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College of Earth and Mineral Sciences

MODELING THE BEHAVIOR OF THE DIELECTRIC PROPERTIES IN LOW FORMATION VOLTAGE ELECTROLYTIC TANTALUM CAPACITORS

A Thesis in

Materials Science and Engineering

by

Angela J. Kramer

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The thesis of Angela J. Kramer was reviewed and approved* by the following:

Elizabeth C. Dickey  
Professor of Materials Science and Engineering  
Associate Director of the Materials Research Institute

Clive A. Randall  
Professor of Materials Science and Engineering  
Director of the Center of Dielectric Studies

Thomas N. Jackson  
Professor of Electrical Engineering

Joan M. Redwing  
Professor of Materials Science and Engineering and Electrical Engineering  
Associate Head for Graduate Studies, Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

With the miniaturization of electronics, there is a continual demand for capacitive components to have greater capacitance per volume with low leakage currents. This research was motivated by the need to understand the impact of low formation voltage dielectrics and high surface area powders on the electrical properties of electrolytic tantalum capacitors. To help address the specific charge \((CV/g)\) loss with decreasing formation voltage (below approximately 12 V), a physical, mathematical model based on the cylindrical geometry of the tantalum anode was developed to qualitatively explain this phenomenon as well as investigate the influence of curvature on the localized electric field and direct-current (D.C.) leakage.

The model developed qualitatively explains the \(CV/g\) behavior and low-voltage \% \(CV/g\) loss observed in experimental data. The model was useful to qualitatively predict the capacitance per volume increase with decreasing particle size. It was found that the \(CV/g\) decreases with decreasing formation voltage due to the presence of the native oxide thickness (which corresponds to the zero formation voltage) becoming a more significant fraction of the total dielectric thickness. Also, since the native oxide is present regardless of tantalum particle size, the percentage of \% \(CV/g\) loss is almost independent of the initial tantalum particle size, although the absolute losses are greater for smaller particle sizes.

The model provided insight into the effects of curvature on electric field, where it was observed that there is electric field enhancement at the anode for features with positive curvature and at the cathode for features of negative curvature. Likewise, there is electric field depletion at the cathode for features with positive curvature and at the anode for features of negative curvature. Since the D.C. leakage current is directly related to the electric field, using the same physical model allows for the effects of particle curvature on the D.C. leakage to be predicted. It was found that for Schottky emission, there is leakage current enhancement at the cathode for
negative curvature features. The leakage due to Schottky emission is predicted to be
inhomogeneous at the cathodes depending on the features curvature. For Poole-Frenkel
conduction, curvature does not affect the leakage current density, but the total leakage current per
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1.1 Electrolytic Tantalum Capacitors

Tantalum pentoxide ($\text{Ta}_2\text{O}_5$) is commonly used as a dielectric material for electronic devices, including electrolytic capacitors [1], dynamic random access memory (DRAM) [2], computers [3], and telecommunications [3]. When tantalum pentoxide is grown under electrolytic conditions, an amorphous, insulating material is formed that is commonly used in energy storage devices, especially in the production of commercial grade electrolytic capacitors [4, 5]. Various companies including Kemet Corporation, AVX Corporation, and Murata Electronics produce commercial electrolytic capacitors. At the end of the fiscal year in 2010, the electrolytic capacitor industry had a net worth of $1.5 billion, and 49% of all capacitors made and sold were electrolytic tantalum capacitors [3]. In September 2010, the electrolytic tantalum capacitor net profit for Kemet Corporation was $248.6 million, where sales were increased by approximately 45% from the previous year [3].

As electronics and electrical circuitry become more advanced, the quantity of ceramic, electrolytic, and polymer film capacitors is growing and becoming more operation-specific. The capacitor industry is tailoring the device production of electrolytic capacitors to succeed in meeting the demands of electronic community. With the miniaturization of electronics, there is a continual demand for components to have an increase in the specific charge of tantalum capacitors as defined by the charge per unit volume or weight ($CV/g$), where $C$ is the capacitance, $V$ is the formation voltage, and $g$ is the weight of the capacitor [6]. In order for the capacitance of the device to increase, there must be an increase in the surface area and/or decrease in the dielectric thickness. Increasing the surface area requires the use of finer powders that have
smaller primary particle sizes [7-9]. The volumetric efficiency of the device is governed by the specific charge, which should value to be as high as possible while remaining cost efficient [5].

Recently oxide growth at lower formation voltages has been investigated as a result of reducing the operating voltage in some electronic devices and the development of ultra-fine tantalum powder capacitors that are applicable only at low formation voltages [5, 8, 10]. It is known that the capacitance is inversely proportional to the thickness of the dielectric; for an electrolytic capacitor the thickness is directly related to the formation voltage in which the oxide is grown. One way to increase the capacitance and specific charge of the material is to reduce the dielectric thickness. Upon decreasing the dielectric thickness, there is a linear reduction in the device formation voltage. Therefore, in assuming that the permittivity of the dielectric does not change with formation voltage, the $CV/g$ should remain constant as a function of formation voltage. However, this is not the case.

Studies have shown that at high formation voltages (and consequently high dielectric thicknesses), the $CV/g$ decreases [11, 12]. During anode formation, the tantalum metal is loosely sintered together creating pores and necks within the anode to maximize surface area [5]. It was found that during anodization at high formation voltages (thicker oxides), some of the necks separating the metal particles and open pores were completely consumed with the formed tantalum oxide [11, 12]. Thus, it is the consumption of necks (and decrease in area) connecting the sintered Ta powder particles during oxide growth that accounts for the % $CV/g$ loss at higher formation voltages [5]. At low formation voltages, it has been found that there is a decrease in the $CV/g$ at formation voltages lower than approximately 12 V [8, 10]. The low voltage $CV/g$ and % $CV/g$ loss dependence on the formation voltage in electrolytic tantalum capacitors was studied for 2.7 and 0.9 μm Ta powders as shown in Figure 1-1, where the % $CV/g$ loss was defined as the percent difference relative to the $CV/g$ at 12V [5]. Figure 1-1 shows that the $CV/g$ decreases with decreasing formation voltage for both particle sizes; the absolute value of the low voltage % $CV/g$
loss is higher in the 0.9 µm powder in comparison to the 2.7 µm powder [5]. At the same time, the relative % CV/g loss is practically identical for these two Ta powders [5]. The decrease of CV/g at low formation voltages limits the miniaturization of electrolytic tantalum capacitors. It is imperative to understand why this happens to understand the limitations of the material and the devices.

Figure 1-1: CV/g and % CV/g loss vs. formation voltage with 0.9 and 2.7 µm Ta powders [5].

The high curvature of the high-surface-area tantalum anodes could also have other implications on the electrical properties of the device. It is known that as the negative (concave) curvature of the material increases, the local electric field concentration increases. This, in turn, has effects on the electrical properties of the devices. Electrode-limiting leakage mechanisms are strongly affected by this increase in field concentration, in that the current density is directly proportional to the exponential of the field. If there is a high localized electric field at the anode
or cathode electrodes, then it is expected that the localized current density will increase at the electrode as well. Therefore, curvature of the tantalum anodes could have major consequences on the electrical properties of the device.

1.2 Objectives

The objective of this research is to create a physical model to help explain the dielectric properties observed in electrolytic tantalum capacitors. A mathematical representation is formulated that best describes the physical characteristics of electrolytic tantalum capacitors. The model is used to describe the scaling behavior of the specific charge (CV/g) with particle size for anodic oxide formed at low formation voltages. This model is also used to understand the general effects of curvature on the electric field within the oxide and on different D.C. leakage mechanisms.
Chapter 2

Literature Review of Tantalum Oxide

2.1 Tantalum Electrolytic Capacitors

A parallel plate capacitor is composed of an insulating material between two conducting materials, where the capacitance is defined as:

\[ C = \frac{\varepsilon_r \varepsilon_0 A}{t} \]  \hspace{1cm} \text{Equation 1}

where \( C \) is the capacitance, \( A \) is the area, \( \varepsilon_r \) is the material’s relative permittivity, and \( \varepsilon_0 \) is the permittivity of free space, and \( t \) is the thickness [13]. With the application of an electric field, there is a charge build up at the metal/oxide interface causing the separation of charge to form an energy potential, which can be released quickly when needed [13]. Capacitive devices are commonly found in many consumer electronics, including cell phones, televisions, computers, and internally implanted heart defibrillators.

Electrolytic tantalum capacitors are not processed to form perfect parallel plate capacitors; instead these capacitors are porous pellets that have both necks and pores after sintering, as shown in Figure 2-1. Their processing consists of tantalum metal powder, which serves as the anode, being pressed into pellets which are then sintered to connect the Ta metal powders without initiating grain growth that would consume the necks and pores of the anode [5]. In this way, the capacitor can have a greater capacitance due to its larger surface area. After sintering, the anodes are dipped into an electrolyte solution to undergo anodic oxidation to form
the dielectric. The samples are then infiltrated with a cathodic material, e.g. MnO₂ or a conductive polymer to create the capacitor.

