 6V, and 8V)

<table>
<thead>
<tr>
<th>Variable</th>
<th>4V Imag</th>
<th>4V Real</th>
<th>6V Imag</th>
<th>6V Real</th>
<th>8V Imag</th>
<th>8V Real</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{dl}$, $\mu$F</td>
<td>51.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48.1</td>
<td>4.4</td>
</tr>
<tr>
<td>$R_{eb}$, $\Omega$</td>
<td>6.12*10^6</td>
<td>7.15*10^6</td>
<td>1.22*10^7</td>
<td>1.37*10^7</td>
<td>1.56*10^7</td>
<td>1.56*10^7</td>
<td>1.37*10^7</td>
<td>0.12</td>
</tr>
<tr>
<td>$R_s$, $\Omega$</td>
<td></td>
<td>95.86</td>
<td>93.9</td>
<td>89.6</td>
<td>93.1</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$, V/cm</td>
<td>2.27*10^6</td>
<td>2.27*10^6</td>
<td>2.36*10^6</td>
<td>2.24*10^6</td>
<td>2.37*10^6</td>
<td>2.26*10^6</td>
<td>2.30*10^6</td>
<td>0.06*10^6</td>
</tr>
<tr>
<td>$k_1^{00}$, mol/s*cm$^2$</td>
<td>0.175*10^{-17}</td>
<td>0.646*10^{-17}</td>
<td>6.80*10^{-17}</td>
<td>3.13*10^{-17}</td>
<td>1.40*10^{-17}</td>
<td>2.19*10^{-17}</td>
<td>1.59*10^{-16}</td>
<td>2.46*10^{-16}</td>
</tr>
<tr>
<td>$k_2^{00}$, mol/s*cm$^2$</td>
<td>5.00*10^{-15}</td>
<td>3.54*10^{-15}</td>
<td>3.56*10^{-15}</td>
<td>3.40*10^{-15}</td>
<td>3.57*10^{-15}</td>
<td>2.99*10^{-15}</td>
<td>3.68*10^{-15}</td>
<td>0.68*10^{-15}</td>
</tr>
<tr>
<td>$k_5^{00}$, mol/s*cm$^2$</td>
<td>4.22*10^{-16}</td>
<td>4.26*10^{-16}</td>
<td>4.55*10^{-16}</td>
<td>4.63*10^{-16}</td>
<td>4.12*10^{-16}</td>
<td>3.90*10^{-16}</td>
<td>4.28*10^{-16}</td>
<td>0.27*10^{-16}</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>0.550</td>
<td>0.551</td>
<td>0.578</td>
<td>0.586</td>
<td>0.575</td>
<td>0.580</td>
<td>0.570</td>
<td>0.016</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>0.173</td>
<td>0.116</td>
<td>0.065</td>
<td>0.120</td>
<td>0.057</td>
<td>0.145</td>
<td>0.113</td>
<td>0.045</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.290</td>
<td>0.290</td>
<td>0.291</td>
<td>0.290</td>
<td>0.291</td>
<td>0.292</td>
<td>0.291</td>
<td>0.001</td>
</tr>
</tbody>
</table>
6.2.4 Evaluation of Optimization Procedure

6.2.4.1 Steady State Conditions

The current and thickness are not fit directly via the regression analysis and are a somewhat independent reality check for assessing whether the parameters are feasible. Because the current of the system is measured directly and the film thickness can be approximated by the formation voltage or capacitance measurements, the physical validity of the regression parameters can be evaluated by comparing the experimental and calculated thickness and current values.

A comparison between the calculated and experimental steady-state thickness is shown in Figure 6-4; the thickness predicted by the PDM, calculated from the literature anodization constant [92, 93], and by measuring the capacitance at 1000 Hz are shown. The PDM thickness is determined using the parameters in Table 6-4 and equation [6-2. It is noted that in calculating the thickness from the capacitance the dielectric constant is assumed to be 23.9. Also, subsequent experiments have shown that the oxide thickens slowly over the 24 hour potentiostatic hold at the formation voltage; the anodization time for the literature anodization constant was not specified, but it is assumed it is on the order of minutes rather than hours. These two realities explain why the thickness as measured by the capacitance is not in better agreement with the other calculations.

The steady state current calculated from the PDM parameters in Table 6-4 and equation 6-1 is not in agreement with the current measured experimentally. The experimental current is (1.09±0.05)*10^-7 A/cm², however the Faradaic current calculated by the PDM is 3.3*10^-12 A/cm². It is important to consider whether the measured steady state current is dominated by the Faradaic processes (an ionic current) or the leakage of electrons through the oxide (electronic current.) It has been demonstrated that during the growth of the oxide the ionic current accounts for >99% of the current.[4, 54] However, given the extreme passivity of tantalum oxide after long anodization times, it could be that the
The electronic current is significant after the formation voltage has been applied for an extended time.

**Figure 6-4:** Comparison between the steady state thickness as calculated by the PDM using the parameters in Table 6-4, and the literature anodization constant, and as calculated from the capacitance at 1000 Hz assuming a dielectric constant of 23.9.

The PDM described above includes an element for the electronic resistance of the oxide in the equivalent circuit (Figure 6—2). The resistance determined from the optimization procedure was used to calculate an electronic current via Ohm’s Law. Table 6-5 shows the experimental steady state current, the total ionic current calculated by the PDM, and the electronic current calculated from the resistance of the equivalent circuit element. There is an obvious discrepancy in that the calculated electronic current is greater than the experimental current. Using the basics of DC circuitry, the sum of the current due to the $R_{eh}$ resistor and the Faradaic impedance should equal the total current. The optimized equivalent circuit reported here predicts DC currents that are of the same order of magnitude as the experimental current but slightly higher.
**Table 6-5:** Experimental current, steady state current calculated from the PDM parameters, and the electronic current determined by optimizing the PDM equivalent circuit to the impedance spectra.

<table>
<thead>
<tr>
<th>Formation Voltage, V</th>
<th>Experimental Current A/cm²</th>
<th>PDM, Total Ionic Current A/cm²</th>
<th>PDM Electronic Current A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1.06 \times 10^{-7}$</td>
<td>$3.26 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$1.05 \times 10^{-7}$</td>
<td>$3.26 \times 10^{-12}$</td>
<td>$6.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>6</td>
<td>$1.16 \times 10^{-7}$</td>
<td>$3.26 \times 10^{-12}$</td>
<td>$9.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>8</td>
<td>$1.07 \times 10^{-7}$</td>
<td>$3.26 \times 10^{-12}$</td>
<td>$1.2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The PDM allows for the measured current to be separated into components due to the production of tantalum interstitials and oxygen vacancies. Using the parameters in Table 6-4 and equation 6—11, the current due to oxygen vacancy production is $3.80 \times 10^{-13}$ A/cm² and due to tantalum interstitials is $2.88 \times 10^{-12}$ A/cm² at the steady state condition. These currents are depicted graphically in Figure 6-5. It is predicted that the current should be independent of the voltage for an n-type film.

**Figure 6-5:** Steady state current where the total current (top plot) is displayed along with the current due to tantalum interstitials (middle plot) and oxygen vacancies (lowest plot).
6.2.4.2 Simulated Impedance Spectra

The impedance spectra predicted by calculating the impedance from the PDM parameters compare well with the experimental spectra. The calculated and experimental spectra are displayed in Bode Plots in Figure 6-6 (4V anodization), Figure 6-7 (6V anodization) and Figure 6-8 (8V Anodization). The Nyquist plots for the experimental and calculated impedance are less enlightening but are shown because their use is ubiquitous in the literature and familiar to scientists; the comparisons are shown in Figure 6-9 (4V anodization), Figure 6-10 (6V anodization), and Figure 6-11 (8V anodization.)

Figure 6-6: Bode representation showing the goodness of fit between the experimental and calculated impedance spectra for oxide formed to 4V vs. SCE.
Figure 6-7: Bode representation showing the goodness of fit between the experimental and calculated impedance spectra for oxide formed to 6V vs. SCE.

Figure 6-8: Bode representation showing the goodness of fit between the experimental and calculated impedance spectra for oxide formed to 8V vs. SCE.
Figure 6-9: Nyquist representation showing the goodness of fit between the experimental and calculated impedance spectra for oxide formed to 4V vs. SCE. The frequency is labeled for a couple of data points.

Figure 6-10: Nyquist representation showing the goodness of fit between the experimental and calculated impedance spectra for oxide formed to 6V vs. SCE.
While the simulated and experimental spectra appear to agree well, it is important to quantify both the goodness of fit and the uniqueness of the fit. By eye, the agreement obtained here is as good or better than optimization reported for other systems in the literature. [20, 83] It is generally not good scientific practice to judge model optimization solely by visual inspection:

“To be genuinely useful, a fitting procedure should provide (i) parameters, (ii) error estimates on the parameters, and (iii) a statistical measure of goodness-of-fit…Unfortunately, many practitioners of parameter estimation never proceed beyond item (i). They deem a fit acceptable if a graph of data and model ‘looks good.’ This approach is known as chi-by-eye. Luckily, its practitioners get what they deserve.” [191]
In an effort to quantify the goodness of fit, chi-squared ($\chi^2$) values were determined; this requires an estimation of the error in the measured data. The error for the impedance data were calculated as the standard deviation ($\sigma$) between the collected data and the K-K transform of the data. This is considered to be a liberal estimation of the error. Chi-Squared values are readily calculated from:

$$\chi^2 \equiv \sum_{i=1}^{N} \left( \frac{y_i - y(x_i; a_1, a_2, \ldots, a_n)}{\sigma_i} \right)^2$$  \[6-13\]

A general rule of thumb is that $\chi^2$ value should be approximately equal to the number of degrees of freedom for a good fit.[191] In this case, there are 52 data points and 12 fitting parameters; therefore there are 40 degrees of statistical freedom. A typical plot of the experimental data and optimized model of the real and imaginary components of the impedance is shown in Figure 6-12. For the real component, $\chi^2 = 111$ and for the imaginary component, $\chi^2 = 47$. Therefore, from a statistical analysis, the optimization result is not great but is satisfactory considering the large number of optimized parameters.

**Figure 6-12:** Determining the goodness of fit between the impedance calculated from optimized PDM and the experimental spectra.
6.2.4.3 Sensitivity Analysis

In order to assess the sensitivity of the calculated impedance to the model parameters, a sensitivity analysis was carried out. Each variable was pushed from its optimized value by ± 25%; the real and imaginary components of the impedance were calculated using the non-optimized values. The sensitivity of the magnitude of the impedance is presented for when the parameters are increased by 25% of the optimized value in Figure 6-13, Figure 6-14, and Figure 6-15. The sensitivity of the impedance to each parameter is plotted, where the sensitivity, S, is defined as:

\[ S = \frac{|Z - Z_0|}{|x - x_0|} \quad 0.25 \]

\[ 6.14 \]

**Figure 6-13**: Sensitivity of the calculated impedance to the value of the optimized parameters, \( R_s \), \( R_{eh} \), \( k_1^\infty \), and \( \alpha_1 \). Starting from the optimized values, parameters were increased 25% and then the impedance was calculated for 4V anodization.
Figure 6-14: Sensitivity of the calculated impedance to the value of the optimized parameters, $\alpha$, electric field, $k_2$, $k_5$ and $\alpha_2$. Starting from the optimized values, parameters were increased 25% and then the impedance was calculated for 4V anodization.

Figure 6-15: Sensitivity of the calculated impedance to the value of the constant parameters, $n$, $\beta$, $\varphi f/s$. Starting from the optimized values, parameters were increased 25% and then the impedance was calculated for 4V anodization.
6.3 Discussion

A point defect model (PDM) has been developed for anodic tantalum oxide. Parameters have been determined by using non-linear regression to optimize the PDM to electrochemical impedance spectra. The rate constants and transfer coefficients provide a fundamental, physical model for the formation and steady state conditions of the oxide. This model can be used to predict how oxide formation would be affected by environmental variables such as pH, applied stress or strain, or a host of other conditions.

While the oxide thickness predicted by the PDM is in adequate agreement with the thickness determined by other methods, the calculated current is not. This discrepancy could be due to

i.) the presence of a significant electronic current, which could be due to leakage through the oxide or due to extraneous currents specific to the electrochemical cell

ii.) over-reliance on the $R_{ct}$ term of the electrical analog during the optimization procedure

The goodness of fit achieved by the optimization procedure is deemed satisfactory; however, it is more difficult to make conclusions concerning the uniqueness of the fit. Sensitivity analysis shows that the impedance calculated by the model is indeed sensitive to the parameters.

In the course of optimizing the model to the experimental impedance, it was observed that the Warburg impedance of the model did not impact the calculated impedance. Changing the Warburg terms by many orders of magnitude produced only a very slight change in the impedance at the lowest two frequency points (0.01 and 0.02 Hz). Therefore, for the range of frequencies studied in this work, the Warburg impedance can be neglected.
An improved optimization procedure can be devised so that experimentally determined properties of the system can be used as constraints during the non-linear regression procedure. This will increase the statistical number of degrees of freedom, help insure that the parameters are physically reasonable, and improve the reproducibility of the optimization results.
Chapter 7: Constrained Bi-Layer Point Defect Model of Anodic Tantalum Oxide

7.1 Comparison of Constrained and Unconstrained PDMs

The methodology of Chapter 6 closely follows work reported for similar systems.[21, 22, 79] The model described in Chapter 6 was developed with the assumption that the total oxide thickness (inner layer + outer layer) is linear with the reported anodization constant for the system, \( L \, (\text{nm}) = 1.8 \times V_f + 2.6 \).[92] However, as shown in 3.2.6 and 4.4.5, the oxide thickness grows with time even after several days of anodization, thus the real oxide thickness is significantly greater. Using the knowledge gained from empirical investigations, an improved bi-layer model is presented here in Chapter 7. Knowing the growth rate of the individual oxide layer provides reasonable estimates for the ionic current due to the generation of tantalum interstitials and oxygen vacancies. These quantities can be calculated from the PDM parameters; therefore, the growth laws can be used to constrain the optimization of the PDM. Also, the thickness of the oxide has a significant effect on the calculated Faradaic impedance; therefore it is important to use an accurate assessment of oxide thickness during optimization of the PDM to electrochemical impedance spectra (EIS).

7.2 Introduction: Anodic Oxide Growth Models

Anodic oxides form by an ionic conduction mechanism. Under an applied electric field, metal atoms from the anode and oxygen atoms from the electrolyte cooperatively migrate to form a metal oxide. Researchers have expressed surprise at learning that cationic species are outwardly mobile[52] but have accepted the experimental evidence despite an incomplete understanding of the mechanism of ionic transport. In interpreting their results on anodic tantalum, Shimizu, et. al.[47], cite Mott’s liquid theory reported for the oxidation of silicon.[192] In this theory, the entire volume of the oxide is composed of “frozen-in dipoles” during anodic oxidation. A group of perhaps 20 ions is collectively excited into a liquid state; the vibrational moments between the ions are sufficiently large for the cohort of ions to act as a liquid droplet. On the time order of \( 10^{-12} \) s, M and O
atoms move past each other creating the alleged dipole. This dipole increases the electric field in the nearby region, thus encouraging other sets of M and O atoms to become excited into a liquid droplet.[47] This qualitative description of a solid with liquid properties can explain how tantalum interstitials are able to transit a precipitated, and hence thermodynamically stable, layer of oxide.

It has been demonstrated that oxide growth is purely interfacial; oxide growth occurs at the metal/oxide interface via the inward migration of oxygen and at the oxide/electrolyte interface via the outward migration of metal.[193] The experimental conditions during the anodic oxidation of tantalum may result in the continuous precipitation of oxide rather than dissolution. Whereas the electrochemical dissolution current for anodic Al₂O₃ was measured at 0.3μA/cm², the dissolution of Ta₂O₅ was less than the detection limit of 0.003 μA/cm².[39] As shown in Section 3.3 of this work, the oxide continues to grow even after the applied formation voltage is reduced and then held for 100 hours.
7.3 Qualitative Point Defect Model

Figure 7-1 depicts the complete point defect model (PDM) envisionable for the tantalum-oxygen system. The PDM is frequently invoked to characterize the passivity of oxide films on metals.[20, 81, 87, 189] The mathematical process described below is based closely on the derivation published for Alloy 22,[21] although it has been modified to explicitly account for oxide growth by the outward migration of tantalum interstitials.

![Figure 7-1: Schematic of the possible point defect reactions in anodic tantalum. Ta= metal atom, VTa’ = cation vacancy on the tantalum sublattice, VO’’ = oxygen vacancy on the oxygen sublattice of the oxide, Ta+i’ = interstitial metal cation, TaTa = tantalum cation on the tantalum sublattice of the oxide, OO = oxygen anion on the oxygen sublattice of the oxide, Ta+; tantalum cation in the solution.](image)

Because tantalum oxide is an n-type semiconductor[64], tantalum vacancies can be treated as minority carriers and disregarded, also there is no evidence in the literature to suggest that the oxidation state of tantalum is anything other than +5 whether tantalum is in the anodic oxide or the aqueous state. This assumption results in $\Gamma = \chi$, which simplifies the model considerably. It has been previously concluded that reactions (I) (II) (IV) (V) and (VI) are lattice conservative, i.e., they do not result in movement of the...
oxide interfaces with respect to the laboratory frame of reference. Reactions (II) and (VII) are lattice non-conservative and are responsible for the formation and dissolution of the oxide, respectively.

Due to the low solubility of tantalum and the absence of a complexing agent in the electrolyte, interstitials remain at the interface where they are hydrolyzed. The bi-layer PDM for tantalum oxide is shown schematically in Figure 7-2.