![Figure 2-1: Electron micrographs of sintered tantalum powder that show the anode morphology [14].](image)

2.1.1 Anodic Oxidation

For capacitor devices, the tantalum oxide must be uniform, stable, and thicker than the native oxide present on tantalum metal [15]. To grow amorphous oxides to thicknesses ranging from nanometers to micrometers, electrochemical techniques have been employed. To form an anodic oxide, an anode (tantalum metal) and cathode (e.g. platinum metal) are submersed in a conducting electrolyte, in which a bias is applied between these two electrodes [1]. Oxidation reactions occur at the anode and reduction processes occur at the cathode [1]. With the application of the bias, an electric field forms across the oxide that causes the oxide to grow as the tantalum and oxygen atoms migrate [1, 16].

2.1.2 Permittivity of Anodic Tantalum

The permittivity of anodic tantalum oxides depends on the formation conditions and has been reported at values ranging from 18 to 28 [17-20]. The large range in the relative permittivity
of the material is due to the growth conditions and electrolyte of the anodic oxide, as shown in Table 2-1. However, other processing steps can also affect the permittivity. When anodized films are annealed to temperatures greater than 200 °C, there is an increase in the capacitance and resistance measurements [21]. It has been postulated that this is due to the Ta metal substrate taking oxygen from the adjacent oxide creating an oxygen gradient through the dielectric. If the films are re-anodized, the dielectric properties, except for the permittivity of the material, are restored to the original values prior the annealing [21]. It was observed that the permittivity is slightly increased from the annealing step and is due to an increase in the medium range order and crystallinity of the material [21]. Another factor in determining the value of the permittivity of the material is its stoichiometry. If the oxide is sub-stoichiometric, the permittivity of the material will be lower than the permittivity of stoichiometric Ta$_2$O$_5$ [17].

The value of the permittivity is also affected by the presence of an incorporated species into the dielectric film during anodization. For incorporated phosphorus, the dielectric constants were inferred from wet capacitance measurements and are recorded in Table 2-2, where the inner layer (that lacks the phosphorous incorporation) was assumed to have a permittivity of 27.6 [22]. It was found that the permittivity of the material is lower when phosphorous is present in the oxide [22]; likewise, the permittivity decreases with increasing concentration of phosphoric acid used in the electrolytic solution [22].

**Table 2-1: Relative permittivity for various formation conditions of anodic tantalum oxide.**

<table>
<thead>
<tr>
<th>Permittivity</th>
<th>Electrolyte</th>
<th>Other Formation Conditions</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.2 ± 0.7</td>
<td>0.01% citric acid</td>
<td>1 mA/cm$^2$, hold 1 hour, 1 kHz, on sputtered Ta</td>
<td>[23]</td>
</tr>
<tr>
<td>24.7</td>
<td>0.01% citric acid</td>
<td>1.5 mA/cm$^2$</td>
<td>[24]</td>
</tr>
<tr>
<td>18.5</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.7 mA/cm$^2$, 25 °C, thickness &lt;18.5 nm</td>
<td>[17]</td>
</tr>
<tr>
<td>27.5</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.7 mA/cm$^2$, 25 °C, thickness &gt;18.5 nm</td>
<td>[17]</td>
</tr>
<tr>
<td>28.2 ± 0.9</td>
<td>0.06 wt% H$_3$PO$_4$</td>
<td>20 °C</td>
<td>[25]</td>
</tr>
</tbody>
</table>
Table 2-2: Variation in the relative permittivity of anodic tantalum oxide due to incorporated phosphorus [22].

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Fraction of Film with Incorporated Phosphorus</th>
<th>Permittivity of Non-Phosphorus Incorporated Layer</th>
<th>Permittivity of Phosphorus Incorporated Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M H₂SO₄</td>
<td>NA</td>
<td>27.6</td>
<td>NA</td>
</tr>
<tr>
<td>0.001 M H₃PO₄</td>
<td>0.48</td>
<td>26.7</td>
<td>25.9</td>
</tr>
<tr>
<td>0.01 M H₃PO₄</td>
<td>0.50</td>
<td>26.0</td>
<td>24.2</td>
</tr>
<tr>
<td>0.1 M H₃PO₄</td>
<td>0.49</td>
<td>24.0</td>
<td>21.3</td>
</tr>
<tr>
<td>1 M H₃PO₄</td>
<td>0.51</td>
<td>23.8</td>
<td>20.3</td>
</tr>
<tr>
<td>10 M H₃PO₄</td>
<td>NA</td>
<td>20.8</td>
<td>NA</td>
</tr>
<tr>
<td>14.7 M H₃PO₄</td>
<td>0.63</td>
<td>17.8</td>
<td>12.2</td>
</tr>
</tbody>
</table>

2.1.3 Growth of Anodic Tantalum

Depending on the electrolyte (species and concentration), temperature, and applied current density, the rate of oxide formation will vary. It is well known that for a given applied constant current density, the voltage is linear with time and the slope depends on the magnitude of the applied current density. It is also known that the anodic oxide can be grown uniformly and has a dielectric thickness that is linear with formation potential governed by:

\[ t = aV_f \]  

Equation 2

where \( V_f \) is the formation potential and the proportionality constant \( a \) is termed the anodization constant [1, 17, 18].

Commonly in industry anodic oxide formation is done in an aqueous or aqueous/ethylene glycol mixture in combination with phosphoric acid to form the electrolyte [4, 15, 26, 27]. There are several reasons for these choices in electrolyte. Phosphoric acid is used due to the greater
thermal stability of the resulting oxide that is associated with the incorporated phosphate in the formed oxide [4, 15, 26]. The incorporation of phosphorous in the dielectric material limits diffusion of the oxygen from the solution into the tantalum metal, increases the oxide film dielectric strength at elevated temperatures, and encourages the formation of a flaw free, uniform (even over portions of underlying damaged Ta bodies) anodic layer [4, 15, 26].

Temperature during formation is important for several reasons: 1. It is well known that the temperature of formation will increase the growth rate [28], and 2. An oxide that is grown at a fast rate will consequently create heat due to the reaction that does not dissipate causing the oxidation temperature to be significantly higher. Torrisi did a study on tantalum foils where oxides were anodized from 5 to 500 V and at temperatures ranging from 0 to 200 °C to determine a correlation of thickness with voltage and temperature [28]. It was determined that for foils anodized at increasing temperatures with a fixed voltage, the oxide thickness increased [28]. During oxide growth both oxygen and tantalum ions move, allowing for oxide formation to occur at both the metal-oxide and oxide-electrolyte interfaces. Marker experiments have shown that the oxygen ion current contributes to about 75% of the total oxide growth, where the oxide growth is dependent on both anodization temperature and current [29, 30]. Therefore, an increase in the anodization temperature increases the oxygen ion migration, which causes the thickness of the anodic oxide to increase.

During formation the applied current density can be a determining factor in the total oxide thickness and in generating excess heat that does not dissipate [1]. When choosing how much current density to apply during formation, one must consider how much current can be passed through the oxide safely without over heating the system. By increasing the temperature during oxide growth, the probability of breakdown due to Joule heating increases and can ultimately cause crystallization of the amorphous oxide, which in turn will increase the materials conductivity and decrease its breakdown voltage.
2.1.4 Anodization Constants

The anodization constant, from Equation 2-2, is the thickness of oxide formed per applied volt. As discussed above, the anodization constant is dependent on several parameters including: temperature, electrolyte type and concentration, growth rate, and length of time held at formation voltage. Thus, the value of this constant is only constant for a specified anodization procedure.

Various anodization constants and their experimental growth conditions are listed in Table 2-3.