<table>
<thead>
<tr>
<th>Ta</th>
<th>Inner Layer</th>
<th>Outer Layer</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)Ta</td>
<td>Ta&lt;sup&gt;5+&lt;/sup&gt; + 5e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>(3)Ta&lt;sup&gt;5+&lt;/sup&gt; + $\frac{5}{2}$ H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;(s) + 5H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>(2)Ta</td>
<td>Ta&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;ta&lt;/sup&gt; + $\frac{5}{2}$ V&lt;sup&gt;••&lt;/sup&gt; + 5e&lt;sup&gt;-&lt;/sup&gt;</td>
<td>(4)V&lt;sup&gt;••&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; + 2H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Figure 7-2: Schematic of the proposed point defect model for n-type anodic tantalum. The inner layer forms at the tantalum/oxide interface due to the production of oxygen vacancies. The outer layer forms as tantalum interstitials react with anions from the electrolyte at the oxide/solution interface.

It is assumed that the rate limiting step for oxide growth is the formation of point defects at the metal/oxide interface. Thus, the diffusion of tantalum interstitials and oxygen vacancies is not considered in this derivation. It is noted that previous attempts to optimize a PDM to electrochemical impedance spectra were unsuccessful in determining the Warburg coefficient, which describes the diffusion of oxygen vacancies. The model was only sensitive to the Warburg term at extremely low frequencies, and it is not trivial to extend the experimental data to include lower frequencies. For this reason, the transport of defects is not considered in deriving the impedance response of the system; however, at low frequencies (< 0.02 Hz) the diffusion of defects may influence the measurable impedance of the system.

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7.4 Constraints Determined for Anodic Tantalum Oxide formed in Phosphoric Acid

As described in Chapter 3.2.6.4, the growth rate of tantalum oxide on sputter deposited tantalum anodes was determined using Fourier transform infrared (FT-IR) reflectance spectroscopy and transmission electron microscopy (TEM). Order of magnitude estimates of the oxide thickness and current due to oxide formation can be readily obtained from this information. By knowing the growth laws of the individual inner and outer layers of oxide, the current attributed to the formation of tantalum interstitials and oxygen vacancies can be determined.

7.4.1 Oxide Thickness

7.4.1.1 Inverse Logarithmic Growth Laws

To a first approximation, the growth kinetics of anodic tantalum have been described using an inverse logarithmic growth law,[7, 59]

\[ \frac{1}{L} = A - b \ln(t) \]  \hspace{1cm} [7-1]

which is an approximate solution of the thickness-time relationship described by the High Field Model (HFM). The oxide thickness is \( L \), \( t \) is time of anodization, and \( A \) and \( B \) are constants. Rearranging [7.4] gives:

\[ L(nm) = \frac{1}{A - b \ln(t, \text{sec})} \]  \hspace{1cm} [7-2]

The growth rate of the oxide is given as
\[
\frac{dL}{dt} = \frac{b}{t(b*\ln t - A)^2} \quad [7-3]
\]

**Table 7-1:** Parameters of the inverse logarithmic growth laws determined for tantalum oxide formed to 70V in 0.1 M H$_3$PO$_4$. The thickness of the oxides at various anodization times was determined by quantifying FT-IR reflectance spectra.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>A (cm$^{-2}$)</th>
<th>B (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>9.64 ± 0.11*10^4</td>
<td>2351 ± 120</td>
</tr>
<tr>
<td>Inner</td>
<td>2.10 ± 0.10 *10^5</td>
<td>6277 ± 980</td>
</tr>
<tr>
<td>Outer</td>
<td>1.80 ± 0.06 *10^5</td>
<td>3542 ± 570</td>
</tr>
</tbody>
</table>

**7.4.1.2 Direct Logarithmic Growth Law**

The direct logarithmic law is a physically more accurate description[12] of the growth laws of anodic tantalum oxide; the reasons for this and the definitions of $a'$ and $b'$ are discussed in Section 3.2.6.1.

\[
L = L_0 + \frac{1}{b'} \ln(1 + a'b \exp(-b'L_0)t) \quad [7-4]
\]

In this case, $L_0$, is the oxide thickness when the formation voltage has been reached. The oxide growth rate for the logarithmic growth law is

\[
\frac{dL}{dt} = \frac{a'}{a'bt + e^{b'L_0}} \quad [7-5]
\]
Table 7-2: Parameters of the direct logarithmic growth laws determined for tantalum oxide formed to 70V in 0.1 M H$_3$PO$_4$. The thickness of the oxides at various anodization times was determined by quantifying FT-IR reflectance spectra.

<table>
<thead>
<tr>
<th>Oxide Layer</th>
<th>a' (cm$^{-1}$)</th>
<th>b' (cm$^{-1}$)</th>
<th>L$_0$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>243 ± 270</td>
<td>(2.18 ± 0.08)*10$^6$</td>
<td>(11.1 ± 0.1)*10$^{-6}$</td>
</tr>
<tr>
<td>Inner</td>
<td>219 ± 150</td>
<td>(4.56 ± 0.29)*10$^6$</td>
<td>(5.6 ± 3.8)*10$^{-6}$</td>
</tr>
<tr>
<td>Outer</td>
<td>248 ± 96</td>
<td>(4.40 ± 0.05)*10$^6$</td>
<td>(5.7 ± 1.1)*10$^{-6}$</td>
</tr>
</tbody>
</table>

7.4.2 Current Density

The growth rate can be used to predict the ionic current density at any given time using Faraday’s law.[89]

\[
i = \frac{dL}{dt} \frac{zF}{M} \rho \]

[7-6]

where $z$ is the number of moles of electrons needed to form a mole of oxide, $F$ is Faraday’s constant, $\rho$ is the density of the oxide (8.03 g/cm$^3$), and $M$ is the molecular mass of the oxide.

The determination of the growth laws are reproduced from Chapter 3. The parameters in Table 7-1 (inverse logarithmic law) and Table 7-2 (direct logarithmic law), allow for the prediction of the ionic current at any particular time of anodization. After 24 hours of anodization, both growth laws predict that the ionic current density would be ~90 nA/cm$^2$. Table 7-3 shows the ionic current densities predicted for the formation of the inner layer (due to the formation of oxygen vacancies) and of the outer layer (due to the formation of tantalum interstitials.)
Table 7-3: Current densities after 24 hours of anodization predicted from inverse logarithmic and direct logarithmic growth laws.

<table>
<thead>
<tr>
<th>Current Density nA/cm²</th>
<th>dL/dt (86,400 s) cm/s</th>
<th>Formed Defect (Layer)</th>
<th>Growth Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 ± 6</td>
<td>2.53*10⁻¹²</td>
<td>( V_o ) (Inner)</td>
<td>Logarithmic</td>
</tr>
<tr>
<td>46 ± 10</td>
<td>2.63*10⁻¹²</td>
<td>( T_{ai} ) (Outer)</td>
<td>Logarithmic</td>
</tr>
<tr>
<td>66 ± 32</td>
<td>3.78*10⁻¹²</td>
<td>( V_o ) (Inner)</td>
<td>Inverse Logarithmic</td>
</tr>
<tr>
<td>37 ± 12</td>
<td>2.10*10⁻¹²</td>
<td>( T_{ai} ) (Outer)</td>
<td>Inverse Logarithmic</td>
</tr>
</tbody>
</table>

The oxide thickness for anodization in 0.1 M H₃PO₄ for 50 minutes is given by:

\[
L(nm) = (1.83 \pm 0.06)V_f + 2.6 \quad [7-7]
\]

Where \( V_f \) is the applied potential versus the hydrogen reduction potential. Tantalum oxide thickens considerably between 50 minutes of applied potential and the 24 hours typically applied in these studies. The oxide thicknesses after 50 minutes and 24 hours of anodization are shown in Table 7-4 for the formation voltages studied herein. These values are assumed to be \( L \), the total thickness of oxide. Throughout the optimization procedure in Chapter 6, the oxide thickness was assumed to be the thickness at 50 minutes of anodization. However, in Chapter 7, the model directly sets the oxide thickness to the values after 24 hours of anodization. The measured currents after 24 hours of anodization are shown in Table 7-4 for anodization at each formation voltage. The DC bias (formation voltage) was applied during the measurement.
Table 7-4: Oxide thickness after 24 hours of anodization as determined by the anodization constant and the inverse logarithmic growth law.

<table>
<thead>
<tr>
<th>Formation Voltage, vs H⁺/H₂ potential</th>
<th>L After 50 minutes, nm</th>
<th>L after 24 hours, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.24</td>
<td>7.1</td>
<td>20.8</td>
</tr>
<tr>
<td>4.24</td>
<td>10.4</td>
<td>24.0</td>
</tr>
<tr>
<td>6.24</td>
<td>14.0</td>
<td>27.7</td>
</tr>
<tr>
<td>8.24</td>
<td>17.7</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Table 7-5: Experimental current after anodization for 24 hours.

<table>
<thead>
<tr>
<th>Formation Voltage, V</th>
<th>Experimental Current, A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.06*10⁻⁷</td>
</tr>
<tr>
<td>4</td>
<td>1.05*10⁻⁷</td>
</tr>
<tr>
<td>6</td>
<td>1.16*10⁻⁷</td>
</tr>
<tr>
<td>8</td>
<td>1.07*10⁻⁷</td>
</tr>
</tbody>
</table>

7.5 Quantitative Point Defect Model

7.5.1 Definition of Terms

The potential drops at the film/solution interface and the metal/film interface are:

\[
\phi_{fo} = \phi_{f} - \phi_{s} = \alpha V + \beta pH + \phi_{fo}^{*}
\]

\[
\phi_{mf} = \phi_{m} - \phi_{f} = (1-\alpha)V - \beta pH - \phi_{fo}^{*} - EL
\]

where \( \alpha \) is the polarizability of the oxide/solution interface, i.e., \( \alpha = d\phi_{fo}/dV \), \( \beta \) is the pH dependence of the potential drop across the oxide/solution interface, i.e., \( \beta = d\phi_{fo}/dPH \).
and L is the thickness of the entire oxide layer. It is worthwhile to note that as the film grows thicker, the potential drop at the metal film interface decreases. It is the size of this potential drop that determines the rate at which point defects will be produced at the metal/film interface. When the energy required to inject a point defect into the oxide is greater than the potential drop, the oxide will cease to thicken.

The standard rate constants, $k_{ij}^{00}$, which are independent of pH are defined as[20, 21]:

$$k_1^{00} = k_1^0 e^{5\gamma \alpha_i \beta \phi H} e^{5\gamma \alpha_i \phi_i}$$  \hspace{1cm} [7-10]

$$k_2^{00} = k_2^0 e^{5\gamma \alpha_i \beta \phi H} e^{5\gamma \alpha_i \phi_i}$$  \hspace{1cm} [7-11]

$$k_3^{00} = k_3^0 e^{-5\gamma \alpha_i \beta \phi H} e^{-5\gamma \alpha_i \phi_i}$$  \hspace{1cm} [7-12]

$$k_4^{00} = k_4^0 e^{-2\gamma \alpha_i \beta \phi H} e^{-2\gamma \alpha_i \phi_i}$$  \hspace{1cm} [7-13]

$$k_5^{00} = k_5^0$$  \hspace{1cm} [7-14]

The transfer coefficient of the $i^{th}$ reaction is denoted as $\alpha_i$; $\gamma = F/RT$ and $K = EF/RT$ where F is Faraday’s constant, R is the ideal gas constant, T is the temperature, and E is the electric field in the oxide. The rate constants, defined as $k_i^0$, are functions of the electrolyte pH and also depend on the standard potential drop at the film/electrolyte interface, which is denoted as $\phi_{f/s}^0$. In the course of these studies, $\beta$ is taken to be -60mV/pH[64, 72] and $\phi_{f/s}^0$ was taken to be -0.1V after initial optimization of the PDM to EIS spectra.
Table 7-6: Summary of abbreviated symbols, \(a_i\) and \(b_i\).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(a_i, V^{-1})</th>
<th>(b_i, cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(5 \gamma \alpha_1 (1 - \alpha))</td>
<td>(5 \alpha_1 K)</td>
</tr>
<tr>
<td>2</td>
<td>(5 \gamma \alpha_2 (1 - \alpha))</td>
<td>(5 \alpha_2 K)</td>
</tr>
<tr>
<td>3</td>
<td>(\gamma \alpha_3 \alpha)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>(2 \gamma \alpha_4 \alpha)</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Having discussed a qualitative description of the PDM and defined some of the symbolic variables in the system, the derivation of the Faradaic impedance of the point defect reactions commences.

### 7.5.2 Derivation of the Faradaic Impedance

The film/electrolyte interface is defined as \(x = 0\) and the metal/film interface is defined as \(x = L\). The change in the total film thickness is the sum of the changes of the inner and outer layers minus any dissolution of the oxide. As mentioned previously, the dissolution is expected to be extremely low. The oxide, \(\text{Ta}_5\text{O}_5\), is defined as \(\text{MO}_{\chi/2}\) where \(\chi = 5\).

The change in the inner layer thickness with time is given by

\[
\frac{dL_{il}}{dt} = -\frac{2 \Omega}{5} \frac{J_O}{\Omega k_s C_h^{n}}
\]

where the first term on the right side corresponds to film growth at the metal/barrier layer interface, the second to dissolution of the barrier layer at the barrier layer/outer layer interface, \(\Omega\) is the molar volume of oxide per cation, and \(J_O\) is the flux of oxygen vacancies defined as:
The change in the outer layer thickness with time is given by

\[ \frac{dL_{OL}}{dt} = -\Omega^* J_i \]  \hspace{1cm} [7-17]

where \( J_i \) is the flux of tantalum interstitials, and is expressed as:

\[ J_i = -D_i \frac{\partial C_i}{\partial x} - 5KD_i C_i \]  \hspace{1cm} [7-18]

The change in the oxide thickness with respect to time is then:

\[ \frac{dL}{dt} = -\frac{2* \Omega^* J_O}{5} - \Omega^* J_i - \Omega^* k_5^* C_{H^+}^n \]  \hspace{1cm} [7-19]

where \( k_5 \) is the rate of oxide dissolution, \( C_{H^+} \) is the concentration of hydrogen ions at the barrier oxide/outer layer interface, and \( n \) is the order of reaction with respect to \( C_{H^+} \).

The Faradaic current is given by

\[ I = F \left[ -5J_i^{\text{eff}} - 5J_O^{\text{eff}} \right] \]  \hspace{1cm} [7-20]

where \( F \) is Faraday’s constant. Table 7-6 defines the symbols \( a_i \) and \( b_i \). These are employed to make the derivation more compact and less frightening to math-phobic readers.
**Table 7-7:** Initial and boundary conditions for determining the rate of change of oxide thickness with respect to time.

<table>
<thead>
<tr>
<th>Initial Conditions</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t = 0$</td>
<td>$t &gt; 0, x = 0$; film/electrolyte interface</td>
</tr>
<tr>
<td>$C_i(x) = C_i^0(x)$</td>
<td>$J_i(0) = -k_2^0 e^{(a_1 V)} C_i(0)$</td>
</tr>
<tr>
<td>$C_O(x) = C_O^0(x)$</td>
<td>$J_O(0) = -\frac{5}{2} k_2^0 e^{(a_1 V)} C_O(0)$</td>
</tr>
<tr>
<td>$t &gt; 0, x = L$ ; oxide/film interface</td>
<td>$J_i(L) = -k_2^0 e^{(a_1 V)} e^{(-b_2 L)}$</td>
</tr>
<tr>
<td></td>
<td>$J_O(L) = -\frac{5}{2} k_2^0 e^{(a_2 V)} e^{(-b_2 L)}$</td>
</tr>
</tbody>
</table>

Using the initial and boundary conditions defined in Table 7-7 and the simplified notation allowed by the symbols in Table 7-6, the change in thickness can be expressed as:

\[
\frac{dL}{dt} = \Omega \sum \left[ k_1^0 e^{(a_1 V)} e^{(-b_1 L)} + k_2^0 e^{(a_2 V)} e^{(-b_2 L)} - k_5^n C_{H^+}^n \right]
\]  

[7-21]

Likewise the total current can be expressed as

\[
I = SF \sum \left[ k_1^0 e^{(a_1 V)} e^{(-b_1 L)} + k_2^0 e^{(a_2 V)} e^{(-b_2 L)} \right]
\]  

[7-22]

The Faradaic admittance is obtained by taking the total differential of equation 7-22, noting that the independent variables are voltage and oxide thickness and dividing by the perturbation in voltage, $\delta V$, to yield:

\[
Y_f = \frac{\delta I}{\delta V} = I^V + I^L \frac{\Delta L}{\Delta V} + I^{C_i(0)} \frac{\Delta C_i(0)}{\Delta V}
\]  

[7-23]

In the case of tantalum, it is assumed that the oxidation state of tantalum interstitials does not change when the specie either forms oxide or dissolves into the electrolyte. Referring to Figure 7-1, $\Gamma = \chi$, thus the current, $I^{C_i(0)}$ is zero. This assumption simplifies the Faradaic impedance to

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\[ Y_f = \frac{\delta I}{\delta V} = I^V + I^L \frac{\Delta L}{\Delta V} \quad [7-24] \]

The AC perturbing signal used in electrochemical impedance spectroscopy causes \( V \) and \( L \) to vary with time as:

\[
\delta V = \Delta V e^{j\omega t} \quad \text{and} \quad \delta L = \Delta L e^{j\omega t} \quad [7-25]
\]

The derivatives of these expressions with respect to time are:

\[
\frac{d(\delta V)}{dt} = j\omega \Delta V e^{j\omega t} \quad \text{and} \quad \frac{d(\delta L)}{dt} = j\omega \Delta L e^{j\omega t} \quad [7-26]
\]