<table>
<thead>
<tr>
<th>Anodization Constant (a) (nm/V)</th>
<th>Electrolyte</th>
<th>Growth Rate/Formation Voltage</th>
<th>Temperature (°C)</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>[18]</td>
</tr>
<tr>
<td>1.84</td>
<td>Held for 20 hours, corrected for surface roughness</td>
<td></td>
<td></td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>1.87</td>
<td></td>
<td></td>
<td>85</td>
<td></td>
<td>[25, 32]</td>
</tr>
<tr>
<td>1.62</td>
<td></td>
<td>1mA/cm²</td>
<td>25</td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>1.73±0.03</td>
<td>0.06wt% H₃PO₄</td>
<td>45µA/cm²</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[25]</td>
</tr>
<tr>
<td>2.02±0.10</td>
<td>0.06wt% H₃PO₄</td>
<td>45µA/cm²</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[25]</td>
</tr>
<tr>
<td>1.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[1]</td>
</tr>
<tr>
<td>1.78</td>
<td>0.06wt% H₃PO₄</td>
<td>100mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.76</td>
<td>0.06wt% H₃PO₄</td>
<td>10mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.87</td>
<td>0.06wt% H₃PO₄</td>
<td>1mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.91</td>
<td>0.06wt% H₃PO₄</td>
<td>0.1mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>2.21</td>
<td>0.06wt% H₃PO₄</td>
<td>45µA/cm² to 100V</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>2.45</td>
<td>0.06wt% H₃PO₄</td>
<td>45µA/cm² to 100V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.67</td>
<td>0.06wt% H₃PO₄</td>
<td>5mA/cm² to 150V</td>
<td>20</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.84</td>
<td>0.06wt% H₃PO₄</td>
<td>5mA/cm² to 150V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[32]</td>
</tr>
<tr>
<td>1.29</td>
<td>0.5M H₂SO₄</td>
<td>0.7mA/cm²</td>
<td>25</td>
<td>Impedance</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Table 2-3: Anodization constants for anodic tantalum oxide formed under various conditions.
### Table

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Concentration</th>
<th>Current Density</th>
<th>Time (s)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.17</td>
<td>0.06wt% H₃PO₄</td>
<td>0.01mA/cm² to 100V</td>
<td>85</td>
<td>Microtomed TEM</td>
<td>[34]</td>
</tr>
<tr>
<td>1.61±0.01</td>
<td>0.1M H₃PO₄</td>
<td>70 V for 2 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.83±0.01</td>
<td>0.1M H₃PO₄</td>
<td>70 V for 60 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.85±0.01</td>
<td>0.1M H₃PO₄</td>
<td>70 V for 90 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>2.13±0.01</td>
<td>0.1M H₃PO₄</td>
<td>70 V for 6135 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.83±0.01</td>
<td>0.1M Na₂SO₄</td>
<td>70 V for 2 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.90±0.01</td>
<td>0.1M H₃PO₄</td>
<td>50 V for 60 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.88±0.07</td>
<td>0.1M H₃PO₄</td>
<td>13.2 V for 60 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.9±0.01</td>
<td>0.1M H₃PO₄</td>
<td>6.2 V for 60 seconds</td>
<td>25</td>
<td>Microtomed TEM</td>
<td>[14]</td>
</tr>
<tr>
<td>1.83±0.04</td>
<td>0.1M H₃PO₄</td>
<td>20-100V for 50 minutes</td>
<td>25</td>
<td>Infared Spectroscopy</td>
<td>[14]</td>
</tr>
<tr>
<td>2.3</td>
<td>0.1wt% H₃PO₄</td>
<td>2-12V for 3-5.5 hours</td>
<td>80</td>
<td>Microtomed TEM</td>
<td>[5]</td>
</tr>
</tbody>
</table>

#### 2.1.5 Native Oxide

When a metal is exposed to air, it is unstable and thermodynamically prefers to form a metal-oxide layer on the metal’s surface [1]. This occurs by most metal’s tendency to form cations through electron loss, allowing a reaction with oxygen (or nitrogen) in air to form an oxide. While many metals are inclined to oxidize, some metals, like palladium, platinum, and gold, do not react with the atmosphere at all. For metals when it is thermodynamically unfavorable for passive oxide formation, the d-bands of the electronic structure are filled and/or the d-bands cross the Fermi level. For metals like aluminum, titanium, and tantalum, the oxide formed at the metal-atmosphere interface is protective, allowing for the principal metal to retain its integrity, preventing the environment from further reactions with the metal [1, 18]. This layer is called either the passive layer or “native oxide” layer. This very thin (usually on the order of
10’s of atoms or a few nanometers thick) passive layer allows for metals like tantalum to be widely used for the protection of equipment in very corrosive environments [1].

For tantalum metal, there is a clear distinction between the amorphous native oxide and the crystalline tantalum metal as shown in Figure 2-2. It is well known that a native oxide with a thickness of 1.8 to 3.5 nm is present on the tantalum anode prior to anodization [5, 17, 18, 35, 36] and is independent of initial tantalum particle size [5].

Figure 2-2: TEM cross-section of the amorphous tantalum oxide and crystalline tantalum metal interface [5].

To study the effect of subsequent electrochemical anodization on the initial native oxide, the oxygen mobility of $^{16}$O and $^{18}$O isotopes has been studied [30, 36, 37]. When the initial anodization is performed in an $^{18}$O electrolyte, a thin layer (on the order of nanometers) of $^{16}$O oxide (native oxide) is observed at the metal/oxide interface [36, 38]. This implies that the oxygen atoms of the native oxide never leave their position at the metal/oxide interface. Thus, the $^{18}$O atoms must be added at either the oxide/electrolyte interface or in the native oxide/anodic oxide interface.

The anodic oxide growth law is modified from Equation 2-2 to account for the thickness of the native oxide:
where $t_0$ is the native oxide thickness [5, 18]. Various native oxide thicknesses and their substrates are listed in Table 2-4.

**Table 2-4: Native oxide thicknesses present at the Ta metal/oxide interface.**

<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>[14]</td>
</tr>
<tr>
<td>2.3</td>
<td>L vs. V intercept, TEM</td>
<td>Sputtered</td>
<td>[25]</td>
</tr>
<tr>
<td>0.8</td>
<td>L vs. V intercept, TEM</td>
<td>Sputtered</td>
<td>[25]</td>
</tr>
<tr>
<td>3.5</td>
<td>$^{18}$O,$\alpha$ spectroscopy</td>
<td>Chemically polished</td>
<td>[38]</td>
</tr>
<tr>
<td>2.0</td>
<td>Wet capacitance</td>
<td>Polished w/ jeweler’s rouge</td>
<td>[35]</td>
</tr>
<tr>
<td>1.8-2.0</td>
<td>Extrapolation of $1/C$ vs. $V$ plot</td>
<td>Chemically polished</td>
<td>[18]</td>
</tr>
<tr>
<td>1.5</td>
<td>XPS</td>
<td>Chemically polished</td>
<td>[17]</td>
</tr>
<tr>
<td>3.3±0.5</td>
<td>L vs. V intercept, TEM</td>
<td>Sintered Ta</td>
<td>[5]</td>
</tr>
</tbody>
</table>

The effect of the native oxide on anodization has been studied by Kerrec, et al., where it was found that the dielectric properties of thin anodic oxides (formation voltages $< 15.2$ V) are different than thick anodic oxides (formation voltages $> 15.2$ V) [17]. The dielectric constant for thin oxides was found to be 18.5, however for thick oxides the dielectric constant was determined to be 27.5 [17]. The difference in dielectric properties is due to the presence and influence of the native oxide, which has been found to be sub-stoichometric with a lower permittivity [17]. For thin oxides (formation voltage $< 15.2$ V), the native oxide makes up a larger percentage of the overall oxide film, which lowers the overall permittivity of the film [17]. Macagno and Schultze also studied electrolytic tantalum oxide formed at low formation voltages (thin oxide films), where they determined that for thin films ($t < 8$ nm), the oxide behaved similarly to an n-type semiconductor due to the incorporation of the native oxide, where the donor density was very high and exhibited Mott-Schottky behavior at negative potentials ($E < 0$ V) [18]. However, thicker oxides ($t > 10$ nm) exhibited characteristics of pure insulating dielectrics since the donor density
decreases with increasing film thickness [18]. For thin films, it is very important to consider the space charge within the n-type semiconductor, which for thicker films, can be neglected [18]. The presence of a native oxide influences the dielectric and electrical properties of the anodic oxide since anodic oxides formed at low formation voltages are thinner and the native oxide comprises a higher percentage of the total oxide.

Using X-ray photoelectron spectroscopy (XPS), Kerrec et al. determined that for anodic oxide thinner than 15 nm, there was the presence of sub-stoichiometric oxides in the thin layers of TaOₓ (the (II) and (V) oxidation states of tantalum) [17]. This determined that post anodization the tantalum oxide film is heterogeneous, where a tantalum monoxide (TaO) layer is present between the tantalum metal and the outer anodic tantalum pentoxide (Ta₂O₅) layer [17]. For thick anodic oxides, although the films were mainly composed of tantalum pentoxide, they still contained a small amount of the sub-oxide (not more than 3 mol %) [17]. Even after anodization, the native oxide was found to be between the Ta and Ta₂O₅ layers [39]. It has been suggested that the initial presence of a native oxide after anodization produces an oxide with high leakage current due to the increased conductivity associated with the native oxide [40].

2.2 D.C. Leakage and Conduction Mechanisms in Anodic Tantalum

The basic conduction mechanisms of Ta₂O₅ films are controlled by the material’s composition, including the point defect concentration, and affect the leakage current and thermal stability [41, 42]. The leakage current density and conduction mechanism of these films are very sensitive to the material’s imperfections, including oxygen vacancies, impurities, or the crystallization of amorphous Ta₂O₅ [43-45]. On average, common values for the D.C. leakage current for anodic tantalum films are found to create a hysteresis on the order of 10⁻⁷ to 10⁻¹² A/cm² at fields measured from -2.5 MV/cm, to +2.5 MV/cm, and back to -2.5 MV/cm [20],
however a detailed list of recorded leakage current mechanisms for films grown under different conditions are listed in Table 2-5. From the table it is apparent that the conduction mechanism depends on the process and conditions in which the oxide is formed. The conduction mechanism for tantalum electrolytic capacitors is not accurately described by one mechanism, but a combination of multiple mechanisms to represent the transient and steady state leakage current [44].

**Table 2-5: Conduction mechanisms reported for tantalum oxide.**

<table>
<thead>
<tr>
<th>Oxide Thickness (nm)</th>
<th>Growth Method</th>
<th>Conduction Mechanism</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;85</td>
<td>Plasma-enhanced CVD</td>
<td>Trap-limited Poole-Frenkel</td>
<td>[46]</td>
</tr>
<tr>
<td>50</td>
<td>Sputter Ta, thermal oxide</td>
<td>Poole-Frenkel</td>
<td>[47]</td>
</tr>
<tr>
<td>20-220</td>
<td>Rf sputtered</td>
<td>Modified Poole-Frenkel (bulk limited)</td>
<td>[48]</td>
</tr>
<tr>
<td>60-1350</td>
<td>Rf sputtered</td>
<td>High field condition: Bulk limited</td>
<td>[48]</td>
</tr>
<tr>
<td>60-1350</td>
<td>Rf sputtered</td>
<td>Low voltage condition: electrode limited Modified Field Emission</td>
<td>[48]</td>
</tr>
<tr>
<td>10-30</td>
<td>Reactive rf sputtered</td>
<td>Poole-Frenkel</td>
<td>[49]</td>
</tr>
<tr>
<td>4-9</td>
<td>Anodized, 0.5% H₂SO₄, 100 μA/cm²</td>
<td>Electron Tunneling, Fowler Nordheim (anodic direction)</td>
<td>[50]</td>
</tr>
<tr>
<td>4-9</td>
<td>Anodized, 0.5% H₂SO₄, 100 μA/cm², In or Au cathode</td>
<td>Schottky emission (cathodic direction)</td>
<td>[50]</td>
</tr>
<tr>
<td>22</td>
<td>Anodized</td>
<td>Defect enhanced tunneling</td>
<td>[51]</td>
</tr>
<tr>
<td>120</td>
<td>Anodized, 0.01M citric acid, ~2.0 mA/cm², Pt cathode</td>
<td>Schottky</td>
<td>[20]</td>
</tr>
<tr>
<td>40</td>
<td>Anodized, model MIM structure</td>
<td>Schottky at low voltages, Poole-Frenkel at high voltages</td>
<td>[44]</td>
</tr>
<tr>
<td>32</td>
<td>Anodized, Au and Pt cathode</td>
<td>Schottky at low voltages, Poole-Frenkel at high voltages</td>
<td>[52]</td>
</tr>
<tr>
<td>10-20</td>
<td>Sputter Ta, anodized in 1% Na₂SO₄</td>
<td>Schottky</td>
<td>[53]</td>
</tr>
<tr>
<td>15-40</td>
<td>Rapid thermal Annealing, T₀v=400°C, t= 15 s</td>
<td>Poole-Frenkel</td>
<td>[54]</td>
</tr>
<tr>
<td>40</td>
<td>Rapid thermal Annealing, T₀v=400°C, t= 30 s</td>
<td>Schottky</td>
<td>[54]</td>
</tr>
<tr>
<td>15-40</td>
<td>Rapid thermal Annealing, T₀v=500°C, t= 15 s</td>
<td>Poole-Frenkel</td>
<td>[54]</td>
</tr>
<tr>
<td>15-40</td>
<td>Rapid thermal Annealing, $T_{ox}=500°C$, $t=30$ s</td>
<td>Poole-Frenkel</td>
<td>[54]</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------</td>
<td>---------------</td>
<td>-----</td>
</tr>
<tr>
<td>15-40</td>
<td>Rapid thermal Annealing, $T_{ox}=550-600°C$, $t=15$ s</td>
<td>Schottky</td>
<td>[54]</td>
</tr>
<tr>
<td>15-40</td>
<td>Rapid thermal Annealing, $T_{ox}=550-600°C$, $t=30$ s</td>
<td>Poole-Frenkel</td>
<td>[54]</td>
</tr>
</tbody>
</table>

Most commonly, Schottky emission and Poole-Frenkel conduction are observed in anodic films [20, 44, 52, 55]. Schottky emission is observed for electrode-limiting current transport found at low applied voltages and the mechanism tends to switch from Schottky to Poole-Frenkel when the current transport becomes bulk-limited at higher applied voltages. More information regarding Schottky emission and Poole-Frenkel conduction will be discussed later in this thesis. From previous work done by Liu, the current-voltage (IV) measurements, as shown in Figure 2-3, were performed on electrolytic tantalum capacitors, consisting of Ta-Ta$_2$O$_5$-MnO$_2$ with a rated voltage of 44 V (an equivalent formation voltage of approximately 73 V) and tested at 100°C, to determine the leakage mechanisms present within the system [56]. It was found that the D.C. leakage mechanism at low fields was due to the interface controlled Schottky emission, however at approximately 36 V, the leakage mechanisms change at high fields to bulk controlled Poole-Frenkel conduction [56]. This work agrees well with what was modeled by Ramprasad for metal-insulator-metal (MIM) capacitors; during the transient region the conduction mechanism was described by trap assisted tunneling [44]. Upon reaching steady-state, for low voltages Schottky emission is observed and for higher voltages there is a switch to Poole-Frenkel conduction [44]. Other authors have observed a change in the conduction mechanism when going from low electric fields to high fields, including the work done by Mead who reported that the conduction mechanism switched from Ohmic to Poole-Frenkel conduction in Ta-Ta$_2$O$_5$-Au systems [52].
Figure 2-3: IV data for electrolytic tantalum capacitors where (A) the data is plotted to model the Schottky emission leakage mechanism and (B) is plotted to model the Poole-Frenkel conduction [56].

The conduction mechanism of the material controls the current transport within the material and how it contributes to the degradation of the dielectric. It is important to know the conduction mechanism of the material in order to predict how the current will change as a function of curvature depending on if the mechanism is a bulk or electrode-limiting process. Understanding how the conduction mechanism and likewise the leakage current behaves allows for the properties of the dielectric to be more predictable and more controllable when working to create high quality electrolytic capacitors with low leakage current and high thermal stability.

2.2.1 Effects of Curvature on the Leakage Current

The electric field is enhanced at areas of negative curvature and depleted at areas of positive curvature, as shown by Lacoste et al. in Figure 2-4 [57].
Figure 2-4: As the feature’s curvature fluctuates between positive and negative curvature, there is a shift in the diffuse charge and the tangential field (thick arrows) and the electric field has a higher density at areas of negative curvature and less dense at areas of positive curvature [57].

For electrode-limited leakage current conduction mechanisms, like Schottky emission, the current density is proportional to the electric field, where a field enhancement will similarly increase the localized leakage current. In previous work done by Zhang, the effects of curvature of porous silicon formed on n-type silicon via an anodic HF solution were investigated, where it was found that for pores with negative curvature, as the radius of curvature decreased (decreasing particle or pore size), the electric field on the surface is greatly increased [58]. A schematic of the silicon/electrolyte interface to demonstrate the feature’s curvature is shown in Figure 2-5.

Figure 2-5: (A) is a SEM micrograph of the individual pores that increase in size from the surface to the bulk, and (B) A schematic of the silicon/electrolyte interface of
spherical shape with \( r_0 \) representing the radius of curvature and \( x_d \) the width of the space charge layer [58].