Returning to equation 7-24, attention is focused on determining the change in thickness with respect to the change in voltage, \( \Delta L/\Delta V \). The full differential of equation 7-21 is given by:

\[
\frac{d(\delta L)}{dt} = \Omega \left[ a_1 k_1^e e^{(a,V)} e^{(-b,L)} \delta V - b_1 k_1^e e^{(a,V)} e^{(-b,L)} \delta L + a_2 k_2^e e^{(a,V)} e^{(-b,L)} \delta V - b_2 k_2^e e^{(a,V)} e^{(-b,L)} \delta L - a_3 k_3^e e^{a,V} C_H^n \delta V \right] \quad [7-27]
\]

and substituting Equations 7-25 and 7-26 into 7-27 and then rearranging, yields the expression:

\[
j\omega \ast \Delta L e^{j\omega t} = \Omega (a_1 k_1^e e^{(a,V)} e^{(-b,L)} \delta V + a_2 k_2^e e^{(a,V)} e^{(-b,L)} - a_3 k_3^e e^{a,V} C_H^n \Delta V e^{j\omega t} e^{b,L}) \Delta L e^{j\omega t}
\]

\[
- \Omega (b_1 k_1^e e^{(a,V)} e^{(-b,L)} \delta L + b_2 k_2^e e^{(a,V)} e^{(-b,L)} \Delta L e^{j\omega t} e^{b,L}) \Delta L e^{j\omega t} \quad [7-28]
\]

By the simple wonders of algebraic manipulation,
\[ \frac{\Delta L}{\Delta V} = \frac{\Omega(a_1k_1^oe^{(a,V)}e^{-b,L}) + a_2k_2^oe^{(a,V)}e^{-b,L} - a_5k_5^oe^{a,V}C_{H^+}^0}{j\omega + \Omega(b_1k_1^oe^{(a,V)}e^{-b,L}) + b_2k_2^oe^{(a,V)}e^{-b,L}} \] [7-29]

It is now trivial, although ugly, to substitute [7.29] into [7.24] to express the Faradaic admittance as:

\[ Y_f = 5F\left[ a_1k_1^oe^{a,V}e^{-b,L} + a_2k_2^oe^{a,V}e^{-b,L} \right] - \]
\[ 5F\left[ b_1k_1^oe^{a,V}e^{-b,L} + b_2k_2^oe^{a,V}e^{-b,L} \right]* \frac{\Omega(a_1k_1^oe^{(a,V)}e^{-b,L}) + a_2k_2^oe^{(a,V)}e^{-b,L} - a_5k_5^oe^{a,V}C_{H^+}^0}{j\omega + \Omega(b_1k_1^oe^{(a,V)}e^{-b,L}) + b_2k_2^oe^{(a,V)}e^{-b,L}} \]

It is assumed that the oxidation state of Ta is the same in the oxide, at the electrolyte/oxide interface, and in the electrolyte (i.e., \( \Gamma = \chi \)). Therefore, the pre-

exponential for Reaction 5 is zero (\( a_5=0 \)) and reaction 5 does not explicitly have an impact on the Faradaic admittance. Thus the expression simplifies slightly to:

\[ Y_f = 5F\left[ a_1k_1^oe^{a,V}e^{-b,L} \right] - \]
\[ 5F\left[ b_1k_1^oe^{a,V}e^{-b,L} + b_2k_2^oe^{a,V}e^{-b,L} \right]* \frac{\Omega(a_1k_1^oe^{(a,V)}e^{-b,L}) + a_2k_2^oe^{(a,V)}e^{-b,L}}{j\omega + \Omega(b_1k_1^oe^{(a,V)}e^{-b,L}) + b_2k_2^oe^{(a,V)}e^{-b,L}} \]

Although it may not have been clearly stated, this simplification has been made by prior investigators.[20] It is noted that the oxide thickness, \( L \), is typically dependent on Reaction 5. From equation 7-31 it is clear that the Faradaic admittance depends on the oxide thickness, \( L \), which is how \( k_5^{00} \) was determined by optimization of the PDM on electrochemical impedance spectra (EIS) by previous researchers studying other systems. However, in this work, it is accepted that the dissolution of tantalum does not occur at a measurable rate. Rather, the thickness, \( L \), used in equation 7-31 was determined by the values Table 7-4. Thus, equation 7-31 is the Faradaic impedance is measurable by EIS.
This concludes the calculation for determining the Faradaic impedance of the tantalum-oxide system when it is pushed from equilibrium by a small perturbing AC voltage.

**7.5.3 Expression of the Experimental Impedance**

Experimentally, the Faradaic impedance cannot be measured directly because other impedance producing components are present in the system. The geometric capacitance of the oxide is considered and is described by the parallel plate model of a capacitor as:

\[
C_g = \frac{A\varepsilon_0\varepsilon}{L}
\]  

[7-32]

where \( A \) is the area, \( \varepsilon_0 \) is the permittivity of free space, and \( \varepsilon \) is the permittivity of the oxide. The electronic resistances of the oxide layers, \( R \), are simply defined as

\[
R = \frac{\rho*L}{A}
\]  

[7-33]

where \( \rho \) is the oxide resistivity and \( L \) corresponds to that for the oxide being considered (barrier or outer layer). The solution resistance, as well as any resistance inherent to the leads and contacts is included in the term \( R_s \). The equivalent circuit for a bi-layer structure is used for the optimization procedure and is depicted in Figure 7-3.
Figure 7-3: Bi-layer equivalent circuit model.

The impedance of the equivalent circuit shown in Figure 7-3 is:

\[
Z_{\text{Total}} = \frac{1}{Z_{C_{1e}}^{-1} + Z_{e,h}^{-1} + Z_{O_L}^{-1} + Z_{C_{OL}}^{-1}} + R_s \tag{7-34}
\]

\[
Z_{\text{Total}} = \frac{1}{j \omega C_{IL} + Y_f + R_{e,h}^{-1} + R_{OL}^{-1} + j \omega C_{OL}} + R_s \tag{7-35}
\]

This concludes the derivation of the cell impedance during the electrochemical impedance spectroscopy measurements.

7.6 Optimization of the PDM

7.6.1 Optimization Procedure

Impedance spectra described in section 5.1 are analyzed. The real and imaginary components of the total impedance, \(Z_{\text{Total}}\), were used for optimizing the impedance predicted by the PDM on the experimental impedance. The expressions for the real and imaginary components are intimidating and are shown in Appendix B. Non-linear regression was performed using DataFit version 9.0.59 software from Oakdale.
Engineering. A flow chart of the process used in optimizing the model to the EIS spectra is shown in Figure 7-4. For each experimental EIS spectra, optimizations were performed on eight variants of the experimental immitance:

1.) $Z'$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
2.) $\ln(Z')$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
3.) $Z''$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
4.) $\ln(Z'')$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
5.) $\frac{1}{Z'}$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
6.) $\ln(\frac{1}{Z'})$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
7.) $\frac{1}{Z''}$ vs. $\log_{10}(\text{Freq}, \text{Hz})$
8.) $\ln(\frac{1}{Z''})$ vs. $\log_{10}(\text{Freq}, \text{Hz})$

where $Z'$ is the real component of the impedance, $Z''$ is the imaginary component of the impedance; $Z$ is used to denote a generic immitance component. Initial parameter values were chosen to approximate the plots of $Z$ vs. $\log_{10}(\text{Freq}, \text{Hz})$ and $\ln(Z)$ vs. $\log_{10}(\text{Freq}, \text{Hz})$. Optimizations were then performed iteratively on these two data sets until the parameters converged to similar values. In practice, optimization to the plots of $\ln(Z)$ vs. $\log_{10}(\text{Freq}, \text{Hz})$ was more beneficial when the initial values of the parameters were far from the values needed to minimize the error function. The final optimizations reported here were performed on the plots of $Z$ vs. $\log_{10}(\text{Freq}, \text{Hz})$. It was crucial to use both representations of the data ($Z$ and $\ln Z$) in order to determine appropriate initial values for the optimization parameters. For an impedance spectra collected at a particular formation voltage, there are four sets of optimized parameters determined by optimizing $Z'$, $Z''$, $(Z')^{-1}$, and $(Z'')^{-1}$. These four sets of parameters allow for the assessment of the reproducibility of the optimization procedure.
Approximate $C_{IL}$, $C_{OL}$, $R_{OL}$, $R_{ct}$, and $E$ using bulk properties

Determine reasonable $a$, $k$, $\alpha$ values that calculate experimental $\ln Z'$

Perform regression analysis on model parameters to satisfy $\ln Z'$

Optimize model to impedance for $\ln Z'$, and $\ln Z''$, $Z'$, and $Z''$

Agreement of Parameters from $\ln Z'$, $Z'$, $\ln Z''$ and $Z''$

Using Parameters from previous step as initial values:
Calculate $\ln 1/Z'$ and $\ln 1/Z''$ and perform regression

Agreement of parameters from regression analysis to $Z'$, $Z''$, 1/$Z'$, and 1/$Z''$

Calculate $L$, $I$, $\rho$, $\varepsilon$, $\chi^2$

Compare calculated and experimental $M'$, $M''$, $\varepsilon'$, $\varepsilon''$, $Z'$, $Z''$, $Y'$, and $Y''$

**Figure 7-4:** Flow chart depicting the process used in optimizing the PDM to the experimental EIS spectra.
7.6.2 Optimized Parameters

The values, averages, and standard deviations of the parameters from each optimization are shown in Table 7—8 ($V_f = 2V$), Table 7-9 ($V_f = 4V$), Table 7—10 ($V_f = 6V$), and Table 7—11 ($V_f = 8V$). The average values of all of these parameters are given in Table 7—12. The purpose of studying several formation voltages is to add credence to the results; the standard rate constants, transfer coefficients, and polarizability of the oxide/solution interface are expected to be independent of formation voltage. However, scientists should be responsible and ethical in designing experiments that demonstrate reproducibility. While the tables and plots given below may seem repetitive, they are important for demonstrating the transparency of the procedure.

Table 7-8: Parameters determined by optimizing the PDM to the real and imaginary components of the impedance and admittance for oxide formed to 2V vs. SCE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Z'$</th>
<th>$(Z')^{-1}$</th>
<th>$Z''$</th>
<th>$(Z'')^{-1}$</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.106</td>
<td>0.102</td>
<td>0.112</td>
<td>0.114</td>
<td>0.109</td>
<td>0.006</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.060</td>
<td>0.059</td>
<td>0.062</td>
<td>0.065</td>
<td>0.061</td>
<td>0.003</td>
</tr>
<tr>
<td>$E, V/cm$</td>
<td>$8.47*10^6$</td>
<td>$8.01*10^6$</td>
<td>$8.32*10^6$</td>
<td>$8.05*10^6$</td>
<td>$8.21*10^6$</td>
<td>$0.022*10^6$</td>
</tr>
<tr>
<td>$R_s, \Omega$</td>
<td>87</td>
<td>85</td>
<td></td>
<td>86</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$C_{IL}, \mu F$</td>
<td>$3.52*10^{-6}$</td>
<td>$3.60*10^{-6}$</td>
<td>$3.50*10^{-6}$</td>
<td>$3.43*10^{-6}$</td>
<td>$3.51*10^{-6}$</td>
<td>$0.07*10^{-6}$</td>
</tr>
<tr>
<td>$C_{OL}, \mu F$</td>
<td>$3.30*10^{-6}$</td>
<td>$3.40*10^{-6}$</td>
<td>$3.20*10^{-6}$</td>
<td>$3.08*10^{-6}$</td>
<td>$3.25*10^{-6}$</td>
<td>$0.14*10^{-6}$</td>
</tr>
</tbody>
</table>
Table 7-9: Parameters determined by optimizing the PDM to the real and imaginary components of the impedance and admittance for oxide formed to 4V vs. SCE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Z'$</th>
<th>$(Z')^I$</th>
<th>$Z''$</th>
<th>$(Z'')^I$</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.110</td>
<td>0.110</td>
<td>0.108</td>
<td>0.115</td>
<td>0.111</td>
<td>0.003</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.065</td>
<td>0.064</td>
<td>0.066</td>
<td>0.066</td>
<td>0.065</td>
<td>0.001</td>
</tr>
<tr>
<td>$E, \text{ V/cm}$</td>
<td>$1.108*10^6$</td>
<td>$1.103*10^6$</td>
<td>$1.109*10^6$</td>
<td>$1.094*10^6$</td>
<td>$1.103*10^6$</td>
<td>$0.007*10^6$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.4320</td>
<td>0.4339</td>
<td>0.4332</td>
<td>0.4332</td>
<td>0.4331</td>
<td>0.0008</td>
</tr>
<tr>
<td>$k_{100}$</td>
<td>$7.25*10^{-9}$</td>
<td>$5.98*10^{-9}$</td>
<td>$6.27*10^{-9}$</td>
<td>$6.27*10^{-9}$</td>
<td>$6.44*10^{-9}$</td>
<td>$0.56*10^{-9}$</td>
</tr>
<tr>
<td>$k_{200}$</td>
<td>$8.70*10^{-11}$</td>
<td>$8.59*10^{-11}$</td>
<td>$9.15*10^{-11}$</td>
<td>$8.98*10^{-11}$</td>
<td>$8.85*10^{-11}$</td>
<td>$0.26*10^{-11}$</td>
</tr>
<tr>
<td>$R_{OL}, \Omega$</td>
<td>$5.70*10^6$</td>
<td>$5.71*10^6$</td>
<td>$6.70*10^6$</td>
<td>$5.91*10^6$</td>
<td>$6.00*10^6$</td>
<td>$0.48*10^6$</td>
</tr>
<tr>
<td>$R_s, \Omega$</td>
<td>85.0</td>
<td>80.0</td>
<td></td>
<td></td>
<td>82.5</td>
<td>3.5</td>
</tr>
<tr>
<td>$C_{IL}, \mu F$</td>
<td>2.85</td>
<td>2.80</td>
<td>2.77</td>
<td>2.75</td>
<td>2.79</td>
<td>0.04</td>
</tr>
<tr>
<td>$C_{OL}, \mu F$</td>
<td>2.63</td>
<td>2.45</td>
<td>2.34</td>
<td>2.52</td>
<td>2.49</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Table 7-10: Parameters determined by optimizing the PDM to the real and imaginary components of the impedance and admittance for oxide formed to 6V vs. SCE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Z'$</th>
<th>$(Z')'$</th>
<th>$Z''$</th>
<th>$(Z'')'$</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.109</td>
<td>0.107</td>
<td>0.102</td>
<td>0.100</td>
<td>0.105</td>
<td>0.004</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.061</td>
<td>0.061</td>
<td>0.062</td>
<td>0.056</td>
<td>0.060</td>
<td>0.003</td>
</tr>
<tr>
<td>$E, \text{V/cm}$</td>
<td>$2.54 \times 10^6$</td>
<td>$2.44 \times 10^6$</td>
<td>$2.48 \times 10^6$</td>
<td>$2.53 \times 10^6$</td>
<td>$2.50 \times 10^6$</td>
<td>$0.05 \times 10^6$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.4349</td>
<td>0.4384</td>
<td>0.4380</td>
<td>0.4480</td>
<td>0.4398</td>
<td>0.0057</td>
</tr>
<tr>
<td>$k_{100}$</td>
<td>$4.73 \times 10^{-9}$</td>
<td>$4.68 \times 10^{-9}$</td>
<td>$3.86 \times 10^{-9}$</td>
<td>$5.41 \times 10^{-9}$</td>
<td>$4.67 \times 10^{-9}$</td>
<td>$0.63 \times 10^{-9}$</td>
</tr>
<tr>
<td>$k_{200}$</td>
<td>$5.25 \times 10^{-11}$</td>
<td>$5.53 \times 10^{-11}$</td>
<td>$5.79 \times 10^{-11}$</td>
<td>$5.57 \times 10^{-11}$</td>
<td>$5.54 \times 10^{-11}$</td>
<td>$0.22 \times 10^{-11}$</td>
</tr>
<tr>
<td>$R_{OL, \Omega}$</td>
<td>$6.55 \times 10^6$</td>
<td>$4.34 \times 10^6$</td>
<td>$12.13 \times 10^6$</td>
<td>$6.19 \times 10^6$</td>
<td>$7.30 \times 10^6$</td>
<td>$3.36 \times 10^6$</td>
</tr>
<tr>
<td>$R_s, \Omega$</td>
<td>73.0</td>
<td>72.0</td>
<td></td>
<td></td>
<td>72.5</td>
<td>0.7</td>
</tr>
<tr>
<td>$C_{IL, \mu F}$</td>
<td>2.54</td>
<td>2.44</td>
<td>2.48</td>
<td>2.53</td>
<td>2.50</td>
<td>0.05</td>
</tr>
<tr>
<td>$C_{OL, \mu F}$</td>
<td>2.25</td>
<td>2.15</td>
<td>1.95</td>
<td>2.25</td>
<td>2.15</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Table 7-11: Parameters determined by optimizing the PDM to the real and imaginary components of the impedance and admittance for oxide formed to 8V vs. SCE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Z'</th>
<th>(Z')'</th>
<th>Z''</th>
<th>(Z'')'</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 )</td>
<td>0.106</td>
<td>0.110</td>
<td>0.106</td>
<td>0.106</td>
<td>0.107</td>
<td>0.002</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>0.066</td>
<td>0.063</td>
<td>0.062</td>
<td>0.061</td>
<td>0.063</td>
<td>0.002</td>
</tr>
<tr>
<td>E, V/cm</td>
<td>1.574*10^6</td>
<td>1.549*10^6</td>
<td>1.574*10^6</td>
<td>1.598*10^6</td>
<td>1.574*10^6</td>
<td>0.020*10^6</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.427</td>
<td>0.440</td>
<td>0.435</td>
<td>0.420</td>
<td>0.431</td>
<td>0.009</td>
</tr>
<tr>
<td>( k_{100} )</td>
<td>1.91*10^-9</td>
<td>3.92*10^-9</td>
<td>5.40*10^-9</td>
<td>2.01*10^-9</td>
<td>3.31*10^-9</td>
<td>1.67*10^-9</td>
</tr>
<tr>
<td>( k_{200} )</td>
<td>5.29*10^-11</td>
<td>4.89*10^-11</td>
<td>5.84*10^-11</td>
<td>3.04*10^-11</td>
<td>4.77*10^-11</td>
<td>1.22*10^-11</td>
</tr>
<tr>
<td>( R_{OL} )</td>
<td>6.37*10^6</td>
<td>3.72*10^6</td>
<td>13.6*10^6</td>
<td>12.0*10^6</td>
<td>8.93*10^6</td>
<td>4.66*10^6</td>
</tr>
<tr>
<td>( R_s )</td>
<td>68.0</td>
<td>75.8</td>
<td></td>
<td></td>
<td>71.9</td>
<td>5.5</td>
</tr>
<tr>
<td>( C_{IL} ), ( \mu F )</td>
<td>2.25</td>
<td>2.26</td>
<td>2.27</td>
<td>2.53</td>
<td>2.33</td>
<td>0.14</td>
</tr>
<tr>
<td>( C_{OL} ), ( \mu F )</td>
<td>1.85</td>
<td>1.75</td>
<td>1.52</td>
<td>1.65</td>
<td>1.69</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Table 7-12: Average parameters in (previous 4 tables) determined for oxides formed to 2V-8V.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2V</th>
<th>4V</th>
<th>6V</th>
<th>8V</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>0.109</td>
<td>0.111</td>
<td>0.105</td>
<td>0.107</td>
<td>0.108±0.004</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>0.061</td>
<td>0.065</td>
<td>0.060</td>
<td>0.063</td>
<td>0.062±0.003</td>
</tr>
<tr>
<td>$E, \text{ V/cm}$</td>
<td>0.821*10$^6$</td>
<td>1.103*10$^6$</td>
<td>1.361*10$^6$</td>
<td>1.574*10$^6$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.3547</td>
<td>0.4331</td>
<td>0.4398</td>
<td>0.431</td>
<td>0.415±0.038</td>
</tr>
<tr>
<td>$k_{100}$</td>
<td>4.56*10$^{-9}$</td>
<td>6.44*10$^{-9}$</td>
<td>4.67*10$^{-9}$</td>
<td>3.31*10$^{-9}$</td>
<td>4.1±1*10$^{-9}$</td>
</tr>
<tr>
<td>$k_{200}$</td>
<td>4.80*10$^{-11}$</td>
<td>8.85*10$^{-11}$</td>
<td>5.54*10$^{-11}$</td>
<td>4.77*10$^{-11}$</td>
<td>5.1±0.7*10$^{-11}$</td>
</tr>
<tr>
<td>$\rho_{\text{OL}}, \Omega\text{cm}$</td>
<td>14±1*10$^{-12}$</td>
<td>8.5±0.7*10$^{-12}$</td>
<td>9.0±0.4*10$^{-12}$</td>
<td>10±5*10$^{-12}$</td>
<td>10.4±3.8</td>
</tr>
<tr>
<td>$\varepsilon_{\text{OL}}$</td>
<td>24.27±0.48</td>
<td>19.8±0.98</td>
<td>19.8±1.3</td>
<td>17.6±1.5</td>
<td>19.9±2.0</td>
</tr>
<tr>
<td>$\varepsilon_{\text{IL}}$</td>
<td>22.43±0.94</td>
<td>22.3±0.35</td>
<td>23.0±0.4</td>
<td>24.2±1.4</td>
<td>23.4±1.1</td>
</tr>
</tbody>
</table>

The model was grossly insensitive to $R_{e,h}$, the electronic resistance of the inner layer of oxide; thus the accuracy of $R_{e,h}$ cannot be assessed using this technique. The values used in the optimization are given in Table 7-13, but they should not be afforded much worth. They are provided here for the benefit of any individual who wishes to exactly reproduce the optimizations reported here.

Table 7-13: Parameter values (in $\Omega$) used for the resistance of the inner layer of oxide during optimization of the PDM to EIS. The model was insensitive to the value of $R_{e,h}$. These values have no physical meaning.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>Z'</th>
<th>Y'</th>
<th>Z''</th>
<th>Y''</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6.98*10$^6$</td>
<td>6.98*10$^6$</td>
<td>6.98*10$^6$</td>
<td>6.98*10$^6$</td>
</tr>
<tr>
<td>6</td>
<td>6.98*10$^6$</td>
<td>7.31*10$^6$</td>
<td>6.98*10$^6$</td>
<td>6.98*10$^6$</td>
</tr>
<tr>
<td>8</td>
<td>6.98*10$^6$</td>
<td>7.90*10$^6$</td>
<td>6.97*10$^6$</td>
<td>6.27*10$^6$</td>
</tr>
</tbody>
</table>
Previous point defect models have assumed that the electric field in the oxide should not depend on the formation voltage. However, because a significant fraction of the oxide thickness is attributed to the extended anodization time rather than the formation voltage, this expectation is no longer valid. In the case of tantalum oxide, the electric field varies with the formation voltage because the linear anodization constant is no longer the paramount variable in defining the oxide thickness. The plot of electric field versus formation voltage is shown in Figure 7-5.

![Electric field calculated by the PDM as a function of the formation voltage.](image)

**Figure 7-5:** Electric field calculated by the PDM as a function of the formation voltage.

### 7.6.3 Goodness of Fit

#### 7.6.3.1 Nyquist and Bode Representations

The Bode and Nyquist plots for the experimental impedance and the impedance calculated by the PDM are shown in Figure 7-6 (2V), Figure 7-7 (4V), Figure 7-8 (6V), and Figure 7-9 (8V). These representations are the most common way of reporting the immitance in the literature, and the model fits the data very well as judged by the eye.
Figure 7-6: Bode and Nyquist plots of the impedance calculated by the PDM where the model was optimized to the real and imaginary components of the impedance for an oxide formed to 2V vs. SCE.
Figure 7-7: Bode and Nyquist plots of the impedance calculated by the PDM where the model was optimized to the real and imaginary components of the impedance for an oxide formed to 4V vs. SCE.
Figure 7-8: Bode and Nyquist plots of the impedance calculated by the PDM where the model was optimized to the real and imaginary components of the impedance for an oxide formed to 6V vs. SCE.
Figure 7-9: Bode and Nyquist plots of the impedance calculated by the PDM where the model was optimized to the real and imaginary components of the impedance for an oxide formed to 8V vs. SCE.
7.6.3.2 Immitance Functions

In evaluating the goodness of fit, it is important to consider several immitance functions, which can be easily determined from the complex impedance. The complex admittance, \(Y\), is given by

\[
\frac{1}{Z} \equiv Y = Y' - jY'' \tag{7-36}
\]

where \(Y'\) is the real component and \(Y''\) is the imaginary component of the admittance. In terms of the real and imaginary components of the impedance, the components of the admittance are:

\[
Y_{\text{Real}} = \frac{Z'}{Z'^2 + Z''^2} \tag{7-37}
\]

And

\[
Y_{\text{Imag}} = \frac{Z''}{Z'^2 + Z''^2} \tag{7-38}
\]

The modulus, \(M\), is defined as[194]

\[
M \equiv j\omega C_C Z = M' - jM'' \tag{7-39}
\]

where \(\omega\) is the angular frequency and \(C_C\) is the capacitance of the free space of the system given by

\[
C_C = \frac{\varepsilon_0 \times A}{L} \tag{7-40}
\]

where \(\varepsilon_0\) is the permittivity of free space, \(A\) is the electrode area, and \(L\) is the thickness of the dielectric. The components of the modulus in terms of the impedance components are:
The permittivity, \( \varepsilon \), is the inverse of the modulus, \( M \), where the components in terms of the impedance components are:

\[
M_{\text{Real}} = Z'' C \omega_c \tag{7-41}
\]

and

\[
M_{\text{Imag}} = Z' C \omega_c \tag{7-42}
\]

The imaginary component of the impedance fits the experimental spectra very well, but there is some discrepancy between the experimental and calculated real impedance from approximately 1-10 Hz. Ideally, this discrepancy should not exist, but it has not been possible to resolve this issue at the present time. The visual agreement between experimental and calculated impedance and phase angle in the Bode plot is superior to results published for a wide variety of systems in the electrochemical literature. This raises the question of whether the general methodology used by many impedance spectroscopists obscures the weaknesses of their models.
Figure 7-10: Real and imaginary components of the impedance calculated by the PDM where the model was determined by optimizing the model to the components of the impedance for an oxide formed to 2V vs. SCE.

Figure 7-11: Real and imaginary components of the impedance calculated by the PDM where the model was determined by optimizing the model to the components of the impedance for an oxide formed to 4V vs. SCE.
Figure 7-12: Real and imaginary components of the impedance calculated by the PDM where the model was determined by optimizing the model to the components of the impedance for an oxide formed to 6V vs. SCE.

Figure 7-13: Real and imaginary components of the impedance calculated by the PDM where the model was determined by optimizing the model to the components of the impedance for an oxide formed to 8V vs. SCE.
The real and imaginary components of the admittance (top plots) and the magnitude of the admittance (bottom plot) calculated from optimizing PDM to the impedance are compared to the experimental spectra in Figure 7-14 (2V), Figure 7-15 (4V), Figure 7-16 (6V), and Figure 7-17 (8V). The excellent agreement observed for the magnitude of the admittance emphasizes the observation that examining the magnitude of an immitance function can obscure the weaknesses of the scientist’s proposed model.

The real and imaginary components of the modulus (top plots) and the magnitude of the modulus (bottom plot) calculated from optimizing PDM to the impedance are compared to the experimental spectra in Figure 7-18 (2V), Figure 7-19 (4V), Figure 7-20 (6V), and Figure 7-21 (8V).

The real and imaginary components of the permittivity calculated from optimizing PDM to the impedance are compared to the experimental spectra in Figure 7-22 (2V) Figure 7-23 (4V), Figure 7-24 (6V), and Figure 7-25(8V).
Figure 7-14: Real and imaginary components and magnitude of the admittance calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 2V vs. SCE.
Figure 7-15: Real and imaginary components and magnitude of the admittance calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 4V vs. SCE.
Figure 7-16: Real and imaginary components and magnitude of the admittance calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 6V vs. SCE.
Figure 7-17: Real and imaginary components and magnitude of the admittance calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 8V vs. SCE.
Figure 7-18: Real and imaginary components and magnitude of the modulus calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 2V vs. SCE.
Figure 7-19: Real and imaginary components and magnitude of the modulus calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 4V vs. SCE.
Figure 7-20: Real and imaginary components and magnitude of the modulus calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 6V vs. SCE.
Figure 7-21: Real and imaginary components and magnitude of the modulus calculated by the PDM where the model was determined by optimizing the model to the real and imaginary components of the impedance for an oxide formed to 8V vs. SCE.
Figure 7-22: Real and imaginary components of the permittivity calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 2V vs. SCE.
Figure 7-23: Real and imaginary components of the permittivity calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 4V vs. SCE.
Figure 7-24: Real and imaginary components of the permittivity calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 6V vs. SCE.
As described above, the optimization procedure was performed on real and imaginary components of the admittance. The results of those optimizations are shown in Figure 7-26 (2V), Figure 7-27 (4V), Figure 7-28 (6V), and Figure 7-29 (8V). They concur with the observations made by determining an optimized impedance and then transforming the optimized impedance into admittance.

**Figure 7-25:** Real and imaginary components of the permittivity calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 8V vs. SCE.
Figure 7-26: Real and imaginary components of the admittance calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 2V vs. SCE.
Figure 7-27: Real and imaginary components of the admittance calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 4V vs. SCE.
Figure 7-28: Real and imaginary components of the admittance calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 6V vs. SCE.
Figure 7-29: Real and imaginary components of the admittance calculated by the PDM where the model was determined by optimizing the model to the components of the admittance for an oxide formed to 8V vs. SCE.
7.6.3.3 Chi-Squared Values

While the “chi-by-eye” technique is frequently invoked in evaluating whether or not a fit “looks” good, it is worthwhile to quantitatively assess the goodness of fit using Chi squared ($\chi^2$) values. Chi squared values are used to evaluate the goodness of fit between experimental and calculated spectra.

An estimate of the standard deviation, $\sigma$, in the experimental data is required to calculate a $\chi^2$ value.

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - (y_i, x_i)}{\sigma_i} \right)^2$$  [7-45]

The standard deviations of the real and imaginary components of the impedance were taken as the standard deviation between the experimental component and the component calculated from the Kramers-Kronig transforms. It is straightforward to calculate the standard deviation of the magnitude of the impedance by propagating the uncertainty associated with the individual components, the magnitude of the impedance is simply the vector sum of the real and imaginary components:

$$Z_{Mag} = \left[ (Z')^2 + (Z^*)^2 \right]^{1/2}$$  [7-46]

The method described herein for calculating the standard deviation begins with calculating the standard deviations of the real and imaginary components.

$$Z_{Mag} = \left[ \left( (Z' \pm \sigma_{Z'}) \right)^2 + \left( (Z^* \pm \sigma_{Z^*}) \right)^2 \right]^{1/2}$$  [7-47]

Using standard uncertainty propagation[195], the standard deviation of the impedance magnitude, $\sigma_Z$, is given as
\[
\sigma_Z = \frac{Z_{Mag}}{2} \sqrt{\frac{(2 \times Z')^2 \sigma_{Re}^2 + (2 \times Z'')^2 \sigma_{Im}^2}{(Z')^2 + (Z'')^2}}
\]

Where \(Z_{Mag}\) is the impedance magnitude, \(Z'\) is the real component, and \(Z''\) is the imaginary component. These values are reported in Table 7-14 for each data set.

**Table 7-14**: Chi-squared values determined for the impedance magnitude.

<table>
<thead>
<tr>
<th>Formation Voltage</th>
<th>(\chi^2) Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>4.04</td>
</tr>
<tr>
<td>6</td>
<td>3.66</td>
</tr>
<tr>
<td>8</td>
<td>0.59</td>
</tr>
</tbody>
</table>

On the basis of these values, it is concluded that the goodness of fit between the experimental and PDM calculated impedance is good. The uniqueness of fit is a much more difficult entity to assess. There exist many solutions to the model that will provide an equally good fit to the data. Therefore, it is imperative to judge the model by whether it can make realistic prediction in accordance with observations. The question of how sensitive the calculated impedance is to the optimized parameters is determined by sensitivity analysis.

### 7.6.4 Sensitivity Analysis

In order to assess the sensitivity of the calculated impedance to the model parameters, a sensitivity analysis was carried out. Each variable was pushed from its optimized value by + 25%; the real and imaginary components of the impedance were calculated using the non-optimized values. The sensitivity of the impedance to each parameter is plotted, where the sensitivity, \(S\), is defined as:
\[ S = \frac{|Z - Z_0|}{|x - x_0|} = \frac{|Z - Z_0|}{0.25} \]  

Figure 7-30 shows the sensitivity of the real component of the impedance to each parameter of the model. The calculated impedance is sensitive to α, E, C_{OL}, R_{OL} at most frequencies and is sensitive to C_{IL} at high frequencies. The real impedance calculated by the model depends relatively weakly on k_i and α_i, and is totally insensitive to R_{e,h}.

Similar results are observed for the sensitivity of the imaginary component of the impedance in Figure 7-31. The calculated imaginary component is most sensitive to the electric field, E, α, and C_{OL}. It is most dependent on R_{OL} at low frequencies, but this dependency drops off rapidly as the frequency increases. The rate constants, transfer coefficients and C_{IL} affect the high frequency impedance.
Figure 7-30: Sensitivity of the PDM to the parameter values. The sensitivity of the real impedance calculated by the PDM for the rate constants, transfer coefficients, electric field, and interface polarizability (top plot) and for the bulk properties of the oxide (bottom plot).
Figure 7-31: Sensitivity of the PDM to the parameter values. The sensitivity of the imaginary impedance calculated by the PDM for the rate constants, transfer coefficients, electric field, and interface polarizability (top plot) and for the bulk properties of the oxide (bottom plot).
7.6.5 Properties Predicted by PDM

The legitimacy of the numerical values determined via optimization of the point defect model to EIS data can be evaluated by comparing measurable properties of the system to quantities predicted from the PDM parameters. Namely, the thickness of the inner and outer layers and the current can be measured. These values can be used to constrain the optimization procedure and will reduce the statistical degrees of freedom of the model.

7.6.5.1 Oxide Thickness

The derivation for formulas that calculate the oxide thickness and current density from PDM parameters follows.

The continuity equations,

\[
\frac{\partial C}{\partial t} = -\nabla \cdot J \quad [7-50]
\]

Are written as, where \( \nabla \) is the operator \( \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k} \), \( \hat{i} \), \( \hat{j} \), and \( \hat{k} \) are unit Cartesian vectors and \( J \) is the flux. These equations are solved to yield the concentration of the transported species as a function of x, y, and z and time. For a one-dimensional model, equation 7-50 reduces to

\[
\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} J_x \quad [7-51]
\]

For the flux of tantalum interstitials and oxygen vacancies, equation 7-51 gives:

\[
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + 5D_iK \frac{\partial C_i}{\partial x} \quad [7-52]
\]

\[
\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} + 2D_OK \frac{\partial C_O}{\partial x} \quad [7-53]
\]
The initial and boundary conditions are given in Table 7-7.