It was found that the field strength increased when the radius of curvature was close to or smaller than the width of the space charge layer of a planar surface; the smaller the radius of curvature (i.e. smaller pore sizes), the smaller the space charge layer thickness, and the larger the electric field [58]. It was also determined that the radius of curvature was the determining factor for the reactions and current density of the pores, where the increase in curvature increases the number of energy levels for electron tunneling to occur [58]. Zhang reported that for a planar material the energy range for tunneling was 180 mV, however for features of curvature the energy range for tunneling was 470 mV [58]. Matsuo et al., studied the effects of curvature on the leakage current on oxide-nitride-oxide films, where it was found that there was an increase in leakage via the direct tunneling mechanism was due to rough surfaces or surfaces of varying curvature [59]. It was found that for concave (negative curvature) areas, the electric field concentration was enhanced at the electrode and caused an increase in the direct tunneling of electrons through the film [59]. Duffy et al., investigated the junction leakage of MOS transistors; it was found that the curvature of the junction significantly affects the electric field, where sharper or increased negative curvature leads to enhanced electric fields and thus increased current densities [60]. Duffy et al. determined that the increase in current density with reverse bias was due to the increase in the depletion layer width and an increase in local electric field [60].

Other work has been done by Levi et al., where depending on the heat treatment of Ni foils prior to BaTiO\(_3\) deposition, it was observed that pores in the dielectric were analogous to the profiles of the underlying Ni grain boundary grooves [6]. It was found that the pores had an effect on the leakage current of the device, where a reverse bias Schottky emission governs the current in areas where the Ni grain boundaries are absent [6]. However, in areas where the Ni grain boundaries were present, the barrier at the cathode became ineffective causing a larger leakage.
current to dominate by the forward biased Schottky barrier at the anode [6]. It was proposed that the curvature of the Ni grain boundary causes electric field enhancement across the metal/ceramic interface as shown in Figure 2-6 [6]. This reduces the barrier height of the reverse Schottky barrier allowing electrons to flow from the cathode through the insulating film and then be blocked at the forward biased Schottky barrier at the anode [6].

![Figure 2-6: Local electric field enhancement shown by the ratio of local field and average field [6].](image)

As shown, for various electronic systems, there was electric field enhancement at concave (negative curvature) surfaces. Since the electric field and current density are usually directly related, it is logical to conclude that the increase in the localized electric field will likewise create an increase in the localized leakage current which in turn increases the probability of device failure.

2.3 Dielectric Breakdown

Dielectric materials degrade due to physical or chemical changes within the material, where in all cases, breakdown occurs when high enough fields are applied [41]. Some of the most important factors affecting breakdown strength include dielectric thickness, temperature, ambient atmosphere, electrode shape and composition, surface finish, field frequency and waveform, porosity, crystalline anisotropy, amorphous structure, and composition [61]. Specifically,
breakdown occurs when the thermal energy of the crystal lattice/electrons reaches a value upon application of an electric field so that the conductivity rapidly increases, leading to permanent damage of the material. Dielectric breakdown in electrolytic tantalum capacitors can occur mainly by two mechanisms, Joule heating (thermal breakdown) and avalanche breakdown [1, 16].

Thermal breakdown occurs when there is current flow through the dielectric resulting in heat generation, known as Joule heating. When the rate of heat dissipation is slower than the rate of heat generation, Joule heating causes the insulating resistance of the dielectric to decrease and allows for more current to flow through the material until breakdown occurs [62]. Electrical breakdown occurs when electrons are energized from the valence band to the conduction band, causing a pathway for current to flow through the material. The avalanche effect happens when electrons are accelerated by an applied electric field, which provides them with enough energy to ionize atoms and produce more electrons [1]. Each time electrons are produced, they continue to multiply creating this avalanche effect [1].

As discussed in the previous section, the curvature of the Ta anode is expected to have a profound effect on the nature of the localized electric field. The electric field affects the probability of electron injection at the cathode into the dielectric material, which leads to the facilitation of dielectric breakdown. However, breakdown is predominantly due to the thickness of the film and the electric field has a minimal effect. It has been found that several breakdown processes are thickness dependent; for thin films the breakdown strength is proportional to the reciprocal of the square root of the dielectric thickness ($E_B \propto t^{-1/2}$) for both thermal and avalanche breakdown [62].

According to Paskaleva, et al. the breakdown electric field for amorphous films is the average applied electric field at which the current density through the dielectric exceeds $4 \times 10^{-4}$ A/cm$^2$ [43]. Avalanche breakdown occurs at relatively low temperatures and in short times. In general, the electrical breakdown strength for Ta$_2$O$_5$ films is found to be between $1 \times 10^6$ and $8 \times$
Kadary and Klein observed breakdown on oxide films when the oxide was grown via an electrolytic solution with a Cr-Au cathode contact on sputtered tantalum [63]. It was found that the rate of breakdown increased exponentially with applied field and the breakdown field was observed to be between 6.1 to 6.7 MV/cm [63]. These values are comparable to what was reported by Burn and Smith where the breakdown field was found to be 5 MV/cm, as shown in Figure 2-7, which compares the energy density, breakdown field and dielectric constant for various energy storage materials [64].

![Graph: Comparison of energy density, breakdown field strength, and dielectric constant for various energy storage materials](image)

**Figure 2-7:** Comparison of energy density, breakdown field strength, and dielectric constant for various energy storage materials [64].
Chapter 3

Modeling the Contribution of the Native Oxide on the Specific Capacitance of Low Formation Voltage Anodic Tantalum Oxide [5]

3.1 Introduction

With the miniaturization of electronics, there is a continual demand for components to have greater capacitance per volume ($CV/g$). To increase the capacitance, either the insulating material must have an increased surface area and/or there must be a decrease in the dielectric thickness. Therefore, to achieve greater capacitance, capacitors must be made with either tantalum anodes with smaller particle sizes and/or oxides grown at lower formation voltages, which correspond to thinner oxides.

The $CV/g$ for electrolytic tantalum capacitors is expected to remain at a constant value regardless of formation voltage (assuming there is no change in permittivity, thickness, and weight or volume of the dielectric material). Industry has found evidence of % $CV/g$ loss with decreasing formation voltage (below approximately 12 V) [8, 10]. Freeman, et al., found that the $CV/g$ decreases with decreasing formation voltage regardless of particle size and the absolute value of the low voltage % $CV/g$ loss is higher for the smaller particle powder anodes [5]. At the same time, the percentage % $CV/g$ loss is practically identical for these two Ta powders [5]. The % $CV/g$ loss is a relatively new issue that materialized from the reduction in the operating voltage of some digital electronic devices and the use of ultrafine Ta powders, which can only be used in conjunction with low formation voltages [5].
3.2 Objectives

This research is motivated by the need to understand the impact of low formation voltage dielectrics and high surface area powders on the electrical properties of electrolytic tantalum capacitors. A model was developed that explains the low voltage % CV/g loss (which was compared to experimental data from Kemet Corporation).

3.3 Model for Electrical Properties of Anodic Tantalum

The model for the electrical properties of electrolytic Ta capacitors was based on cylindrical shaped features, composed of both positive (convex) and negative (concave) curvatures and asymmetric electrodes, as shown in Figure 3-1, where the reference state for the definition of curvature is defined at the cathode – oxide interface.

Figure 3-1: Schematic of positive (A) and negative (B) curvature features used in modeling the electrical properties of anodic Ta, where: $R_0$ is the distance to the initial Ta anode, $R_1$ is the distance to the Ta anode-oxide interface after the Ta is consumed during anodization, $R_2$ is the distance to the oxide-cathode interface, $t$ is the total Ta$_2$O$_5$ oxide thickness, and $r$ is the Ta consumed during oxide formation.

Curvature, $\kappa$, is defined as the change in surface area over the change in volume ($dA/dV$); in a cylindrical coordinate system, the curvature is represented by,
where \( r \) is the radius of the cylinder and \( h \) is the cylinder length.

### 3.4 Specific Charge \((CV/g)\)

An idealized model was developed to describe the scaling behavior of \( CV/g \) with particle size. The model was based on cylindrical features, as shown in Figure 3-1. The cylindrical model was chosen because it best represents the geometry of near-spherical particles once they are sintered together.

The total capacitance through the dielectric can be considered a series of capacitors, and thus can be written in integral form,

\[
\frac{1}{C_{\text{tot}}} = \int_{R_i}^{R_f} \frac{1}{dC} = \int_{R_i}^{R_f} \frac{dr}{2\pi r h \varepsilon_0 \varepsilon_r}
\]

**Equation 5**

Thus, the total capacitance is,

\[
C_{\text{tot}} = \frac{2\pi h \varepsilon_0 \varepsilon_r}{\ln \left( \frac{R_f}{R_i} \right)}
\]

**Equation 6**

To determine how the capacitance varies as a function of the formation voltage (dielectric thickness), the terms \( R_f = R_i + t \) and \( R_i = R_i' - 0.408t \) are substituted into the equation for the total capacitance as described in Equation 3-3, where the \( \text{Ta}_2\text{O}_5 \) thickness is governed by the anodization voltage according to Equation 2-3. The 0.408 prefactor accounts for the molar volume change upon anodization.