At steady state, the concentrations of the point defects at the interfaces will be constant, i.e., \( \frac{\partial C}{\partial t} = 0 \).

\[
\frac{\partial^2 C_i}{\partial x^2} + 5K \frac{\partial C_i}{\partial x} = 0 \quad [7-54]
\]

\[
\frac{\partial^2 C_O}{\partial x^2} + 2K \frac{\partial C_O}{\partial x} = 0 \quad [7-55]
\]

The solutions to these linear, second order differential equations are of the form:

\[
C_i(x) = A_i \cdot e^{(-5Kx)} + B_i \quad [7-56]
\]

and

\[
C_O(x) = A_O \cdot e^{(-2Kx)} + B_O \quad [7-57]
\]

Using the boundary conditions in Table 7-7 to solve for B gives the expressions:

\[
B_i = \frac{k^{e.a} e^{-bL}}{5KD_i} \quad [7-58]
\]

\[
B_O = \frac{5k^{e.a} e^{-bL}}{4KD_O} \quad [7-59]
\]

The flux of the tantalum interstitials and oxygen vacancies are:

\[
J_i = -5KD_i B_i \quad [7-60]
\]

\[
J_O = -2KD_O B_O \quad [7-61]
\]

It is now necessary to consider the change in thickness with respect to time. It is conventional to assume a constant thickness at steady state, which implies that the growth
in the oxide, as embodied by reactions 1 and 2 must be equal to the dissolution of the oxide, i.e., reaction 5.

At steady state, it might be expected that \( \frac{dL}{dt} = 0 \), thus equation 7-19 simplifies to:

\[
-\frac{2}{5} J_0 - J_i = k_5^o C_{H^+}^{n_i}
\]  \hspace{1cm} [7-62]

Substituting equations 7.58—7.61 and rearranging results in

\[
k_5^o C_{H^+}^{n_i} = k_1^o e^{a_i V} e^{-b_i L} + k_2^o e^{a_i V} e^{-b_i L}
\]  \hspace{1cm} [7-63]

and the thickness, the sum of the inner and outer layers would be

\[
L = \left( \frac{a_1 + a_2 - a_5}{b_1 + b_2} \right) V - \frac{1}{b_1 + b_2} \ln \left( \frac{k_5^o}{k_1^o + k_2^o} C_{H^+}^{n_i} \right)
\]  \hspace{1cm} [7-64]

Making the appropriate substitutions for \( a_i \) and \( b_i \) then simplifying results in the expression

\[
L = \frac{1}{E} \left[ (1 - \alpha) V - \frac{1}{5 \gamma \alpha_1 + 5 \gamma \alpha_2} \ln \left( \frac{k_5^o}{k_1^o + k_2^o} C_{H^+}^{n_i} \right) \right]
\]  \hspace{1cm} [7-65]

As shown in Chapter 3.3, the dissolution rate of tantalum oxide relative to the growth rate of the oxide is too small to measure. The total oxide thickness calculated from equation [7.65] when it is assumed that \( k_1^{00} = 200 \times k_5^{00} \) or that \( k_1^{00} = 2,000 \times k_5^{00} \) is shown in Table 7-15 for each optimization. The calculated thickness of the oxide is relatively insensitive to the magnitude of \( k_5^{00} \) when it is assumed to be this small. The thickness calculated by the PDM is in close agreement with thicknesses predicted from the formation voltage and empirical growth laws shown in Table 7-4.
Table 7-15: Total oxide thickness calculated from equation 7-65 using the PDM parameters determined in each optimization.

<table>
<thead>
<tr>
<th>Ratio of $k_i^{00}:k_s^{00}$</th>
<th>Vf vs SCE</th>
<th>L, nm</th>
<th>L, nm</th>
<th>L, nm</th>
<th>L, nm</th>
<th>L, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re Z</td>
<td>Re Y</td>
<td>Im Z</td>
<td>Im Y</td>
<td>Average</td>
<td></td>
</tr>
<tr>
<td>1: 200</td>
<td>2</td>
<td>20.52</td>
<td>20.37</td>
<td>20.63</td>
<td>20.90</td>
<td>20.6±0.2</td>
</tr>
<tr>
<td>1:2000</td>
<td>2</td>
<td>21.81</td>
<td>21.77</td>
<td>21.88</td>
<td>22.15</td>
<td>21.9±0.2</td>
</tr>
<tr>
<td>1: 200</td>
<td>4</td>
<td>23.89</td>
<td>23.93</td>
<td>23.85</td>
<td>24.07</td>
<td>23.9±0.1</td>
</tr>
<tr>
<td>1:2000</td>
<td>4</td>
<td>24.82</td>
<td>24.87</td>
<td>24.79</td>
<td>24.99</td>
<td>24.87±0.09</td>
</tr>
<tr>
<td>1: 200</td>
<td>6</td>
<td>27.63</td>
<td>27.57</td>
<td>27.59</td>
<td>27.41</td>
<td>27.6±0.1</td>
</tr>
<tr>
<td>1:2000</td>
<td>6</td>
<td>28.41</td>
<td>28.36</td>
<td>28.40</td>
<td>28.26</td>
<td>28.36±0.07</td>
</tr>
<tr>
<td>1: 200</td>
<td>8</td>
<td>31.53</td>
<td>31.35</td>
<td>31.15</td>
<td>31.48</td>
<td>31.4±0.2</td>
</tr>
<tr>
<td>1:2000</td>
<td>8</td>
<td>32.20</td>
<td>32.03</td>
<td>31.83</td>
<td>32.16</td>
<td>32.1±0.2</td>
</tr>
</tbody>
</table>

7.6.5.2 Current Density Calculated by the PDM

The steady state current is attributed to the production of tantalum interstitials and oxygen vacancies and is expressed as:

\[
I = I_{Ta}^i + I_{Vo}^i \quad [7-66]
\]

where

\[
I_{Ta}^i = 5F* k_i^* e^{5\gamma i (1-a)V} e^{-5\gamma i E_F L} \quad [7-67]
\]

\[
I_{Vo}^i = 5F* k_{2}^* e^{5\gamma i (1-a)V} e^{-5\gamma i E_F L} \quad [7-68]
\]

The oxide thicknesses in Table 7-4 were used in calculating I from equations 7-67 and 7-68. The currents determined from the parameters of each optimization procedure are shown in Table 7-16.
Table 7-16: Current densities calculated for the production of tantalum interstitials and oxygen vacancies from the PDM parameters. The results of each optimization were used to calculate the current densities from equations 7-67] and 7-68].

<table>
<thead>
<tr>
<th>Defect</th>
<th>$V_f$ vs SCE</th>
<th>$I_e$, nA/cm$^2$</th>
<th>$I_i$, nA/cm$^2$</th>
<th>$I_d$, nA/cm$^2$</th>
<th>$I_o$, nA/cm$^2$</th>
<th>$I_t$, nA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re Z</td>
<td>Re Y</td>
<td>Im Z</td>
<td>Im Y</td>
<td>Average</td>
<td></td>
</tr>
<tr>
<td>$Td_i$$^+$</td>
<td>2</td>
<td>33.41</td>
<td>33.30</td>
<td>28.80</td>
<td>32.95</td>
<td>32±2</td>
</tr>
<tr>
<td>$V_o$$^*$</td>
<td>2</td>
<td>35.96</td>
<td>29.49</td>
<td>33.75</td>
<td>37.10</td>
<td>34±3</td>
</tr>
<tr>
<td>$Td_i$$^+$</td>
<td>4</td>
<td>32.13</td>
<td>29.07</td>
<td>29.70</td>
<td>33.32</td>
<td>31±2</td>
</tr>
<tr>
<td>$V_o$$^*$</td>
<td>4</td>
<td>30.12</td>
<td>31.67</td>
<td>26.43</td>
<td>38.34</td>
<td>32±4</td>
</tr>
<tr>
<td>$Td_i$$^+$</td>
<td>6</td>
<td>36.23</td>
<td>34.74</td>
<td>43.33</td>
<td>35.73</td>
<td>38±4</td>
</tr>
<tr>
<td>$V_o$$^*$</td>
<td>6</td>
<td>43.34</td>
<td>37.57</td>
<td>36.43</td>
<td>41.07</td>
<td>40±3</td>
</tr>
<tr>
<td>$Td_i$$^+$</td>
<td>8</td>
<td>39.09</td>
<td>36.86</td>
<td>33.32</td>
<td>35.40</td>
<td>36±2</td>
</tr>
<tr>
<td>$V_o$$^*$</td>
<td>8</td>
<td>39.56</td>
<td>38.12</td>
<td>30.75</td>
<td>33.85</td>
<td>36±4</td>
</tr>
</tbody>
</table>

For all PDM optimizations to each EIS data set, the predicted current densities calculated by the PDM are $34 \pm 4$ nA/cm$^2$ for tantalum interstitials and $35 \pm 5$ nA/cm$^2$ for oxygen vacancies. Thus the total ionic current due to the anodic oxidation of tantalum after $>24$ hours of applied voltage is thus $69 \pm 6$ nA/cm$^2$.

7.7 Discussion

A point defect model (PDM) for anodic tantalum oxide formed in phosphoric acid has been developed that considers the empirical growth laws for the system. A compact bi-layer structure forms where the inner layer of oxide forms due to the production of oxygen vacancies at the metal/oxide interface and the outer layer forms by the combination of outwardly mobile tantalum interstitials with anions at the film/solution interface. PDMs
for previous systems assumed dissolution of the oxide, however, it has been shown that tantalum oxide does not dissolve at a measurable rate. The bi-layer PDM was described using an equivalent circuit having two groups of elements in series. Empirical investigation of the growth laws provided constraints, such as ionic current densities and oxide thicknesses to the PDM.

The parameters of the PDM were determined by a rigorous optimization procedure to electrochemical impedance spectroscopy (EIS) spectra. The agreement between the experimental immitance functions and the immitance calculated by the PDM were examined. While the magnitude of calculated immitance functions were generally in close agreement with the experimental values, discrepancies can be found when the real and imaginary components are examined separately. The Bode plots, which are typically displayed by impedance spectroscopists, exhibit excellent agreement between the experimental and calculated values. However, when the real and imaginary components are compared separately, significant discrepancies can be observed. This raises the general question of whether scientists are obscuring the weaknesses of their impedance optimizations.

The proposed PDM was not sensitive to the value of $R_{c,h}$, thus it is not possible to compare the relative resistivities of the inner and outer layers from these experiments. The lack of oxide dissolution and the subsequent continual oxide thickening means that the formed oxide thickness does not solely depend on the applied formation voltage. Rather, the time of anodization has a greater effect on the thickness when the formation voltage is small. Because of this, the electric field in the oxide is not expected to be constant for experiments at different formation voltages. Lower formation voltage oxides are expected to have a lower electric field, which is confirmed by optimization of the PDM to EIS spectra.

This work is the first effort to describe tantalum anodization using defect chemistry reactions. The point defect model described herein provides a physical, mechanistic model for the formation of anodic oxides. While many descriptions of ionic conduction
and anodic oxidation have been proposed over several decades, this work stands out because it is a deterministic model. Therefore, it can be adjusted to predict the effects of experimental changes in the growth method.
Chapter 8: Conclusions

The mechanism of tantalum anodization is a longstanding area of scientific inquiry. In 1935 Verwey ([58] cited in [55]) described anodic oxides as cation conductors that grow by the outward migration of metal. Vermilyea studied the kinetics of formation and the properties of formed oxides throughout the 1950’s[7, 8, 15, 23, 70, 113, 196-199]. Lawrence Young began publishing on the mechanism of anodic tantalum oxides in 1954[4, 200] and continues to publish on the topic.[190] From a cursory search of the literature, it is evident that tantalum anodization has been thoroughly studied; thus it is not a trivial task to contribute new knowledge concerning the anodization of tantalum.

This dissertation presents a fresh perspective and methodology for describing the process of anodic oxidation on tantalum. A quantitative point defect model (PDM) is determined to describe the formation of a bi-layer oxide. While the growth and properties of anodic tantalum oxide have been studied previously, this work analyzed the anodic film as two distinct materials.

Experiments reported in the literature provide excellent guidance in developing a tenable model that describes how anodic oxides come into being from their parent metal. Reports on the properties of tantalum oxide as a function of growth conditions provide a context for thinking about how oxides form; a careful examination of the literature results in many constraints for how oxides can form and reduces the number of necessary experiments, thus interpretation of the literature is an important aspect of this dissertation. “They say that three weeks in the lab will save you a day in the library every time”[201] A physical model of anodization must account for all observed phenomena, or in the words of Einstein it must not “surrender the adequate representation of a single datum of experience.” [19]

By interpreting experimental findings in the literature (Chapter 2) and studying the properties of formed oxides as a function of anodization time and voltage (Chapters 3 and
4), clear requirements for a tenable model of tantalum anodization can be outlined. The model must recognize that:

1.) the oxide forms a bi-layer structure in some electrolytes where the outer layer contains species incorporated from the outer layer at a constant concentration.[34, 53, 54] and Sections 3.2.1, 3.2.2, and 4.4.1.

2.) dissolution of tantalum oxide is minimal in non-fluorinated electrolytes. [39] and Section 3.3

3.) the entire oxide is compact and not porous. [92, 172, 173] Sections 3.2.1 and 4.4.3.

4.) the order of oxygen atoms is conserved during anodization. [33]

5.) tantalum atoms are mobile during anodization. [14]

6.) oxide growth occurs at the metal/oxide and the oxide / electrolyte interfaces. [24-29]

7.) oxide growth does not occur in the bulk of the oxide. [193]

8.) oxide growth does not occur at the inner layer / outer layer interface. [53]

Tantalum oxide challenges the conventional description of anodic oxide structures, which often have a compact barrier layer and porous, precipitated outer layer. Both the inner layer, which is pure tantalum oxide and the outer layer, which contains phosphate incorporated from the electrolyte, are compact.

Electrochemical studies on tantalum oxide typically define the oxide thickness strictly as a function of formation voltage. However, as shown in Section 3.2.6, the oxide thickness depends significantly on the time that the formation voltage is applied. As discussed in Chapter 5, the EIS experiments require the formation voltage to be applied for 24 hours in order for the oxide to reach a pseudo-steady state condition. Therefore, the real oxide thickness is anticipated to be significantly greater than the thickness predicted from the anodization constant.

Electrochemists often use wet electrical measurements in order to measure the thickness of formed thin films. Thickness is extracted by measuring the high frequency
capacitance, assuming the dielectric constant, and calculating the oxide thickness from the parallel plate capacitor equation, \( L = \varepsilon_0 \varepsilon_r A / C \). However, the dielectric constant of tantalum oxide is a function of the applied field, [157] and as shown in Figure 4-20 of this work, it may also depend on the length of time that the formation voltage is applied. Furthermore, the dielectric constant can vary depending on growth or deposition conditions. As shown in Table 2-14, the reported dielectric constant varies from 18 to 30 depending on how the measurement is made. Coulometry is also used to determine formed oxide thickness, but this technique assumes that the current efficiency of formation is 100%. This technique leads to the puzzling finding that oxides formed in phosphoric acid form at efficiencies greater than 100%. This means that the amount of oxide formed is greater than the passage of a particular current would predict. The electrochemical techniques of capacitance and/or coulometry are not sufficiently accurate for determining the thickness of a thin film.

It is preferable to have an external method for measuring the oxide thickness as wet electrochemical measurements require unwarranted assumptions of the dielectric constant of the material. In this work, oxide thickness is measured ex-situ using two independent methods: spectroscopic ellipsometry and FT-IR reflectance spectroscopy calibrated by TEM imaging. The direct logarithmic growth law was parameterized by measuring the oxide thicknesses as a function of anodization time. The oxide thicknesses were quantified using FT-IR reflectance spectroscopy; the relation between IR absorbance and oxide thickness was calibrated using TEM bright field imaging. Due to the fortuitous absorption band characteristic of incorporated phosphate, FT-IR reflectance spectroscopy is a convenient and reliable method for determining the thickness of the individual inner and outer layers of oxide formed in phosphoric acid. This empirical determination of growth laws (Section 3.2.6.4) for the inner and outer layers of oxide provides realistic constraints for the thickness of the oxide. These growth laws also allow for calculation of the Faradaic current due to the production of tantalum interstitials and oxygen vacancies at any time of anodization.
As shown by TEM imaging (3.2.1) and SE (4.4.3) the entire anodic oxide on tantalum is a compact material and no evidence of porosity has been observed for anodization of tantalum in dilute phosphoric acid. Therefore, the total thickness of the oxide is considered as a barrier layer in determining the Faradaic response of the anodic oxide film.

The empirical studies presented in Chapter 3 allow for constraint of the PDM. The PDM described in Chapter 6 does not use an independent method for determining the oxide thickness during the optimization procedure; rather, it was assumed that the oxide thickness was very close to the thickness predicted by the anodization constant.

The calculated impedance response was observed to be strongly dependent on the oxide thickness, this fact is obvious from inspection of the equation for the Faradaic admittance (Equation 7-31) During the optimization of the unconstrained model in Chapter 6, the oxide thickness was a function of the PDM parameters; however in Chapter 7 it is set to a constant value during the optimization.

The (PDM) describes the formation of anodic oxide using point defect reactions. Because tantalum oxide is n-type (Section 5.3 and [64]) the dominant defect species can be tantalum interstitials and/or oxygen vacancies. Tantalum interstitials and oxygen vacancies form at the metal/oxide interface. The outer layer forms by outward migration of tantalum; because the solubility product of tantalum is extremely low in non-fluorinated electrolytes, when tantalum interstitials reach the oxide/electrolyte interface they are hydrolyzed by oxyanions. The strong positive charge of the interstitial at the interface attracts oxygen \(O^2\) and phosphate \((PO_4)^{3-}\) ions to the interface. The formation of the inner layer is attributed to the formation of oxygen vacancies at the metal/oxide interface. The rate controlling step is the production of point defects at the metal/oxide interface, and the diffusion of charged species is not considered in the impedance expression.
The PDM presented in Chapter 7 provides a model based on activated complex theory. This model provides kinetic rate constants and thermodynamic transfer coefficients for the production of oxygen vacancies and tantalum interstitials. Parameters of the PDM were determined using electrochemical impedance spectroscopy (EIS.) This transient technique is used to probe the impedance response of a formed oxide and has been used previously to characterize platinum[20, 79], zirconium[83, 165], alloy 22[21, 22], and iron[80, 81]. The rate constants, transfer coefficients, and polarizability of the oxide/solution interface did not vary with formation voltage. For the production of tantalum interstitials, the standard rate constant is $4.1 \pm 1 \times 10^{-9}$ mol/cm*s and the transfer coefficient is $0.108 \pm 0.004$. For the production of oxygen vacancies, the standard rate constant is $5.1 \pm 0.7 \times 10^{-11}$ mol/cm*s and the transfer coefficient is $0.062 \pm 0.003$. The polarizability of the oxide/solution interface is $0.415 \pm 0.038$. The dielectric constants of the inner and outer layers are $23.4 \pm 1.1$ and $19.9 \pm 2$, respectively; these values are measured with the electric field applied. Because the oxide thickness was a strong function of anodization instead of a strict function of the formation voltage, the electric field in the oxide was linear with formation voltage.

It was determined that the frequency range probed using EIS was too high to measure the impedance due to the transmission of defect species through the oxide. Attempts to include a Warburg term in the impedance were unsuccessful as the model was completely insensitive to its values. The impedance calculated by the PDM and the equivalent electronic circuit was insensitive to the electronic resistance of the inner layer.

In order for a model to be scientific, it must be capable of failing, i.e., hypotheses must be capable of being disproved. There must be rubrics by which models can be evaluated in an objective manner. In this work, the growth rate of the individual oxide layers is determined empirically; these growth rates allow for the determination of the ionic current attributed to tantalum interstitials and to oxygen vacancies at any time of anodization. As shown in Chapter 7, the parameters of the PDM correctly predict the ionic currents due to the formation of oxygen vacancies and tantalum interstitials. Comparisons were made between the experimental immitance functions and the
immitance functions calculated from the PDM. The magnitude of the impedance, admittance, modulus, and permittivity agree well for the experiments and the model. However, if the real and imaginary components are examined separately, deviations can be observed in the frequency range of 10-100 Hz.

The PDM accounts for the observed characteristics of formed anodic tantalum oxide. It is unique in its mechanistic, physical description of anodic oxide formation. It also provides a quantitative model that can be tested under various conditions.

The optical properties of the inner and outer layer of oxide are determined by the application of spectroscopic ellipsometry analysis. Oxides formed in 0.1 M Na$_2$SO$_4$ exhibit a compact, mono-layer structure, while oxides formed to $\geq$ 13 V in 0.1 M H$_3$PO$_4$ exhibit a bi-layer structure. The band gap is defined as the onset of absorption of $\varepsilon_2$, and occurs at a lower energy when phosphate is incorporated in the oxide. For oxide formed to 70 V in 0.1 M H$_3$PO$_4$, the inner layer of oxide has a band gap of 4.467 ± 0.002 eV while the outer layer has a band gap of 3.86 ± 0.06 eV. Monolayer oxide formed in 0.1 M Na$_2$SO$_4$ has a band gap of 4.00 ± 0.02 eV. The lower onset of absorption for the outer layer of oxide is likely due to the incorporated phosphate; phosphorus may act as a dopant by providing additional energy levels near the band edge. This analysis suggests that the inner layer of oxide formed in 0.1 M H$_3$PO$_4$ does not have the same optical properties of oxide formed in 0.1 M Na$_2$SO$_4$ as has been previously assumed.

The optical properties of oxides formed in 0.1 M H$_3$PO$_4$ are dependent on formation voltage; for thin oxides (formation voltage 2 – 6 V) a mono-layer optical model was used to describe the oxide, and the complex dielectric function of thin oxides is more similar to the complex dielectric function of oxide containing incorporated phosphate than it is to pure tantalum oxide. This is shown in Figure 4-17.

The length of time that the 70 V formation voltage was applied also has an effect on the optical properties of the oxide. As shown in Figure 4-20, the band gaps of the inner and outer layers of oxide decrease with increasing anodization time. Electrochemists often
use the high frequency capacitance as a measure of oxide thickness, however, these results indicate that the dielectric constant is a function of anodization time. This limits the certainty of thickness measurements measured by capacitance because the permittivity is not a constant value.

At extended anodization times, the relative thickness of the phosphate containing layer decreases. Growth of the outer layer, which forms by Ta migration, is either halted or significantly slowed at extended anodization times. Relative to the outer layer, the inner layer grows faster at extended anodization times. This suggests that once a critical thickness has been reached, the production and/or migration of tantalum interstitials is reduced relative to the production and/or migration of oxygen vacancies. It is interesting to ponder what effect the incorporated phosphate in the outer layer may have on the point defect reactions at the metal/oxide interface. Incorporated phosphate inhibits oxidation of tantalum, [37] but it may influence tantalum interstitials and oxygen vacancies differently.

Prior to this work, kinetic models of tantalum anodization treated the formation of oxide as a single process. The kinetic rate constants and thermodynamic rate constants responsible for the formation of each layer are reported as part of a quantified PDM. The growth laws and optical properties for the individual oxide layers are reported, and the PDM is in agreement with the measured growth laws. The point defect model described herein provides a physical, mechanistic description of the formation of anodic oxides. While many descriptions of ionic conduction and anodic oxidation have been proposed over several decades, this work stands out because it is a deterministic model. Therefore, it can be adjusted to predict the effects of experimental changes in the growth method.
Chapter 9: Future Work

9.1 Consideration of Anode Curvature and its Effects on Anodic Oxides

9.1.1. Motivation

As the electronics industry trends towards miniaturization, no component is free from the pressure to increase its volumetric efficiency and simultaneously reduce its cost. In the case of electrolytic capacitors, there is a push to maximize the CV (capacitance*voltage) per device volume. Electrolytic capacitor anodes are fabricated by sintering and pressing fine metal particles to form a high surface area, low volume anode. As the particle size of the metal powder is reduced, anodes with smaller feature sizes are produced. Figure 9-1A shows a FE-SEM image of sintered tantalum powder prior to compression. Figure 9-1B shows a cross sectional SEM image of a commercial tantalum electrolytic capacitor. While many studies have been completed on the anodization and characterization of tantalum oxide, they are largely limited to planar anodes. The industry currently uses anodes with micron-sized particles, and further miniaturization may be limited by curvature effects that dominate at higher curvature.

A: Sintered tantalum powder used in fabricating anodes for electrolytic capacitors.
B: Cross-section of a commercial electrolytic capacitor.

Figure 9-1: Electron micrographs indicating anode morphology of commercial capacitors.
9.2. Definition of Curvature and Gibbs-Thomson Effect

As can be seen in Figure 9-1B, the geometry of the anode in an electrolytic capacitor is complicated. Whereas the vast majority of anodization studies have been completed on planar substrates, the geometry of anodes is much more complex in real-world applications. As the particle size of the anodes is reduced, the thickness of the oxide will approximate (or possibly be greater than) the thickness of the anode. If this is the case, our knowledge of how bulk systems behave may no longer apply. Also, as the particle size is reduced, the curvature of the anodes will become increasingly important.

Curvature is defined as the change in area with respect to volume (dA/dV); in the case of a sphere, the curvature, $\kappa$, is $2/r$. Figure 9-2A is a schematic depicting the definition of curvature. It is well established that the curvature has important repercussions for the stress distribution in thermal metal oxides[202-204]. The Gibb-Thomson effect[205, 206] also predicts that the concentration of defect species will be dependent on the curvature[206]. The chemical potential, $\mu$, depends on $r$, the radius of curvature, when the curvature is on length scales of $10^{-7}$ to $10^{-9}$ m:

$$\Delta \mu = \mu_{\text{Curve}} - \mu_{\text{Flat}}$$  \hspace{1cm} [9-1] \\
$$\Delta \mu = \frac{2\gamma_{SV} \Omega_{Ta_2O_5}}{r}$$  \hspace{1cm} [9-2] \\

where $\gamma_{SV}$ is the solid/vapor surface energy and $\Omega$ is the molar volume. The concentration of defects depends on the chemical potential:

$$C_0 = k' \exp\left(\frac{-Q}{k_BT}\right)$$  \hspace{1cm} [9-3] \\
$$C_\kappa = k' \exp\left(\frac{-Q + \Delta \mu}{k_BT}\right)$$  \hspace{1cm} [9-4] \\
$$C_\kappa = C_0 \exp\left(\frac{-2*\Omega*\gamma_{SV}}{r*k_BT}\right)$$  \hspace{1cm} [9-5] \\

Where $C_0$ is the concentration of defects in a planar system and $C_\kappa$ is the concentration in a curved system. As shown in Figure 9-2B, the concentration of defects is predicted to be
higher at concave surfaces with a negative curvature but lower at convex surfaces with positive curvature. As the particle size of anodes is further decreased, the resulting extreme curvatures may pose fundamental barriers that could limit the mechanical and/or electrical stability of the metal/oxide system.

**Figure 9-2:** Definition of curvature and its predicted effect on the distribution of defect species.

It is hypothesized that the trend in decreasing the feature size of metal anodes may limit the achievable quality of the dielectric layer. The small feature size of the anodes results in anodes and dielectric films with extremely high curvature. The anticipated repercussions of curvature in anodic oxide films should be explored at micron and sub-micron feature sizes. Three suggested points to consider are:

1.) Effect of stress and curvature on the anodization process

2.) Effect of curvature on the distribution of point defects (Gibbs-Thomson effect)

3.) Distribution of electric field during anodization and during the use of the device
9.3. Literature Review on Stress in Oxides

While the electrochemistry [64, 207] and chemical nature [47, 100, 208] of anodized tantalum have been well characterized, the influence of growth stress has been marginally examined. Although growth stresses during anodic oxidation have been extensively studied for some valve metals, research on tantalum has been limited in scope. [199, 209] Growth stresses in thermal tantalum oxide have been studied in a planar geometry [199, 210, 211] and on hollow cylinders with radii in the centimeter range [204]. An analytical solution for stress distribution in the Si-SiO$_2$ system has been derived in cylindrical coordinates by Hsueh and Evans [212]. Solutions are provided for oxide growth at i.) the metal/oxide interface and ii.) the oxide/atmosphere interface. [212]

9.3.1 Stress on Planar Substrates

The formation of growth stress in anodic oxide films has been studied rather extensively for several metals including Al [209, 213-218], Ti [214, 215, 219, 220], Ni [214, 221], Zr [222, 223], Pd [224], and W [225, 226], yet studies specifically on Ta are limited in scope. [199, 209]. There is a general consensus in the literature that fast growth rates, rather galvanostatic or potentiodynamic, are associated with lower levels of stress. It is interesting to note that growth conditions that trend with increasing stress typically trend with the propensity for oxide crystallization.

The molar volume per cation of tantalum oxide is significantly greater than the molar volume of metal consumed during anodic oxidation. If oxide growth occurs at the metal/oxide interface, the molar volume mismatch results in stress in both the metal and oxide layers. A schematic of why the molar volume mismatch could produce stress is shown in Figure 9—3. Such growth stress has long been reported in the literature beginning with Pilling and Bedworth, who introduced the ratio:

\[
PBR = \frac{\text{Molecular Wt. Oxide} \times \text{Density of Metal}}{\text{Formula Weight of Metal} \times \text{Density of Oxide}} = 2.5 \text{ For Ta}_2\text{O}_5 \quad [9-6]
\]
for calculating the sign and magnitude of the stress. In the case of tantalum, the oxide layer will be under compressive stress, and the metal will be under a tensile stress. Compressive stress is defined as a negative stress, and tensile stress is defined as positive. If oxide growth is occurring at the metal/film interface, this growth stress should be considered regardless of geometry.

![Oxide and Metal Diagram](image)

**Figure 9-3:** Schematic showing that the metal oxide will be in compression while the metal will be in tension.

### 9.3.2: Stress in metal oxide systems on curved substrates

An analytical solution for stress distribution in the Si-SiO₂ system has been derived in cylindrical coordinates by Hsueh and Evans[212]. Solutions are provided for oxide growth at i.) the metal/oxide interface and ii.) the oxide/atmosphere interface. It is proposed that the Hsueh and Evans model can be extended to calculate the stress distribution in the anodic tantala system on convex surfaces. It is crucial to have an understanding of where oxide growth occurs during tantalum anodization because this is vital in calculating the stress in the oxide film. Literature indicates that oxide growth in anodic tantala occurs at both the metal/oxide and the oxide/solution interfaces.[53]
In the planar case of anodic oxidation, growth stress will occur at the metal/oxide interface, but there is no a-priori reason for growth stress to occur at the oxide/solution interface. [199] If the metal/oxide interface is a curved surface, then growth stresses will occur regardless of the location of oxide growth. For a concave surface, the radial and tangential stress will have the same sign. In the case of growth via oxygen ingress, the stress will be compressive while it will be tensile for growth via cation egress.[227] This is shown schematically in Figure 9-4.

On a convex surface, the radial and tangential stresses will have opposite signs.[202] Oxide growth by pure oxygen ingress results in radial compressive stress and tangential tensile stress; oxide growth by pure cation egress results in radial tensile stress and tangential compressive stress.[227] This is shown schematically in Figure 9-5.
A: The radial and tangential stresses are compressive.  
B: The radial and tangential stresses are tensile.

**Figure 9-4:** Radial and tangential stresses on a concave surface depend on the location of the growth front of the oxide.

A: The radial stress is compressive, and the tangential stress is tensile.  
B: The radial stress is tensile, and the tangential stress is compressive.

**Figure 9-5:** Radial and tangential stresses on a convex surface depend on the location of the growth front of the oxide.

Compared to a planar surface, a convex surface will have a higher maximum shear stress, and a concave surface will have a lower maximum shear stress. Thus, on a concave
surface, the oxide will have a greater resistance to interfacial fracture, but a lower resistance on a convex surface.[202]

Hollow tantalum cylinders (outside diameter: 1.27 cm, inside diameter 0.281 cm to 1.216 cm) were annealed in an oxygen environment so that the oxide scale could be examined on both convex and concave surfaces.[204]. The scale on the concave surfaces was thinner than on the convex surface but showed little variation with the radius of curvature. There is some indication that the oxide scale might be thicker on substrates with higher curvature.[204]

9.3.3 Analytical solution of stress in cylindrical coordinates

An analytical solution has been derived in cylindrical coordinates for oxidation induced stresses in the Si-SiO₂ system.[212] The oxidation strain in the metal is determined by solving the differential equation

\[ \frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} - \frac{u}{r^2} = 0 \]  \hspace{1cm} [9-7]

and for the oxide film

\[ \frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} - \frac{u}{r^2} = \frac{de^T}{dr} + \frac{(1-2\nu_f) e^T}{(1-\nu_f)} \]  \hspace{1cm} [9-8]

Where \( u \) is the radial replacement, \( r \) is the position \( e^T \) is the oxidation strain and \( \nu_f \) is Poisson’s ratio of the oxide film. Boundary conditions to the above equations are selected to separately solve for oxidation at the metal/film interface and at the film/atmosphere interface. As shown in Figure 9-6, The initial radius of the metal cylinder is defined as ‘b’ and the metal radius after oxidation is defined as ‘a.’
Figure 9-6: Definition of the initial (prior to oxidation) and final (after oxidation) radii of a metal cylinder as used in the growth stress model of Hsueh and Evans.[212]

The boundary conditions are set by noting that there is no displacement, $u$, at $r = 0$. The radial displacement and radial stress must be continuous at $r = a$, thus stipulating:

$$u^m(a) = u^f(a) \quad [9-9]$$
$$\sigma^m_r(a) = \sigma^f_r(a) \quad [9-10]$$

Finally, the radial stress at the environment surface must be zero:

$$\sigma_r^f(b) = 0 \quad [9-11]$$

The results for dilational oxidation at the metal/oxide interface are shown in Hsueh and Evans work.[212]

The stress distribution depends critically on the ratio, $a/b$, which emphasizes the fact that careful considerations must be made when dealing with a film that approximates the dimensions of the substrate.

It is proposed that this model of oxidation on silicon can be applied to the anodic oxidation of tantalum. In reality, it is not straightforward to describe the anodic oxidation of tantalum as being simply due to the egress of tantalum cations or the ingress of oxygen anions; literature suggests that oxide growth occurs simultaneously by both processes.
9.4. Inclusion of Stress in the Point Defect Model

As described in chapter 6, the PDM describes oxide growth in terms of defect chemistry reactions. The following derivation was conceived by Dr. Digby Macdonald, thus he is deserving of the credit for the derivation below; it is reproduced here so as not to be lost to posterity. The application of this theory to the anodization of tantalum is the work of this author.