The specific charge \((CV/g)\) can then be defined as,
where $\rho$ is the density of Ta. This equation provides the $CV/g$ scaling as a function of the particle size. For constant anodization voltage, $CV/g$ increases as the particle size decreases as shown in Figure 3-2, which is a result of the surface area per volume increase with decreasing particle size.

The experimental $CV/g$ data for particle sizes 0.9 and 2.7 µm, shown in Figure 3-2, are lower than the values predicted by the ideal model due to the model’s assumption that the features are perfect, separated cylinders. In commercial powders there is a distribution of particle sizes and a significant loss in surface area as the powders are sintered into a solid body [5].

\[
\frac{CV}{g} = \frac{2\varepsilon_r \varepsilon_0 V_f}{\rho R_i^2 \ln \left[ 1 + \frac{(aV_f + t_0)}{R_0 - 0.408(aV_f + t_0)} \right]}
\]

Equation 7

Figure 3-2: Capacitance scaling ($CV/g$) as a function of particle size. Line predicted from Equation 3-4, where the $V_f = 12$ V, and points are experimental data from Figure 1-1 [5], where the solid circles are experimental data taken by Freeman et al. and the solid line was modeled in this work [5].

The $CV/g$ behavior as a function of formation voltage is plotted in Figure 3-3, where the results are qualitatively consistent with what is observed experimentally over the range of $0 - 12$ V. As shown in Figure 3-3, as the formation voltage decreases (in turn decreasing the oxide thickness), there is a decrease in the $CV/g$. In comparing the model to the experimental data there is a greater decrease in the absolute value for the smaller particle size (0.9 µm). Again there is an
offset between the experimental and theoretical values due to the surface area loss during sintering of the powders [5].

![Graph](image)

Figure 3-3: CV/g as a function of formation voltage, where the smaller primary size is 0.9 µm and the larger primary particle size is 2.7 µm. The maximum in the CV/g for the small and large particle sizes excluding necking defects are shown on the left of the plot, where the solid squares and solid circles are experimental data taken by Freeman et al. and the dotted lines were modeled in this work [5].

For the larger particle size anodes, the experimental CV/g asymptotically approaches a value of approximately 40,000 µCV/g, where for the smaller particle size anodes, experimentally there is a maximum in the CV/g at around 12 V. At formation voltages greater than 12 V, the high formation voltage CV/g mechanisms begin to dominate, which include the complete anodization through some of the interparticle necks and the closure of pores by the oxide [11, 12]. The idealized, cylindrical model does not incorporate these mechanisms and are thus not observed in the calculations at higher formation voltages. These results of the experimental data emphasize that the particle morphology control becomes extremely important in smaller particle size powders to prevent high formation voltage % CV/g loss [5].

The % CV/g loss relative to the CV/g at 12 V (prior to the onset of high formation voltage losses) is plotted in Figure 3-4. The percentage loss in CV/g clearly highlights the scaling effect because the relative loss is nearly independent of the particle size. The % CV/g loss is slightly
higher in the experimental data compared to the theoretical model, where the differences may arise from the geometric ideality of the theoretical model. However, the model captures the overall trends of the % CV/g losses.

Figure 3-4: % CV/g loss, where the thickness includes the native oxide thickness, for the 2.7 and 0.9 µm capacitors as a function of formation voltage, where the solid squares and solid circles are experimental data taken by Freeman et al. and the dotted lines were modeled in this work [5].

Further analysis of Equation 3-8 shows that the CV/g roll-off is very sensitive to the value of \( t_0 \). In Figure 3-5, the CV/g is constant for \( t_0 = 0 \) and the low voltage CV/g roll-off increases with increasing values of \( t_0 \). Although it would be tempting to conclude from Figure 3-5 that varying the native or thermal oxide thickness can control the low formation voltage CV/g roll-off, this, however, is not the case. As shown by Freeman, et al., when the initial oxide was made thicker via thermal oxidation, the growth of the anodic oxide converged to that predicted by Equation 2-4 upon exceeding the initial thermal oxide thickness [5]. This suggests that the \( t_0 \) in Equation 2-4 corresponding to the zero-V thickness, is a constant for a given anodization condition and that the growth law cannot be changed by simply varying the initial oxide thickness [5].
Figure 3-5: CV/g as a function of formation voltage with varying $t_0$ in Equation 3-8 for an initial particle size of 0.9 µm.

3.5 Conclusions

It was shown that the geometrical model for capacitance qualitatively explains the low voltage % CV/g loss, and agrees well with the experimental data observed and provided by Kemet Corporation. The model was useful to quantitatively predict the capacitance per volume increase with decreasing particle size. It was found that the $CV/g$ decreases with decreasing formation voltage due to the presence of the native oxide thickness (which corresponds to the zero formation voltage) becoming a more significant fraction of the total dielectric thickness. Also, since the native oxide thickness is independent of tantalum particle size, the percentage of % CV/g loss is almost independent of the initial tantalum particle size, although the absolute losses are greater for smaller particle sizes.
Chapter 4

Modeling the Effects of Curvature on the D.C. Leakage and Breakdown of Anodic Tantalum Oxide

4.1 Introduction

It has been commonly accepted that the leakage mechanisms that dominate in electrolytic tantalum capacitors are not due to simply one mechanism, but are commonly the combination of multiple mechanisms to accurately describe the transient and steady-state leakage current [44, 52, 55]. Most commonly, Schottky emission and Poole-Frenkel conduction are observed [20, 44, 52, 55]. In identifying the relevant conduction mechanisms, information about the underlying transport mechanisms responsible for D.C. leakage and correlations between the leakage mechanism and the degradation of the dielectric can be determined. This allows for the dielectric properties to be more predictable and controllable to create high quality electrolytic capacitors with low leakage and thermal stability.

It is also known that for thinner dielectrics, the D.C. leakage current increases [65]. The increase % CV/g loss and D.C. leakage current at low formation voltage dielectrics is a major restriction on the miniaturization of Ta capacitors.

4.2 Objectives

This research is motivated by the need to understand the D.C. leakage of electrolytic tantalum capacitors. To do this, the effect of the Ta powder particles’ curvature on the localized electric field was investigated. A model was developed to predict the effects of particle curvature on Schottky emission and Poole-Frenkel conduction mechanisms compared to planar features.
4.3 Model for Electrical Properties of Anodic Tantalum

The model for the electrical properties of electrolytic Ta capacitors was again based on cylindrical shaped features, composed of both positive and negative curvatures and asymmetric electrodes, as shown in Figure 3-1.

4.3.1 Electric Field Distribution of Features with Curvature

In order to derive the electric field as a function of curvature for such cylindrical features, a combination of Gauss’s Law and Maxwell’s equations can be defined as,

\[ \Phi = \int E \cdot dA = \frac{Q_{enc}}{\varepsilon_0 \varepsilon_r A} \]

Equation 8

where \( \Phi \) is the electric flux, \( E \) is the electric field, \( A \) is the area, \( Q_{enc} \) is the charge enclosed in the Gaussian surface, \( \varepsilon_0 \) is the permittivity of free space, and \( \varepsilon_r \) is the dielectric permittivity of the oxide material. The charge enclosed for a dielectric material is equivalent to

\[ Q_{enc} = C_{tot} V_{app} \]

Equation 9

where \( C_{tot} \) is the total capacitance and \( V_{app} \) is the applied voltage. After rearranging Equation 4-2 and simplifying for a cylindrical shaped capacitor, the electric field as a function of radius is,

\[ E(r) = \frac{Q_{enc}}{\varepsilon_0 \varepsilon_r A} = \frac{C_{tot} V_{app}}{\varepsilon_0 \varepsilon_r (2\pi rh)} \]

Equation 10
After substituting the equation for the total capacitance, Equation 3-3, into Equation 4-3, the electric field distribution as a function of curvature for a cylindrical capacitor is given as

\[ E(r) = \frac{V_{\text{app}}}{r} \frac{1}{\ln\left(\frac{R_2}{R_1}\right)} \]

Equation 11

The electric field for the planar substrate, \( E^0 \), can be defined from Equation 4-4 as,

\[ E^0 = \frac{V_{\text{app}}}{R_2 - R_1} \]

Equation 12

When the electric field is plotted as a function of position inside the dielectric material, \( r \), Figure 4-1, there is electric field enhancement at the anode and depletion at the cathode for Ta features with positive curvature. Figure 4-2 shows that there is electric field depletion at the anode and enhancement at the cathode for features of negative curvature. In both cases, the electric field decays by \( 1/r \) through the dielectric.