The predicted effects of stress in the oxide film can be incorporated into the PDM by including a stress term in the chemical potential. Previously, we assumed that the chemical potential could be accounted for by:

\[ \bar{\mu}_i = \mu_i^0 + RT \ln(a_i) + ZF \phi_i \]  \hspace{1cm} [9-12]

Where \( \mu^0 \) is the standard chemical potential, \( a \) is the activity, \( Z \) is the number of electrons, \( F \) is Faraday’s constant, and \( \phi \) is the potential. The effects of stress on the chemical potential can be accounted for by introducing the term \( \sigma V \), which is the product of the stress and the partial molar volume of the species. Thus, the expression for chemical potential is now

\[ \bar{\mu}_i = \mu_i^0 + RT \ln(a_i) + ZF \phi_i + \sigma V_i \]  \hspace{1cm} [9-13]

Rate constants are related to the chemical potential by

\[ k_i = \tau \frac{k_B T}{h} e^{-\frac{\Delta \mu^*}{RT}} \]  \hspace{1cm} [9-14]

where \( \tau \) is a statistical thermodynamic constant, \( k_B \) is Boltzman’s constant, and \( h \) is Planck’s constant. We can then express the rate constants as
\[ k_i = k_i^{00} * e^{\alpha_i (1-\alpha) \chi \frac{F}{RT} V} * e^{-\alpha_i \epsilon \chi \frac{F}{RT} L} * e^{-\alpha_i \beta \chi \frac{F}{RT} pH} * e^{-\alpha_i \Delta (\sigma \bar{V})} \]  \[9-15\]

where the symbols are defined in Table 7.1. Although a quantitative analysis of the predicted stress has not been derived, we expect the oxide film to be under compressive stress, while an equal tensile equal stress must exist in the metal. To date, a quantitative analysis of the predicted stress has not been determined, but it is anticipated that Hseuh’s methodology can be used to calculate the stress on a convex surface. Finite element method (FEM) simulations of the stress could substitute for an analytical solution.

9.5. Evaluating the Significance of Stress to the PDM via Order of Magnitude Approximations

It is worthwhile to take a Fermi approach (order of magnitude approximation) in examining how stress in the oxide would be expected to influence the rate constants of the PDM. While we do not have a quantitative description of the stress distribution, we can make order of magnitude approximations to predict the results.

For film growth at the metal/film interface via the reaction

\[ m \rightarrow k_i M_M + \frac{\chi}{2} V_O^- + \chi e^- \]  \[9-16\]

The change in stress is given by:

\[ \Delta(\sigma_R, V_R) = \sigma_m \bar{V}_{M_M} + \sigma_m \bar{V}_{e^-} + \frac{\chi \sigma_m}{2} \bar{V}_O^- - \chi \sigma_m \bar{V}_m = \sigma_m \Delta V_R \]  \[9-17\]

where \( \bar{V} \) represents molar volume. The molar volume of a tantalum atom in Ta\(_2\)O\(_5\) is calculated to be 26.95 m\(^3\)/mol while that of an oxygen atom is 10.78 m\(^3\)/mol. The molar volume of tantalum is 10.87 m\(^3\)/mol. For tantalum oxide, these values are approximations determined from the density and molar mass. It is particularly troublesome to determine what the molar volume of an oxygen vacancy would be.
Although we do not address the determination of the molar volume here, we can examine what effect the molar volume would have on the strain energy.

For tantalum atoms in $\text{Ta}_2\text{O}_5$, the molar volume was allowed to vary between 0 m$^3$/mol and twice the volume of its estimated value. The molar volume of an oxygen vacancy in $\text{Ta}_2\text{O}_5$ is allowed to vary between the molar volume of an oxygen atom in $\text{Ta}_2\text{O}_5$ and zero. The molar volume of an electron is assumed to be zero. The numerical expressions for these conditions are shown in Table 9-1.

**Table 9-1:** Mathematical description of the allowed molar volumes of atoms and vacancies.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar Volume m$^3$/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{V}<em>{Ta</em>{\text{a}}}$</td>
<td>$26.95(1-\delta_{Ta})$; -1 $\leq$ $\delta_{Ta}$ $&lt; 1$</td>
</tr>
<tr>
<td>$\bar{V}_{e^{-}}$</td>
<td>0</td>
</tr>
<tr>
<td>$\bar{V}_{Ta}$</td>
<td>10.87</td>
</tr>
<tr>
<td>$\bar{V}<em>{O</em>{V}}$</td>
<td>$10.78(1-\delta_{O})$; 0 $&lt; \delta_{O}$ $&lt; 1$</td>
</tr>
</tbody>
</table>

The stress in anodic zirconia has been reported to be on the order of magnitude of $10^8$ Pa [228]. Thus, if we set the stress to 1 GPa, we can estimate the effect that the molar volumes of the defects would have on the strain energy. First, if we hold the molar volume of tantalum in $\text{Ta}_2\text{O}_5$ constant, we can see the effect of the molar volume of an oxygen vacancy on the strain energy of the system. As $\delta_{Ta}$ and $\delta_{O}$ are varied, the strain energy stays within the same order of magnitude, $10^{10}$ Joules/mole. This is illustrated by Figure 9-7.
1 GPa Stress and $\delta_{Ta} = 0$
Y-axis is Strain Energy, J/mol

1 GPa Stress and $\delta_{Ta} = 0.5$
Y-axis is Strain Energy, J/mol

1 GPa Stress and $\delta_{Ta} = -0.5$
Y-axis is Strain Energy, J/mol

**Figure 9-7:** The influence of the molar volume of an oxygen vacancy on the strain energy of the system.

Because the molar volume of the oxygen vacancy and metal site do not play a large role in determining the strain energy, we set $\delta_{Ta}$ and $\delta_{O}$ to 0.5, which effectively sets the oxygen vacancy to one-half the volume of an oxygen atom in Ta$_2$O$_5$. This enables us to estimate the system’s change in energy as a function of stress.

**Figure 9-8:** Strain energy as a function of assumed stress.

- **A:** Strain energy as a function of stress in the GPa range.
- **B:** Strain energy as a function of stress in the MPa range.
The change in chemical potential associated with the growth of anodic tantala via the production of oxygen vacancies is 103 kJ/mol $\text{Ta}_2\text{O}_5$. Setting this to be the reference state of zero stress, we can evaluate how additional stress will affect the change in the chemical potential and hence the rate constant.

For relatively small strains, i.e. in the kPa range, the chemical potential is in the range of 20-40 kJ/mol, depending on the size of the vacancies. This is a significant energy in comparison to the chemical potential determined by optimizing EIS data to the PDM. Therefore, it is worthwhile to consider the effects of stress on the rate constants.

### 9.6 Derivation of the Impedance that Considers the Potential Drop Across an Oxide Formed by both Tantalum Interstitial and Oxygen Vacancy Migration

The PDM has been modified by accounting for the potential drop across the outer layer in expressing the rate constants.[83, 165] The potential drop has been expressed as the product of the resistance of the outer layer and the experimentally measured current of the cell. Thus the rate constants for the formation of tantalum interstitials and oxygen vacancies are affected by the reduced potential at the metal/oxide interface. Previously the relationship between the applied voltage and rate constant was of the form

$$k'_i = k''_i e^{dV} \quad [9-18]$$

However, correcting for the potential drop across the outer layer results in the relationship

$$k'_i = k''_i e^{d(V-IR_e)} \quad [9-19]$$

Where $V$ is the applied voltage, $I$ is the experimental current of the cell and $R_{OL}$ is defined as
\[ R_{\text{OL}} = \frac{\rho L_{\text{OL}}}{Q} \]  \[ \text{[9-20]} \]

Where \( \rho \) is the resistivity of the electrolyte in the pores, \( L_{\text{OL}} \) is the thickness of the outer layer, and \( Q \) is the porosity of the outer layer.

In the case of zirconium, the outer layer is notably porous. However, as shown by TEM analysis (Section 3.2.1) and ellipsometry (Section 4.4.3), the outer layer is compact. Under non-thickness limited (NTL) growth conditions, porosity <5% has been observed using TEM imaging, however examination of oxides formed in dilute phosphoric acid has never revealed evidence of porosity. In Ai’s treatment of the impedance expression for zirconium, reaction 2 (the production of oxygen vacancies) is the only reaction that must be considered in forming the compact layer. However, in the case of tantalum, both reactions 1 and 2 (production of tantalum interstitials and oxygen vacancies) result in the formation of a compact layer. Therefore, the expression for the Faradaic admittance is more complicated. In the case of tantalum, it is straightforward to calculate the Faradaic impedance, however, when the real and imaginary components of the impedance are separated, the result is monstrously intimidating.

The rate constants for the production of tantalum interstitials and oxygen vacancies are of the form:

\[ k_i = k^o_i e^{a_i (V-IR_{\text{a}})} e^{b_i L_{\text{b}}} e^{c_i \alpha_i (\beta_i H + \phi_{\text{e}})} \]  \[ \text{[9-21]} \]

where \( a_i \) and \( b_i \) are defined in Table 9-2.
Table 9-2: Abbreviated symbols, $a_i$ and $b_i$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$a_i, \text{V}^{-1}$</th>
<th>$b_i, \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$5\gamma\alpha_1 (1 - \alpha)$</td>
<td>$5\alpha_1 K$</td>
</tr>
<tr>
<td>2</td>
<td>$5\gamma\alpha_2 (1 - \alpha)$</td>
<td>$5\alpha_2 K$</td>
</tr>
</tbody>
</table>

The Faradaic current response is given by:

$$\delta I = \chi F[(a_1 k_1 + a_2 k_2)\delta V - (b_1 k_1 + b_2 k_2)\delta L - (a_1 k_1 + a_2 k_2)\delta I]$$ [9-22]

Defining:

$$\delta V = \Delta V e^{j\omega t} \quad \text{and} \quad \delta L = \Delta L e^{j\omega t} \quad \text{and} \quad \delta I = \Delta I e^{j\omega t}$$ [9-23]

The derivatives of these expressions with respect to time are:

$$\frac{d(\delta V)}{dt} = j\omega \Delta V e^{j\omega t} \quad \text{and} \quad \frac{d(\delta L)}{dt} = j\omega \Delta L e^{j\omega t} \quad \text{and} \quad \frac{d(\delta I)}{dt} = j\omega \Delta I e^{j\omega t}$$

Making the appropriate substitutions results in:

$$\Delta I^* e^{j\omega t} = \chi F[(a_1 k_1 + a_2 k_2)\Delta V - (b_1 k_1 + b_2 k_2)\Delta L - (a_1 k_1 + a_2 k_2)\Delta I^* e^{j\omega t}]$$ [9-24]

$$\frac{\Delta I}{\Delta V}(1 + a_1 k_1 + a_2 k_2) + \frac{\Delta L}{\Delta V}(b_1 k_1 + b_2 k_2) = \chi F(a_1 k_1 + a_2 k_2)$$ [9-25]

The Faradaic admittance is determined by solving for $\Delta I/\Delta V$

$$Y_F = \frac{\Delta I}{\Delta V} = \frac{\chi F(a_1 k_1 + a_2 k_2) - \frac{\Delta L}{\Delta V}(b_1 k_1 + b_2 k_2)}{1 + a_1 k_1 + a_2 k_2}$$ [9-26]

Now to determine $\Delta L/\Delta V$
\[
\frac{dL}{dt} = \Omega \left[ k_1^* e^{a_1(V - IR_{OL})} e^{-b_1 L} + a_2 k_2^* e^{a_1(V - IR_{OL})} e^{-b_2 L} - k_3^* C_H^a \right] \quad [9-27]
\]

\[
\frac{d\delta L}{dt} = \Omega \left[ a_1 k_1^* e^{a_1(V - IR_{OL})} \delta V - b_1 k_1^* e^{a_1(V - IR_{OL})} \delta L - a_1 R_{OL} k_1^* e^{a_1(V - IR_{OL})} \delta I + a_2 k_2^* e^{a_1(V - IR_{OL})} \delta L - a_2 R_{OL} k_2^* e^{a_1(V - IR_{OL})} \delta I \right] \quad [9-28]
\]

\[
jo\Delta L e^{j\omega} = \Omega \left[ a_1 k_1 \Delta V e^{j\omega} - b_1 k_1 \Delta L e^{j\omega} - a_1 R_{OL} k_1 \Delta I e^{j\omega} + a_2 k_2 \Delta V e^{j\omega} - b_2 k_2 \Delta L e^{j\omega} - a_2 R_{OL} k_2 \Delta I e^{j\omega} \right] \quad [9-29]
\]

\[
\Delta j\omega = \Omega \left[ a_1 k_1 \Delta V - b_1 k_1 \Delta L - a_1 R_{OL} k_1 \Delta I + a_2 k_2 \Delta V - b_2 k_2 \Delta L - a_2 R_{OL} k_2 \Delta I \right] \quad [9-30]
\]

Solving for \( \Delta L/\Delta V \)

\[
\frac{\Delta L}{\Delta V} = \frac{\Omega (a_1 k_1 + a_2 k_2)}{jo + \Omega b_1 k_1 + \Omega b_2 k_2} - Y_F \left[ \Omega a_1 R_{OL} k_1 + \Omega a_2 k_2 R_{OL} \right] \quad [9-31]
\]

Substituting \( \Delta L/\Delta V \) into the Equation 9—26 gives:

\[
Y_F = \left[ \chi F (a_1 k_1 + a_2 k_2) \right] \left[ \frac{jo + \Omega b_1 k_1 + \Omega b_2 k_2 \Delta V - [\Omega a_1 k_1 + \Omega a_2 k_2 \Delta L - b_1 k_1 + b_2 k_2][b_1 k_1 + b_2 k_2]}{[jo + \Omega b_1 k_1 + \Omega b_2 k_2][1 + a_1 k_1 + a_2 k_2] - [\Omega a_1 R_{OL} k_1 + \Omega a_2 k_2 R_{OL}][b_1 k_1 + b_2 k_2]} \right] \quad [9-32]
\]

This is the expression for the complex Faradaic admittance where a potential drop is assumed across the oxide where the oxide forms by the production and migration of both tantalum interstitials and oxygen vacancies. The experimental impedance of such a system is represented by the equivalent circuit in Figure 9-9. The total impedance of this
The circuit is given in equations [9-33] and [9-34]. The real and imaginary components of the impedance predicted by the PDM are shown at the end of this chapter.

![Bi-layer equivalent circuit model](image)

**Figure 9.9:** Bi-layer equivalent circuit model.

\[
Z_{\text{Total}} = \frac{1}{Z_{C_\text{e}}^{-1} + Z_{f}^{-1} + Z_{e,h}^{-1}} + \frac{1}{Z_{C_\text{OL}}^{-1} + Z_{C_\text{e}}^{-1}} + R_s \tag{9-33}
\]

\[
Z_{\text{Total}} = \frac{1}{j\omega C_{\text{IL}} + Y_f + R_{e,h}^{-1}} + \frac{1}{R_{\text{OL}}^{-1} + j\omega C_{\text{OL}}} + R_s \tag{9-34}
\]

The potential drop obtained by taking the product of the experimental current and the resistance of the outer layer is a measurable fraction of the applied formation voltage as shown in Table 9-4. Serious questions remain as to whether the potential drop should be accounted for in the tantalum/tantalum oxide system. This modification of the PDM was made for the case of zirconium, which has a porous, outer layer. However, tantalum oxide forms a compact bi-layer structure where the two layers are differentiated by chemistry, but both layers are compact. The magnitude of the potential drop (resistance of the outer layer * experimental current) is calculated by using the resistance of the outer...
layer (R_{OL}) determined from the PDM in Chapter 7. These values are shown in Table 9-3. Assuming that this methodology is valid, the potential drop is a significant fraction of the applied voltage.

**Table 9-3:** Potential drop across the oxide layer and its value relative to the applied formation voltage.

<table>
<thead>
<tr>
<th>Formation Voltage, V_f</th>
<th>Experimental Current, A</th>
<th>R_{OL} from PDM, Ω</th>
<th>I*R_{OL}, V</th>
<th>I*R_{OL}/V_f *100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.24</td>
<td>1.802*10^{-7}</td>
<td>8.755*10^6</td>
<td>1.58</td>
<td>70.5</td>
</tr>
<tr>
<td>4.24</td>
<td>1.785*10^{-7}</td>
<td>6.00*10^6</td>
<td>1.07</td>
<td>25.2</td>
</tr>
<tr>
<td>6.24</td>
<td>1.972*10^{-7}</td>
<td>7.30*10^6</td>
<td>1.44</td>
<td>23.1</td>
</tr>
<tr>
<td>8.24</td>
<td>1.819*10^{-7}</td>
<td>8.93*10^6</td>
<td>1.62</td>
<td>19.7</td>
</tr>
</tbody>
</table>
Table 9-4: Key for matching the symbolism used in the derivation of the experimental impedance to the symbolism used in separating the real and imaginary components of the impedance.

<table>
<thead>
<tr>
<th>Symbol used in expression of Re or Im Component below</th>
<th>Corresponding terms as defined above</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>C_{OL}</td>
</tr>
<tr>
<td>G</td>
<td>C_{IL}</td>
</tr>
<tr>
<td>R</td>
<td>R_{OL}</td>
</tr>
<tr>
<td>Q</td>
<td>R_{IL}</td>
</tr>
<tr>
<td>d</td>
<td>Ω</td>
</tr>
<tr>
<td>A</td>
<td>a_{1}k_{1}+a_{2}k_{2}</td>
</tr>
<tr>
<td>B</td>
<td>b_{1}k_{1}+b_{2}k_{2}</td>
</tr>
<tr>
<td>c</td>
<td>χ^{F}</td>
</tr>
</tbody>
</table>
Imaginary Component of the Impedance

\[
\frac{H w}{g + H^2 w^2}
\]

\[
(G w) \left( \frac{\alpha c ((1 + A) B d - A B d R) w^2}{((1 + A) B d - A B d R)^2 + w^2} + \frac{A c w^2}{((1 + A) B d - A B d R)^2 + w^2} \right)
\]

\[
(AB d w) \left( \frac{1}{Q + \frac{(-A B d + A B c d) ((1 + A) B d - A B d R)}{((1 + A) B d - A B d R)^2 + w^2} + \frac{A c w^2}{((1 + A) B d - A B d R)^2 + w^2}} \right)
\]

\[
(A^2 B c d w) \left( \frac{1}{Q + \frac{(-A B d + A B c d) ((1 + A) B d - A B d R)}{((1 + A) B d - A B d R)^2 + w^2} + \frac{A c w^2}{((1 + A) B d - A B d R)^2 + w^2}} \right)
\]

\[
(A^2 B c d R w) \left( \frac{1}{Q + \frac{(-A B d + A B c d) ((1 + A) B d - A B d R)}{((1 + A) B d - A B d R)^2 + w^2} + \frac{A c w^2}{((1 + A) B d - A B d R)^2 + w^2}} \right)
\]
Real Component of the Impedance
(continues on next page)
Appendix A: Formalism of the Admittance used for PDM Optimization using the Unconstrained Model of Chapter 6.

\[ Y_f = \chi F \left[ a_1 k_1^0 e^{\alpha_1 V} e^{-b_1 L} + a_2 k_2^0 e^{\alpha_2 V} e^{-b_2 L} \right] - \chi F \left[ b_1 k_1^0 e^{\alpha_1 V} e^{-b_1 L} + b_2 k_2^0 e^{\alpha_2 V} e^{-b_2 L} \right] \frac{a_2/b_2}{1 + j \omega \frac{1}{\Omega k_2^0 b_2 e^{a_2 V} e^{-b_2 L}}} \]

194.72=x/F/RT, 5 = x=valence state

<table>
<thead>
<tr>
<th>Symbol used in algorithm below</th>
<th>Corresponds to variable in Table IIIA.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>m1</td>
<td>( \alpha_1 )</td>
</tr>
<tr>
<td>m2</td>
<td>( \alpha_2 )</td>
</tr>
<tr>
<td>k100</td>
<td>( k_1^{00} )</td>
</tr>
<tr>
<td>k200</td>
<td>( k_2^{00} )</td>
</tr>
<tr>
<td>k500</td>
<td>( k_5^{00} )</td>
</tr>
<tr>
<td>e</td>
<td>E</td>
</tr>
<tr>
<td>p2</td>
<td>( \phi_{0f/s} )</td>
</tr>
<tr>
<td>p1</td>
<td>( \beta )</td>
</tr>
<tr>
<td>wa</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>x</td>
<td>( \chi ) and ( \delta )</td>
</tr>
<tr>
<td>e1</td>
<td>e</td>
</tr>
<tr>
<td>Cdl</td>
<td>( C_{dl} )</td>
</tr>
<tr>
<td>Rs</td>
<td>( R_s )</td>
</tr>
</tbody>
</table>

Imaginary part:

\( F1 = 2.241 \) (applied potential, SHE = SCE + 0.241)
\( F2 = 2.47 \) (pH)
\( F3 = (194.72^{*}(1-m)^{m2})/(194.72^{*}m2*e)^{F1-1}/(194.72^{*}m2*e)\log(k500/(k200*exp(-m2*194.72*(p1*F2+p2)))*(10^{(-F2)})^{n}) \)
\( F4 = 96486.7^{*}(194.72^{*}m1^{*}(1-m)^{5*}k100*exp(-m1*194.72^{*}(p1*F2+p2))*exp(194.72^{*}m1^{*}(1-m)^{F1})*exp(-194.72^{*}m1*e^{F3})+194.72^{*}m2^{*}(1-m)^{5*}k200*exp(-m2*194.72^{*}(p1*F2+p2))*exp(194.72^{*}m2^{*}(1-m)^{F1}))*exp(-194.72^{*}m2*e^{F3})) \)
\( F5 = -e/(1-m)^{F4} \)
\( F6 = (1-m)/e \)
\( F7 = 1/(w^{*} k200*exp(-m2*194.72^{*}(p1*F2+p2))*exp(194.72^{*}m2^{*}(1-m)^{F1})*exp(-194.72^{*}m2*e^{F3})+194.72^{*}e^{m2}) \)
\( F8 = F4+F5*F6/(1+(2^{*}3.1415926^{*}(10^{x})*F7)^{2}) \)
\[ F9 = -F5 \cdot F6 \cdot 2 \cdot 3.1415926 \cdot (10^x) \cdot F7 / (1 + (2 \cdot 3.1415926 \cdot (10^x) \cdot F7)^2) \]

\[ Y = -((F9 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.0000000000088542 / F3) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.0000000000088542 / F3))^2) + 1 / Re)^2 + ((F9 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.0000000000088542 / F3)^2) - 1 / (2 \cdot 3.1415926 \cdot (10^x) \cdot Cdl) \]

**Real part:**

\[ F1 = 2.241 \]
\[ F2 = 2.47 \]
\[ F3 = (194.72 \cdot (1-m) \cdot m2) / (194.72 \cdot m2 \cdot e) \cdot F1 - 1 / (194.72 \cdot m2 \cdot e) \cdot \log(k500 / (k200 \cdot \exp(-m2 \cdot 194.72 \cdot (p1 \cdot F2 + p2)))) / (10 \cdot (-F2))^n \]
\[ F4 = 96486.7 \cdot (194.72 \cdot m1 \cdot (1-m) \cdot 5 \cdot k100 \cdot \exp(-m1 \cdot 194.72 \cdot (p1 \cdot F2 + p2)) \cdot \exp(194.72 \cdot m1 \cdot (1-m) \cdot F1) \cdot \exp(-194.72 \cdot m1 \cdot e \cdot F3) + 194.72 \cdot m2 \cdot (1-m) \cdot 5 \cdot k200 \cdot \exp(-m2 \cdot 194.72 \cdot (p1 \cdot F2 + p2)) \cdot \exp(194.72 \cdot m2 \cdot (1-m) \cdot F1) \cdot \exp(-194.72 \cdot m2 \cdot e \cdot F3)) \]
\[ F5 = -e / (1-m) \cdot F4 \]
\[ F6 = (1-m) / e \]
\[ F7 = 1 / (w \cdot k200 \cdot \exp(-m2 \cdot 194.72 \cdot (p1 \cdot F2 + p2)) \cdot \exp(194.72 \cdot m2 \cdot (1-m) \cdot F1) \cdot \exp(-194.72 \cdot m2 \cdot e \cdot F3)) \cdot 194.72 \cdot e \cdot m2 \]
\[ F8 = F4 + F5 \cdot F6 / (1 + (2 \cdot 3.1415926 \cdot (10^x) \cdot F7)^2) \]
\[ F9 = -F5 \cdot F6 \cdot 2 \cdot 3.1415926 \cdot (10^x) \cdot F7 / (1 + (2 \cdot 3.1415926 \cdot (10^x) \cdot F7)^2) \]
\[ Y = ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.0000000000088542 / F3)^2) + 1 / Re)^2 + ((F9 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) / ((F8 / (F8^2 + F9^2)) + (2 \cdot 3.1415926 \cdot (10^x)) \cdot (-0.5) \cdot w) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.0000000000088542 / F3)^2) + Rs \]
Appendix B: Formalism of the Admittance for PDM Optimization using the Bi-Layer Constrained Model of Chapter 7

Table B-1: Symbols used for coding in the DataFit program

<table>
<thead>
<tr>
<th>Symbol in DataFit</th>
<th>Symbol in Table 6-1</th>
<th>Constant or Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$\alpha_1$</td>
<td>Variable</td>
</tr>
<tr>
<td>A2</td>
<td>$\alpha_2$</td>
<td>Variable</td>
</tr>
<tr>
<td>P</td>
<td>$\alpha$</td>
<td>Variable</td>
</tr>
<tr>
<td>Cil</td>
<td>$C_{IL}$</td>
<td>Variable</td>
</tr>
<tr>
<td>Col</td>
<td>$C_{OL}$</td>
<td>Variable</td>
</tr>
<tr>
<td>Rol</td>
<td>$R_{OL}$</td>
<td>Variable</td>
</tr>
<tr>
<td>Re</td>
<td>$R_{IL}$</td>
<td>Variable</td>
</tr>
<tr>
<td>Rs</td>
<td>$R_s$</td>
<td>Variable</td>
</tr>
<tr>
<td>k100</td>
<td>$k_{1}^{(0)}$</td>
<td>Variable</td>
</tr>
<tr>
<td>k200</td>
<td>$k_{2}^{(0)}$</td>
<td>Variable</td>
</tr>
<tr>
<td>V</td>
<td>V</td>
<td>Constant</td>
</tr>
<tr>
<td>L</td>
<td>L</td>
<td>Constant</td>
</tr>
<tr>
<td>g</td>
<td>$\gamma$</td>
<td>Constant</td>
</tr>
<tr>
<td>c</td>
<td>$\chi_F$</td>
<td>Constant</td>
</tr>
<tr>
<td>d</td>
<td>$\Omega$</td>
<td>Constant</td>
</tr>
<tr>
<td>Y</td>
<td>Z</td>
<td>Dependent Variable</td>
</tr>
<tr>
<td>x</td>
<td>Frequency, Hz</td>
<td>Independent Variable</td>
</tr>
<tr>
<td>w</td>
<td>$2\pi x$</td>
<td>Independent Variable</td>
</tr>
</tbody>
</table>

Table B-2: Constants assumed in calculating the relationship between $k_i^{(0)}$ and $k_i^{00}$

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.4</td>
<td>pH meter</td>
</tr>
<tr>
<td>T</td>
<td>298 K</td>
<td>STP</td>
</tr>
<tr>
<td>$\beta$</td>
<td>-0.060 V</td>
<td></td>
</tr>
<tr>
<td>$\phi_{0s}$</td>
<td>-0.10</td>
<td></td>
</tr>
</tbody>
</table>

The following terms are defined in order to simplify the algebraic expressions:

\[ \gamma' = \chi' \gamma = \frac{\chi_F}{RT} \quad [B-1] \]
\[ a_1 = \gamma' \alpha_1 (1 - \alpha) \quad [B-2] \]
\[ a_2 = \gamma' \alpha_2 (1 - \alpha) \quad [B-3] \]
\[ b_1 = \gamma' E \alpha_1 \quad \text{[B-4]} \]
\[ b_2 = \gamma' E \alpha_2 \quad \text{[B-5]} \]
\[ k_1^o = k_1^o \exp(46.9 \ast \alpha_1) \quad \text{[B-6]} \]
\[ k_2^o = k_2^o \exp(46.9 \ast \alpha_2) \quad \text{[B-7]} \]

The Faradaic admittance given in equation 7-31 can be simplified to
\[ Y_F = c'A' - c'B' \frac{\Omega A'}{j \omega + \Omega B'} \quad \text{[B-8]} \]

where
\[ A' = a_1 k_1^o e^{(aV - b_i L)} + a_2 k_2^o e^{(aV - b_i L)} \quad \text{[B-9]} \]
\[ B' = b_1 k_1^o e^{(aV - b_i L)} + b_2 k_2^o e^{(aV - b_i L)} \quad \text{[B-10]} \]

The real component of the impedance from equation [B-8] is:
\[
\text{Re}(Z) = \frac{A' \chi}{\left( \frac{A'B'\chi \omega \Omega}{B'2 \Omega^2 + \omega^2 + \omega^* C_{IL}} \right)^2 + \left( \frac{A' \chi - A'B'^2 \chi \Omega^2}{B'2 \Omega^2 + \omega^2 + \frac{1}{R_{e,h}}} \right)^2} - \frac{A'B'^2 \chi \Omega^2}{\left( B'2 \Omega + \omega^2 \right)^2 \left( \frac{A'B'\chi \omega \Omega}{B'2 \Omega^2 + \omega^2 + \omega^* C_{IL}} \right)^2 + \left( \frac{A' \chi - A'B'^2 \chi \Omega^2}{B'2 \Omega^2 + \omega^2 + \frac{1}{R_{e,h}}} \right)^2} + \frac{1}{\left( \frac{A'B'\chi \omega \Omega}{B'2 \Omega^2 + \omega^2 + \omega^* C_{IL}} \right)^2 + \left( \frac{A' \chi - A'B'^2 \chi \Omega^2}{B'2 \Omega^2 + \omega^2 + \frac{1}{R_{e,h}}} \right)^2} \ast R_{e,h} + \frac{1}{\left( \frac{\omega^2 C_{OL}^2 + \frac{1}{R_{OL}^2}}{R_{OL}} \right) R_s} \quad \text{[B-11]} \]
The imaginary component from equation [B-8] is:

[B-12]

\[
\text{Im}(Z) = -j \left( \frac{A'B'\chi\Omega\omega}{\left( B'^2\Omega + \omega^2 \right)^* + \left( A'B'\omega\Omega + \omega C_{IL} \right)^2 + \left( A'\chi - \frac{A'B'^2\chi\Omega^2}{B'^2\Omega^2 + \omega^2} + \frac{1}{R_{ch}} \right)^2 + \frac{1}{\omega^2 C_{OL}^2 + \frac{1}{R_{OL}^2}} \right) R_{OL}
\]

The following definitions are made:

F1=a1
F2=a2
F3=b1
F4=b2
F5=A'
F6=B'
F7=B'^2d'^2 + w'^2
F8=A'B'^2cd'^2
F9=A'B'cdw

The expressions entered into DataFit Software

**Real:**

F1 = g*A1*(1-P)
F2 = g*A2*(1-P)
F3 = g*E*A1
F4 = g*E*A2
F5 = F1*k100*exp(46.9*A1)*exp(F1*V)*exp(-F3*L)+F2*k200*exp(46.9*A2)*exp(F2*V)*exp(-F4*L)
\[
F_6 = F_3 \cdot k_{100} \cdot \exp(46.9 \cdot A_1) \cdot \exp(F_1 \cdot V) \cdot \exp(-F_3 \cdot L) + F_4 \cdot k_{200} \cdot \exp(46.9 \cdot A_2) \cdot \exp(F_2 \cdot V) \cdot \exp(-F_4 \cdot L) \\
F_7 = F_6 \cdot d^2 + (6.28 \cdot 10^x)^2 \\
F_8 = F_5 \cdot F_6 \cdot c \cdot d^2 \\
F_9 = F_5 \cdot F_6 \cdot c \cdot d \cdot 6.28 \cdot 10^x \\
Y = \frac{F_5 \cdot c}{(F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2} - \frac{F_8 / F_7 \cdot ((F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2)}{((F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2) \cdot \text{Re}} + \frac{1}{((6.28 \cdot 10^x)^2 \cdot \text{Col}^2 + 1 / \text{Rol}^2) \cdot \text{Rol}} \\
\]

**Imaginary:**

\[
F_1 = g \cdot A_1 \cdot (1 - P) \\
F_2 = g \cdot A_2 \cdot (1 - P) \\
F_3 = g \cdot E \cdot A_1 \\
F_4 = g \cdot E \cdot A_2 \\
F_5 = F_1 \cdot k_{100} \cdot \exp(46.9 \cdot A_1) \cdot \exp(F_1 \cdot V) \cdot \exp(-F_3 \cdot L) + F_2 \cdot k_{200} \cdot \exp(46.9 \cdot A_2) \cdot \exp(F_2 \cdot V) \cdot \exp(-F_4 \cdot L) \\
F_6 = F_3 \cdot k_{100} \cdot \exp(46.9 \cdot A_1) \cdot \exp(F_1 \cdot V) \cdot \exp(-F_3 \cdot L) + F_4 \cdot k_{200} \cdot \exp(46.9 \cdot A_2) \cdot \exp(F_2 \cdot V) \cdot \exp(-F_4 \cdot L) \\
F_7 = F_6 \cdot d^2 + (6.28 \cdot 10^x)^2 \\
F_8 = F_5 \cdot F_6 \cdot c \cdot d^2 \\
F_9 = F_5 \cdot F_6 \cdot c \cdot d \cdot 6.28 \cdot 10^x \\
Y = \frac{F_5 \cdot c}{(F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2} - \frac{F_8 / F_7 \cdot ((F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2)}{((F_9 / F_7 + 6.28 \cdot 10^x \cdot \text{Cil})^2 + (F_5 \cdot c - F_8 / F_7 + 1 / \text{Re})^2) \cdot \text{Re}} + \frac{1}{((6.28 \cdot 10^x)^2 \cdot \text{Col}^2 + 1 / \text{Rol}^2) \cdot \text{Rol}} \\
\]
References


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172. Olszta, M.J., Field-induced Crystallization in Electrochemically Anodized Nb$_2$O$_5$ and Ta$_2$O$_5$ Capacitors. unpublished 2006: University Park, PA.


Jennifer was born Friday, February 13, 1981, 01:13 in Clearfield, Pennsylvania to Donna and Dennis Sloppy. On May 6, 2006 she married Patrick Christopher Ray and began using the alias Jennifer Ray Sloppy. She received a bachelor’s degree in chemistry with minors in physics and mathematics at the Indiana University of Pennsylvania (IUP), Indiana, Pennsylvania in May 2003. She is also a graduate of the Robert E. Cook Honor’s College at IUP. While at IUP, Jennifer studied the biochemical changes of recalcitrant seeds using infrared spectroscopy as a MERCK/AAAS undergraduate research fellow. She completed an undergraduate thesis entitled “Ab initio studies of diamond surfaces.”

During the summers of 2001 and 2002 she was employed by Argonne National Laboratory-West (ANL-W), Idaho Falls, ID as an Energy Research for Undergraduate Laboratory Fellow. While at ANL-W she explored disposal methods for air filters contaminated with hazardous materials and characterized the thermal properties of prototype nuclear fuels. She entered the graduate program of the Materials Science and Engineering Department at Pennsylvania State University (PSU) in August 2003 and was awarded a Graduate Research Fellowship from the National Science Foundation in 2004. Jennifer became involved with the Center for Dielectric Studies at PSU in November 2004 and completed her Ph.D. studies in 2009.