![Figure 4-1: Electric field distribution through the dielectric for a planar substrate and at various radii of curvature, anodes of positive curvature with an initial radius \( (R_0) \) of 1.0 µm, 1.5 µm, and 2.0 µm, where \( V_f = 12 \) V.](image-url)
4.3.2 Effects of Curvature on Leakage Current Mechanisms

4.3.2.1 Schottky Emission

The electrode that controls conduction in the system can be determined by considering the band diagrams for the Ta-Ta$_2$O$_5$-cathode structure under zero bias and under an applied bias that causes band bending, as shown in Figure 4-3, where the band gap for Ta$_2$O$_5$ is 4.5 eV [66], the electron affinity for Ta$_2$O$_5$ is 3.2 eV [67], the band gap for MnO$_2$ is 0.58 to 0.7 eV [68], the electron affinity for MnO$_2$ is 2.06 to 3.03 eV [69], and the work function for Ta is 4.1 eV [66]. It is known that the greater the applied voltage, the greater the band bending. In the Ta-Ta$_2$O$_5$-cathode system, where the system is composed of a positively charged tantalum metal and a negatively charged cathode (n-type MnO$_2$), the charge travels from the cathode to the dielectric creating a forward biased Schottky barrier at the cathode. The Ta-Ta$_2$O$_5$ interface creates an ohmic-like contact that does not play a critical role in the current transport [44]. Whereas the
Ta$_2$O$_5$-cathode interface is the dominant interface in controlling the current transport due to the presence of Fermi-level electrons in the cathode that can move into the conduction band of the dielectric [44]. The barrier height is defined as the potential difference between the Fermi energy of the metal and the band edge where the majority carriers reside. Therefore, for an n-type semiconductor, the barrier height can be expressed as,

$$\phi_B = \phi_m - \chi$$

where $\phi_m$ is the work function of the metal and $\chi$ is the electron affinity [42].

Figure 4-3: Band diagram for the Ta-Ta$_2$O$_5$-MnO$_2$ structure with (A) no applied bias and (B) a forward applied bias; $E_C$ is the conduction band energy, $E_V$ is the valence band energy, $E_F$ is the Fermi energy, $\phi_m$ is the metal work function, and $\phi_B$ is the barrier height [70].

When the leakage current is limited by a Schottky barrier at the electrode interface, the electric field enhancement (as described in Chapter 4.3.1) would increase the Schottky emission [42]. The electron emission occurs by applying an electric field to lower the potential barrier within the dielectric film, as shown by the schematic in Figure 4-4.
Figure 4-4: Schematic of the Schottky emission mechanism, where $E_F$ is the Fermi level energy, $E_C$ is the conduction band energy, $E_V$ is the valence band energy, and $\phi_B$ is the barrier height [70].

The current density in Schottky emission is controlled by an electrode-limited process and is given by the Schottky-Richardson relations:

\[
J_s = \Lambda T^2 \exp\left(\frac{-\phi_B}{k_BT}\right) \exp\left(\frac{\beta_s}{k_BT} E^{1/2}\right)
\]  
\[\text{Equation 14}\]

where

\[
\Lambda = \frac{2qmk_s^2}{(2\pi)^2 h^3}
\]  
\[\text{Equation 15}\]

\[
\beta_s = \left(\frac{q^3}{4\pi\epsilon_0 K_T}\right)^{1/2}
\]  
\[\text{Equation 16}\]

where $\phi_B$ is the barrier height, $E$ is the applied electric field, $k_B$ is the Boltzmann constant, $h$ is Plank’s constant, $q$ is the electronic charge, $\epsilon_0$ is the permittivity of free space, and $K_T$ is the high-frequency dielectric constant of the insulator [48, 49, 55, 71].

In order to investigate how the curvature of the tantalum anodes will affect the Schottky emission in comparison to the planar case, the current density at the cathode for the Schottky emission as a function of curvature was normalized to the current density at the cathode of the Schottky emission for a planar substrate,
where $J_S(R_{\text{cathode}})$ is the Schottky emission as a function of curvature and $J_S^0$ is the Schottky emission for a planar substrate.

When the normalized current density for Schottky emission, Equation 4-8, is plotted as a function of curvature, Figure 4-5, there is a direct correlation between the electric field enhancements at the cathode to the Schottky current density.

![Figure 4-5: Normalized Schottky emission current density for features with both positive and negative curvature of the Ta; the solid line is the predicted model, the solid circles are at positive and negative ~0.9 µm, and the solid squares are at positive and negative ~2.7 µm.](image)

As the radius of curvature becomes more negative, it is shown in Figure 4-1 that the electric field increases at the cathode, the Schottky leakage current also increases. For positively curved features, as the particle size decreases, Figure 4-1 shows that the electric field decreases at the cathode, the Schottky leakage current also decreases. There is Schottky leakage current enhancement at the cathode for negative curvature and leakage current depletion at the cathode for positive curvature relative to an equivalently biased planar capacitor. Thus, preferential leakage at necking sites between the sintered Ta particles is expected.
4.3.2.2 Poole-Frenkel Conduction

In Poole-Frenkel conduction, the leakage current is a bulk limited process, where the barrier of the localized states is lowered due to the field enhanced electron emission from donor centers, as shown in Figure 4-6 [42]. As previously discussed, the Ta metal has a native oxide layer composed of TaO_x that is incompletely oxidized tantalum. This layer creates the donor-like surface states, interface traps, and oxide charges that allows for Poole-Frenkel conduction to occur in the Ta-Ta_2O_5-cathode system [68].

![Figure 4-6: Schematic of Poole-Frenkel conduction, where $E_F$ is the Fermi level energy, $E_C$ is the conduction band energy, $E_V$ is the valence band energy, and $\phi_B$ is the energy levels of the trap [70].](image)

The equation for current density indicative of Poole-Frenkel conduction is represented by,

$$J_{PF} = \mu E \exp \left( \frac{-\phi_B}{2k_B T} \right) \exp \left( \frac{2\beta_{PF} E}{k_B T} \right)$$

Equation 18

where

$$\beta_{PF} = \left( \frac{q^2}{\pi \epsilon r K_T} \right)^{\frac{3}{2}}$$

Equation 19

where $\mu$ is the mobility of electrons in the dielectric [42, 44].

To determine how the anode curvature affects the bulk-limited Poole-Frenkel conduction process in comparison to the planar case, the current density throughout the entire dielectric
material must be taken into account. Thus, the average current density for the Poole-Frenkel effect as a function of curvature was normalized to the current density for the Poole-Frenkel effect for a planar substrate,

\[
\frac{\langle J_{PF}(r) \rangle}{J_{PF}^0} = \frac{\langle E(r) \rangle \exp \left( \frac{2B_{PF}}{k_B T} \sqrt{E(r)} \right)}{E^0 \exp \left( \frac{2B_{PF}}{k_B T} \sqrt{E^0} \right)}
\]

Equation 20

where \( \langle J_{PF}(r) \rangle \) is the average Poole-Frenkel current density as a function of curvature and \( J_{PF}^0 \) is the Poole-Frenkel current density for a planar substrate. The average electric field as a function of curvature, \( \langle E(r) \rangle \), can be defined from Equation 4-4 as,

\[
\langle E(r) \rangle = \frac{V_{app}}{R_s - R_i}
\]

Equation 21

and the electric field for the planar substrate, \( E^0 \), is the same as in Equation 4-5. It is important to note that the average electric field as a function of curvature is independent of curvature. The normalized current density for Poole-Frenkel conduction was plotted as a function of curvature, as shown in Figure 4-7. The result is a straight line regardless of positive or negative curvature, indicating that the Poole-Frenkel current density is constant throughout the dielectric.

![Figure 4-7: Normalized Average Poole-Frenkel current density plotted as a function of curvature.](image)

38
To further consider the bulk effects of the dielectric on the Poole-Frenkel current density, it is important to see how the increase in surface area per volume affects the current per volume,

$$\frac{I_{PF}}{\text{Volume}} = J_{PF} \left( \frac{\text{Surface Area}}{\text{Volume}} \right)$$

Equation 22

where $I_{PF}$ is the Poole-Frenkel current. It is known that a decrease in particle size increases the surface area per volume, as shown in Figure 4-8. Thus, when the Poole-Frenkel current per volume is plotted as a function of particle size, there is an increase in current per volume as the particle size decreases as shown in Figure 4-9. For a given volume, as the particle size decreases, the enhancement in the Poole-Frenkel current is only due to an increase in surface area.

![Figure 4-8: Surface area per volume plotted as a function of particle size.](image)
4.4 Conclusions

The model presented in this work helps provide insight into the effects of curvature on electric field distributions within the dielectric. Curvature is shown to lead to electric field depletion at the cathode for Ta features with positive curvature and electric field enhancement at the cathode for Ta features of negative curvature. The electric field decays by $1/r$ through the dielectric.

The proposed model was used to explore and predict how the difference in curvature of the tantalum anode affects the D.C. leakage current. The current density of both electrode-limiting (Schottky emission) and bulk-limiting (Poole-Frenkel) conduction mechanisms was investigated. For Schottky emission, there is leakage current enhancement at the cathode for negative curvature features. Likewise, there is leakage current depletion at the cathode for positive curvature features. The leakage due to Schottky emission is predicted to be inhomogeneous at the cathodes depending on the feature’s curvature. For Poole-Frenkel or other bulk conduction mechanisms, curvature does not affect the leakage current density, but the total
leakage current per volume scales with the surface area per volume and is thus greater for smaller particle sizes.
Chapter 5
Conclusions and Future Work

5.1 Conclusions

Electrolytic tantalum capacitors are widely used in commercial electronics, and are produced by anodic oxidation of metal anodes. With the miniaturization of electronics, there is a continual demand for components to have greater specific charge (CV/g). It was previously thought that the CV/g for electrolytic tantalum capacitors should remain at a constant value regardless of formation voltage, however this work has shown that this is not the case; at low formation voltages, there is a decrease in the CV/g due to the geometry of the Ta anodes and the presence of the native oxide becoming a more significant fraction of the total dielectric thickness. % CV/g loss is a relatively new issue which materialized from the reduction of operating voltage of some digital electronic devices and the use of ultrafine Ta powders, which can only be used in conjunction with low formation voltages [5].

This research was motivated by the need to understand the impact of low formation voltage dielectrics and high surface area powders on the electrical properties of electrolytic tantalum capacitors. To help address the % CV/g loss with decreasing formation voltage (below approximately 12 V) [8, 10], a mathematical model was developed to explain this phenomenon as well as investigating the effects due to the physical features on the localized electric field and D.C. leakage current.
It was shown that the model developed qualitatively explains the low voltage $\% \, CV/g$ loss, which agrees well with the experimental data observed. The model was useful to qualitatively predict the $CV$ per volume increase with decreasing particle size. It was found that the $CV/g$ decreases with decreasing formation voltage due to the presence of the native oxide thickness (which corresponds to the zero formation voltage) becoming a more significant fraction of the total dielectric thickness. Also, since the native oxide is present and its thickness is independent of tantalum particle size, the percentage of $\% \, CV/g$ loss is almost independent of the initial tantalum particle size, although the absolute losses are greater for smaller particle sizes.

It is equally important to understand the effects of curvature on D.C. leakage of electrolytic tantalum capacitors. Incorporating the geometry of the physical features of the Ta anodes into the leakage current equations predicted the effects of particle curvature on the localized electric field and D.C. leakage. For the localized electric field, it was found that there is electric field depletion at the cathode for features with positive curvature and electric field enhancement at the cathode for features of negative curvature. The electric field decays by $1/r$ through the dielectric. Since Schottky emission is electrode limiting, there is leakage current enhancement at the cathode for negative curvature features. The leakage due to Schottky emission is predicted to be inhomogeneous at the cathode depending on the local curvature. For Poole-Frenkel conduction, curvature does not affect the leakage current density, but the total leakage current per volume scales with the surface area per volume and is thus greater for smaller particle sizes.

Overall, the developed physical model predicts comparable scaling behavior of the specific charge characteristics when compared to the experimental data for electrolytic tantalum capacitors. It is also a useful tool in predicting areas of increased electric field and leakage current for both electrode and bulk controlled mechanisms.
5.2 Future Work

5.2.1 Other Ways to Enhance the Specific Charge in Electrolytic Ta Capacitors

This thesis proposes one possible explanation for the electrical behavior in electrolytic tantalum capacitors. However, one can hypothesize that there could be several other approaches to increase the specific charge of the capacitors.

1. Propose different morphologies of the tantalum anode to increase the specific charge of the device.

The proposed model showed that a perfect cylinder would have an increase in surface area, likewise an increase in specific charge. If the morphology of the ultra-fine powder Ta anodes is controlled or patterned in a way that would eliminate the loss of surface area during sintering and anodization, the overall specific charge could be increased significantly. The specific charge might be increased by changing the morphology of the anode from sintered Ta powder particles, to a large sphere or arbitrary shape that was covered in spikes that were small enough to increase the surface area and yet large enough to not be consumed during anodization at low formation voltages.

2. Determine how the Ta-Ta$_2$O$_5$ interface plays a role in controlling the material’s conduction mechanism.

Current-voltage (I-V), capacitance- voltage (C-V), and thermally stimulated depolarization current (TSDC) measurements have shown that the conduction mechanism in electrolytic tantalum capacitors switches from Schottky emission at low field to Poole-Frenkel conduction at high field. It has also been shown in other works that the potential in which the
change in conduction mechanism occurs is directly related to the properties of the Ta-Ta$_2$O$_5$ interface. The native oxide is a sub-stoichometric oxide [17], creating a high probability for the presence of trapped charges at the Ta-Ta$_2$O$_5$ interface. In work done by Freeman, et al. it was determined that the presence of conductive sub-stoichometric oxide (TaO) particles that form at the Ta-Ta$_2$O$_5$ interface, create areas of localized electrical field in the dielectric, which significantly increases the injection of electrons from the tantalum cathode into the oxide [72, 73].

From the model presented in this work it was shown that curvature has a strong affect on the Schottky emission, but none on the Poole-Frenkel effect. Therefore, it is important to understand this transition region and if the transition in the conduction mechanism has a dependence on curvature. If the presence of the native oxide could be reduced or eliminated, the onset of Poole-Frenkel conduction could be moved to higher applied fields, well out of the operating range of the device.

5.2.2 Curvature Effects on the Electrical Properties of Electrolytic Tantalum Features

In commercial capacitors, the tantalum anode is composed of pressed and sintered tantalum powder. The model presented in this work, predicts areas of high negative curvature to have an increase in leakage and breakdown voltage. These predictions need to be experimentally validated. To do this, a set of experiments are proposed to measure the electrical properties of features with increased positive and negative curvature and then will be compared to the results from the proposed model.
5.2.2.1 Fabrication of Tantalum Pillars and Holes with Various Radii

To study the anodization kinetics as a function of curvature, patterned thin film featured arrays with various radii must be fabricated. From previous work, a procedure was developed to fabricate both positive (pillars) and negative (holes) curvature features in Ta metal substrates for diameters ranging from 0.8 to 3.0 µm. To do this, planar tantalum metals was sputter deposited on Si (100) p-type, boron doped prime wafers using a Kurt J. Lesker CMS-18 deposition chamber. Prior to the deposition of the Ta metal, a titanium (Ti) adhesion layer, platinum (Pt) layer, and tantalum nitride (TaN) layer were deposited on the Si wafer. The Ti, TaN, and Ta layers were deposited via rf-magnetron sputtering and the Pt layer was deposited using dc-magnetron sputtering. The operating conditions during deposition are summarized in Table 5-1. All deposition was done at room temperature (19-22°C) and for the deposition of the TaN the flow rate of N₂ was 2.3-2.5 sccm. The target power, bias, and cathode current for Pt were 190 W, 550 V, and 298 mA.

<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>

After deposition of the metal, the film then undergoes some photolithography steps. This includes the application of an anti-reflecting coating, and either positive or negative photoresist. The photoresist is deposited to about 300 µm thick. The films are then patterned using the GCA 8000 Stepper with a quartz/copper mask and exposed to ultra-violet light to form the hole and pillar arrays at various radii (0.8 to 3.0 µm). The wafers are then etched using a PT Versalock Dual Etch reactive ion etcher (RIE) to etch without etching though the Ta metal (which would
cause charging during anodization). The excess photoresist and anti-reflectant were removed using an oxygen ash.

Anodic oxidation was performed in a model K0235 Princeton Applied Research flat cell. The counter electrode was a platinized mesh. A strip of copper tape was used to make electrical contact to the front of the Ta substrate. The electrolyte was 0.1 M H$_3$PO$_4$ and was exposed to a circular area of 1 cm$^2$ of Ta metal. The applied voltage was increased by automatically stepping the applied voltage 0.5 V every 2 seconds using a Hewlett Packard 4140B pA/DC voltage source and then holding for 60 minutes at the desired formation voltage. The experiments were done at room temperature and for formation voltages ranging from 10 to 70 V.

5.2.3 Curvature Effects on the D.C. Leakage

To study the effects of curvature on the D.C. leakage of the electrolytic tantalum capacitors, the electrical measurements, including current-voltage (I-V), current-voltage-temperature (I-V-T), and thermally stimulated depolarization current (TSDC), will determine the source of leakage current and breakdown strength of the dielectric at various radii of curvature. Measuring the electrical properties of commercial electrolytic tantalum capacitors with various initial particle sizes of the tantalum powder will allow the effects of curvature on the overall device to be determined.
References:


