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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RECEUE
POOLE FRENKEL CONDUCTION IN ANODIC TANTALUM PENTOXIDE

submitted in partial fulfilment of the requirements of a doctorate degree in experimental solid state physics at the University of Ottawa

by Carla J. Miner

1985

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POOLE FRENKEL CONDUCTION IN ANODIC TANTALUM PENTOXIDE FILMS

Abstract:

The current-voltage-temperature (I-V-T) behavior of anodic tantalum pentoxide films was studied as a function of the physical properties of the oxide. Oxide thickness was varied by controlling anodizing conditions, and the oxide dielectric constant was varied by incorporation of nitrogen. A third property, device area, was photolithographically defined. Finally, the absolute level of conductivity was changed by heating the anodized oxide in vacuum or under a reducing atmosphere. While agreement could be obtained between the predictions of standard Poole-Frenkel theory and the I-V behavior observed at any one temperature with the use of arbitrary constants, agreement could not be obtained over a range of temperatures without significant temperature variation in the physical properties of the oxide such as the dielectric constant. The anomalous temperature behavior was explained by extending Poole-Frenkel theory to include a transition from uncompensated to partially compensated donor statistics at a critical temperature. The theory was also extended to include spatially nonuniform donor distributions, and thus was able to explain the observed asymmetry in current with respect to zero bias.
This thesis describes a study of conduction in anodic tantalum pentoxide films. Since amorphous thin film oxides have peculiarities all their own, a brief introduction to the factors controlling conduction is given in Part I, section 1. The goal of the investigation was to determine which conduction process was responsible for the dramatic current-voltage (I-V) non-linearity observed for electric field strengths between $10^6$ V/m and $10^8$ V/m. Included in Part I, section 2 is a summary of the proposed mechanisms other than Poole Frenkel conduction.

Preliminary results indicated that the non-linearity could best be described by the Poole Frenkel theory. The model is based on field assisted ionization of localized impurity states in the band gap. A detailed description of Poole Frenkel conduction comprises Part II. It is necessary to examine the model, in its simple and various modified forms, for its applicability to the anodic oxide device. In the concluding section of Part II, a sequence of experiments is proposed to test the model.

The results of those tests are documented in Part III, along with a description of the measurement and analysis techniques. In Part IV the results are discussed. The major conclusion is that Poole Frenkel theory, as it is presently used, does not adequately describe all of the observed behavior. Specifically, the magnitude of non-linearity as a function of temperature
cannot be reconciled with the measured electrical and optical properties of the oxide. In addition, there is no provision in the model for the degree of I-V asymmetry with respect to zero bias that is observed in some samples.

In Part IV, section 2, it is shown that the two presently used forms of Poole Frenkel theory are valid for certain temperature and doping conditions. The anomalous temperature dependence of I-V behavior shown by the samples studied is evidence of a transition between the two. This analysis allows a physical interpretation of the mechanisms by which nitrogen incorporation and heat treatments affect conduction.

In Part IV, section 3, a model based on spatially non-uniform donor distributions is proposed to account for the I-V asymmetry. Numerical simulations are employed to show that the predictions of the model are consistent with the observed behavior.
ACKNOWLEDGEMENTS

Most of the experiments reported in this work were performed in the Advanced Technology Laboratory of Bell-Northern Research in support of a program to create a new liquid crystal messaging terminal. To multiplex such a display, the voltage contrast threshold of the individual liquid crystal picture elements must be sharpened. Previous research had shown that this could be possible if each picture element were connected to a device with non-linear current-voltage (I-V) characteristics. My main responsibility to the program was to determine the causes and methods of control of I-V non-linearity in the devices proposed for use in these liquid crystal displays.

It is a pleasure to acknowledge two members of the project team with whom I shared the responsibility for the preparation of the devices: Mr. Blair MacLaurin, and Mr. Grant Este. I also wish to acknowledge the contribution of Dr. David Smith of the University of British Columbia, who measured the oxide thickness and index of refraction using the ellipsometer of the Electrical Engineering Department. Special thanks are due to my managers over the course of the project: Dr. David R. Baraff and Dr. Richard W. Streeter, for their encouragement and support, and for providing a work environment conducive to research. Much credit is also due Dr. William D. Westwood, who besides being an invaluable source of information concerning thin films in general
and tantalum thin films in particular, asked the question that proved to be central to this thesis: namely, "What is meant by intermediate compensation?". I would also like to thank Bell-Northern Research for providing me with a post graduate award to enable the completion of this work on a full time basis.

Finally, I must express my loving thanks to my husband Bob and my son Glen for their (usually) uncomplaining forbearance of the consequences of part-time wife and mother.
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<td>E</td>
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<tr>
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<td>h_</td>
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<td>m</td>
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<td>m_s</td>
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<td>m_o</td>
<td>free electron mass</td>
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- $m^*$ - effective electron mass
- $n_0$ - index of refraction
- $n$ - free electron carrier density
- $n_a$ - density of unionized acceptors
- $N_a$ - total density of acceptors
- $N_c$ - conduction band effective density of states
- $N_e$ - effective conduction band density of states (page 31)
- $n_d$ - density of unionized donors
- $N_d$ - total density of donors
- $N_{d+}$ - density of ionized donors
- $n_{ex}$ - extrapolated zero bias carrier density (page 137)
- $n_i$ - density of traps
- $n_k$ - normalizing carrier density (pages 74-75)
- $n_0$ - density of Poole Frenkel carriers at zero bias
- $N_0$ - constant $n_0$ which is independent of $x$
- $n_t$ - density of occupied traps
- $N_t$ - total density of traps
- $N_t^*$ - characteristic trap energy density (page 33)
- $n_t(E)$ - density of traps / energy (page 33)
- $N(E_F)$ - density of electron states at the Fermi energy level

- $p$ - density of holes
- $P$ - pressure
- $\overline{P}$ - dipole moment
- $P(\xi)$ - probability of electron emission from donor
- $q$ - electronic charge
- $q_i$ - ion coordinates
- $R$ - hop length
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<tr>
<td>$r$</td>
<td>generalized 3-D radial coordinate</td>
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<tr>
<td>$r_{\text{eff}}$</td>
<td>radial position such that $E = E_c - \frac{1}{r_{tb}}$</td>
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<tr>
<td>$r_o$</td>
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<td>$r_p$</td>
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<td>voltage</td>
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<td>$V_c$</td>
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<td>$V_n$</td>
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<td>$V_{\text{in}}$</td>
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<td>$w$</td>
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<td>$\nu$</td>
<td>frequency (e.g. an attempt to escape frequency)</td>
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<td>$\xi$</td>
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PART I - BACKGROUND

1. ANODIC OXIDE FILMS: AN INTRODUCTION

Early in the development of the science of electrochemistry, it was discovered that if the anode in a simple water electrolysis cell was made from one of a limited number of metals, known as valve metals, oxygen evolution no longer occurred. Instead, uniform layers of oxide were built up on the anode. The name valve metal derives from the observation of strong current rectification in the manner of vacuum tube "valves", for the anodic oxides of Ta, Al, Nb, Zr, Hf and W. Anodic oxides are not restricted however, to these metals. Other metals such as Bi, Sb, Sn and Ti, and semiconductors such as Si, Ge, and GaAs also form stable anodic oxides provided care is exercised in the choice of an electrolyte in which the oxide is relatively insoluble. Thus the anodic oxide studied in this work, tantalum pentoxide, is only one member of a large family of technologically important materials. Likewise, the topic of electronic conduction is only one property among many that interest scientists working with anodic oxides. These other interests are covered in such standard texts as "Anodic Oxide Films" by L. Young (1), and "Electrochemistry at Semiconductor and Oxidized Metal Electrodes" by S. R. Morrison (2).

The intrinsic properties of anodic oxides contribute one main advantage and numerous limitations to a study of electronic
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conduction. The advantage is the excellent uniformity of film properties, especially film thickness, as discussed in detail below. The limitations are also discussed as the topic is progressively narrowed from thin films in general, to amorphous anodic tantalum pentoxide thin films in particular.

Anodic films are uniquely uniform due to the "self-healing" property of anodic film growth. During anodization, thin regions, which are consequently high field regions, experience rapid film growth until any asperity is smoothed out. The uniformity of such films can greatly exceed that attained by other thin film deposition techniques. For example, the intense interference colors of anodic Ta$_2$O$_5$ films appear uniform over large areas, as well as on a microscopic scale, even though the eye is capable of discerning changes in optical thickness as small as 10 nm. Because the electric field is nearly constant during oxide film growth, the absolute thickness of the oxide is controlled by the anodizing voltage, and to a lesser degree by the current density and electrolyte temperature (3). Thus for a particular parent metal, one speaks of an anodizing constant relating thickness to voltage. The anodizing constant for Ta for example, ranges from 1.52 to 1.94 nm/V, depending on the crystalline phase and impurity content of the parent metal (4). The ability to grow very thin, uniform films of known thickness is used as a tool, in fact, for sectioning metal samples (5). The enhanced control over material
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properties afforded by the anodization process is also of great use in solid state research - especially in conduction studies such as this.

Properties of Thin Films:

Conduction in thin films differs on several points from that usually seen in bulk semiconductors. In the latter, current density is linearly related to electric field through a voltage independent resistivity. However, in films as thin as these (10 nm to 10 μm), high field effects are encountered even at reasonably low voltages. Resistivity becomes decidedly non-linear. In the samples discussed here, it drops from a high of $10^7 \text{ohm-m}$ to a low of $10^4 \text{ohm-m}$ as electric field strength approaches the value present during anodizing. The small thickness of the samples and their high resistivity may also allow space charge regions to extend throughout the film's thickness, and thus modify conduction processes greatly (6). For example, current transients with time constants varying up to many minutes are frequently observed as a result of space charge effects (7). A conduction model, space charge limited current (SCLC) is commonly put forward to explain conduction behavior, and thus warrants closer examination in the following section. Electrode to electrode tunnelling will not be discussed since the films considered here are too thick (i.e. >10 nm) for this mechanism to be significant.
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In addition, conduction in thin films differs from that in bulk semiconductors because the influence of surfaces is emphasized in the thin sample. To begin with, there are limitations on the theory of electron propagation which become significant in small specimens (8). Besides these geometric effects, one must consider that material parameters of thin films will not necessarily be the same as bulk values (9-11). Finally, as dimensions shrink, contacts become increasingly important. A contact controlled conduction model, Schottky emission, is also discussed in the following section.

Properties of Amorphous Thin Films:

Next, the amorphous nature of the anodic oxide must be taken into consideration. In the first place, it complicates the attempt to model behavior with theories developed for crystalline materials. Also, on the basis of thermodynamic arguments, it can be shown that amorphous materials are, at best, metastable (12). Slow, irreversible drift of characteristics is seen accompanying long term voltage stress (13) and temperature cycling (14). In some cases, there is evidence for a concurrent increase in crystallinity (15). This, too, must be considered in the design and implementation of conduction experiments.
Properties of Anodic Amorphous Thin Films

The anodic amorphous thin film is a system that compounds the idiosyncracies mentioned above with a few more derived from the method in which the film is made. Four features of anodic films are important to consider in a conduction model: 1) the inevitably large impurity level, 2) the frequent occurrence of flaws in the form of microscopic pores and fissures, 3) the possibility of stoichiometry variations throughout its thickness, and 4) the predisposition of these films to carry current ionically rather than electronically.

1) The predominant impurities in anodic films formed in aqueous electrolytes are water (or OH) (16) and to a lesser or greater degree, depending on anion size; the electrolyte itself (17). At one extreme, anodizing in phosphoric acid leads to considerable phosphorus incorporation in the outer half of the film as detected by Auger and XPS (X-ray Photoelectron Spectroscopy) profiling (18). The two halves show quite different chemical properties (e.g. etch rates) (19), structural properties (e.g. rates of recrystallization under electron beam irradiation) (20) and optical properties (e.g. optical constants) (21). To limit this effect, the films studied in this work were anodized in dilute citric acid. The large size of the citric acid anion is such that electrolyte incorporation is unlikely. Auger and SIMS (Secondary Ion Mass Spectroscopy) analysis did not detect a carbon component traceable to the electrolyte. Water, which was
likely present, would not be detected by this analysis technique.

Other impurities from the parent metal or surface contamination can enter the oxide during growth. Early work with bulk Ta foil (99.9% pure) was particularly susceptible to metallic impurities. References to the related effect of cleaning procedures on oxide resistivity can also be found (22). The work described here deals with oxides grown on Ta thin films sputtered from 99.999% pure targets and subsequently processed under clean room conditions.

2) A major concern with metallic impurities is their firmly established connection with flaws and anomalous conduction behavior (23-25). This is the second feature of anodic oxides to be considered. Vermilyea demonstrated flaw controlled conduction by electrochemically decorating current carrying filaments distributed across the sample (26). Recent work with high resolution TEM (Transmission Electron Microscopy) has confirmed the importance of much smaller defect sites (as small as 10 nm across) to catastrophic breakdown, and field induced recrystallization (20). Flaw conduction was shown to be responsible for the rectification that was previously thought to be characteristic of oxide coated valve metals (27). Surfaces polished prior to oxide growth (22) and counter electrodes evaporated at oblique angles (27) were shown to reduce leakage currents in accordance with a model of flaw dominated conductivity. The possibility of flaw conduction must be
recognized, and hopefully eliminated from the samples used before conduction models are examined. One must determine whether the observed conduction takes place uniformly through the whole film or only at local flaws where physical properties can be dramatically different from what can be measured macroscopically.

A series of tests were proposed (28) to identify nominally flaw free films: current density - voltage characteristics should be nearly symmetric with respect to zero bias, and should be independent of device area, and ambient moisture level. This last criterion arises from the historical use of gold as a counter electrode. This metal tends to bridge flaws in the oxide and reduce the effect of flaws on conduction, and yet leave a void into which water may penetrate and alter charge injection from the contact (28). Strongly adherent metallizations, as are used in this study, are not expected to be affected by atmospheric moisture in this way.

3) The third consequence of anodic oxidation is the belief that the film has a varying stoichiometry throughout its thickness (29). Tracer experiments determined that both the oxygen and the metal move from the respective interfaces to a line approximately in the center of the film where successive layers of oxide form (30). During anodization, both species of ions are en route through the stoichiometric oxide to the center line; when anodization is halted these ions are frozen in place. One expects that the outer layer is oxygen rich and the inner layer is oxygen.
deficient. The effect can be reduced by holding the anodizing voltage constant until current density has dropped to levels associated with electronic conduction alone. This practice was observed in this work.

The variation in stoichiometry is expected to alter J-V behavior in the finished device. A conduction model described by Sasaki (31) claims that the variation is large enough for the formation of a p-i-n diode. The model proposed in this work relies on the existence of a spatially non-uniform donor density distribution, which may be related to the stoichiometry variations. The donor density distributions are studied by comparing the behavior of films seeing various heat treatments, which are thought to change the composition profile (32).

Concerning the final feature of anodic films, ionic conduction in its own right is a possibility since field strengths used for conductivity measurement may be as large as those used during anodization. Also anodization takes place at room temperature, but conductivity tests may be done at elevated temperatures where ionic conduction will be enhanced. One of the major sources of poor reproducibility and long term drift in amorphous materials is thought to be ionic transport. The scope of this work does not include ionic processes. In these experiments, therefore, field strengths were kept relatively low, and electrical behavior was periodically checked against control samples which had not been voltage stressed up to that point.
Properties of Amorphous Anodic Tantalum Oxide Thin Films:
Restricting the topic under discussion to anodic tantalum pentoxide itself brings out a few more points that must be considered when comparing conduction data from various laboratories. Small differences in anodizing behavior and oxide properties such as index of refraction are noted when different phases of Ta are used (33). Bulk Ta foil is polycrystalline body centered cubic (b.c.c. or α-Ta) whereas sputtered and evaporated thin films may be b.c.c. or an impurity stabilized tetragonal phase, β-Ta (34). High oxide conductivity is often associated with sputtered b.c.c. films which tend to be highly stressed and exhibit poor film to substrate adhesion and high oxide flaw density (35,36).

Although, as noted before, metallic impurities in bulk Ta affect conductivity levels by introducing flaws, the bulk properties of the sputtered Ta film and its nominally flaw free anodic oxide may be altered by reactive sputtering. Intentional (or inadvertant) doping can occur by the incorporation of gases such as N₂, O₂, H₂, and CH₄, into the Ta during deposition which then become part of the oxide during growth (37-39). Thus, the cleanliness and base pressure of the sputtering system are important factors. Deliberate additions of N₂ into the sputtering atmosphere can lead to the deposition of nitrogen doped Ta, Ta₂N or TaN films and the subsequent growth of tantalum oxy-nitride.
dielectrics. The procedure becomes a novel method of changing the oxide properties to test the conduction models proposed (40, 41).

An additional experimental variable that affects conduction is the practice of heat treating the oxide after growth. This may operate by driving off water (42), inducing crystallinity (15), diffusing counter electrode material into the oxide (43), or modifying the Ta-Ta$_2$O$_5$ interface (14). This interface is normally abrupt in the anodic film. Physical analysis has shown that the interface width is less than 2 nm (44). In thermally grown oxides, the oxygen concentration decreases throughout the layer (45). It has been proposed by Smyth et al. (14) that the interface in the thermally treated anodic oxide is substantially broadened. They attribute the latter to the propensity of tantalum to dissolve oxygen at elevated temperatures. This effect is reduced when thin films of tantalum or tantalum nitride are used, since their capacity to store the dissolved oxygen is reduced (38, 39).

The types of heat treatments reported vary from the nominally untreated films, to those with photolithographically defined counter electrodes ($T_{\text{max}} = 150^\circ\text{C}$), to those which are baked under high vacuum, air or N$_2$ atmospheres at temperatures up to 400$^\circ$C where crystallization begins. Here we report quantitative changes in impurity densities caused by vacuum baking ($T_{\text{max}} = 150^\circ$C, $P = 10^{-4}$ Pa), and hydrogen annealing ($T_{\text{max}} = 350^\circ$C in flowing 10% H$_2$-N$_2$ mixtures).

From theoretical considerations it is clear that a contact
limited conduction process is more likely in a-thin film than in a thick one. Therefore it would not be surprising if some conduction models apply to certain ranges of thicknesses and not to others. In the following section film thickness will be noted with any experimental observations from the literature. Film thickness is limited in anodic Ta₂O₅ by the onset of what is inaccurately known as field recrystallization. At that point current is diverted from the growth of normal amorphous oxide to breakdown sites where small crystallites form, and progressively displace the pre-existing oxide (46). Many researchers study films which approach that thickness (approximately 500 nm), whereas the samples used here are nominally 50 nm thick.

Finally, because Ta₂O₅ has a large band gap and is amorphous, the density of states at the Fermi energy within the band gap may be non-zero. This can lead to various forms of hopping conduction (47) such as are discussed in Part II.
Summary:

To conclude, the relatively simple fabrication and well controlled macroscopic properties of the anodic oxide make it an attractive choice of subject matter in the study of conduction in amorphous materials. The thinness of the film allows the investigation of high field and space charge related phenomena. The possibility of interference from contact and surface related phenomena is recognized, as is the possibility of long term stability problems due to the amorphous nature of the film. An anodic oxide has unique properties derived from its method of growth: e.g. the high and variable impurity level, and a stoichiometry which may vary throughout the film thickness. Electronic conduction, representative of the oxide in general, must be distinguished from flaw dominated and ionic processes. The study is aided by the facility to modify conduction behavior in a controlled manner by 1) the choice on anodizing parameters, 2) the formation of doped oxides on reactively sputtered tantalum, and 3) the use of various heat treatments after growth.
PART I - BACKGROUND

2. ALTERNATIVE CONDUCTION MODELS

Previous Approaches:

Investigations of anodic oxides have usually been undertaken in the context of an intended application. For example, material aspects have been studied in conjunction with the use of these films as decorative or protective finishes (48). They have also been studied as a means by which thin film resistors may be trimmed and stabilized (49). More important is the wide use of anodic oxides of tantalum and aluminum in electronic devices. Some examples of these devices are capacitors (50), MOS structures (51-53), electroluminescent displays (54), and thin film transistors (55,56). Work in these areas has concentrated on reducing conduction and defects, and improving a-c dielectric properties. Thus capacitance and dissipation factor receive considerable attention in the literature.

This thesis addresses the high field conduction properties of anodic tantalum pentoxide, where current density rises rapidly with increasing voltage. Because the usefulness of many thin oxide devices is limited by excessive conduction in that regime, this topic has been dealt with in a number of theoretical and experimental papers. In contrast to earlier applications, however, the non-linearity of high field conduction in anodic tantalum oxide has recently become a desired attribute. Tantalum pentoxide MIM (Metal - Insulator - Metal) devices have been used
as non-linear resistors for threshold control in liquid crystal displays (57). Because the material used in this study has been optimized for the latter application, it should be noted that it has higher conductivity than the type of tantalum oxide generally described in the literature. Also note that some of the work cited in this section deals with gas phase anodized and sputtered \( \text{Ta}_2\text{O}_5 \), as well as other anodic oxides. The conduction behavior of \( \text{SiO}_x \), a more distantly related amorphous oxide which is usually evaporated, is also described for comparison.

Conduction Models:

In this section three high field conduction models are discussed: contact limited conduction, space-charge limited conduction, and hopping conduction. These are the main alternatives to the conduction model advocated here; namely Poole Frenkel theory. These are not competing models in the sense that one is right and the others are wrong, but rather each has a range of applicability depending on such parameters as oxide thickness, temperature, electric field strength, impurity density and contact characteristics. In general terms, the proposed models differ in one of three characteristics: mobility is either high and crystal-like, or low and phonon assisted; conduction is either contact or bulk limited; and the charge carriers are either electrons or holes. Quantitative estimates of these physical properties of \( \text{Ta}_2\text{O}_5 \) vary widely depending on the
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Conduction model used to explain the observed behavior.

For example, a mobility of $2 \times 10^{-1} \text{m}^2/\text{V-s}$ (58) has been estimated for $\text{Ta}_2\text{O}_5$ from a space charge limited conduction model, yet an interpretation of similar data based on Poole-Frenkel theory has yielded a value of $7.5 \times 10^{-3} \text{m}^2/\text{V-s}$ (59). Hall effect measurements would resolve the discrepancies. However, even if a sample could be made without the usual underlayer of unanodized Ta, conductivity is non-ohmic at the current levels necessary for Hall voltage measurement. To the author's knowledge, other techniques such as photo-Hall (60), EBIC (Electron Beam Induced Current) (61) or time of flight measurements (62) have not been attempted with $\text{Ta}_2\text{O}_5$. Theoretical approaches to estimating mobilities are severely hampered by the general lack of information about oxide band parameters. All that has been reported about $\text{Ta}_2\text{O}_5$, for instance, is its band gap of 4.6 eV (63, 64). In amorphous materials the concept of a uniquely defined mobility and a band gap is replaced by that of the mobility gap (65). Over a narrow range of energies corresponding to the band edges in crystalline semiconductors, mobility drops precipitously from values comparable to the single crystal (i.e. $\mu > 0.01 \text{m}^2/\text{V-s}$) to very low, but non-zero values in the gap (i.e. $\mu < 0.001 \text{m}^2/\text{V-s}$). There is, therefore, a dichotomy among conduction models: those advocating low mobility transport via localized states in the gap without excitation to the conduction band, and those proposing activated processes with high mobility.
transport through extended states in the conduction band. Both Poole-Frenkel and Schottky conduction assume the latter condition, while hopping conduction is based on the former. Space charge limited conduction is often found in low mobility materials, but as such does not specify the mode of carrier transport.

Another distinction among the models is the importance attached to the contacts. If the current limiting step in conduction is the passage of charge carriers across a potential barrier at the interface, it is a fundamentally different problem from one where the resistance of the interior of the material dominates. The former should be sensitive to choice of electrode material, while the latter should have identical electrical behavior in both bias polarities. Unfortunately, these distinctions are not as clear as one would hope. The existence of surface states can pin the Fermi energy at a particular level irrespective of electrode material \( \text{(66)} \), while the symmetry of so-called bulk conduction assumes homogeneity throughout the dielectric, and the absence of internal electric fields, both questionable assumptions.

Unless otherwise noted, the dominant charge carrier is assumed to be the electron. While this is not an uncommon assumption, it should be noted that the matter has yet to be settled conclusively. As mentioned, Hall effect measurements of carrier type are not possible. Some supporting evidence is
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present in the form of the cold cathode behavior of Ta₂O₅ in electroluminescent devices (54). Light emission is dependent on the injection of hot electrons from the oxide into the semiconductor. The energy distribution of these electrons has been reported recently by O'Clock and Feisil (67). Also, extensive scintillation studies of tantalum anodizing behavior near breakdown have led to a successful impact ionization theory, based on the assumption of electron injection from the electrolyte and rapid removal from the oxide (68). The model also requires holes to be deeply trapped and deduces from experimental data a hole mobility of $10^{-11} \text{m}^2/\text{V-s}$. Furthermore, short circuit photocurrent experiments by Hoenig reported by Thomas (69) point to electron conduction. On the basis of additional photoconductivity results, Thomas proposes a Fermi energy level 1.4 eV below the conduction band, and thus n-type conductivity. In contrast, Gubanski and Hughes show that SCLC in Ta₂O₅ is strongly affected by choice of counter electrode material, and conclude that they are observing hole injection (70). This contradicted the previous SCLC data for Ta₂O₅. Both observations could be reconciled if like in Nb₂O₅ (71), hole and/or electron injection in Ta₂O₅ may also be favoured by certain sample preparation methods.
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Contact Limited Conduction - Schottky Barriers

Theory of Barrier Formation:

The process of supply or extraction of charge carriers at the contacts may be the rate determining step in the passage of current from one electrode to the other (72). Interfacial potential barriers similar to that shown in Figure <i>1</i> can arise as a result of the thermodynamic requirement that the Fermi energies of the two materials align upon contact. This is accomplished by the transfer of electrons between the two; the flow being from the material with the lower work function (defined as the energy difference between the vacuum level and the Fermi level) to that with the higher work function. In the metal the work function is denoted \( \Phi_m \), whereas in the insulator the work function is the sum of the electron affinity \( q_X \) and the separation of the Fermi energy and the conduction band, \( qV_n \). The final position of the conduction band in the insulator with respect to the metal Fermi energy is directly related to the respective work functions and the density of surface states which can supply (or take up) a portion of the transfer electrons. Those electrons not coming from (or ending up in) the surface states are extracted from (or injected into) the bulk of the insulator forming a depletion (or accumulation) layer adjacent to the metal interface. The doping density of the insulator will determine how far the layer will extend into the bulk of the
Figure 1. Energy Band Diagram of Metal Semiconductor Contact

a) The vacuum levels of the metal and the semiconductor determine the relative positions of the Fermi energy level in each when they are widely spaced.

b) Upon contact, the Fermi energies align due to a flow of electrons from the material with the smallest work function into that with the largest work function. Thus, a potential barrier of height \( q\phi = q(\phi_m - \chi) \) and a depletion region of width \( w \) are created.
insulator. In imperfect insulators with semiconductor-like doping densities the layer is a few tens of nanometers thick, whereas the very low carrier concentrations of normal insulators will often force this region to extend completely from one side of the sample to the other. This latter configuration is known as the Mott or punch-through Schottky barrier. The electric field, $\xi$, in the normal insulator sample is uniform and equal to the ratio of the sum of the applied voltage, $V$, plus the internal depletion voltage, $V_{in}$, (for dissimilar opposing contact metals) to sample thickness, $d$, i.e.

$$\xi = \frac{V + V_{in}}{d}$$  \hspace{1cm} <1>$$

In imperfect insulators and semiconductors, on the other hand, both the electric field, which has a maximum at the interface, and the depletion/accumulation layer thickness, $w$, increase with increasing reverse bias as given by: (72)

$$w = \sqrt{\frac{2\varepsilon_0}{qN_d}} (V_{in} + V - kT/q)$$  \hspace{1cm} <2>$$

and

$$\xi_{max} = \frac{2}{w} (V_{in} + V - kT/q)$$

$$= \frac{2qN_d}{\varepsilon_0} \frac{(V_{in} + V - kT/q)}{\sqrt{\varepsilon_0}}$$  \hspace{1cm} <3>$$

where $\varepsilon$ = high frequency dielectric constant
$N_d$ = impurity density
$T$ = temperature

(19)
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The size and voltage dependence of this layer's width may be inferred from the bias behavior of capacitance. In extreme cases, insulators with large interfacial defect or impurity concentrations, and/or sufficiently high surface state densities, exhibit features of both the semiconductor-like depletion layer, which can quickly respond to changes in bias, and the normal insulator, whose carrier concentrations respond relatively slowly due to deep trapping and/or space charge effects. The combination can lead to some interesting history effects and other non-equilibrium behavior as described by Simmons and Nadkarni (73) that will not be considered here.

Current - Voltage - Temperature Behavior:

The emission of carriers over the barrier at the metal interface is analogous to the case of the well-known vacuum diode. By considering the distribution of electrons in the metal, with energies sufficient to surmount the barrier and trajectories in the appropriate direction, one arrives at the Richardson relationship between J, the current density and T, temperature. Modifications must be made in insulators and semiconductors to take into account the carrier effective mass (72).

Thus:

\[ J = A T^2 \exp\left(-\frac{q\phi}{kT}\right) \]  \hspace{1cm} (4)
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\[ A^* = \frac{4\pi q m^* k^2}{h^3} \quad <5> \]

where \( q \phi \) is the barrier height

\( m^* \) is the effective mass

\( A^* \), the effective Richardson coefficient, can be further adjusted to take into consideration quantum mechanical reflection, tunnelling probabilities, and optical phonon backscattering, but its value remains on the same order of magnitude as the free space value of \( 1.2 \times 10^6 \, A/(m^2 K^2) \).

The current density - voltage behavior of the Schottky barrier is not immediately obvious in this expression because the barrier height is also voltage dependent. Consider the detailed Figure <2>. A carrier at a distance \( x \) from the interface experiences a force due to the depletion region field, an externally applied field, \( \xi \), and an "image force" due to an induced charge located in the metal at \(-x\). As shown in the figure, the fields have the net effect of lowering the barrier under appropriate bias conditions. The amount of barrier lowering is derived by differentiating an expression that gives the energy of the charge as a function of distance from the interface given by:

\[ E(x) = \frac{\xi x}{4\pi \varepsilon_0 (2x)^2} - q \xi x \quad <6> \]
Figure 2: Energy Barrier Lowering in Metal Semiconductor Contacts

The detailed picture of the metal-semiconductor interface must take into account the image force arising from electrons in the metal which take up positions mirroring any fixed charges in the semiconductor depletion region. The potential energy for carriers in the semiconductor is the sum of the depletion region potential (approximately linear in x on this scale) and a Coulombic image force potential which varies as 1/x. The peak height of the barrier to current flow is reduced by an amount Δqϕ. An external applied field of the appropriate polarity increases the slope of the depletion potential, and in turn further lowers the interfacial barrier.
the energy has a maximum at
\[ x = \frac{q}{\sqrt{16\pi \varepsilon_0 \varepsilon}} \]
with the value
\[ E_{\text{max}} = E_c - \frac{q^2 \varepsilon_{\text{max}}}{4\pi \varepsilon_0} \]
Since the \((E_c - E_{\text{max}})\) is equal to \(\Delta q\phi\), equation (8) leads to the expanded \(J-\xi\) expression for both the Schottky barrier at the reversed biased imperfect insulator (semiconductor-like) \(\rightarrow\) metal contact of doping density \(N_d\), and thickness \(d\):

\[ J = A^* T^2 \exp(-q\phi_0) \exp \left[ \frac{q \xi_{\text{max}}}{kT \sqrt{4\pi \varepsilon_0 \varepsilon}} \right] \]

and the punch-through barrier in normal insulators:

\[ J = A^* T^2 \exp(-q\phi_0) \exp \left[ \frac{q (V_{\text{in}} + V)}{kT \sqrt{4\pi \varepsilon_0 \varepsilon d}} \right] \]

or recast in terms of current density, \(J\), and voltage, \(V\):

\[ J = K_{\text{sch}} \exp \left( \beta_{\text{sch}} \sqrt{V} \right) \]

where
\[ K_{\text{sch}} = A^* T^2 \exp(-q\phi_0) \]

and
\[ \beta_{\text{sch}} = \frac{1}{kT} \sqrt{\frac{q^3}{4\pi \varepsilon_0 \varepsilon d}} \]
assuming \(V_{\text{in}}\) is small compared to \(V\)
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Hybrid Theories:

Contact barriers surely exist in almost all metal-insulator-metal systems. It is apparent therefore that in a normal insulator the effects of the contacts are usually overshadowed by those of the highly resistive bulk. Occasionally for less resistive materials, narrow depletion layer contact barriers can form which have appreciable influence on the conductivity of the sample for certain ranges of voltages and temperatures. Simmons (74) examined in detail the theoretical characteristics of a metal-imperfect insulator-metal system where the resistances of the contacts and the bulk were similar. Current flow over the barrier followed the normal Schottky equation <9>, where the electric field was calculated to take into consideration the uneven division of the voltage between the contact and the bulk. He found that for low voltages, current rose very steeply with increasing bias when most of the voltage was dropped over the narrow depletion layers. At higher voltages the influence of the bulk became increasingly dominant until the J-V curves were essentially identical with normal Poole Frenkel curves. This is shown schematically in Figure <3>. There is a transition between a low field, thickness independent behavior to a high field Poole Frenkel behavior which is strongly dependent on sample thickness.

In a similar fashion Frank and Simmons (75) discussed the effect of space charge on contact controlled conduction. In the
Figure 3: Theoretical Schottky to Poole Frenkel J-V Transition

Plotted is the theoretical current density - voltage (J-V) behavior of metal-insulator-metal devices with three different insulator thicknesses, d. The low field behavior, for voltage below \( \sim 10 \text{ V} \), is dominated by Schottky emission over a potential barrier at the cathode and is therefore independent of d. The high field behavior is dominated by Poole Frenkel emission from donors in the insulator bulk and exhibits an asymptotic slope proportional to \( 1/\sqrt{d} \) on this type of plot. From Simmons (74)
PART I - BACKGROUND

case where the work function of the metal contacts is less than that of the insulator, injecting contacts are formed. Current passes from one electrode to the other over a potential maximum in the interior which is also known as a virtual cathode. As current increases, the size of the accumulation region shrinks in accordance with SCLC (space charge limited conduction) theory. Eventually, the supply of carriers from the emitting contact is unable to keep up with the extraction of carriers from the accumulation region. At that point the virtual cathode becomes coincident with the real cathode and contact limited conduction takes over. The I-V curves for a variety of combinations of barrier heights, carrier mobilities and concentrations were calculated. The common features were a low voltage, bulk controlled regime where current rises steeply, and a high voltage, thickness independent regime which asymptotically approaches the usual Schottky behavior. A schematic diagram of the typical behavior is given in Figure <4>.

Pulfrey, Shousha and Young (76) made a theoretical study of conduction behavior for a range of insulator properties. They were able to identify major regions on a graph of current density versus the product of donor density and sample thickness where either Poole Frenkel, Schottky or space charge limited conduction dominated.
Figure 4: Theoretical SCLC to Schottky J-V Transition

![Graph showing current density vs. square root of voltage for different conditions.]

*Graph legend*:
- SCLC
- Schottky

Plotted is the theoretical current density - voltage (J-V) behavior of 1 μm thick metal-insulator-metal devices showing a transition between space charge limited conduction (SCLC) at low voltages to Schottky emission over the interfacial barrier of height qφ. When either mobility, μ, or the ratio of the densities of carriers to occupied traps, μ/d, is reduced the upper voltage limit of the SCLC dominated range increases. From Frank and Simmons (75)
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Experimental Evidence:

Unambiguous identification of Schottky barrier controlled conduction is hampered by the close similarity of its I-V-T (current-voltage-temperature) behavior to that of Poole Frenkel conduction. Thus many experimental results, initially reported as exhibiting Schottky behavior have been subsequently re-interpreted as Poole Frenkel conduction and vice versa. Additional tests are required. For instance, if a strong contact work function dependence is established, then Poole Frenkel conduction can be ruled out. This has been done by Hacskalyo for very thin (2.7 to 8.3 nm) Al$_2$O$_3$ films with Zn, Sn and Au contacts (77). Flannery and Pollack have also compared I-V-T characteristics of very thin (2.4 nm) plasma anodized Ta$_2$O$_5$ films with Au contacts (78) with similar behavior reported by Namba on 14 nm thick, wet anodized Ta$_2$O$_5$ with Al contacts (79). Good agreement with the Schottky model was obtained. In addition, the values of the physical parameters estimated from low temperature tunnelling currents agreed with those derived from the high temperature Schottky curves. C.Mead, working with ZnO$_x$ was able to relate the voltage intercept on the ln(I) vs $\sqrt{V}$ curve to the theoretical contact potential difference (80).

Simmons' predicted transition from Schottky to Poole Frenkel I-V behavior upon increasing bias has been convincingly demonstrated in a number of systems. In SiO$_x$ for instance,
Hartman, Blair and Bauer (81), Hirose and Wada (82), Inagaki, Adachi and Nitta (83), and Stuart (84,85) have presented data showing the characteristic steeply rising, thickness independent behavior at low bias, diverging into $\ln(I) vs \sqrt{V}$ behavior with slopes dependent on thickness. In $\text{Ta}_2\text{O}_5$, the effect is more elusive. Matsumoto (86) presented a probable example, but only after subtracting the effects of a shunt resistance from the data. P.L. Young (87) on the other hand, only saw this phenomenon in abnormally conductive $\text{Ta}_2\text{O}_5$ films.

Less clear examples, with no corroborating work function evidence, can be tentatively assigned to Schottky conduction on the basis of three tests. First, the temperature dependence of the I-V characteristics should predict a barrier height consistent with that given another technique such as photoconductivity. Second, strong rectification should occur when dissimilar contacts are used. Third, punch-through conditions must be consistent with the doping levels and insulator thickness observed. Under these criteria, the rectifying 6 nm evaporated aluminum oxide sample of Antula (88) is probably exhibiting Schottky conduction. Antula was also able to show agreement with Schottky predictions on the changes in conductivity when a known quantity of dopant was electrochemically drawn into the film. Likewise, the thinnest of the $\text{Ta}_2\text{O}_5$ films studied by O'Clock (89) exhibited $\ln(I) vs \sqrt{V}$ behavior that can be attributed to Schottky emission. Note that this was not the conclusion drawn in that
work. An error had been made in the value of the dielectric constant and the correct value does in fact give good agreement with theory.

As one final example, Pulfrey et al. (90) attributed the \( \ln(I) vs \sqrt{V} \) characteristics demonstrated by wet anodized Ta\(_2\)O\(_5\) with Au or In contacts to Schottky conduction for the Ta positive polarity. The other polarity also showed \( \ln(I) vs \sqrt{V} \) behavior, but with a slope more in line with Poole-Frenkel predictions. Interestingly, the application of a high voltage stress removed the rectification, increased conductivity by several orders of magnitude and the \( \ln(I) vs \sqrt{V} \) slope for both polarities became the "Schottky" value. As will be explained in a following section the nonrectifying behavior is more likely to be due to Poole-Frenkel conduction. The re-interpretation of Pulfrey's and other workers' "Schottky" behavior will be discussed there.

Table I summarizes some of the experimental evidence for Schottky emission in insulators, emphasizing its predominance in thin films.
### TABLE 1

Experimental Evidence for Schottky Conduction

<table>
<thead>
<tr>
<th>DEVICE STRUCTURE</th>
<th>THICKNESS (nm)</th>
<th>EVIDENCE</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-Ta$_2$O$_5$-Au</td>
<td>2.4</td>
<td>J-V (Ta +ve)</td>
<td>78</td>
</tr>
<tr>
<td>Al-Al$_2$O$_3$ { Zn, Sn, Au }</td>
<td>2.7 to 8</td>
<td>J-V-Ø metal</td>
<td>77</td>
</tr>
<tr>
<td>Si-Si$_3$N$_4$-Al</td>
<td>8</td>
<td>J-V</td>
<td>91</td>
</tr>
<tr>
<td>Al-mica-Al</td>
<td>5</td>
<td>$\varnothing_{J-V=\varnothing}$ photo</td>
<td>92</td>
</tr>
<tr>
<td>Al { GeO$_2$-Al, Al$_2$O$_3$-Al, polymerized silicon oxid-Al }</td>
<td>&lt;10</td>
<td>J-V</td>
<td>93</td>
</tr>
<tr>
<td>Al-GaSe-Au (single crystal)</td>
<td>60</td>
<td>$\varnothing_{J-V=\varnothing}$ photo</td>
<td>94</td>
</tr>
<tr>
<td>Al-Al$_2$O$_3$-Al</td>
<td>6 and 17</td>
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<td>88</td>
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<td>Ta-Ta$_2$O$_5$-Au</td>
<td>9</td>
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<td>89</td>
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</table>
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Space Charge Limited Conduction

Theory:

One of the frequently called upon conduction models in the study of anodic oxide films is space charge limited conduction - SCLC. This model considers the injection of electrons and/or holes into the dielectric in a manner analogous to a vacuum diode. In this model, a limitless supply of carriers is available at one electrode. These are injected into the material until the space charge that is built up repels new additions of charge. The flow of current is therefore dependent on the balance between the injection rate, as determined by the voltage, and the extraction rate, as determined by the carrier mobility and insulator thickness. A much abbreviated summary of the results will be presented here as a basis for comparison with Poole Frenkel conduction. The interested reader is referred to the definitive work on the subject by Lampert and Mark (95) for the details.

The development of the I-V relationships for SCLC begins with the trap free insulator of thickness d, dielectric constant ε, carrier concentration n, and mobility μ. In later discussions, traps of varying energy depths, and then hole currents and recombination centers will be added. Neglecting diffusion currents, the relation between current density J and electric field E is given by:

\[ J = n q \mu E \]  \hspace{1cm} (14)
PART I - BACKGROUND

Poisson's equation gives us:
\[ \nabla \cdot D = \rho(x, y, z) \]  \hspace{1cm} \text{<15>}

But for dc current conditions,
\[ D = \varepsilon \varepsilon_0 \xi \]  \hspace{1cm} \text{<16>}

therefore, in one dimension
\[ \frac{d\xi}{dx} = \frac{n(x) q}{\varepsilon \varepsilon_0} \]  \hspace{1cm} \text{<17>}
\[ J = \varepsilon \varepsilon_0 \frac{d\xi}{dx} \xi \mu \]  \hspace{1cm} \text{<18>}

Upon integration, with \( \xi(0) = 0 \), we have:
\[ \xi(x) = \frac{2Jx}{\varepsilon \varepsilon_0 \mu} \]  \hspace{1cm} \text{<19>}
\[ V(x) = \int_0^d \xi(x) \, dx = \frac{8Jd^3}{9\varepsilon \varepsilon_0 \mu} \]  \hspace{1cm} \text{<20>}
\[ J = \frac{9\varepsilon \varepsilon_0 \mu^2}{8} \]  \hspace{1cm} \text{<21>}

Note that below a threshold voltage the current density due
to drift of thermally generated carriers, \( n_0 \), i.e. the ohmic component,
overshadows the SCLC component. Setting the two components equal,
\[ J = qn_0 V_c = \frac{9\varepsilon \varepsilon_0 \mu}{8} \frac{V_c^2}{d^3} \]  \hspace{1cm} \text{<22>}

yields the crossover point voltage \( V_c \).
\[ V_c = \frac{8n_0 q d^2}{9 \varepsilon \varepsilon_0} \]  \hspace{1cm} \text{<23>}

Expressed in another way, SCLC is dominant only if the injected carriers can transit the sample before they are
thermally relaxed.

If there are traps present in the dielectric, they will reduce the amount of space charge current by immobilizing a portion of the injected carriers. The occupancy of the trap level is given by:

\[ n_t(x) = \frac{N_t}{1 + \frac{1}{g} \exp \left[ \frac{E_t - E_f(x)}{kT} \right]} \tag{24} \]

and the free electron density is given by:

\[ n(x) = N_c \exp \left[ \frac{E_f(x) - E_e}{kT} \right] \tag{25} \]

where

- \( n_t \) - density of occupied traps
- \( N_t \) - density of traps
- \( g \) - degeneracy factor ( = 2 for singly charged donors)
- \( E_c \) - conduction band energy
- \( E_t \) - trap energy
- \( E_f \) - Fermi energy
- \( N_c \) - conduction band effective density of states

For clarity, let

\[ N_c' = N_c \exp \left[ \frac{E_t - E_c}{2kT} \right] \tag{26} \]

\[ = N_c \exp \left[ \frac{-E_t}{2kT} \right] \tag{26} \]

therefore, combining (24), and (26)

\[ n_t(x) = N_t \left[ 1 + \frac{N_c'}{n(x)} \right]^{-1} \tag{27} \]

(31)
PART I - BACKGROUND

Note that for shallow traps, i.e. \( E_F \) below \( E_t \),

\[
 n_t(x) = N \frac{n(x)}{N_c} \tag{28} 
\]

\[
 \frac{n(x)}{n_t(x)} = \frac{N_t}{N_c} = \theta, \text{ independent of } V \tag{29} 
\]

Thus for shallow traps

\[
 J = \frac{9 \varepsilon \varepsilon_0 \theta V^2}{8 \frac{d^3}{s^3}} \tag{30} 
\]

But for deep traps where \( E_F \) is above \( E_t \)

\[
 n_t(x) \sim N_t ; \theta = 1 \tag{31} 
\]

and

\[
 J = \frac{9 \varepsilon \varepsilon_0 V^2}{8 \frac{d^3}{s^3}} \tag{32} 
\]

This is just as in the trap free case (equation \( <21> \), page 30). Thus one would expect that if the Fermi energy were made to pass through the energy level of a trap, through increased injection, for instance, then current density should increase rapidly from the shallow trap regime, where \( J \propto \theta V^3 \) to the trapped filled conditions of equation \( <32> \). Since \( n(x)/n_t(x) = \theta \) can be very small (for example \( 10^{-7} \)), the increase in current density can be very dramatic. The transition points between ohmic and shallow trap conditions, shallow and trap filled regimes, are used to estimate the thermally generated carrier density, and the trap density.

Exponents of \( V \) higher than 2 are possible, if the traps have an exponential energy distribution of the form
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\[ n_t(E) = N_t^* \exp \left[ \frac{E - E_c}{kT_f} \right] \]

where \( n_t(E) \) = trap density / unit energy

\( T_f \) = a characteristic temperature

\( N_t^* \) = a characteristic trap density / unit energy

It can be shown that for these conditions (33)

\[ J = q \mu N_c \left[ \frac{\varepsilon \varepsilon_0}{qN_t kT_f} \right]^S V^{S+1} \]

\[ \frac{d^{2S+1}}{d^2} \]

where \( s = \frac{T_f}{T} \)

Two carrier injection arises from the arrangement of an electron injecting cathode, a hole injecting anode and a suitable density of recombination centers in between. The theoretical treatment is more involved (97), but leads to four distinct J-V regimes: a low field ohmic region, a \( V^2 \) region, then VCNR (voltage controlled negative resistance), followed by a high current region where:

\[ J \propto e \mu \mu_n V^3 \frac{d^2}{d^5} \]

where \( \tau \) = an average carrier lifetime

\( \mu_p \) = hole mobility

\( \mu_n \) = electron mobility

The full range of expected SCLC J-V behavior is sketched in Figure <5>.

One further identifying feature of SCLC is the characteristic current transient as shown in Figure <6>. This subject has been
Theoretical current density - voltage (J-V) behavior of the various forms of space charge limited conduction (SCLC) is shown in this graph. In the simple, trap free, single carrier SCLC, low field ohmic $J \alpha V$ and higher field SCLC $J \alpha V^2$ regimes are seen (a). When shallow traps are present both the ohmic and SCLC relations hold as before, but at much reduced current levels (b). Deep traps, on the other hand, can have J-V behavior identical to the trap free case. However, because the Fermi level shifts with increased injection, a trap may be considered shallow at low voltage and deep at higher voltage. Consequently its J-V behavior can show a nearly vertical transition between shallow $J \alpha V^2$ and deep $J \alpha V^2$ relations (c). In the case where injection occurs at both electrodes, ohmic, then simple $J \alpha V^2$ behavior is followed by voltage controlled negative resistance (VCNR) and finally a high current $J \alpha V^3$ regime. From Lampert and Mark (95).
The space charge in an insulator takes a finite period of time to establish its final distribution. As a result, the transient behavior of current with time takes on the characteristic form shown. Current at $t = 0$ tends to a value equal to approximately one half its steady state value. Also, it will overshoot the steady state mark by up to 21% before finally decreasing. In the presence of trapping, the transient is overlaid with a general decrease proceeding with time. For strong trapping the overshoot can be completely obscured. From Lampert and Mark (95).
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dealt with in detail by Lampert (98), Many and Rakavy (99), and Lindmayer (100). An explanation is given below based upon the treatment of Lampert (98). The transient is composed of three portions: the initial rise stage from \( t=0 \) to \( t_1 \) (when the injected charge uniformly fills the volume between the cathode and the charge front which has not yet reached the anode); the relaxation stage from \( t=t_1 \) to \( t_2 \); and the steady state stage for \( t>t_2 \). The analysis of the initial rise stage is particularly simple, since the electric field is a linear function of distance between the cathode and the charge front (space charge is uniform), and is constant between the charge front and the anode (zero space charge). Also, the analysis yields quantitative estimates of both the magnitude and time of current overshoot.

The current density in the initial rise time period is the sum of conduction and displacement terms. The conduction term is, in turn, made up of drift and diffusion terms, but the diffusion term can be neglected for insulators, and for moderate electric field strengths (101). Thus

\[
J(x,t) = q n(x,t) \xi(x,t) + \frac{\partial}{\partial t} \xi(x,t) \quad <36>
\]

From Poisson's equation \( n(x,t) \) can be evaluated, i.e.

\[
n(x,t) = -\frac{\xi(x,t)}{\varepsilon_0} \quad <37>
\]

\[
J(x,t) = \varepsilon_0 \left[ \mu \xi(x,t) \frac{\partial}{\partial t} \xi(x,t) + \frac{\partial}{\partial t} \xi(x,t) \right] \quad <38>
\]

Current density is the same throughout the thickness of the
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sample, therefore it can be averaged over x from the cathode to the anode. Thus:

\[ J(t) = \frac{ce_0}{d} \left[ \mu \int_0^d \xi(x,t) \, dx + \frac{2}{\delta_t} \int_0^d \xi(x,t) \, dx \right] \]

\[ = \frac{ce_0}{d} \left[ \frac{\mu \xi^2(d,t)}{2} + \frac{3V}{\delta_t} \right] \]

\[ = \frac{ce_0 \mu}{2d} \xi^2(d,t) \]

(39)

assuming \( \xi(0) = 0 \), and \( V \) is constant.

If \( J \) is evaluated at the anode \( (x = d) \) during the initial rise time, then the only component is the displacement term because the charge front has not yet reached the anode. Therefore, combining (36) and (39)

\[ \frac{3V}{\delta_t} \xi(d,t) = \frac{\mu}{2d} \xi^2(d,t) \]

(40)

which can be integrated from \( t=0 \) to \( t \) to yield

\[ \frac{1}{\xi(d,0)} - \frac{1}{\xi(d,t)} = \frac{\mu t}{2d} \]

(41)

but since \( \xi(d,0) = V/d \)

\[ \xi(d,t) = \frac{1}{d} \left( \frac{V}{V - \frac{\mu t}{2d}} \right) \]

(42)

where \( t_o = d/\nu = d^2/\mu V \) is the transit time in the absence of

(35)
space charge effects. It is obvious that the electric field at the anode (which is the same as that at the leading front) is larger than the steady state value of $V/d$, and grows with time. Substitution of this result into <39> gives an expression for current density in the initial rise time

$$J(t) = \frac{cc_0 \mu V^2}{2d^3} \left[ \frac{1}{1 - t/2t_o} \right]^2$$  \hspace{1cm} (43)

Note that $J(0)$ is equal to

$$\frac{cc_0 \mu V^2}{2d^3}$$

which is slightly less than one half of the steady state value calculated on page 30 (equation <21>).

To calculate the amount of current overshoot, note that it occurs when the transit of the leading front is complete at $t_1$. Therefore:

$$\int_0^{t_1} \mu \xi (d,t) \alpha t = d$$

$$= \frac{2 \mu t_o V}{d} \ln \left( \frac{1 - t_1}{2t_o} \right)$$

which implies

$$t_1 = 2 t_o \left( 1 - \frac{1}{\sqrt{e}} \right) = 0.787 \ t_o$$  \hspace{1cm} (44)

Therefore, evaluating <43> at $t_1$ gives,

$$J(t_1) = 1.21 J(t>>t_o)$$  \hspace{1cm} (45)

In a similar fashion, the relaxation stage has been examined with typical results shown in Figure <6> following page 33.
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Hybrid Theories:

A number of theoretical papers combine SCLC with one or more other effects. As mentioned, Frank and Simmons (75) studied the effect of Poole Frenkel trap depth lowering on the transition between contact controlled conduction and SCLC. Later Edwards and Jones extended the work to a variety of trap energy distributions (102). Nicolet (103) and later Sworakowski (104) both attended to the problem of spatially non-uniform trap distributions. In general, however, the predictions hold that for some range of current and voltage and for some $s$, the researcher should observe:

\[ J \propto \frac{V^{s+1}}{d^{2s+1}} \]

<47>

Experimental Evidence:

Good examples of SCLC in a variety of insulators can be found in Lampert and Mark's book (95) on the subject. An early report of SCLC in an anodic oxide was made by Hickmott (71). $J \propto V^{3/4}$ behavior, typical of two carrier SCLC was observed in anodic $\text{Nb}_2\text{O}_5$ if the counter electrode was a high work function metal: e.g. gold, while $J \propto V^2$ behavior, corresponding to one carrier injection was found with a low work function material: e.g. indium. Electrode dependent behavior was also reported for this material by Sciri and Chabicovsky (105), although they saw one carrier SCLC with evaporated Au electrodes and Poole Frenkel characteristics if the gold electrodes were sputtered. The full
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range of expected two carrier SCLC behavior, including VCNR was seen by Taylor and Lalevic (106) in TiO$_x$. A report on Al$_2$O$_3$ by Mason and Nathoo (107) shows complex behavior, complicated by drift, which has certain features similar to SCLC.

In Ta$_2$O$_5$, however, most of the well documented observations have come from researchers at the University College of North Wales. The point in mentioning this fact is that the experimental method of preparing the oxide is common to all these papers. In 1973, Aris and Lewis (58) reported work done on thick oxides (160 to 500 nm), formed by anodization in phosphoric acid. They observed current rectification, with the anodic (Ta positive) polarity yielding much higher currents than the cathodic (Ta negative) polarity. Above a voltage threshold, and for films thicker than 200 nm, $J$ was proportional to $V^2 d^{-3}$. The low voltage behavior was attributed to a Poole Frenkel trap emptying mechanism. The forward bias currents were analyzed with a Schottky model, although as will be shown later, a Poole Frenkel model is just as appropriate. The analysis yields a value for the (high frequency) dielectric constant which they incorrectly use for determining the mobility in the reverse SCLC regime where the static dielectric constant should have been used. The error amounts to just under a factor of 5; therefore, the order of magnitude of effective mobility is essentially unchanged at $10^{-14}$ m$^2$/V-s. A slightly different value is deduced from the shape of the charging current transients. Effective mobility is the
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product of 0 from equation <29> and the true mobility. From their estimate of trap depth energy (.44 eV) and density (in excess of $10^{24} \text{m}^{-3}$), the true mobility is calculated to be $10^{11} \text{m}^2/\text{V-s}$. This is much lower than the electron mobility quoted in other sources (59) and is, in fact, inconsistent with transport in extended states.

Their coworkers, Jones and Hughes, (11) prepared oxides in the same manner on sputtered Ta films (b.c.c. phase). The J-V curves appear the same, showing a rapid rise due to Poole Frenkel trap emptying, followed by a $J \propto V^2 \text{d}^{-3}$ region for the Ta electrode positively biased. They correct the mistake with respect to dielectric constant, and determine a trap density of $10^{25} \text{m}^{-3}$ and an effective mobility of $10^{16} \text{m}^2/\text{V-s}$. The transient response agreed with these values.

The third paper from the group then appeared, authored by Cubanski and Hughes (70). The only change in structure is the use of gold counter electrodes instead of aluminum ones. In the course of their temperature studies they discovered that the films were rectifying and space charge dominated when freshly prepared — but exhibited low leakage symmetric $\ln(J) \propto \sqrt{V}$ behavior after being heated in vacuum. In fact, the original characteristics could be restored by re-exposure to the atmosphere. They attributed the change to oxygen diffusion. However, as mentioned previously, moisture is also a likely culprit. The significance they drew from this behavior was that
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if conduction was controlled by conditions at the anode, then, contrary to previous assumptions, the SCLC observed was actually hole injection. A note that can be added as proof is the similarity between the mobility calculated by these workers and that deduced from anodization studies by Kadavy and Klein \(10^{10} \text{m}^2/\text{V-s}\) (68). A final observation was that TSC (thermally stimulated current) scans of both the rectifying and nonrectifying samples had high temperature regions where the sense of current flow was opposite to convention, indicating non-uniform internal fields.

A summary of the experimental evidence for SCLC is given in Table II. This presentation of the data highlights the very low mobilities usually observed, and the association of SCLC with anodic oxide films thicker than 100 nm.


<table>
<thead>
<tr>
<th>DEVICE STRUCTURE</th>
<th>THICKNESS (nm)</th>
<th>EVIDENCE</th>
<th>$N_t$ ($m^{-3}$)</th>
<th>$\mu$ ($m^2/Vs$)</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-Ta$_2$O$_5$-Al</td>
<td>160-510</td>
<td>$J \alpha V^2$, $J_{-t}$</td>
<td>$10^{24}$</td>
<td>$10^{-16}$</td>
<td>58</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-Au</td>
<td>300-500</td>
<td>$J \alpha V^2$, $J_{-t}$</td>
<td></td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-Al</td>
<td>300</td>
<td>$J \alpha V^2$, $J_{-t}$</td>
<td>$10^{24}$</td>
<td>$10^{-16}$</td>
<td>11</td>
</tr>
<tr>
<td>Al-Al$_2$O$_3$-Al -Au</td>
<td>50-130</td>
<td>$J \alpha V^2$, $J_{-t}$</td>
<td></td>
<td></td>
<td>107</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-NiCr:Au</td>
<td>500</td>
<td>$J \alpha V^2$</td>
<td>$10^{24}$</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>Nb-Nb$_2$O$_5$-Au</td>
<td>160</td>
<td>$J \alpha V^2$</td>
<td>$10^{25}$</td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>Ti-TiO$_2$-Cr</td>
<td>2000</td>
<td>$J \alpha^3$, VCNR</td>
<td></td>
<td></td>
<td>106</td>
</tr>
<tr>
<td>Nb-Nb$_2$O$_5$-Au -In</td>
<td>100-270</td>
<td>$J \alpha^3d^{-5}$, $J \alpha^2$</td>
<td></td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-NiCr-Au</td>
<td>190-350</td>
<td>$J \alpha V^2$</td>
<td>$10^{24}$</td>
<td></td>
<td>109</td>
</tr>
<tr>
<td>Si-Y$_2$O$_5$-Au</td>
<td>160</td>
<td>$J \alpha V^2$</td>
<td>$10^{19}$</td>
<td>$10^{-8}$</td>
<td>110</td>
</tr>
</tbody>
</table>
Hopping Conduction

Theory:

As the name suggests, hopping conduction describes the process by which carriers move through an insulator or semiconductor via a discrete number of jumps between localized states. The distinction between such a process and Poole-Frenkel conduction, where carriers also "hop" from one localized state to another, is that the true hopping carrier never reaches the conduction (or valence) band. Its mobility is much lower, usually less than $10^{-4} \text{m}^2/\text{V-s}$. Both electrons and holes can hop. In addition, the combination of an electron and the polarization induced potential well that surrounds it, known collectively as the polaron, can also hop. Polarons only form in those ionic lattices where the electron is moving sufficiently slowly that the lattice has time to distort in response to the charge. Also, since to move a polaron, the lattice distortion around the electron is dragged along, the effective mass of the hopping entity is larger. Both these effects limit polaron hopping to low mobility materials. The two types of hopping - that of electrons along a band of localized states at the Fermi energy, and that of polarons - will be discussed in this section. The aim will be to produce the appropriate $J-V-T$ (current density - voltage - temperature) equations. The study of hopping and polarons is much more extensive than can be covered here. Extensive reviews
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covering additional topics such as the frequency dependence of conductivity, and the optical properties of systems of hopping carriers are found in "Electronic Processes in Noncrystalline Materials" by N. F. Mott, and E. Davis (47).

1 - Variable Range Hopping:

Low Field Behavior:

The Fermi energy of the non-degenerate semiconductor or insulator lies within the band gap between the valence and conduction bands. The band gap of a perfect crystal is characterized by the lack of allowed electron states, whereas within the band gap of an amorphous material or a heavily doped and compensated semiconductor a small but non-zero number of states are present. Thus in a perfect crystal carriers must be activated to the appropriate band to participate in conduction. The electrons within a kT or so of the Fermi energy in an amorphous or highly doped sample, however, are able to hop from one allowed state to another without necessarily reaching the conduction band. As expected, the principles that govern the two processes are quite different. A distinction can also be made between the hopping conductor, and a metallic sample which also has allowed states at the Fermi level. In contrast to metallic samples, the states at the Fermi energy in an amorphous semiconductor or insulator which exhibit hopping conduction are

(43)
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too few to overlap significantly. It is the overlap which leads to the formation of extended states and gives rise to band-like conduction properties.

Consider an insulator with a distribution of localized states at the Fermi energy. The probability of a successful hop depends on the energy difference, $\Delta E$, between the origin and destination state, and the overlap of the wave functions of the two states. To quantify the overlap, let the potential in the vicinity of a localized state be given by:

$$\psi(r) = \psi_0 \exp(-\eta r)$$  \hspace{1cm} (48)

where

$$\eta = \sqrt{\frac{2m^* \xi}{\hbar}}$$

$\xi$ - the ionization energy of the state

$m^*$ - the effective mass of the carrier

For the materials being studied here the radius of the localized states, given by $1/\eta$, is on the order of a few tenths of nanometers. In this notation the overlap factor in the hopping probability is given by $\exp(-2\eta R)$; where $R$ is the hopping distance. If we compare hopping to the analogous process of ion diffusion then it is possible to define a diffusion coefficient $D$ for hopping:

$$D = \nu R^2 \exp\left(-\frac{\Delta E}{kT}\right) \exp\left(-2\eta R\right)$$  \hspace{1cm} (49)
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where \( \nu \) is the attempt-to-escape frequency (which some authors have set to the lattice vibrational frequency of \( 10^{12}\text{s}^{-1} \))

Mobility may then be ascertained by use of the Einstein relationship \( \mu = qD/kT \).

\[
\mu = \frac{q \nu R}{kT} \exp \left( \frac{-W_D}{kT} \right) \exp \left( -2\eta R \right) \tag{50}
\]

and thus

\[
J = nq \mu \xi
\]

\[
= q^2 \nu R^2 \xi N(E_F) \exp \left( -\frac{W_D}{kT} - 2\eta R \right) \tag{51}
\]

where \( n = N(E_F) kT \)

The minimum spacing of energies in the band of localized states has been estimated by Mott (111) to be

\[
W_{\text{min}} = \frac{3}{4\pi R^3N(E_F)} \tag{52}
\]

At low temperatures, all transitions will be to states separated by this value, so that

\[
J = q^2 \nu R^2 \xi N(E_F) \exp \left( -2\eta R - \frac{3}{4\pi R^3N(E_F)kT} \right) \tag{53}
\]

Clearly, the exponential has a maximum when

\[
2\eta = \frac{9}{4\pi R^3N(E_F)kT} \tag{54}
\]

or

\[
R = \sqrt[3]{\frac{9}{8\pi N(E_F)kT}} \tag{55}
\]

(45)
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If it is assumed that conduction is dominated by these optimal jumps, then

\[ J = q^2 v R^2 \xi N(E_F) \exp \left( -\frac{8nR}{3} \right) \]  \hspace{1cm} (56)

\[ v = q^2 v R^2 \xi N(E_F) \exp \left[ \frac{T_0}{T} \right] \]  \hspace{1cm} (57)

where \( T_0 = \frac{18.1 n^3}{N(E_F) k} \)  \hspace{1cm} (58)

This is known as the Mott law for variable range hopping. The numerical prefactor in (58) varies from 5 to 20 depending on the averaging technique used.

At high temperatures, the limitation on successful hops will not be the supply of thermal energy, but rather the overlap factor \( \exp(-2nR) \). Under these conditions the observed activation energy will be \( \hbar \omega_{\text{max}} \) which is equal to the mean spread in energies within the band of localized states. The hallmark of variable range hopping is, therefore, an Arrhenius plot of \( \ln(J/V) \) vs \( 1/T \) which is not linear. A typical example is shown in Figure (7). The activation energy derived from such a plot decreases continuously as temperature decreases, and the low temperature behavior is better fitted with \( \ln(J/V) \) set equal to a linear function of \( T^{-4} \). Because the low temperature behavior is so distinctive it is most often used to test the applicability of the model to experimental data.

Related low temperature hopping conduction models have been proposed. For instance, if the density of states at the Fermi
The activation energy of conductivity in a system exhibiting variable range hopping is a constant at high temperatures when the carrier hops between nearest neighbors of a fixed energy separation, $\xi_0$. Below a transition temperature, $T_c$, the carrier may not possess sufficient energy to make a transition to these sites, and will instead be forced to find a more distant site whose energy separation is smaller. Thus the observed activation energy drops at low temperature.
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energy is allowed to vary with energy, analysis has shown (113):

\[
\ln \sigma = -T^s(b) \tag{59}
\]
\[
s = \frac{b+1}{b+4} \tag{60}
\]

where

\[
N(E) = |E-E_F|^b \tag{61}
\]

Note that for \( b=0 \) (constant density of states), Mott's hopping law is recovered. In the experimental work accompanying this analysis, an exponent of \( 0.40 \pm 0.05 \) was found for a number of amorphous semiconductors including Si, GaAs, GaP, and InP.

It has also been pointed out that for films whose thicknesses are comparable, or less than, the hop distance, conductivity becomes thickness dependent, and \( S(b) \) of equation \( 59 \) approaches \( 1/3 \) (114-116).

High Field Behavior:

So far hopping has only been shown to produce ohmic behavior. The model has been extended to higher electric fields (117-122). It is assumed that for each jump of length \( R \) the electron picks up an amount of energy \( q\mathcal{E}R \). The effective activation energy is then \( W-q\mathcal{E}R \) and current density is

\[
J = K_H \xi \exp \left( \frac{q\mathcal{E}R}{kT} \right) \exp \left[ -\frac{T_0}{T} \right]^k \tag{62}
\]

where

\[
K_H = \frac{q^2 \nu R^2 n}{kT}
\]

\( c \) is a constant less than unity introduced by Pollak

(47)
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and Riess (119) to take into account that the path from one site to another has only a component exactly parallel to the field. Their percolation methods gave a typical value of \( c \) to be .17.

At medium field strengths a significant number of transitions are made "upstream", against the electric field. For those jumps the barrier is increased. The net current density is given by (117,118,120,121):

\[
J = 2 K_H \xi \exp\left[\frac{T_0}{T}\right] \sinh \left\{ \frac{qFR}{kT} \right\} \leq 63\right.

Shklovskii (121,122) and Hill (117) both extended the work to high fields. In Shklovskii's treatment

\[
J \propto \exp\left[ \frac{qER}{kT} \right]^{1/1+\nu} \quad \nu=0.9 \leq 64\right.

Hill on the other hand, finds that at higher fields, the electron gains enough energy to reach the conduction band, and thus no longer qualifies as a true "hopping" carrier. In fact, his treatment shows that the differences between hopping conduction and Poole's law for field assisted ionization of closely spaced donors become negligible as \( \xi \) increases. Poole's law will be discussed in Part II as an extension to Poole Frenkel conduction.

In all of these treatments, \( R \) is temperature dependent. At low temperature the electron must hop a longer distance to find a site that differs by only the small amount of thermal energy.
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available, whereas at high temperature, the electron can jump to any of the nearest neighbours. Thus $R$ should decrease with increasing temperature.

ac Conductivity:

Although the temperature and field dependences of hopping conduction should suffice to distinguish between hopping and the other conduction models proposed for Ta₂O₅, most researchers rely upon on further signature: that is, the ac conductivity $\sigma(\omega)$ at low frequencies ($10^{-3}$ to $10^5$ Hz) for hopping conduction is found to be proportional to $\omega^s$ where $0.8 < s < 1$. The derivation of the detailed expression is found in reference 123. The main result is quoted below to permit the evaluation of experimental evidence from the literature; even though the ac properties of the films in this study were not examined in any depth.

$$\sigma(\omega) = 2.5q^2 kT \left( \frac{n}{u_0} \right)^{2n-5} \left\{ \ln \left( \frac{\nu}{\omega} \right) \right\}^4$$  \hspace{1cm} (65)

where $n =$ hopping carrier density

$n =$ overlap parameter (equation (48), page 44)

$u_0 =$ disorder parameter

$\nu =$ phonon frequency (10¹² s⁻¹)

For low frequency measurements, Mott estimates the frequency dependence of $(\ln(\nu/\omega))^4$ to be approximately $\omega^{-2}$, yielding an $s$ of .8.

(49)
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In contrast, the high frequency conductance was found to be

\[ \sigma(\omega) = \left( \frac{\pi \omega n}{\nu_0} \right)^2 \eta \eta^5 \left\{ \ln \left( \frac{\nu_0}{\eta \omega} \right) \right\}^4 \]  \hspace{1cm} (66) \]

where \( \nu_0 \) was defined in equation (48), page 44.

An \( \omega^2 \) response is often found in insulators and semiconductors. However, other phenomena can also give rise to an \( \omega^2 \) response (e.g. series resistance), so that the high frequency response is not conclusive evidence for hopping conduction.
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11 - Polaron Hopping

Low Field Behavior:

Because polaron hopping is completely analogous to electron hopping, the basic equations describing J-V-T behavior is the same as in equation (51) page 45, repeated here.

\[ J = q^2 \nu R^2 \xi N(E_F) \exp \left[ -\frac{\frac{6a}{kT} - 2\eta R}{\xi} \right] \]  

(51)

In this case however, the nature of the hopping carrier, the polaron, contributes to the form and temperature dependence of the hopping activation energy \( E_a \) (125-127). In the hopping of the polaron, there are two energies to be considered: that needed to form the polaron, \( \nu_p \), and that needed to overcome any energy difference between the origin and the destination states, \( \nu_D \). To calculate \( \nu_p \), let the distortion energy of an ion be expressed in terms of a displacement from an equilibrium position \( q_1 \). A parabolic expression with the value of zero at the minimum might be:

\[ E_1(x) = A (x-q_1)^2 \]  

(67)

Let a second ion have a similar energy form, but a minimum value of \( \nu_D \) i.e.

\[ E_{II}(x) = A (x-q_2)^2 + \nu_D \]  

(68)

These two sites are shown schematically in Figure 8.
Figure 8: Schematic of the Intra-site Transfer of a Polaron

Any displacement of ions I and II from their equilibrium positions \( q_1 \) and \( q_2 \) results in a parabolic increase in each of their potential energies \( E_I \) and \( E_{II} \). The equilibrium energies of the two sites differ by \( W_D \).

Adding an electron to site one contributes an energy \( B \cdot (x - q_1) \), creating a polaron with total energy \( E_I' \). The activation energy for the formation of the polaron is \( W_P \).

For electron transfer to occur the electron energy on site I, \( B \cdot (x - q_1) \), must equal that on site II, \( B \cdot (x - q_2) + W_D \).

A suitable configuration can be formed by allowing both ions to distort. The optimal distortion, shown here, has an activation energy of \( \zeta_n \).
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Now if an electron were placed adjacent to the first ion, its energy expression becomes:

\[ E_I(x) = A(x - q_1)^2 - B(x - q_1) \]  \( \text{<69>} \)

which has a minimum at:

\[ (x - q_1) = \frac{B}{2A} = q_0 \]  \( \text{<70>} \)

Thus the amount of energy required to produce a system of an electron and a distorted lattice is:

\[ \Delta W_p = E_I(q_0) - E_I(q_0) = \frac{B^2}{4A} - Aq_0^2 \]  \( \text{<71>} \)

Although it may require \( \Delta W_p \) to create a polaron, it takes somewhat less than that value to shift the polaron from one lattice site to another. The necessary condition is that the electron have the same energy in both sites, i.e.

\[ B(x - q_1) = B(x - q_2) + \Delta W_0 \]  \( \text{<72>} \)

The energy required to produce the distortion of the lattice corresponding to this configuration is:

\[ \xi_a = A(x - q_1 - q_0)^2 = A(x - q_1 - \frac{\Delta W_0}{B})^2 \]  \( \text{<73>} \)

The energy of the system with site one with \( (x - q_1) = q_0 \) and site two with \( (x - q_2) = q_0 \), as in equation \( \text{<72>} \)

\[ (x - q_1) = \frac{q_0}{2} + \frac{\Delta W_0}{2B} \]  \( \text{<74>} \)

(52)
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Therefore:

\[ \zeta_a = A \left( \frac{W_D}{2B} - \frac{q_0}{2} \right)^2 + A \left( \frac{q_0}{2} - \frac{W_H}{2B} \right)^2 \]

\[ = 2A \left\{ \left( \frac{W_H}{2B} \right)^2 + \frac{q_0 W_D}{2B} + \frac{q_0^2}{4} \right\} \]

\[ = \frac{Aq_0^2}{2} + \frac{W_H}{2} + \frac{Aq_0^2}{2B} \quad \ldots \tag{76} \]

Let \( W_H = \zeta_a (W_D = 0) = Aq_0^2/2 \), then

\[ \zeta_a = W_H + W_D + \frac{W_H^2}{16 W_H} \quad \ldots \tag{77} \]

Note that the energy to shift a polaron in the absence of \( W_D \), i.e., \( W_H \), is one half of the energy required to create the polaron. From known values of \( W_p \), polaron hopping energies of on the order of \( 0.5 \, \text{eV} \) can be estimated (126).

The transfer of the electron can be made in two ways: adiabatically, and nonadiabatically.

1) Two conditions must hold for the adiabatic case: the excited state where a polarization well exists for both sites (Figure 8) must persist long enough, and the separation between the wells must be small enough that the electron makes many passes back and forth between the sites. This resonance lowers \( \zeta_a \) further below \( W_p/2 \) (125). The J-V-T expression (51) (page 45) becomes:

\[ J = \frac{q^2 v a^2 \zeta n}{kT} \exp \left( -\frac{\zeta a}{kT} \right) \quad \ldots \tag{78} \]

Note that the closely spaced ions imply that the overlap factor, \( \exp(-2aR) \approx 1 \), and that \( R = a \), where \( a \) is the nearest
PART I - BACKGROUND

neighbour separation.

2) In the nonadiabatic case, the electron transition is not probable, therefore the resonance effect is negligible. Also, the overlap factor must be retained. Therefore equation (51) remains unchanged.

Schnakenberg (127) has examined the temperature dependence of the hopping activation energy when more than one type of phonon (acoustic and optical) are involved. His analysis predicts a change in \( \zeta_0 \) from \(-W_H + W_D/2\) (equation (76), page 53) to \( W_D \) as temperatures drop below \( \Theta_D/2 \). \( \Theta_D \) is the Debye temperature, which ranges in oxides similar to \( Ta_2O_5 \) between 400 and 800 K. \( W_D \) itself is estimated to be on the order of \( kT \) (118).

High Field Behavior:

As in electron hopping, conductivity becomes nonohmic when the polaron picks up an energy \( q\xi R \) which is an appreciable fraction of the hopping activation energy. Therefore, using the same arguments, for moderate fields:

\[
J(\xi) = \frac{J(0) \sinh \left( \frac{c q R \xi}{2kT} \right)}{c q R \xi \frac{2kT}{2kT}} <79>
\]

and for high fields:

\[
J(\xi) = J(0) \exp \left( \frac{c q R \xi}{kT} \right) <80>
\]

As mentioned before, \( c \) is a number to take into account that
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not all jumps are exactly parallel with the field. Also, as mentioned before, $R$ is temperature dependent, decreasing to the limit of nearest neighbour spacing as temperature increases. In some work it is evident that the number of sites "passed over" at room temperature can be substantial - in a variety of transition metal ion glasses Austin and Sayer found the hopping distance appeared to be 4 to 17 times the intersite spacing (118). They attributed this to the enhancement of the local electric field around the site due to fluctuations in the local well depths.

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Experimental Evidence:

Hopping conduction is well documented in amorphous semiconductors (113, 114, 116, 128-130), heavily doped single crystals (131-134) and transition metal oxide single crystals (135). In this section, the emphasis is on those materials most similar to Ta$_2$O$_5$. Only two examples of hopping conduction in Ta$_2$O$_5$ itself are found. Both cases rely heavily upon the examination of the frequency dependence of ac conductivity. In Savinova's study (136) $\sigma$ was found to be proportional to $\omega^s$ where $s = .95$ for frequencies between $10^{-1}$ and $10^3$ Hz, and temperatures between 300 and 400 K. Bryksin et al. (137) also examined the ac conductivity of Ta$_2$O$_5$. In the range of 1 to $10^5$ Hz, $s$ was found to be .95 at room temperature but somewhat smaller at higher temperatures. Thus variable range hopping was inferred. Bryksin et al. also looked at the temperature and field dependence of dc conductance. Mott's law, equation (57) was observed for an extended temperature range (77 - 400 K) and equation (62) relating electric field and conductance was observed for $\xi$ between 2 and $3.8x10^6$ V/m. A characteristic hop length of 1.81 nm, independent of temperature, was calculated from the data. The number of sites participating was also calculated to be on the order of $10^{26}$ m$^{-3}$.

Also noteworthy are the examples of SiO$_x$ studied by Frost and Jonscher (138), and the Cr$_2$O$_3$ studied by Barbe and Herman.
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(139). In both cases, the ac conductivity indicated hopping, while the dc behavior was best analyzed using the Poole Frenkel model. These models are compatible, since the ac behavior is controlled by the easiest transition, whereas the dc behavior is controlled by the hardest transition (140).

The experimental evidence for hopping conduction in $\text{Ta}_2\text{O}_5$ and related compounds are summarized in Table III.
<table>
<thead>
<tr>
<th>DEVICE STRUCTURE</th>
<th>THICKNESS (nm)</th>
<th>EVIDENCE</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-Ta₂O₅-C</td>
<td>200</td>
<td>σ ~ ω⁻⁰·₉₅</td>
<td>136</td>
</tr>
<tr>
<td>Ta-Ta₂O₅</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>175</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ ~ ω⁻⁰·₉₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inσ ~ ξ (limited range)</td>
<td>137</td>
</tr>
<tr>
<td>Si-Cr₂O₃-Al</td>
<td>100</td>
<td>σ ~ ω⁻⁰·₉₅ LF</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ ~ ω² HF</td>
<td></td>
</tr>
<tr>
<td>Sc-Sc₂O₅-In</td>
<td>10-15</td>
<td>σ ~ ω⁻⁰·₅ &lt;ω&lt;1</td>
<td>141</td>
</tr>
<tr>
<td>Au-(V₂O₅)(P₂O₅)-Au</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ ~ ω⁻⁰·₇₃ &lt;ω&lt;0·₈₆</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ζσ=f cn(T)</td>
<td></td>
</tr>
<tr>
<td>Au-SiO₅-Al</td>
<td>220-620</td>
<td>σ ~ ω⁻⁰·₆</td>
<td>143-144</td>
</tr>
<tr>
<td>Al-AlN-Al</td>
<td>125</td>
<td>σ ~ ω⁻₀·₈₃</td>
<td>145</td>
</tr>
<tr>
<td>Al-Si₃N₄-Al(Ti)</td>
<td>120</td>
<td>lnσ ~ T⁻¹/₂</td>
<td>146</td>
</tr>
<tr>
<td>Al-biotite-Au mica</td>
<td>10⁵</td>
<td>lnσ ~ T⁻¹/₂</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lnσ ~ ξ</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ζσ=f cn(T)</td>
<td></td>
</tr>
<tr>
<td>Au-{NiF₂}³−Au(6F)</td>
<td>500</td>
<td>lnσ ~ T⁻¹/₂</td>
<td>148</td>
</tr>
</tbody>
</table>
PART II - THEORY

1. POOLE FRENKEL CONDUCTION THEORY

In this section a detailed Poole Frenkel conduction theory will be presented. To begin with, simple one dimensional analysis will be put forward, followed by an extension to three dimensions. Then field enhanced ionization of non-Coulombic potential wells will be discussed. This will set the stage for a description of the current density - voltage - temperature (J-V-T) behavior expected when Poole Frenkel barrier lowering controls conductivity. Although this thesis is concerned only with dc conductivity, field enhanced barrier lowering is of concern in the interpretation of DLTS (Deep Level Transient Spectroscopy) (149,150), FATSIC (Field Assisted Thermally Simulated Ion Current) (151), photoconductivity (152,153) and ac conductivity (154) results, as well. As in the discussions of alternate conduction models, this section will conclude with a description of the various hybrid models that combine the Poole Frenkel effect with other conduction models, and with a summary of the experimental evidence for Poole Frenkel conduction reported in the literature.
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Poole Frenkel Barrier Lowering - One Dimensional Analysis:

Poole Frenkel conduction arises from the interaction between a large electric field and the potential well surrounding a donor or an acceptor. The term donor (or acceptor) is meant precisely. By definition, a donor is charged when empty and neutral when filled. There are other configurations, for example, traps, which do not experience Poole Frenkel barrier lowering because they are charged when full and neutral when empty. The reason for this distinction will become clear in the following discussion. First, consider as Frenkel did in 1938 (155), the isolated donor in a crystalline semiconductor. Solid state theorists have shown that the behavior of an electron in the vicinity of the donor may be described with surprising accuracy by making slight modifications to the predicted behavior of an electron near a singly charged positive ion (156). Because the escaping electron sees an attractive force due to the net positive charge on the ionized donor, the potential well is Coulombic, as in the hydrogen atom. However, an effective electron mass and an effective dielectric constant are used to take into consideration the other core electrons between the positive ion and the electron under study. Furthermore, these constants are characteristic of the matrix, not the source of the imperfection, which may be an impurity atom or misplaced host atom, because the orbit of the extra electron encompasses many host atoms. The orbital frequency of the extra electron is such that the core electrons are not polarized.
Therefore the dielectric constant used in the model is the high frequency one. An appropriate measure of the high frequency dielectric constant is the square of the index of refraction. This distinction is particularly important in Ta$_2$O$_5$ which has a low frequency dielectric constant of 21 to 29 (157) and a high frequency dielectric constant of 4.4 to 5 (158). In fact, this can be used to distinguish between electronic Poole Frenkel barrier lowering and an analogous process which enables ions to move from potential well to potential well under the influence of an electric field (159-161). In the latter case, the low frequency dielectric constant is appropriate.

Thus a modified Coulomb's law gives the shape of the potential well surrounding an arbitrary imperfection as:

$$E(r) = \frac{q}{4\pi \varepsilon_0 r^5} \quad \tag{81}$$

As shown in Figure 9a, this form of potential implies a spherically symmetric barrier of height $\zeta = E_C - E_d$ to an electron attempting to escape from the vicinity of the impurity into the conduction band. The superposition of an applied electric field, as shown in Figure 9b, distorts the potential barrier, and reduces its height for trajectories with a component parallel to the field. If the field is applied in the positive x direction, then the total potential energy of the electron is given (in 1 dimension) by

$$\tag{61}$$
Figure 9: Energy Band Diagram of Poole-Frenkel Potential Well

(a) The potential well formed around a donor has a spherically symmetric shape defined by Coulomb's law.

(b) An external electric field can distort the potential well, making it easier for the electron to escape in the field direction. The amount of barrier lowering $\Delta \xi$ is proportional to the square root of applied electric field.
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\[ E(x) = E_c - \frac{q^2}{4\pi\varepsilon_0} - q \xi x \]  \hspace{1cm} <82>

Differentiating with respect to \( x \) locates the peak in the positive \( x \) direction

\[ x_p = \frac{\sqrt{q}}{p \sqrt{4\pi\varepsilon_0}\varepsilon_{\max}} \]  \hspace{1cm} <83>

which implies a barrier lowering of

\[ \Delta\varepsilon_d = \frac{\sqrt{\frac{q}{p \varepsilon_0}}} {4\varepsilon_0} = \alpha \]  \hspace{1cm} <84>

Thus in this one dimensional analysis the enhancement in emission probability, \( P(\xi) \) over the zero field probability, \( P(0) \) is:

\[ \frac{P(\xi)}{P(0)} \exp\left(\frac{\alpha}{kT}\right) \]  \hspace{1cm} <85>

Poole-Frenkel Barrier Lowering - Three Dimensional Analysis:

There is an obvious difficulty with this simple theory: emission is enhanced for all trajectories with a component aligned with the field. Many researchers have considered this aspect (65, 162-165). Equation <82> is replaced by

\[ E(r, \theta) = -\frac{q^2}{4\pi\varepsilon_0} - q \xi r \cos \theta \]  \hspace{1cm} <86>

where \( \theta \) = the angle between the escape trajectory and the field direction.

By differentiating \( E(r, \theta) \) with respect to \( r \) and setting the result to zero, the angle dependent barrier lowering can be
PART II - THEORY

evaluated:

\[ \Delta \alpha_d \approx \sqrt{\frac{q^2}{\pi E_0} \cos \theta} = a \sqrt{\cos \theta} \]  \(<87>\)

In order to obtain the total emission enhancement ratio different methods of spatial averaging over all \( \theta \) were used by the different researchers. Connell et al. (162) used an exact numerical method.

Hartke (163) integrated over the "forward hemisphere" (i.e. for \(-\pi/2 < \theta < \pi/2\)). Emission into the "reverse hemisphere" was considered to be unaffected by the electric field. This approach yields:

\[ \frac{P(\theta)}{P(0)} = \left[ \frac{kT}{\alpha} \right]^2 \left[ 1 + \left( \frac{\alpha}{kT} - 1 \right) \exp \left( \frac{\alpha}{kT} \right) \right] + \frac{1}{2} \]  \(<88>\)

Note that the "\(1/2\)" term is the constant term arising from the "reverse hemisphere" emission. See Figure <10>.

Jonscher (65) set the reverse term to zero — implying no reverse emission. Hill (164) proposed that an appropriate approximation would be to let the barrier at \((r, r-\theta)\) in the "reverse" direction be increased by the same amount that the barrier at \((r, \theta)\) had been decreased. The resultant expression is:

\[ \frac{P(\theta)}{P(0)} = 2 \left( \frac{kT}{\alpha} \right)^2 \left[ \left( \frac{\alpha}{kT} \right) \cosh \left( \frac{\alpha}{kT} \right) - \sinh \left( \frac{\alpha}{kT} \right) \right] \]  \(<89>\)

Ieda et al. (165), on the other hand, introduced the concept that given the availability of thermal energy, the in the form of

(63)
Figure 10: Field Dependence of Different Emission Enhancement Ratios

In this diagram the Poole-Frenkel emission enhancement ratio is plotted against the dimensionless parameter $\alpha/kT$ (defined on page 62) for the following models:

- One dimensional equation <85> page 62
- Hartke <88> page 63
- Hill <89> page 63
- Ieda et al. <91> page 64
- Onsager/Pai (one step process) <93> page 65

Note that the slopes of these plots are the same for $\alpha/kT > 5$, corresponding to a voltage of 0.6 V for the devices considered here.
In the procedure of Ieda et al. (165) the edge of the Coulombic potential well is set to be where the energy of the escaping electron is within $\zeta_{th}$ of the conduction band. In this manner an effective radius, $r_{eff}$, and an effective donor depth $\zeta_d(d)$ can be defined for all trajectories.
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lattice phonons, the carrier need only reach within $\xi_{th}$ of the band edge to be considered ionized. This assumption permits the definition of an effective potential well depth, $\xi_{eff}(0)$ for all carrier trajectories as shown in Figure 11. It is then possible to integrate over all $\theta$ in a simple manner. Two regimes become apparent. At low fields the carrier is ionized before reaching the peak of the barrier, so that the enhancement ratio is:

$$\frac{P(\xi)}{P(0)} = 2\xi_{th} \frac{kT}{\alpha^2} \sinh \left( \frac{\alpha^2}{4kT \xi_{th}} \right)$$  \hspace{1cm} (90)

But at high fields, the radial position of the peak of the barrier, $r_p(\theta)$ is within $r_{eff}(0)$ for some portion of the "forward hemisphere", so that:

$$\frac{P(\xi)}{P(0)} = \left( \frac{kT}{\alpha} \right)^2 \left( \frac{\alpha}{kT} - 1 \right) \exp \left( \frac{\alpha}{kT} - \frac{\xi_{th}}{2kT} \right)$$

$$\times \left( \frac{\xi_{th}}{kT} \exp \left[ \frac{-\alpha^2}{2kT \xi_{th}} \right] + \exp \left[ \frac{\xi_{th}}{2kT} \right] \right)$$  \hspace{1cm} (91)

Equations (89-91), (91) and (93) are compared against the one dimensional equation (85), page 62 on Figure 10. Note that for high electric fields the slopes of the enhancement ratio vs $\sqrt{\xi}$ curves are identical. Only at low fields are differences evident. Also, each of the three dimensional approaches characteristically produce near ohmic behavior at very low fields.

So far, all of the Poole Frenkel conduction models have expressed the emission enhancement ratio in terms of the barrier

(64)
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height alone. The implication is that the nature of the escape process is little effect on the observed electrical behavior. In contrast, the Onsager approach (166-169) explicitly considers the three-dimensional diffusion process (Brownian motion) in the presence of a specified potential. The equation to be solved is:

\[
\frac{\partial f}{\partial t} = -\frac{kT}{q} \mu \text{div} \left[ \exp \left( -\frac{E(r, \theta)}{kT} \right) \right] \text{grad} f \exp \left( -\frac{E(r, \theta)}{kT} \right) \tag{92}
\]

where \( E(r, \theta) \) is given by equation (86) page 62. 

\( f \) is the probability function.

\( \mu \) is mobility.

The solution in the case of the electron originating at a donor for steady state is:

\[
\frac{P(\varepsilon)}{P(0)} = \frac{J_1 \left( \frac{q \varepsilon}{kT} \right)}{2 \pi \varepsilon} \quad J_1 \text{ = Bessel function of first order} \tag{93a}
\]

\[
= 1 + \frac{1}{2!} \left( \frac{q \varepsilon}{kT} \right)^2 + \frac{1}{2 \cdot 3!} \left( \frac{q \varepsilon}{kT} \right)^4 + \frac{1}{3 \cdot 4!} \left( \frac{q \varepsilon}{kT} \right)^6 + \cdots \tag{93b}
\]

The subsidiary assumptions are:

1) carrier is delocalized if \( r > \frac{1}{2} \left[ \frac{q \varepsilon}{4 \pi \varepsilon_0 kT} \right]^2 \)

2) \( \exp \left[ \frac{q \varepsilon r \cos \theta}{kT} \right] - 1 \) for \( r < \frac{1}{2} \left[ \frac{q \varepsilon}{4 \pi \varepsilon_0 kT} \right]^2 \)

3) negligible screening

4) negligible overlap of adjacent potential wells

Pai (167) considered the ramifications to the Poole Frenkel conduction situation. His results are also shown on Figure (10).
A simple formula which replicates equation (93b) for \(\xi\) in the range of \(10^6\) to \(10^9\) V/m is given by Adamec and Calderwood (168):

\[
\frac{P(\xi)}{P(0)} = 0.531 \left[ \frac{kT}{\alpha} \right]^{0.75} \exp \left[ \frac{\alpha}{kT} \right]
\]

The Onsager formulation is especially useful in describing the electric field dependence of recombination events where the electron and hole are initially separated (166, 167, 169, 170). The change in boundary conditions has a profound effect on the field dependence of the enhancement ratio, as shown in Figure 12. The high field ln \(\ln \frac{P(\xi)}{P(0)}\) linear in \(\sqrt{\xi}\) behavior is lost and instead the enhancement ratio tends to saturate at high fields. There is one situation that might be encountered in an insulator to which this form may apply. Suppose the carrier begins its escape from a neutral trap within the Coulombic potential well (171, 172). The Onsager formulation for initially separated charges must be used. Plans et al. (171) call this the two-step process, and find experimental evidence for it in the case of the release of photogenerated carriers in TSC (Thermally Stimulated Current) spectra.

Poole-Frenkel Barrier Lowering - Non-Coulombic Potentials:

At this point, it could be noted that field-enhanced emission need not be restricted to Coulombic potentials. Other potentials such as the screened Coulombic (173-177) and those of
The field dependence of the emission enhancement ratio predicted by the Onsager model is compared for the one and two-step processes. In case (a) the electron begins its escape from the center of the potential well, while in case (b) the electron starts its second step of the escape process from a distance of 1.5 nm away from the center. $\alpha/kT$ which is proportional to $\sqrt{\xi}$ was defined on page 62. From Pai (167)
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the form $E(r) \propto \exp^{-m}$ have been considered (172, 174-176, 178-179).
While strictly speaking the resulting conduction formulae are not "Poole-Frenkel-like" in nature, it is instructive to consider them here for comparison.

The screened Coulombic or Yukawa potential (173-172) has been studied in the context of donor ionization. The potential energy of the electron in the vicinity of the donor has the form:

$$E(r, \theta) = \frac{\alpha^2}{\epsilon_0} \exp\left(-\frac{r}{r_o}\right) + \frac{q\epsilon r \cos\theta}{r_o}$$

where $r_o$ is the shielding length.

As in conventional Poole Frenkel analysis, the energy equation <95> is differentiated with respect to radius and set equal to zero to locate the barrier extrema. In this case, however, the process must be done numerically. Martin et al. (173) presented analysis that showed that the Yukawa potential only deviates significantly from the Coulombic potential when $r_o$ is less than 10 nm. Kahut and Schirmeister (177) give theoretical enhancement ratio curves for a range of electric fields, screening lengths, dielectric constants and temperatures. They present an estimate of the screening length:

$$r_o = \sqrt{\frac{kT \epsilon \epsilon_0}{g^2 N_d}}$$

where $T_g$ is the temperature at which the defects were formed

$N_d$ is the density of charged donors
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Although this expression was proposed for glasses, it can serve as a first-order approximation for amorphous Ta₂O₅. Given the material properties of Ta₂O₅, equation (96) implies that in excess of $10^{-22}$ m⁻³ charged defects are required to reduce the screening length to less than 10 nm. Thus consideration of the Yukawa potential is necessary only when donors are dense and shallow (i.e., charged at room temperature). The strong temperature dependence of conductivity in Ta₂O₅ demonstrates that conduction is not dominated by shallow levels, and thus the Yukawa potential can be safely approximated by the Coulombic one.

Another class of potentials that has been considered (172, 174-176, 178-179) is of the form:

$$E(r) = A r^{-m}$$

where $A$ is a constant, or slowly varying function of $r$.

This yields a one-dimensional field induced barrier lowering of the form:

$$\frac{F(\xi)}{F(0)} = \exp\left(\frac{m+1}{kT} \left[ \frac{A}{m} \frac{q^2}{m} \right] \frac{m+1}{m} \frac{1}{m} \right)$$

Marshall and Miller (179) also used a truncation procedure similar to what Feda et al. (165) used with the Coulombic potential in order to extend the work to three dimensions.

The Coulombic potential is the special case where $m=1$. Other exponents are also physically meaningful.
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1) \( m=2 \) corresponds to the dipole potential energy:

\[
E(r,\phi) = -\frac{q\delta \cos \phi}{4\pi \varepsilon_0 r^2}
\]

which may arise from a complex of two oppositely charged centers (173), or from a dipolar molecular impurity (180). In this case the amount of barrier lowering is dependent on the angle between \( \zeta \) and \( \bar{\phi} \).

ii) \( m=3 \) is the quadrupole potential energy which may arise from lattice strain around a substitutional isoivalent impurity (172).

iii) \( m=4 \) is the polarization potential which has been used to describe that around neutral traps (173).

Two other potential wells with similar field dependent enhancement ratios have been considered. They are the system of multiple overlapping Coulombic wells (164), and the square well (173, 181). Both lead to Poole's law (155, 164):

\[
\frac{P(\xi)}{P(0)} = \exp (B\xi)
\]

where \( B \) is a constant.

To summarize, the field enhanced ionization of a deep impurity in a semiconductor or an insulator has a variety of theoretical forms governed by the assumed shape of the potential well. The most general form is \( E(r)=Ar^{-m} \) which leads to an enhancement ratio that increases exponentially as \( \xi \) to the
exponent of $\frac{m}{(m+1)}$ for $1 \leq m < 4$. Only the Coulombic form ($m=1$) expected for simple donors or acceptors leads to the Poole Frenkel effect. The screened Coulombic or Yukawa potential should be used at high charge densities. By correctly taking into account the possibility of emission in all directions, ohmic behavior is predicted at low field strengths with the Coulombic potential. At high field strengths, however, all Coulombic forms approach the simple one dimensional form, i.e.:

$$\frac{P(\varepsilon)}{P(0)} = \exp \left[ \frac{\alpha}{kT} \right] = \exp \left[ \frac{1}{kT} \sqrt{\frac{3 \varepsilon}{\pi \varepsilon_{0}}} \right]$$

<85>'

In this work, therefore, the various conduction models will be tested in the high field regime. The low field behavior does not yield much additional information, as was noted by Hrivnak (176). The primary reason being that the close similarity between the various three dimensional Poole Frenkel models at low fields precludes distinguishing which model is most appropriate.
Current - Voltage - Temperature Behavior:

Electric field enhanced emission will lead to electric field dependent carrier concentration and thus nonohmic current - voltage behavior if and only if the source of carriers is a partially ionized donor (or acceptor) level. In the following discussion, the expressions relating current to voltage in the presence of Poole Frenkel barrier lowering will be derived.

In the most general system containing acceptors and donors, the expression for charge neutrality is (182):

\[ n + n_d - \frac{N_a}{N_d} + N_a = p + n_a + N_d \tag{101} \]

where

\( n \) = the density of free electrons
\( N_d \) = the density of donors
\( n_d \) = the density of un-ionized donors
\( p \) = the density of free holes
\( N_a \) = the density of acceptors
\( n_a \) = the density of un-ionized acceptors

Let us consider an \( n \) type material. This implies that \( p \) and \( n_a \) are negligible. Now

\[ n = N_c \exp \left( \frac{E_F - E_C}{kT} \right) \tag{102} \]

where \( N_c \) = the conduction band effective density of states
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\( E_F \) = the Fermi energy

\( E_C \) = the conduction band energy

Also

\[
\frac{N_d}{1 + \frac{1}{\varphi} \exp \left( \frac{E_d - E_F}{kT} \right)} = \frac{N_d}{1 + \frac{N_c}{2n} \exp \left( \frac{-\xi_d}{kT} \right)}
\]  \( <103> \)

where \( E_d \) = the donor energy level

\( \xi_d = E_C - E_d \), the donor activation energy

\( \varphi \) = ground state degeneracy of the impurity level ( \( \varphi = 2 \) )

For the sake of brevity, let:

\[
N_c' = \frac{N_c}{2} \exp \left( \frac{-\xi_d}{kT} \right)
\]  \( <104> \)

Therefore, from \( <102> \)

\[
n = N_d - N_a - \frac{N_d}{1 + \frac{N_c'}{n}}
\]  \( <105> \)

which yields a quadratic expression in \( n \):

\[
n^2 + n (N_c' + N_a) - N_c' (N_d - N_a) = 0
\]  \( <106> \)

with a physically acceptable solution

\[
n = -\frac{1}{2} \left( N_a + N_c' \right) + \frac{1}{2} \left( (N_C' + N_a)^2 + 4 N_c' (N_d - N_a) \right)^{1/2}
\]  \( <107> \)

This formula has two simple approximations as described below.
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CASE I - Uncompensated Donors

Let \( N_a \) be very small. In addition, let \( N_d \gg N_c \) to ensure that these levels are partially ionized for Poole Frenkel barrier lowering to be significant. In this case equation (107) has an approximation of

\[
\bar{n} \approx \sqrt{N_c N_d} \exp \left[ -\frac{\zeta_d}{2kT} \right] \exp \left[ \frac{1}{2kT} \sqrt{\frac{3e}{\pi \epsilon_0}} \right]
\]

And in the presence of Poole Frenkel barrier lowering in the high field limit where from page 62:

\[
\Delta \zeta_d = \sqrt{\frac{3e}{\pi \epsilon_0}}
\]

Thus

\[
\bar{n} = \sqrt{N_c N_d} \exp \left[ -\frac{\zeta_d}{2kT} \right] \exp \left[ \frac{1}{2kT} \sqrt{\frac{3e}{\pi \epsilon_0}} \right]
\]

The progression from carrier density to current density can now be made. In well behaved crystalline semiconductors, the relationship between electric field and current density is linear with the constant of proportionality being the product of carrier density, mobility and the electronic charge. Therefore the high field behavior of a semiconductor containing donors (or acceptors) is expected to be of the form:

\[
J = n q \mu \zeta
\]

(73)
and thus

\[ J = \mu q \sqrt{\frac{N N}{c d}} \frac{e^{-\frac{d}{2kT}}}{2kT} \exp\left[\frac{1}{2kT} \sqrt{\frac{3}{q c \epsilon_o}}\right] \]  \hspace{1cm} \tag{111}

This may be recast in terms of the experimental parameters: current density, \( J \), and voltage, \( V \):

\[ J = K_{pf} V \exp(\beta \sqrt{V}) \]  \hspace{1cm} \tag{112}

where

\[ K_{pf} = \frac{n_q u \exp\left[\frac{-d}{2kT}\right]}{d} \]  \hspace{1cm} \tag{113}

\[ \beta = \frac{1}{kT} \sqrt{\frac{3}{4\pi e c \epsilon_o d}} \]  \hspace{1cm} \tag{114}

d = insulator thickness

\[ n_k = \sqrt{\frac{N N c d}{2}} \]

CASE II - Partially Compensated Donors

In this case let the acceptors remain, but in smaller numbers than that of the donors. Furthermore, let \( N_a > N_c \). This condition allows expansion of the square root in equation \( 107 \) as follows:

\[ n = \frac{N_a + N_a}{2} \left( 1 + \frac{4N_c(N_d - N_a)}{N_a} \right) \]  \hspace{1cm} \tag{115}

or

\[ n = \frac{N_c (N_d - N_a)}{N_a} \]  \hspace{1cm} \tag{116}

\[ n = \frac{N_d - N_a}{2N_a} N_c \exp\left[\frac{-d}{2kT}\right] \]  \hspace{1cm} \tag{117}

Therefore in the presence of Poole Frenkel barrier lowering,

\[ n = \frac{N_d - N_a}{2N_a} N_c \exp\left[\frac{-d}{2kT}\right] \exp\left[\frac{1}{kT} \sqrt{\frac{3}{q c \epsilon_o}}\right] \]  \hspace{1cm} \tag{118}

(74)
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which implies

\[ J = \mu q \left( \frac{N_d - N_a}{N_c} \right) \exp \left[ -\frac{\zeta d_0}{kT} \right] \exp \left[ \frac{1}{kT} \sqrt{\frac{3}{\pi \epsilon_0 d}} \right] \]  \hspace{1cm} \text{<119>}

The \( \beta \) that arises from this situation is

\[ \beta = \frac{1}{kT} \sqrt[3]{\frac{q}{\pi \epsilon_0 d}} \]  \hspace{1cm} \text{<120>}

which is twice the one in equation <114>

Also \( K_{pf} \) differs from that in equation <113>, and is instead:

\[ K_{pf} = \mu q \left( \frac{N_d - N_a}{N_c} \right) \exp \left[ -\frac{\zeta d_0}{kT} \right] \]  \hspace{1cm} \text{<121>}

In this work, a compensation index \( \gamma \) is adopted to relate the true barrier lowering \( \Delta C_d \) to the slope of the \( \ln(J/V) vs \sqrt{V} \) curve, hereafter defined to be \( \beta \). That is

\[ \beta = \frac{a}{\gamma kT d} \]  \hspace{1cm} \text{<122>}

\[ = \frac{1}{\gamma kT} \sqrt[3]{\frac{q}{\pi \epsilon_0 d}} \]  \hspace{1cm} \text{<123>}

Where \( \gamma = 1 \) in partially compensated semiconductors

or \( \gamma = 2 \) in uncompensated semiconductors

Other cases may be envisioned involving impurity sites that experience Poole Frenkel barrier lowering; e.g. \( N_a \) may be allowed to increase further to surpass \( N_d \), but then the original equation <102> must be rewritten for p-type material. In these and other cases analogous expressions can be derived. Simmons (6) and Mark
and Hartman (183) have examined these and have found no new forms of the basic carrier concentration equations. The contribution of Yeargan and Taylor (184) was to point out that since $\delta$ is derived from an approximation at the extremes of the permitted population of partially compensating acceptors, then $\gamma$ should vary between 1 and 2.

Recall from the discussion of punch-through Schottky barriers that the Schottky $\delta$, which is the slope of a $\ln(J)$ vs $\sqrt{V}$ plot (equation $\approx 13$, page 22), has a value exactly equal to the slope of a similar curve for Poole-Frenkel conduction if $\gamma$ were 2. This has lead to difficulties in distinguishing the two conduction models, especially since the uncompensated case where $\gamma$ does equal 2 was not originally considered (74, 183, 185). This issue was brought to a head when data was published that appeared to have a Schottky-like $\delta$ (82) even up to thicknesses of 4 $\mu$m, and even when dissimilar contact materials were used. To reconcile the apparently contact controlled J-V behavior with otherwise bulk controlled characteristics, an argument was waged in the literature between the various camps of Jonscher, Hill and associates at Chelsea College (65, 138, 154, 185-187); Simmons and his students (6, 73-75, 188, 189); Mark and Hartman (183); and Yeargan and Taylor (184), until the explanation was found in semiconductor carrier statistics.
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Modifications and Hybrid Theories:

The task remains to test the theory for its validity in the application to anodic Ta$_2$O$_5$ films. Although the above simple theory is derived for an isolated donor in a crystalline semiconductor, it is used to explain the behavior of imperfect amorphous insulators. There is considerable irony in the observation that Poole Frenkel conduction has been rarely reported in crystalline materials (190-196). Jonscher (197) offers an explanation. At the electric field strengths required to significantly increase free carrier concentrations through Poole Frenkel barrier lowering, avalanche breakdown has already occurred in a crystalline solid. Amorphous materials also exhibit avalanche breakdown, but at correspondingly higher fields due to the shortened mean free path of the electron. Nevertheless, the use of single crystal concepts to model amorphous behavior is one assumption of this simple picture of Poole Frenkel conduction that must be examined in detail.

First then, the question must be asked - what parts of the theory survive the transfer from a single crystal to an amorphous solid and what parts must be abandoned? The extensive work with amorphous and liquid semiconductors of the last two decades has established that the basic band structure of the amorphous semiconductor differs from that of the single crystal only in the diffuse nature of the band edges (198,199). There is no longer a precisely defined band gap in the amorphous solid. Instead, a
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continuum of states exists within the "band gap", which are characterized by rapidly decreasing mobility as the energy separation from the approximate band edges increases. Thus, the electronic propagation that takes place in the conduction band may be safely described with single crystal concepts.

The smeared-out band edges do make the concept of a precisely defined activation energy, $E_a$, suspect, however. An electron thermionically emitted from an impurity site does not reach the conduction band after a specific energy gain - but rather it becomes more and more mobile as its energy increases. A spread of activation energies would intuitively seem more appropriate. Fortunately, thermally stimulated conduction and photoconductivity experiments have indicated that in some amorphous materials at least, activation energies are well defined (69,200).

A second concept that can be questioned is that of mobility. In many materials, amorphous (201) and single crystal (202), the electron drift velocity saturates at high electric fields. After that point, mobility is undefined and equation <110>, page 73, must be replaced by:

$$J = n q v_{sat}$$  \[<124]\n
Thus:

$$J \propto \exp \sqrt{E}$$  \[<125]\n
Note that current density has a field dependence through carrier density alone. Jonscher (65) points out that this is
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equivalent to saying that the escaped electron travels to the next nearest site downstream where it is recaptured. In contrast, the simple theory is dependent on the electron spending a mean free time in the conduction band. Under saturated velocity conditions, one observes a linear relationship between \( \ln(J) \) and \( \sqrt{V} \) rather than \( \ln(J/V) \) and \( \sqrt{V} \) as predicted by simple theory. This point has been missed by many workers who have used \( \ln(J) - \sqrt{V} \) relationship indiscriminately. To the author's knowledge the behavior of drift velocity in \( \text{Ta}_2\text{O}_5 \) has not been investigated (203).

One final objection to raise is how does the behavior of an isolated donor relate to the behavior of an assembly of them in a real material with edges and contacts? Are the electrons extracted and replenished through the contacts with little or no expenditure of voltage? The only contact capable of supplying carriers upon demand without significant assistance of an applied electric field is the true ohmic one. Its behavior may be mimicked however by a process by which electrons tunnel directly into deep levels adjacent to the contact with subsequent excitation to the conduction band (65). Interestingly, exactly this kind of interfacial tunnelling was the mechanism proposed to explain the frequency behavior of tantalum oxide capacitors (204). If the contacts' influence is significant, then one of the hybrid models which combine Poole Frenkel conduction with injecting (76) or blocking (74) contact behavior must be used.
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On a different level, the Poole-Frenkel effect has been combined with other emission mechanisms. For instance, Hill proposed that the distorted barrier becomes narrow enough at high fields to permit quantum mechanical tunnelling from the donor core to the conduction band (164). Using the Wentzel-Kramers-Brillouin (W.K.B.) tunnelling approximation, he was able to reduce a rather complicated expression to a two variable system which allows the plotting of experimental \( J \cdot \xi \) data for a range of temperatures on a single graph. \( J \) and \( \xi \) are combined into a new variable, \( J = J \cdot T^{n} \cdot \exp(C_{0}/kT) \) where \( n = 3 \) or 4. Poole-Frenkel mechanisms are identified when \( \delta \) is a hyperbolic function of \( \delta = B\sqrt{\xi}/kT \). This model accounts for the decreased sensitivity to changing temperature at low temperatures due to the increased dominance of tunnelling in that regime, and for the often seen ohmic behavior at low fields. Experimental data for \( SiO_{x} \) were shown to agree with the theory's prediction for a large temperature range.

Martin et al. (173) and Vincent et al. (181) have extended Hill's work by incorporating phonon assisted tunnelling over Coulombic, and non-Coulombic wells. In these models, the carrier is thermally excited to a pseudo-state partway up within the well, from which it may more easily tunnel into the conduction band. For all these models, the effects become more noticeable at lower temperatures.
Experimental Evidence:

The most convincing examples of Poole Frenkel conduction have three characteristics in common: In \((J/\sqrt{V})\) is proportional to \(\sqrt{V}\) and J-V behavior is essentially independent of both electrode work function and bias polarity. Silicon nitride, as studied by Brown et al. (205), and Sze (206) fits the description. In Sze's study, concurrent ohmic and tunnelling components were also identified via temperature dependences. Brown used the wide latitude permitted in the preparation of this material to check the predicted variation in conduction with \(d\) and \(c\). He notes that the observed \(\beta\)'s tended to be 10% higher than was calculated from independent measurements of \(d\) and \(c\). In both studies \(\beta\) was analysed with \(\gamma = 1\).

Silicon oxide has also yielded some convincing examples of Poole Frenkel conduction - although not always recognized as such. The work of Hartman, Blair and Bauer (81) is a case in point. Nonrectifying \(\ln(J) vs \sqrt{V}\) behavior was obtained for four different metal contacts and for thicknesses varying from 1 to 10 \(\mu m\). A Schottky emission interpretation was discarded on the unfavourable comparison of the deduced barrier height and the one observed directly with photoresponse techniques. Other internal inconsistencies were found with the model. However, they also discarded the Poole Frenkel theory, as it was then known, because the \(\beta\) appeared to be Schottky like. This is, of course,
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permissible when $\gamma = 2$. Their data also shows a classic example of the low bias transition from Schottky emission to Poole Frenkel conduction which was not described theoretically for another two years (74). The results of Hirose and Wada (82) on SiO₂ are similar. They originally interpreted it as Poole Frenkel conduction, but this view fell into disfavour (84) because the deduced $\gamma$ was much larger than the accepted value. In fact, the agreement is very good when the uncompensated donor model ($\gamma = 2$) is used. The work of Johansen (207) on SiO₂ is often cited for his attempt to reconcile apparent bulk conduction with Schottky like $\beta$'s. He proposed, (with some expressed misgivings) that Schottky emission could be taking place from islands of "metallic" silicon in the interior of the insulator. Ironically he also mentions the effect of compensation, but misquotes it, and thus expected a $\beta$ twice as large as the "normal" one, and four times as large as the one he observed.

Extensive research has been performed on SiOₓ more recently. A.K. Jonscher and his colleagues have been particularly active in this area (12, 65, 138, 154, 185-187). The three mentioned criteria of Poole Frenkel conduction were demonstrated for an exceptionally wide range of bias conditions in the paper of Jonscher and Ansari (187) ... but for dark currents only. Low levels of light intensity increased the current by a temperature insensitive amount proportional to $\sqrt{V}$. They came to the conclusion that the light was capable of altering the equilibrium
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electron distribution present in the donor sites. The resulting J-V behavior would therefore appear anomalous, but could be brought back into agreement with Poole Frenkel predictions with the use of an effective temperature higher than that of the lattice. Many subsequent papers from this group explore the dynamic J-V behavior, and TSC (thermally stimulated current) properties of SiO\textsubscript{x}, that exhibit Poole Frenkel conduction. Table IV reviews some of the experimental evidence for Poole Frenkel conduction in SiO\textsubscript{x}, Si\textsubscript{3}N\textsubscript{4}, and other materials.

The evidence for Poole Frenkel conduction in tantalum pentoxide generally is not as good. Early work with a variety of metal counter electrodes demonstrated large changes in conductivity, but no clear work function dependence (208). Flow conduction may have been at fault as metal foil was used. Head (209) had also shown ln(J) vs V behavior and analyzed it as Poole Frenkel conduction, but calculated an erroneous dielectric constant. This was pointed out by Schug (210), who re-examined the data in terms of \( \gamma = 2 \). Many other examples since these early ones have been documented. Often data is quoted for one polarity only - the other one being subject to too much drift (209). An interesting observation in this respect is that of Pulfrey, Shousha, and Young (76). Their tantalum oxide films were rectifying until a large voltage was applied in the "drifty" polarity, after which point the films became nonrectifying and obeyed a Schottky law. It is likely that the "before" case
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resulted from a contact barrier that was removed by the voltage stress, after which uncompensated Poole Frenkel conduction due to the bulk was seen.

The compensation index $\gamma$, has been observed by the various workers to be equal to either 1 or 2 (within 23%). Intermediate values have not been documented prior to the work reported in this thesis. Angle and Talley see $\gamma = 1$ for thermal oxides and $\gamma = 2$ for anodic oxides of similar thickness and conductivity (51). Matsumoto (86) changed $\gamma = 1$ behavior to $\gamma = 2$ behavior by vacuum baking the anodized tantalum oxide, whereas P.L. Young (211) sees $\gamma$ go from 2 to 1 with a more gentle heating of r.f. sputtered films. And finally, Gubanski and Hughes (70) fail to see Poole Frenkel conductivity at all unless their tantalum oxide is thoroughly dried. These examples and others of Poole Frenkel conduction in $\text{Ta}_2\text{O}_5$ are also reviewed in Table IV.
### TABLE IV
Experimental Evidence for Poole Frenkel Conduction

<table>
<thead>
<tr>
<th>DEVICE STRUCTURE</th>
<th>THICKNESS (nm)</th>
<th>EVIDENCE</th>
<th>COMPENSATION RATIO, γ</th>
<th>RECTIFICATION RATIO</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-Ta$_2$O$_5$-Al</td>
<td>50-100</td>
<td>J ~ exp ($kT$)</td>
<td>~1 anodic, ~2 thermal</td>
<td>&lt;10</td>
<td>51</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$<em>5$-Al$</em>{Au}$</td>
<td>300-500</td>
<td>J ~ exp ($kT$)</td>
<td>~2</td>
<td>10-100</td>
<td>69</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-Au</td>
<td>87</td>
<td>J-V-T</td>
<td>~2</td>
<td>209</td>
<td></td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-Al</td>
<td>340</td>
<td>J ~ exp ($kT$)</td>
<td>~1 unheated, ~2 heated</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>Si-Ta$_2$O$_3$-Al</td>
<td>70</td>
<td>J ~ exp ($kT$)</td>
<td>~2</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$-Au</td>
<td>27-81</td>
<td>J ~ exp ($kT$)</td>
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<td>&lt;1</td>
<td>89</td>
</tr>
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<td>Ta-Ta$_2$O$_5$-Al</td>
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<td>J-V-T</td>
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<td>&lt;1</td>
<td>59</td>
</tr>
<tr>
<td>Ta-Ta$_2$O$_5$[Au]</td>
<td>14-240</td>
<td>J-V-$\phi_m$</td>
<td>~2 as is, ~1 dried</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td>Al-Al$_2$O$_3$-Al</td>
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<td>J-V-doping</td>
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<td>1</td>
<td>88</td>
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<td>Si-Cr$_2$O$_3$-Al</td>
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<td>J-V</td>
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<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$/Al</td>
<td>60-600</td>
<td>J-V-T</td>
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<td>1</td>
<td>205</td>
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<td>Si$_3$N$_4$/Mo</td>
<td>110-290</td>
<td>J-V</td>
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<tr>
<td>Si$_3$N$_4$/Al</td>
<td>100</td>
<td>J-V-T</td>
<td>~1</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$/Al</td>
<td>100</td>
<td>J-V-T</td>
<td>1</td>
<td>214</td>
<td></td>
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<tr>
<td>Al-SiO$_x$-Al</td>
<td>250-590</td>
<td>J-V-T</td>
<td>~2</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>Al-SiO$_x$-Al</td>
<td>100-1000</td>
<td>J-V</td>
<td>~2</td>
<td>207</td>
<td></td>
</tr>
<tr>
<td>Al-SiO$_x$[Cu, Mg, Ti]</td>
<td>300-1400</td>
<td>J-V-$\phi_m$</td>
<td>~2</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>DEVICE STRUCTURE</td>
<td>THICKNESS (nm)</td>
<td>EVIDENCE</td>
<td>COMPENSATION RATIO, γ</td>
<td>RECTIFICATION RATIO</td>
<td>REF.</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>----------</td>
<td>-----------------------</td>
<td>---------------------</td>
<td>------</td>
</tr>
<tr>
<td>Au-SiOₓ-Au</td>
<td>100-300</td>
<td>J-V</td>
<td>~1 doped ~2 undoped</td>
<td>~1</td>
<td>215</td>
</tr>
<tr>
<td>Al-SiOₓ-Al</td>
<td>500</td>
<td>J-V-T</td>
<td>~1</td>
<td></td>
<td>216</td>
</tr>
<tr>
<td>Ti-TiOₓ-Au</td>
<td>20-60</td>
<td>J-V</td>
<td>~1</td>
<td>1</td>
<td>217</td>
</tr>
<tr>
<td>Mo-NgO-electron beam</td>
<td>5-20</td>
<td>J-V-T</td>
<td>1</td>
<td></td>
<td>196</td>
</tr>
<tr>
<td>Au ( \left{ \text{CaO} _{ \text{P } \text{2} \text{O } \text{5} } \right}<em>{\text{Au}} \left{ \text{ZnO} \right}</em>{\text{Ag}} )</td>
<td>1.2-4.5×10⁴</td>
<td>J-V-T-Ω₂₉₉</td>
<td>1</td>
<td>1</td>
<td>161</td>
</tr>
<tr>
<td>Au ( \left{ \text{CaO} _{ \text{P } \text{2} \text{O } \text{5} } \right}<em>{\text{Au}} \left{ \text{ZnO} \right}</em>{\text{Ag}} )</td>
<td>1.3-2.1×10⁴</td>
<td>J-V-Ω</td>
<td>2</td>
<td>1</td>
<td>160</td>
</tr>
<tr>
<td>Si-Si₃Nₓ-Al</td>
<td>150</td>
<td>J-V-T-c</td>
<td>1</td>
<td></td>
<td>218</td>
</tr>
<tr>
<td>Si ( \left{ \text{SiO₂} \right}<em>{\text{Si}} \left{ \text{SiO₂} \right}</em>{\text{Al}} )</td>
<td>50-120</td>
<td>J-V-T-d</td>
<td>0.96-1.23</td>
<td>\text{fn}(T)</td>
<td>219</td>
</tr>
<tr>
<td>Ag-phthalocyanine-Ag</td>
<td>200-2200</td>
<td>J-V-T-d</td>
<td>1</td>
<td>1</td>
<td>220</td>
</tr>
<tr>
<td>Al ( \left{ \text{Zn} \right}_{\text{Ga}} )</td>
<td>50-500</td>
<td>J-V-Ω</td>
<td>~1 or 2</td>
<td>1</td>
<td>221</td>
</tr>
<tr>
<td>Cd CdSe-Se</td>
<td>5.5</td>
<td>J-V</td>
<td>1</td>
<td>1</td>
<td>193</td>
</tr>
<tr>
<td>Al ( \left{ \text{CdTe} \text{In} \text{Ag} \right}_{\text{Al}} )</td>
<td>723-1165</td>
<td>J-V-T-d-Ω</td>
<td>2</td>
<td>2</td>
<td>222</td>
</tr>
<tr>
<td>In ( \left{ \text{CdF₂} \text{In} \text{Au} \right}_{\text{Au}} )</td>
<td>5.1 mm</td>
<td>J-V-T-Ω</td>
<td>1</td>
<td>1</td>
<td>223</td>
</tr>
<tr>
<td>Au ( \left{ \text{AlN} \right}<em>{\text{Si}} \left{ \text{Al} \right}</em>{\text{Al}} )</td>
<td>100-300</td>
<td>J-V-T</td>
<td>1</td>
<td>1</td>
<td>195</td>
</tr>
<tr>
<td>B₁ ( \left{ \text{FeF₃} \text{Au} \right}_{\text{NIF₂}} )</td>
<td>500</td>
<td>J-V-T-Ω</td>
<td>1</td>
<td>1</td>
<td>148</td>
</tr>
<tr>
<td>Au-hexamethyldisiloxane - Au</td>
<td>800</td>
<td>J-V-T</td>
<td>1</td>
<td></td>
<td>224</td>
</tr>
<tr>
<td>Au-polymethylpentene - Au</td>
<td>5×10⁶</td>
<td>J-V-T</td>
<td>1</td>
<td>1</td>
<td>225</td>
</tr>
<tr>
<td>Al-polystyrene - Ag</td>
<td>60-350</td>
<td>J-V-T-d</td>
<td>2</td>
<td>1</td>
<td>226</td>
</tr>
</tbody>
</table>
PART II - THEORY

2. DEFINITION OF EXPERIMENTAL GOALS

Now that all of the major contenders have been put forward with appropriate supporting evidence, it remains to be seen which conduction model most closely describes the electrical behavior of the Ta₂O₅ films used in this study. All four models predict the existence of a high field regime where current density rises rapidly and superlinearly with increasing voltage. In fact, all four can be made to fit the J-V behavior observed here - for a restricted range of currents and with appropriate choice of values for the disposable parameters in each J-V expression. This is shown in Figure <13> for a typical set of J-V data. The restricted range is understandable, even expected, because more than one conduction mechanism may be operative in each voltage region. Fortunately the disposable parameters do remain open to examination. The main thrust of the work described here is the comparison of the predicted and observed J-V behavior using independently determined values of the material properties that make up these disposable parameters. The addition of the variable, temperature, allows tests of self consistency as well. For example, the value of a physical property may be inferred from J-V behavior at room temperature and from J-T behavior at constant voltage. The properties involved, such as the dielectric constant or film thickness should have little or no temperature

(87)
Figure 13: Comparison of Proposed Models Fitted to J-V Data

Typical J-V data is plotted here and compared to least squares fits to four conduction models: (a) Hopping, (b) Poole Frenkel, (c) Schottky barrier, and (d) Space charge limited conduction.
PART II - THEORY

or voltage dependences in the ranges covered, and so the two inferred values should be the same. Table V presents the J-V-T expressions for Schottky, SCLC, Hopping and Poole Frenkel conduction with the temperature and voltage independent parameters condensed into the single constants the measurements are able to determine. Table V is found on page 91.

An experimental goal that must be achieved prior to J-V study is the exclusion of flaw dominated conduction. The method of sample preparation is designed to reduce flaws. Should they occur, the following test, as recommended by Schwartz and Gresh (28), will set a maximum limit on their size and density. In this experiment, devices are made with areas ranging over three orders of magnitude. The very smallest of the devices, 4 μm by 4 μm in area, are still large compared to the flaws now thought to control catastrophic breakdown (>10 mm in diameter) (20), but the flaws which invalidated much of the early work in anodic conduction would be identified by this test. In addition, flaws in anodized tantalum pentoxide thin films often cluster along the edges of tantalum electrode where etching may leave burrs or promote local lifting of the metal from the substrate. Thus flaw conduction usually depends on device "perimeter" rather than area, and can be identified in this manner.

Once current density has been proven valid, the other geometric property of the device, oxide thickness, can be studied. The thickness dependence of SCLC, \(J \propto d^{-\alpha}\), where
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the exponent, \(-(2s+1)\), is uniquely related to the exponent, \(s+1\), relating \(J\) to \(V^{s+1}\), is significantly different from that of Schottky or Poole-Frenkel conduction where \(J = \exp(\text{constant}/d)\). Therefore, devices with a range of thicknesses were tested. The range is not extensive, only 40 to 65 nm, primarily because the experimental evidence and the proposed hybrid models have suggested that a transition from one conduction mechanism to the other may be expected as thickness is increased.

In all models, conduction is dependent on the dielectric constant which of course varies with frequency. In SCLC, the low frequency, or static dielectric constant is important. For the devices used here, the measurement of capacitance and oxide thickness allows this value to be calculated. For Poole-Frenkel and Schottky conduction equations, the high frequency dielectric constant is required. This was calculated from the index of refraction of the oxide, which was obtained by a combination of reflectance spectrophotometry and ellipsometry techniques (41). In hopping conduction, both dielectric constants enter into the calculation of the radius and energy of the polaron. To explore further the relationship between the optical and electrical properties of the oxide, the dielectric constant of the oxide was varied in a controlled manner by nitrogen doping the parent tantalum film. The pertinent electrical parameters could be then checked to see if they varied in the fashion predicted.

(89)
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The values of mobility and carrier concentration and the details of the interface properties do remain inaccessible in all but the hopping conduction model. Hopping is unique in that all parameters are accessible, and are in many ways interdependent (e.g. hop length and impurity density). Thus only in a hopping analysis can the absolute level of conductivity be compared to model predictions. Large changes in the overall conductivity are attained through heat treatments while other properties may be unaltered. So, even though the physical cause for these changes cannot be quantified for some of the models, annealing does provide very fertile ground for testing these theories over extended conductivity ranges.
TABLE V
Comparison of Proposed Conduction Formulae

Contact Limited Conduction - Schottky Barriers

\[ J_{sch} \propto T^2 \exp \left[ -\frac{q\phi_0}{kT} \right] \exp \left[ \frac{B}{2kT} \sqrt{\frac{V}{d}} \right] \]

Space Charge Limited Conduction - SCLC

\[ J_{sclc} \propto \exp \left[ -\frac{\zeta_d o}{kT} \right] \left[ \frac{\gamma^{s+1}}{\gamma^{2s+1}} \right] \]

Thermally Activated Hopping Conduction

\[ J_{thop} \propto \frac{V}{d} \exp \left[ \frac{CVR}{T d} \right] \exp \left[ -\frac{W}{kT} \right] \]

Variable Range Hopping Conduction

\[ J_{vhop} \propto \frac{V}{d} \exp \left[ \frac{CVR}{T d} \right] \exp \left[ -\frac{T_0}{T} \right] \]

Poole-Frenkel Conduction

\[ J_{pf} \propto \left[ \frac{V}{d} \right]^n \exp \left[ -\frac{\zeta_d o}{\gamma kT} \right] \exp \left[ \frac{B}{\gamma kT} \sqrt{\frac{V}{d}} \right] \]
PART III - EXPERIMENTS

1. SAMPLE PREPARATION AND MEASUREMENT TECHNIQUES

Sample Preparation:

The samples of Ta₂O₅ used in this study were prepared with the basic process sequence shown in Figure 14. The details of this process are described below. First, soda lime or borosilicate glass substrates 2 inches square were thoroughly degreased and rinsed in accordance with standard thin film techniques. Either a dc diode, or planar magnetron sputtering system as previously described in the literature (227, 228) was then loaded with a number of these substrates, and pumped to a base pressure of 10⁻⁴ Pa before the diffusion pump was throttled and high purity argon, the sputtering gas, was admitted into the chamber. After a short pre-sputter period to remove the layer of the target which was exposed to the atmosphere, an etch stop layer of tantalum pentoxide was reductively sputtered in oxygen from a 99.999% pure Ta target. Without breaking vacuum a shutter was then put in place between the target and the substrates and the target was sputtered in pure Ar, or an Ar/N₂ mixture until the stoichiometry of the target was stable. Then the shutter was removed and the substrates were coated with a nominally 200 nm thick layer of tantalum or tantalum nitride. In a few of the earlier experiments; the etch stop layer was formed by depositing a 50 nm Ta layer and converting it to an oxide thermally. The tantalum layer to be anodized was then deposited in the same
Figure 14: Outline of Sample Preparation Sequence

(a) Clean glass substrates are coated with a layer of Ta$_2$O$_5$.

(b) Ta or TaN$_x$ then is sputtered and photolithographically defined.

(c) The metal is partially converted to an oxide by anodization in a weak citric acid electrolyte.

(d) Then a layer of Cr is evaporated and photolithographically defined into strips that intersect the oxide coated tantalum at right angles.
fashion as just described. Next, this tantalum was photolithographically defined into the required base electrode pattern. The etch stop layer of Ta$_2$O$_5$ protected the glass substrate from chemical attack in this step.

Anodization of the oxide took place at room temperature in a 0.1% solution of citric acid monohydrate in de-ionized water. A constant current of 10 A/m$^2$ from a Keithley constant current source was passed through the sample, causing oxide growth, and a linear rise in voltage. When the voltage reached a pre-set limit (30 V, unless otherwise stated) the voltage was held constant until the current had fallen to 10 mA/m$^2$. The behavior of anodizing current and voltage with time is shown schematically in Figure 15. The sample was then carefully rinsed in boiling de-ionized water to remove all surface traces of electrolyte.

The top contact metal used in these experiments was electron-beam evaporated chromium. It was also defined photolithographically. The oxide-coated tantalum lines and the chromium lines intersect each other at right-angles, minimizing the error in area that could be possible through registration difficulties.

During the course of the study both dc diode and magnetron sputtering were used to deposit the first two layers. The latter technique is an improvement on the diode system, featuring a magnetic field to confine the secondary electrons to the target region thus increasing the sputtering rate. As mentioned in the
Formation of the anodic oxide uses both galvanostatic and potentiostatic modes. First a constant current is passed through the cell, causing oxide growth and a linear rise in voltage. Once the desired voltage is reached, it is held constant while current falls as \(1/\text{time}\). The process is halted when current has reached levels that can be attributed to electronic conduction alone. For the samples in this study, total anodizing times were 3-5 mins.
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introduction, the residual gas pressures and impurity levels associated with an individual sputtering system do play an important role in determining the characteristics of the anodic oxide to be formed on the deposited tantalum. This observation was indeed substantiated in our work. Even though the Poole-Frenkel nonlinearity coefficient $\beta$, which is related to insulator dielectric constant and thickness (defined in equation (122), page 75), was reproducible from system to system, the conductivity coefficient, $K_{pf}$, indicative of a doping concentration, was found to be several orders of magnitude lower in oxides formed on magnetron sputtered tantalum, as compared to diode sputtered films.

Four electrode patterns, each designed for a specific type of measurement, were used in this investigation. For optical measurements, broad areas of oxides of different thicknesses were required. For this purpose, centimeter wide tantalum electrodes with a common contact to the anodizing electronics above the electrolyte meniscus were photodefined. Thus the area and appropriate anodizing current could be determined accurately. Also, regions of flawed tantalum that may be present at the edges of the substrate could be avoided. Any such flaw, scratch or pinhole would have thwarted precise control of anodizing parameters, because oxygen evolution there would have short circuited oxide growth. In any case, those samples showing bubbles, or abnormal anodizing I-t behavior were dropped from the
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The experiment. Three other patterns were designed for conductivity measurements. One, shown in figure 16, featured ten devices of each of four different areas with provision made for easy simultaneous access to each device with an edge connector. It was primarily used in the J-V-T experiment. Figure 17 shows an enlarged view of the area test pattern, used to determine the area - current relationship. The fourth pattern featured an array of 32 by 32, 14.2.5 μm square devices, for the purpose of generating statistics on device characteristic uniformity.

Measurement of Optical Properties:

Two parameters that enter the conduction formulae are oxide thickness, d, and index of refraction, n, (as the square root of the high frequency dielectric constant). The first is particularly difficult to measure by simple step height techniques because the oxide grows both above and below the plane of the unananodized metal. In addition the oxide is very chemically stable, complicating attempts to etch a step while preserving the substrate surface.

The method chosen was a combination of reflectance spectrophotometry and ellipsometry. In the former, the reflectance of the oxide coated metal was measured from 187 nm (the cut-off of the quartz optics) to 1000 nm (beyond the position of the zero-th interference peak) in a Perkin-Elmer 3330 Spectrophotometer (kindly made available by the Optical
The mask for the tantalum (a) and chromium (b) levels are shown above. When these patterns are overlapped, 40 devices are formed, 10 of each of the following dimensions: .005" = 125 μm, .010" = 250 μm, .020" = 500 μm, .040" = 1000 μm square.
The tantalum level of the area test pattern is shown above at 3.25x. Devices are formed at the crossover of chromium electrodes (not shown) and the oxide coated tantalum lines connected at right angles to the main tantalum electrodes running from right to left in this diagram. The numbers on the diagram refer to the width of the Ta and Cr lines (respectively) making up the devices in each block outlined with the dotted lines.
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Physics Department of the National Research Council of Canada). The positions of the peaks are related to the product of the index of refraction, \( \tilde{n} \), and the oxide thickness, \( d \) (229,230). Thus a dispersion curve in terms of \( \tilde{n}d \) can be constructed for the entire wavelength range. To separate these two variables, more information is required. Either transmission spectra or a measurement of either \( \tilde{n} \) or \( d \) at a single frequency would suffice. The first option is unavailable; the ever present metal underlayer is opaque; therefore the second option was pursued. Representative samples, including those of the various nitrogen doping concentrations, were prepared and analysed at 632.8 nm (He-Ne laser) by ellipsometry at the Electrical Engineering Department of the University of British Columbia by Dr. David Smith. In this method (231) the absolute phase and amplitude of the light reflecting from a given surface are measured for both the components parallel and at right angles to the plane of incidence. The extra variable permits the independent determination of both \( \tilde{n} \) and \( d \) at the one wavelength and thus provides a reference point to scale the dispersion curve determined from the reflectance data.

Measurement of Electrical Properties:

Current-voltage (I-V) measurements were made using a Keithley constant current source (0.1 nA to 10 mA) and a Keithley electrometer (input impedance \( 10^{14} \Omega \)). Shielding of the
PART III - EXPERIMENTS

electrometer, the constant current source cables and the sample holder was required to reduce electrical noise. The measurement error in current is \( \pm 0.5\% \) (or \( .05 \text{ nA} \), whichever is larger); in device size is \( \pm .25\mu\text{m} \); and in voltage is \( \pm 1 \text{ mV} \). The typical device responded to the first application of a constant current in a manner that saw the voltage rise gradually with an estimated time constant of 1 to 5 seconds. Thereafter, the I-V characteristics could be reproduced, provided the highest bias previously reached was not exceeded. The test procedure, therefore, consisted of increasing the current through the device until the maximum desired level had been reached, then reducing the current in steps and allowing for capacitive discharge before measurements of voltage were made. In this way, true steady state behavior could be determined. A recorder trace of typical charging and discharging phenomena may be seen in Figure 18. In general the range of I-V data is limited by noise in the low current region (\( < .05 \text{ nA} \)), and drift at high fields (\( V > 80\% \) of the anodizing voltage).

In the J-V-T experiment the test limit was kept to a very conservative 15\% of the anodizing voltage to eliminate possible drift. In this experiment three out of the 10 devices of a given size on the mask (Figure 16) were measured at a time. Note that area independence of current density was checked at room temperature. The J-V behavior was re-examined after each temperature excursion and compared to control samples which had
A strip chart recording of voltage vs time is reproduced here showing the transients associated with changing the current flowing through the device to the values indicated. A time constant of the order of seconds and slight hysteresis is evident. Measurements are typically made on the descending bias steps.
been temperature cycled, but not voltage stressed, and to samples seeing no temperature or voltage stress. The vacuum baked and unheated samples exhibited no detectable changes throughout the experiment. The hydrogen annealed samples however did exceed the drift limit of $\Delta I > 3\%$ after the 360 K temperature run and were therefore analysed over a more narrow temperature range.

The problem of control of temperature during J-V-T measurements was studied. A cooling system based on cold nitrogen gas boiled-off from liquid nitrogen (a Delta-type environmental chamber) proved to have too short a thermal time constant. The voltage across a device passing a constant current fluctuated wildly whenever a new "blast" of cold nitrogen was admitted into the chamber. A compressor based refrigeration unit combined with forced air heating was much slower in attaining set points, but could hold that temperature with smaller fluctuations. With the proper choice of thermal mass attached to the substrate, temperatures at the substrate could be kept within at least 0.2 K (the measurement limit of a chromel/alumel thermocouple - voltmeter combination), or more importantly, within the limit of the measurement of voltage across the device, a more sensitive criterion. Icing and/or condensation problems were avoided by one of two methods: an ambient of dry nitrogen inside the test chamber, or a thorough drying bake at 80°C prior to low temperature runs.

A slightly different approach was followed in testing the 32
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by 32 array of 12.5 μm square devices. This mask was the primary tool in the investigation of the thickness and nitrogen doping dependences of J-V behavior. Testing of the entire array was performed by a Rockwell Aim 65 microcomputer, interfaced to an x-y stage, digitally controlled voltage source, instrumentation amplifier (unity gain, 10^14 ohm input impedance) and digital voltmeter. A test voltage was applied to each device individually, and current (i.e. the voltage drop across a precision resistor) was recorded after a software determined settling period. Uniformity and reproducibility of J-V behavior were evaluated on a routine basis in this manner throughout the duration of the project. Well over one thousand substrates of 1024 devices each were mapped. Uniformity and reproducibility were understandably functions of processing parameters. However, in the absence of serious processing problems the following statistics were typical: 1 or 2 devices would be shorted due to particulate contamination prior to anodization, or due to electrostatic discharge, up to 5 would be open due to microcracks where the chromium top metallization steps up over the Ta_2O_5 covered tantalum electrode; and the remainder would show a 3σ standard deviation in current for a given voltage of < 3% on a given substrate of 12.5 μm square devices, and < 5% within a fabrication run of 5 to 25 substrates. As mentioned previously, larger differences did appear between the magnetron and dc diode sputtered based Ta_2O_5. By careful measurement of line widths
using a Nanoline automatic dimension measurement system it was determined that uniformity on a substrate was photolithography limited. For the smaller devices, such as are found on the area test pattern (Figure <17>), these tolerances of ± .25 μm imply larger standard deviations of up to 13%, as was observed. Of the 1024 devices on a substrate, 64 were tested with a more substantial range of voltages, so that the appropriate conduction models could be determined.

Finally, a least squares fit to the J-V data was made with functions appropriate to the various models. A typical set of data and the Poole Frenkel fit is given in Figure <19>. There is a range of voltages covering four orders of magnitude of current density where the ln(J/V) vs √V plot is near ideal. The magnitude of J-V asymmetry with respect to zero bias is also typical. Obviously, there is a $K_{pf}$ for each polarity. Not so obvious is that there is also a slightly different $\beta$ for each polarity, even though the physical parameters making up $\beta$ have no apparent bias dependence. This observation is not in accordance with Poole Frenkel theory, and will be discussed fully in Part IV. For this preliminary analysis, an average of the two $\beta$'s is used.

The high field forms of the Poole Frenkel and hopping conduction equations, appropriate to the fields actually used, were fitted to the data for all but the J-V-T experiment. Thus the $K_{pf}$ and $\beta$ quoted correspond to equations <113>, <121> and <123> found on pages 74 and 75. It was unnecessary to resort to

(100)
A Poole Frenkel plot of current density/voltage vs the square root of voltage is shown for devices with the nominal areas indicated. For clarity, the error bars have been omitted. The relative error in current is +0.5%, in area is +0.5 \( \mu m^2 \), and in voltage is +1 mV.

- line (a) - cathodic polarity (Ta positive with respect to Cr)
- line (b) - anodic polarity (Ta negative with respect to Cr)
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the less common forms of field induced barrier lowering. No integral values of m in the relationship:

\[ \frac{J}{V} \propto \frac{u \alpha}{d} \exp \left[ \frac{-m}{m+1} \right] \]

<98>

could be selected to fit the data with any higher accuracy than the Poole Frenkel model (m = 1). The most accurate fits yielded non-integer values of m, close to \( m \approx 1 \), which were not independent of temperature, oxide thickness and dielectric constant. Because the Poole Frenkel fit is satisfactory for the experimental range of these properties, and in addition permits a physical interpretation of the fitting parameters, it will be the only barrier lowering model discussed in subsequent sections. Likewise, the hop length is calculated from equation <80> (page 54). In the J-V-T experiment the limited voltage range necessitates the use of a full 3 dimensional approach - such as the Onsager formulation (equation <93a>, page 65).
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2. RESULTS

The Effect of Device Area:

To establish whether current could be described in terms of current density, I-V data were obtained for current levels from 5 nA to 255 nA for devices ranging in size from 4 \( \mu \)m x 4 \( \mu \)m to 250 \( \mu \)m x 500 \( \mu \)m. Five substrates of undoped Ta were used (in two different oxide thicknesses) and one each of the 0.6, 0.9, and 1.2 sccm \( \text{N}_2 \) doped Ta. The number of devices available of each size on the area test pattern (32 of the smaller sizes and 128 of the larger) permitted the estimation of the mean deviation in conductivity levels for a particular size of device at 10% to 14%. A few size categories showed anomalously large deviations and thus were not included in this analysis. This is attributed to difficulties with photolithography in the very smallest sized devices and poor step coverage of the chromium over the oxide coated tantalum in certain areas of the substrates.

The data presented in Figures 19&20 are representative of the given device sizes for a particular substrate of 30 V thick undoped oxide devices. Similar behavior was observed with the nitrogen doped and 40 V thick undoped devices. As can be seen in Figure 20, conductivity for a fixed voltage (and thus fixed electric field) scales with area. The error bars shown are the 3\( \sigma \) deviations for all devices tested of that size. Figure 19 is a
Figure 20: Observed Current as a Function of Device Area

The currents interpolated from the data given in Figure 19 for a voltage of 10 V anodic bias (*) and 8 V cathodic bias (o) are plotted against the device area. The error bars on current represent 3σ deviations for all the devices tested of that particular size.
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Poole Frenkel plot of the J-V data for these devices. The logarithm of the ratio of current density to voltage is plotted against the square root of voltage. The J-V data of the devices whose areas vary by more than a factor of six, can be seen to fall on the same curve, confirming that current does scale with area. The largest devices, not plotted, did not fall on this line. For the currents used in the test, only ohmic behavior was observed, presumably because the Poole Frenkel regime had not yet been entered at that bias. The currents required to produce comparable electric fields in devices of this size can be estimated to be approximately 100 \( \mu A \), two orders of magnitude higher than the arbitrarily chosen current limit for this test.

Although this test conforms to that set out by Schwartz and Gresh to identify nominally flaw free films, it is actually verifying that conduction is uniform on the scale of microns. However, there is the additional evidence in the morphology of the oxide observed at 20,000 times magnification in the scanning electron microscope. The oxide appears uniform and featureless. Thus it is concluded that conduction in these devices is not dominated by flaws such as fissures and micropores.
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The Effect of Oxide Thickness:

Once confident that the flaw free conditions can be assumed to exist in the oxides under investigation, we can proceed to examine the effect of oxide thickness. In this experiment, three anodizing voltages (25, 30 and 35 V) were chosen to give samples of three different oxide thicknesses. The standard 32 x 32 pattern was used to give a large number of devices for testing. At the same time, an optical test pattern sample was prepared with anodizing voltages from 15 to 55 V, in 10 V increments.

The ellipsometry results were fitted well with a model consisting of a single homogeneous layer. Figure 21 is a plot of the measured oxide thickness as a function of anodizing voltage. The offset, which appears to indicate no oxide formation until -2 V is measured, is not unusual. It can be explained by the existence of a native oxide. Moreover, only the absolute value of oxide thickness is required for the following analysis of conduction behavior.

The J-V behavior of these films is diagrammed in Figure 22. These data fit the Poole Frenkel relationship, \( -\ln(J/V) = \sqrt{V} \), for over 4 orders of magnitude of current density in the anodic (Ta positive) bias and a somewhat reduced range for the cathodic (Ta negative) bias. In addition, \( \beta \), the Poole Frenkel nonlinearity coefficient defined in equation 123, page 75 is observed to be proportional to \( d^{-\frac{1}{2}} \) as predicted (Figure 23b).
Figure 21: Oxide Thickness as a Function of Anodizing Voltage

Oxide thickness is determined by the anodizing voltage used. The relationship is shown here for β phase of thin film Ta. The calculated anodizing constant is 1.96 nm/V. The absolute error in thickness as determined by ellipsometry is ± 0.5 nm, while the error in voltage is estimated to be ± 0.1 V.
Figure 12. Poole Frenkel Plot for Devices of Various Thicknesses

a) Anodic conductance (i.e., current density / voltage for the Ta positive bias) is shown here for three different oxide thicknesses. The curves should be linear on this plot format if 1-D Poole Frenkel conduction is dominant. Three different thicknesses were obtained by the choice of the following anodizing voltages: (a) 25 V, (b) 30 V, (c) 35 V. As in Figure 19, following page 100, the error bars have been omitted for clarity. The total relative error in conductance is 4% and in voltage is less than 0.001%.
Figure 22: Poole Frenkel Plot for Devices of Various Thicknesses

b) The cathodic conductance for the same devices as shown in part a) of this figure is plotted against \( \sqrt{\text{voltage}} \). For voltages in excess of 50% of the anodizing voltage, a small excess current is observed for this bias polarity. This phenomenon has been observed by other workers (13, 90), and is believed to be caused by the onset of high field ionic conduction. Also seen in curve (c) is the predicted deviation at low fields due to three dimensional effects. (a) 25 V oxide, (b) 30 V oxide, (c) 35 V oxide.
In upper part, the logarithm of current density for a bias of 10 V from Figure <22>, is shown to be a linear function of (oxide thickness)\(^{-1/2}\). In the lower part, the Poole Frenkel nonlinearity coefficient, \( \beta \), is shown to be proportional to (oxide thickness)\(^{-2}\). The error bars on \( \beta \) of 0.03% are statistically derived for a Student's T confidence limit of 95%. Both relationships should hold if Poole Frenkel conduction is dominant. • = anodic bias (Ta positive), + = cathodic bias (Ta negative).
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and current density at a set voltage (10 V is chosen for Figure <23a>) is observed to be an exponential function of $d^{-\frac{1}{2}}$, as predicted in equation <112>, page 74. These relations would also hold for Schottky punch-through conditions, equations <12> and <13>, page 22.

The analysis of the data with respect to the high field hopping model is shown in Figure <24>. The fit is only adequate for conductance greater than 500 Ω/m². As discussed on page 54, the slope of the $\ln(J/V)$ vs $V$ curve in that region is

$$\frac{c q R}{k T d}$$

where $c$ is equal to 0.17

- $R$ is the hop length
- $d$ is the oxide thickness

For all these curves, $R$ is calculated to be $5.2 \pm 0.2$ nm. This is large compared to the value of 1.81 nm found by Bryksin et al. (137) for $\text{Ta}_2\text{O}_5$. If the hop length corresponds to the inter-impurity separation, as might be expected at high temperature, then $N_d$ can be estimated to be on the order of

$$\left[\frac{4\pi R^3}{3}\right]^{-1} \approx 1.8 \times 10^{24} \text{ m}^{-3}$$

This is within the range of values for $\text{Ta}_2\text{O}_5$ derived from other methods. (See for instance Table II, page 41). Thus hopping conduction cannot be ruled out by these observations.

In contrast, the thickness dependence of J-V behavior predicted for both the imperfect insulator - metal contact and
When the hopping model is applied to J-V data covering an extensive range of voltages satisfactory agreement is only attained for the highest voltages. Only in that region does conductance (J/V) increase exponentially with electric field as per equation \(128\), page 91. (a) 25 V oxide, (b) 30 V oxide, (c) 35 V oxide.
the space charge limited conductor cannot be reconciled with the data. The former predicts no thickness dependence, (equation \(<9\), page 22), while the other predicts the existence of an unique \(s\) such that \(J_a V^{s+1}\) and \(J_b d^{-2s+1}\) (equation \(<37\), page 34). Figure <25> presents an analysis of the J-V data within the standard SCLC model. The \(s\) derived from the straightest portion of the J(V) plot is 5.5, while \(s\) predicted from J(d) is 3.3.

The conclusion of this experiment is that the space charge limited conduction, and the imperfect insulator - metal Schottky barrier models are not appropriate to these films, whereas either punch-through Schottky barrier emission or hopping or Poole Frenkel conduction might be occurring.

(106)
If space charge limited conduction were dominant, then these power law plots of current density vs voltage and current density vs oxide thickness (inset) would be linear with exponents of $s+1$ and $-(2s+1)$ respectively. The calculated exponents are $6.5 \pm 0.1$ and $-7.6 \pm 0.1$ for $J > 100$ A/m$^2$, and are thus inconsistent with an unique $s$. As before the error in $J$ is less than 4% and $V$ is 1 mV. (a) 25 V oxide, (b) 30 V oxide, (c) 35 V oxide.
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The Effect of Dielectric Constant:

Small amounts of nitrogen added to the argon used to sputter the tantalum deposited for these experiments had a dramatic effect on both the metal and the anodic oxide properties subsequently formed on it. As the nitrogen flow into the dc diode sputtering chamber was increased the metal resistivity first dropped from the undoped value of \(-2.0 \, \text{ohm} \cdot \text{m}\) to a minimum of \(-0.8 \, \text{ohm} \cdot \text{m}\) at 0.3 sccm (standard cubic centimeters per minute) of ultra pure nitrogen. Between 0.6 and 0.9 sccm, the resistivity rose to a plateau at \(-3.5 \, \text{ohm} \cdot \text{m}\). Beyond the plateau, resistivity rose steadily to insulator like values at 1.5 sccm. These results appear to be typical of diode sputtered tantalum, and are in good agreement with the findings of Gerstenberg (37). A smooth transition in crystallographic phase from undoped 8-Ta to f.c.c TaN at 1.5 sccm N\(_2\) was observed with wide film Debye-Scherer techniques. The intermediately doped films were composed of b.c.c. Ta near the resistivity minimum, and a mixture of Ta\(_2\)N, Ta\(_4\)N\(_5\) and Ta\(_5\)N\(_6\), throughout the plateau region. The two latter phases were not observed by Gerstenberg, but have been reported by Terao (232) for nitrided evaporated tantalum films. The magnetron sputtered tantalum films also went through a similar sequence of phases in good agreement with the literature (233).

To study the changes in oxide properties, three nitrogen flowrates were chosen to compare with the undoped 8-Ta based
PART III - EXPERIMENTS

oxides. These were 0.6, 0.9 and 1.2 sccm. For comparison, note that the argon flowrate was 8 sccm. The interplanar spacings observed are compared to literature values (232-234) in Table VI. The use of flow rate to characterize the nitrogen content of the films can be justified. Given the deposition rate, and the sticking coefficient of nitrogen to tantalum, analysis has shown that all of the nitrogen entering the chamber is gettered by the film, and is not merely pumped away. These particular flowrates were chosen because they span the range of tantalum nitride that forms useful oxides. At flowrates above 1.2 sccm the nitride became so highly resistive that the voltage dropped in the lines leading from the contact above the electrolyte meniscus down to the device area would significantly reduce the thickness of the oxide formed furthest from the contact. In the range between no \( N_2 \) and 0.6 sccm of \( N_2 \), b.c.c. Ta was deposited. These samples did not yield good quality oxides. The anodizing behavior showed evidence of frequent breakdown events during growth, and the interference colors of the oxide were murky and greyed rather than clear and intense, as if containing numerous light scattering centers. Under I-V test, these films were unable to support current in the Poole Frenkel-range without catastrophic breakdown.
Table VI
Summary of X-Ray Analysis - Observed and Reported Interplanar Spacings

<table>
<thead>
<tr>
<th>Observed Interplanar Spacing vs. ( N_2 ) Flowrate (sccm)</th>
<th>Reported Interplanar Spacing vs. Nitride Composition</th>
</tr>
</thead>
</table>
| none 0.6 0.9 1.2                                          | tetrahedral  h.c.p. tetrahedral  
\( \beta\)-Ta  \( \text{Ta}_2\text{N} \)  \( \text{Ta}_5\text{N}_6 \)  \( \text{Ta}_4\text{N}_5 \) |
| 7.260 (nm) .258                                         | .267 (nm) .259                                    |
| 7.244 .247                                             | .248 .248                                         |
| .233 .226                                               | .232 .233                                         |
| .214 .207                                               | .214 .219 .216                                   |
| .143 .140                                               | .152 .152                                         |
| .132 .130                                               | .133 .130                                         |
| .098                                                    | .097 .096                                         |

Deduced Composition:
\( \beta\)-Ta  \( \text{Ta}_2\text{N} \)  \( \text{Ta}_5\text{N}_6 \)  \( \text{Ta}_4\text{N}_5 \)  \( \text{Ta}_3\text{N}_5 \)

? indicates poor correlation between observed and reported spacings. Systematic errors due to film shrinkage is suspected. The sum of all other errors in observed values are estimated to be less than 0.5\%. 

(109)
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For each nitrogen doping level one substrate was processed with the area test pattern, one with the optical measurement pattern and between 4 and 8 with the standard 32 x 32 test pattern of 12.5 μm square devices in each of two thicknesses.

The reflectance spectra of the oxides are shown in Figure <26>, where the 30V oxide of each sputtering condition is compared. The reflectance maxima and minima are shifted to shorter wavelengths and the range of amplitude of the interference effects at high frequencies is reduced with the increasing nitrogen content. In practical terms, the first observation means that the doped films "look ten volts thinner" than the undoped films anodized at the same voltage; and the second gives them their less intense colors. In more theoretical terms, it can be concluded that the effect of nitrogen is to reduce the product of the index of refraction and oxide thickness, nd, and to shift the onset of strong absorption to longer wavelengths. Thomas's photoconductivity study of nitrogen doped tantalum oxide (63) confirms the observation that the absorption edge shifts to longer wavelengths with increasing nitrogen.

The same samples were examined with ellipsometric techniques. The reduction in the product of index of refraction and insulator thickness with doping was shown to be due to a drop in the index of refraction of 10%, as well as a 20% decrease in the thickness of the films prepared at the same anodizing
Figure 26: Reflectance Spectra of N₂-Doped Tantalum Oxides

The amount of light reflected from the oxide coated metal as a function of wavelength is determined by interference effects, and absorption near the band gap. Both are related to the complex index of refraction in the oxide and its parent metal and both are shown by these plots to be affected by nitrogen in the tantalum film. The reflectance curves here are for tantalum sputtered with the following nitrogen flow rates: (a) none, (b) 0.6 sccm, (c) 0.9 sccm, (d) 1.2 sccm. The x-ray composition analysis for these films is given in Table VI.
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voltage. The optical constants determined are listed in Table VII. The observed effect of nitrogen on the anodizing constant is in qualitative agreement with that seen by Kamei and Matsuzaki (19). The undoped Ta$_2$O$_5$ in this experiment is apparently not typical of the β'-Ta based oxides reported previously. The index is almost 10% below literature values (52), and has an imaginary component as well, contrary to common experience. The latter implies absorption at the wavelength used in the ellipsometry. This unexpected absorption is thought to be a consequence of the optimization of the oxides used in this study for the MIM-LCD, which requires much higher levels of conductivity than the usual capacitor application. This point will be discussed in Part IV.

Electrical characterization began with the verification of the expected area and thickness dependences of current. Then J-V data was collected for 64 devices on each of 4 to 8 substrates and Poole Frenkel coefficients were determined in the standard fashion and are given in Table VIII. Analysis using a hopping model is given in Table IX and will be discussed shortly. Under the Poole Frenkel model the main conclusions are that the doped films showed lower conductivity (i.e. smaller K), and greater non-linearity (i.e. larger β). Now that both d and c (c = n$^2$) are known for each film, the expected β may be calculated directly. The ratio of β calculated for γ = 1 to the observed slope of the ln(J/V) vs $\sqrt{V}$ curves, gives the compensation index γ (as defined in equation (122), page 75). All three doped films exhibit

(111)
"normal" Poole-Frenkel $\beta$'s ($\gamma = 1$), conforming to a model of compensated donors, even though $\epsilon$ itself varies from 2.99 to 3.45. These $\beta$'s are inconsistent with the Schottky model. The $\beta$ of the undoped film is also not Schottky-like, and if Poole-Frenkel-like, can only be reconciled with a compensation index between 1 and 2. Interestingly, Thomas also proposes a compensating role for nitrogen in reducing an absorption feature at 2.1 eV that he observed in undoped films, but could not resolve in films made on tantalum with as little as 2% nitrogen (63).

Thus, under the Poole-Frenkel analysis it can be concluded that nitrogen in the oxide has the effect of compensating the donors responsible for conductivity. This explains the larger non-linearity and lower conductivity of the electrical characteristics, and the reduced absorption observed in the ellipsometric study of the optical properties on these films.

The hopping model also leads to the interpretation that nitrogen doping causes a decrease in the number of impurities. This leads to the observed increase in hop length, and decrease in overall conductivity. The values of the hop length given in Table IX do require comment, however. Devices with the highest nitrogen doping exhibit an inferred hopping length of 18.5 nm. This is surprisingly large, and not in agreement with Bryksin's value of 1.81 nm (137). In fact, in most experimental examples of hopping in a range of materials the hop length is on the order of
.5 to 5 nm. To be able to make a conclusion regarding the appropriateness of the hopping model even in the light of these longer than normal hop lengths, an estimate of the activation energy is required.
**TABLE VII**

Optical Properties of Anodic Films on N₂-Doped Tantalum

<table>
<thead>
<tr>
<th>N₂ Flowrate</th>
<th>None</th>
<th>0.6 sccm</th>
<th>0.9 sccm</th>
<th>1.2 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>n⁻(Ta₂O₅N₅₋ₓ)</td>
<td>1.9 ± 1.06</td>
<td>1.86</td>
<td>1.75</td>
<td>1.73</td>
</tr>
<tr>
<td>d(nm)(30 V film)</td>
<td>36.2</td>
<td>43.8</td>
<td>44.8</td>
<td>44.0</td>
</tr>
</tbody>
</table>

- measured by ellipsometry at 632.8nm, relative error = ±1%

**TABLE VIII**

Poole Frenkel Coefficients of Anodic Films on N₂-Doped Ta
(30 V film)

<table>
<thead>
<tr>
<th>N₂ Flowrate</th>
<th>None</th>
<th>0.6 sccm</th>
<th>0.9 sccm</th>
<th>1.2 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B (V⁻¹k)</td>
<td>4.2 ± 0.4</td>
<td>6.4 ± 0.4</td>
<td>8.5 ± 0.1</td>
<td>8.8 ± 0.9</td>
</tr>
<tr>
<td>K (A/Vm²)</td>
<td>7.26 × 10⁻⁶</td>
<td>3.42 × 10⁻¹¹</td>
<td>8.77 × 10⁻¹³</td>
<td>1.78 × 10⁻¹¹</td>
</tr>
<tr>
<td>γ</td>
<td>1.5 ± 0.3</td>
<td>1.2 ± 0.2</td>
<td>0.9 ± 0.1</td>
<td>0.9 ± 0.2</td>
</tr>
</tbody>
</table>

- calculated from J(V) and data of Table VII
- absolute error in log (K) is less than .5

**TABLE IX**

Summary of Hopping Analysis of Anodic Films on N₂-Doped Ta

<table>
<thead>
<tr>
<th>N₂ Flowrate</th>
<th>None</th>
<th>0.6 sccm</th>
<th>0.9 sccm</th>
<th>1.2 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(nm)</td>
<td>5.4 ± 0.4</td>
<td>5.2 ± 0.3</td>
<td>9.3 ± 1</td>
<td>18.5 ± 0.9</td>
</tr>
</tbody>
</table>

- inferred from J(V) and data of Table VII

(114)
The Effect Of Heat Treatments:

As reviewed in the introduction, heat treatments have been shown to make large changes in the level of conductivity in anodic Ta$_2$O$_5$. The use of heat treatments was advocated in this study to see if a conduction model could be demonstrated for a range of conductivity levels, and whether it could identify the causes of those changes. Furthermore, heat treatments were shown to affect the compensation index γ of those films exhibiting Poole Frenkel conduction, as documented in Part II. This was particularly interesting since the γ determined for our undoped samples was 1.5 - midway between the usually observed values of 1 or 2. This corresponds to intermediately compensated donor statistics. That is, these samples are neither uncompensated, nor are they in the regime where partial compensation is said to occur. This was the first report of a significant departure from 1 or 2 conditions, even though intermediate values had been theoretically predicted by Yeargan and Taylor in 1968 (184). It was important to determine whether these films could be pushed into one of the two more well known regimes.

Two types of heat treatments were tried. One consisted of baking the samples with quartz lamps under high vacuum (10$^{-4}$Pa) just prior to the deposition of the chromium top metallization. The maximum temperature reached is estimated to be 150°C. This would be very effective in removing water from the oxide, a
likely impurity. The second method was designed to enhance oxygen vacancies, another proposed source of donors. The samples were placed in a tube furnace at 350°C for 1 hour in a flowing stream of 10% H₂ in N₂. The samples were heated to this temperature and cooled down while in the reducing atmosphere.

The J-V-T pattern (Figure 16) was used. Five substrates from a common sputtering run were processed with each heat treatment and studied over a range of temperatures. Later experiments compared the J-V behavior of vacuum baked and nominally unheated devices on a larger number of 32 by 32 array substrates. The later experiments confirmed the room temperature observations quoted below.

The heat treatments were effective in changing the overall level of conductivity, as shown in Figure 27. This graph compares the three types of devices at 251 K. This temperature is chosen for illustration purposes only. At this temperature all three sample types exhibit relatively simple J-V behavior. The low field effects that are seen will be discussed in the next section. As can be seen, the conductance of the vacuum baked samples was approximately an order of magnitude greater than samples which saw no heat treatment. The hydrogen annealed samples showed a thousandfold increase in conductivity. These changes were stable provided the samples were kept and tested under a dry nitrogen ambient. As already mentioned, the stability of the hydrogen annealed samples degraded in the upper range of

(116)
Heat treatments of various types are shown to have an effect on the Poole Frenkel behavior of anodic tantalum oxides. The solid lines connect the anodic (•) and cathodic (+) J-V data for the unheated oxides. The dashed lines similarly connect the vacuum baked J-V points. Note that both the anodic (•) and cathodic (+) currents have been increased by the heat treatment. Hydrogen annealing increases current by an even larger amount as seen by the data connected by the dash-dot line. Cathodic currents (+) for the hydrogen annealed devices remain larger than anodic currents (•). The lines used here to guide the eye do have physical significance as will be explained in later portions of this thesis.
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J-V-T testing (T > 360 K).

The Poole Frenkel interpretation of the data is discussed first. All samples showed $\ln(J/V) \propto \sqrt{V}$ behavior for electric field strengths in excess of $3 \times 10^8$ V/m. As expected, $u$ did indeed drop in the vacuum baked samples to the $V \sim 2$ condition. Thus either the number of acceptors has been decreased, or the number of donors has been increased. An intuitive suggestion is that water loss during baking is associated with a decrease in the density of a water related acceptor. The hydrogen annealed samples showed a $u$ of 3.12 $V^{-1/2}$ at 251 K - much too low to be reconciled with the index of refraction and the oxide thickness measured prior to heat treatment. It is unclear whether these have been changed by the anneal. That is to say, the hydrogen annealed samples did not show any change in the appearance of the interference colors of the exposed oxide adjacent to the chromium coated devices, and yet the capacitance and dissipation factor of tantalum capacitors were shown by Vermilyea (15) and later Smyth et al (14) to be quite different after annealing, even though in those instances also, the interference colors were not changed. Smyth developed a model to explain the frequency dependent behavior of the annealed capacitor in terms of a blurring of the metal - oxide interface: his so-called conductivity profile. These studies support the suspicion that the transport properties of hydrogen annealed samples can no longer be described with the macroscopic parameters determined for unheated samples.

(117)
An analysis of the data was also made with the hopping model (Figure 28). The hop length at 251 K inferred was 10.3 nm for the unheated samples, 9.4 nm for the vacuum baked samples, and 9.0 nm for the hydrogen annealed samples. The relative error in these values arising from measurement tolerances and sample homuniformity is 5%. If nearest neighbour hopping can be assumed (a reasonable assumption in the temperature range under consideration) then these results imply that the impurity concentration is lowest in the unheated samples, and highest in the hydrogen annealed samples. Therefore water would be a poor candidate for the impurity responsible for a hopping type conduction. From these results it is not clear whether the magnitude of the change in impurity density and thus hop length is sufficient to explain the large increases in conductivity in the heat treated samples. One other parameter that may have changed is the activation energy which will be examined in the next section.

Current - Voltage - Temperature Behavior:

The extra variable of temperature was used to check the Poole Frenkel and hopping models for internal consistency, and to quantify the differences between the three types of samples studied in the last section. It also brought unexpected insights into asymmetry and compensation effects.

The J-V behavior of the three types of samples - unheated,
The data of Figure <27> are replotted in the format expected to produce linear plots at high fields if hopping conduction were dominant. As before, the solid, dash, and dash-dot lines correspond to the unheated, vacuum baked, and hydrogen annealed oxides, respectively; also (+) denote anodic polarity, and (−) denote the cathodic polarity J-V points. In this figure however, the shape of the lines used has no physical significance. Only the anodic hydrogen annealed line approaches the $J \propto \exp(V)$ form expected by equation <128>, found on page 91.
vacuum baked, and hydrogen annealed, was investigated over the range of \(-55^\circ C\) to \(145^\circ C\). Within this range conductivity changed by almost eight orders of magnitude.

In this section, analysis of the data will be attempted with the activated hopping, variable range hopping and Poole Frenkel models.

a) Thermally Activated Hopping:

The restricted voltage range and wide temperature variation brought to light a low field ohmic region. This is seen in the hopping plots Figures <29-31> and more clearly in the Poole Frenkel plots Figures <35-37>, pg 122. Both hopping and the three dimensional Poole Frenkel models predict the existence of such a region. From an Arrhenius plot of conductance \((J/V)\) in the voltage independent region vs \(1/T\), Figure <32>, an activation energy may be calculated. For both the vacuum baked and unheated samples an activation energy of \(E_a = 0.86 \pm 0.04 \text{ eV}\) was deduced. The hydrogen annealed samples, on the other hand, exhibited an activation energy of \(E_a = 0.69 \pm 0.05 \text{ eV}\).

With these values of \(E_a\) it is now possible to calculate the absolute level of conductance predicted by the thermally activated hopping conduction model. Recall equation <51> derived in Part I, page 45, repeated here in an appropriate format:

\[
J = \frac{q^2 \nu R^2 n}{dkT} V \exp \left( - \frac{E_a}{kT}, -2\eta R \right) \tag{51'}
\]
a) On this plot anodic J-V data are shown for a range of temperatures. The estimated errors have been discussed in Figure 22, following page 104. The solid lines are least square fits to equation 128, page 91. The lower than expected conductance at low voltages (where data points are connected by dashed lines) is not explained by the hopping theory.
Figure 29: Hopping J-V-T Behavior of Unheated Oxides

Voltage (V)

Conductance (A/V m²)

b) Cathodic J-V data is shown as a function of temperature in a format expected to produce straight lines if hopping conduction were dominant. As in the a) part of the figure, linear behavior is only observed at high voltages. The deviation from theory is more significant in this polarity.
a) On this plot anodic J-V data are shown for a range of temperatures. The solid lines are least square fits to equation (128), page 91. The hopping model does not explain the dashed portion of the curves.
b) On this plot cathodic J-V data are shown for a range of temperatures. The solid lines are least square fits to equation <128>, page 91. The hopping model does not explain the dashed portion of the curves which deviate more strongly in this polarity.
a) On this plot anodic J-V data are shown for a range of temperatures. The solid lines are least square fits to equation (128), page 91. Note that the fit to the hopping theory prediction of a straight line is significantly better than that exhibited by either the unheated or vacuum baked samples.
b) On this plot cathodic J-V data are shown for a range of temperatures. The solid lines are least square fits to equation (128), page 91. The fit to the hopping theory prediction of a straight line degrades at low bias, as observed in the unheated and vacuum baked oxides.
Figure 32: Temperature Dependence of Low Field Ohmic Conductance

Conductance ($A/Vm^2$)

$10^0$ $10^1$ $10^2$ $10^3$

$10^{-3}$ $10^{-1}$

$1000/T$ ($K^{-1}$)

Temperature behavior of the ohmic conductance at zero bias for the (a) unheated, (b) vacuum baked, and (c) hydrogen annealed samples. The calculated activation energies are $0.86 \pm 0.04$ eV for the vacuum baked and unheated samples, and $0.69 \pm 0.05$ eV for the hydrogen annealed case.
Take as an example the data from Figure <30> for the vacuum baked samples. The following parameters from equation <51'> have been evaluated at 312 K:

\[(\frac{J}{V}) = 2.65 \times 10^{-2} \ A/(V-m^2) \ - \text{observed at low bias}\]

\[\zeta_3 = 0.86 \ \text{eV} \ - \text{from Figure <32>}\]

\[d = 54.7 \ \text{nm} \ - \text{measured by ellipsometry}\]

\[R = 8.4 \ \text{nm} \ - \text{inferred from J-V dependence}\]

\[v = 10^{12} - 10^{13} \ \text{s}^{-1} \ - \text{physical property of solids}\]

\[\exp(-2nR) < 1 \ - \text{the overlap factor}\]

Let us assume nearest neighbour transitions which permits the upper limit of the overlap factor can be taken. This also allows \(n\) to be estimated \(4.0 \times 10^{23} \ \text{m}^{-3}\). Substitution in equation <51'> gives a predicted \((\frac{J}{V})\) value of less than \(3.7 \times 10^{-4} \ A/(V-m^2)\), 70 times smaller than what is observed.

No improvement is made by allowing for hop lengths, \(R\), in excess of the inter-impurity spacing, \(\sigma\). For instance, suppose that the carriers hop to the next nearest neighbour, i.e. \(R = 2a\). Then the estimate of \(n\) would increase to \(3.2 \times 10^{24} \ \text{m}^{-3}\), helping to increase the estimated value of \(\frac{J}{V}\), but at the same time the overlap factor will drop to below \(3.4 \times 10^{-4}\) (assuming that \(1/n < a/2\); i.e. impurity wave functions do not overlap). The net result is that the predicted \(\frac{J}{V}\) in this case must be less than \(1 \times 10^{-6} \ A/(V-m^2)\), over four orders of magnitude too small.

Similarly, the optimized predictions of \(\frac{J}{V}\), assuming nearest neighbour hopping, for the unheated and hydrogen annealed
samples at this temperature are 24 and 14 times too small, respectively. These optimized values are over estimates, since experimental evidence shows that $R$ has not yet reached a high temperature limit (Figure <33>), and thus the overlap factor must be retained. Therefore it is concluded that pure thermally activated hopping is unable to explain the observed J-V-T behavior.

b) Variable Range Hopping:

Figure <33> suggests that the Mott theory for variable range hopping should be considered, even though the experimental temperature range is higher than is usually considered appropriate for this mechanism. An additional argument against variable range hopping is the apparent temperature independence of the observed activation energy. In fact, a plot of the low field conductance vs. $T^{-1/4}$, as per equation <57>, page 46, repeated below also gives a straight line. This equation states that for low bias and low temperature conditions:

$$\frac{J}{V} = \frac{q^2 v R^2 N(E_F)}{d} \exp \left[ \frac{T_0}{T} \right]^{1/4}$$  \hspace{1cm} <57>

$$T_0 = \frac{18.1 \eta^3}{N(E_F) k}$$  \hspace{1cm} <58>

The values of $T_0$ can be calculated from the slopes of the curves plotted in Figure <34>. These are 6.6, 15.5, and 4.8 x10$^{10}$ K for the unheated, vacuum baked and hydrogen annealed samples respectively. They compare poorly with the value of 10$^6$ K
If hop lengths, $R$, calculated from the data of Figures 29-31 (following page 119) for the unheated o, vacuum baked ☐, and hydrogen annealed □ samples are plotted against temperature, then a rough tendency towards smaller hop lengths at higher temperature is observed. Only in the case of the hydrogen annealed oxides can a monotonically decreasing function be drawn through all data points. As before, the error bars on $R$ represent a statistically derived Student's $T$ confidence limit of 95% on the results of the linear regression.
Figure 34: Variable Range Hopping Analysis of Ohmic Conductance

The variable range hopping equation (57), page 46, predicts that the low field ohmic conductance decreases exponentially as $T^{-2}$, as shown in this graph. The three curves shown are for $o$ - unheated, $e$ - vacuum baked, and $□$ - hydrogen annealed samples. As is discussed in the text, however, the slopes and intercepts of these lines predict physically unacceptable hop lengths.
deduced by Bryksin for Ta₂₀₅ (137). Note that the intercepts of the plots on Figure 134 yield an estimate of N(Eₚ). For the vacuum baked sample, for instance, N(Eₚ) is found to be 5.3x10⁴⁵ (J⁻¹ m⁻³)⁻¹, corresponding to a room temperature density of states at the Fermi level of 2.2x10¹⁵ m⁻³. With this value, and the T₀ estimate, 1/₁₀ can be estimated. For the vacuum baked device example 1/₁₀ = 25 nm, an exceptionally large value. It is three times the hop length, and is incompatible with the assumptions of hopping conduction. Therefore both the activated and variable range hopping theories must be discarded as possible explanations of the observed J-V-T behavior in these films.

c) Poole Frenkel Conduction:

In general, when the J-V data is plotted in Poole Frenkel format (i.e. ln(J/V) vs √V), each curve has up to 3 distinct segments. These can be seen in Figures 135-37. The first segment is the low field ohmic region whose activation energy has already been calculated. The next segment is most distinct in the cathodic (Ta negative) polarity in the vacuum baked and unheated samples, but is also present in the anodic (Ta positive) polarity for certain temperatures. It is linear on these Poole Frenkel plots, but with a larger slope than that of the third segment. The third segment is the Poole Frenkel region identified in the previous experiments. A number of conduction models, such as the three-dimensional Poole Frenkel models, Poole Frenkel conduction
Figure <35> Poole Frenkel Plot of Unheated Oxides

a) This is a Poole Frenkel plot for the anodic-bias of the unheated oxides with temperature as a parameter. The estimated errors have been discussed in Figure <22>, following page 104. The solid lines are least square fits to the form predicted by the Poole Frenkel theory discussed in Part IV. The low field behavior is strongly influenced by 3-D effects and thus is curved on this type of plot. The high field behavior for points to the right of the dividing line exhibits a gradual change in slope due to a rise in compensation index when a sufficient number of donors have been ionized.
b) This graph shows the corresponding J-V-T curves for the cathodic bias. The transition between the two compensation regions is more distinct than in the anodic case, but in fact occurs at approximately the same current density for both biases. The behavior can also be fitted with the extended Poole Frenkel theory of this thesis.
Figure 3: Poole-Frenkel Plot of Vacuum Baked Oxides

The anodic J-V-T behavior of the vacuum baked samples is shown in the same format as given in Figure 3 for the unheated oxides. Temperature is given as a parameter. Low-field effects and the mid-field change in slope to the right of the dividing line are also apparent.
Figure <36> Poole-Frenkel Plot for Vacuum Baked Oxides

b) The cathodic J-V-T plots for the vacuum baked samples are shown here. The shape of the J-V-T curves for the two biases are more similar to each other for the vacuum baked samples than for the unheated oxides.
For all-temperatures the current density in hydrogen annealed oxides is much larger than for the same bias applied to unheated or vacuum baked samples. The anodic bias is shown here. The solid lines are fits to the 3-D Onsager-Poole Frenkel model. No mid-field change in slope is observed within the experimental range.
Figure 37: Poole Frenkel Plot for Hydrogen Annealed Oxides

b) The cathodic J-V-T behavior is shown here for the hydrogen annealed samples. The shape of the curves is similar to that of the anodic bias and can be satisfactorily fitted to the Onsager-Poole Frenkel model.
involving a second donor level, or a Schottky contact barrier in series with the Poole Frenkel dominated bulk, were applied to the second segment, without success. The least squares algorithm used to draw the solid lines on Figures 35-37 is guided by the conduction model described in Part IV. All regions are fitted to a Poole Frenkel form, with a smooth change in compensation index at a critical voltage. For low voltages it is necessary to consider the three dimensional emission process.

This discussion shall concentrate on the highest field region which should correspond to one dimensional theory. If Poole Frenkel conduction were operative, then one should observe an activation energy for conductance, $\xi_2$, that decreases with increasing voltage. This is precisely what is seen in Figures 38. One complication in extracting these values from the experimental J-V-T data was that the data was collected as voltage for a set current, while current for a set voltage is required for the activation energy analysis. Therefore for each point in Figure 38, interpolated values of $J(V)$ were used. Analysis was not carried out for voltages in the ohmic or transition regions. In the high field region the decrease in observed activation energy depth is proportional to the square root of applied voltage as predicted from equation 84, page 62. The constant of proportionality is nearly the same for both polarities, and for both the vacuum baked and the unheated samples, even though conductivity is an order of magnitude higher

(123)
Figure 38: Voltage Dependence of Activation Energy.

When the activation energy, $\zeta_a(V)$, is calculated from the slopes of experimental $\ln(J/V)$ vs. $1/T$ plots at equally spaced voltage points it is found to decrease linearly as the square root of voltage. Such behavior is characteristic of Poole Frenkel conduction. Identical behavior is observed for both the unheated (o) and vacuum baked samples (e), even though the magnitude of conduction in the two types of samples differed by a factor of 10. The activation energy for hydrogen annealed samples also decreases linearly with the square root of applied voltage, but both the slope and intercept differ from those observed for unheated and vacuum baked oxides (o).
in the vacuum baked samples. An asymmetry with respect to zero bias is apparent for these two types of samples. In the hydrogen annealed samples, on the other hand, the asymmetry is absent. The slope of the $E_a$ vs $\sqrt{V}$ line was also less at $0.17 \pm 0.01$ eV/V$^2$.

Thus it would appear that the vacuum baked and unheated samples do experience identical Poole-Frenkel barrier lowering operating on the same level. Hydrogen annealing appears to create a new, shallower level. These lines do not extrapolate to the correct zero bias activation energies because the one-dimensional approach leads to an over estimate of $E_a$.

In the section describing the nitrogen doping experiments, the room temperature nonlinearity coefficient $\beta$, was extracted from the $J(V)$ data. Then the compensation index, $\gamma$, was calculated as a ratio of the constant

$$\frac{1}{kT} \sqrt{\frac{q}{\pi \varepsilon_0 d^2}}$$

to $\beta$, the observed slope of the experimental $\ln(J/V) vs \sqrt{V}$ curves. Independently measured values of the pertinent physical parameters enabled accurate calculation of $\beta$. In a similar fashion, $\gamma$ may also be calculated from the slope of the experimental $E_a$ vs $\sqrt{V}$ plots. That is

$$\Delta E_a = \frac{1}{kT} \sqrt{\frac{q}{\pi \varepsilon_0 d}} \delta^{\gamma=0}$$

Thus it may seem possible to calculate $\gamma$ from $J(T)$ as well as $J(V)$. However, when this is tried, the inferred $\gamma$ is $0.6 \pm 0.1$
PART III - EXPERIMENTS

for both the vacuum baked and unheated samples. This is inconsistent with the previously calculated $\gamma$'s of 2 and 1.5 respectively. Even for the hydrogen annealed samples, there is some doubt as to $c$ and $d$, a similar discrepancy is found when the slope $\Delta E_0/\Delta V$ is compared to the product of $S$ and $T$.

Consider the temperature dependence of $S$ itself (Figures 39-41). A similar calculation shows $\beta$ rises much too rapidly with decreasing temperature to be consistent with the $\gamma$'s calculated at room temperature, or for any other $\gamma$ between 1 and 2. These graphs suggest the eventual answer to the dilemma... above room temperature $S$ does follow a proper $\gamma = 2$ line (as is dotted in on the Figure), consistent with independent measurement of $c$ and $d$. Intuition might suggest that at lower temperatures $\gamma$ is dropping to the $\gamma = 1$ state, causing a rise in $S$. Part IV will back up intuition with a detailed theory of the compensated semiconductor, which predicts this effect.

At this point however, the conclusion must be made that standard Poole Frenkel theory is unable to explain the observed $J-V-T$ behavior.

(125)
The temperature dependence of $\beta$ for the unheated oxides is shown here for the anodic (•) and cathodic (*) polarities. Error bars correspond to a Students' T 95% prediction interval. Clearly the data departs from the $\gamma = 2$ line predicted by standard theory. The solid line is the prediction of the extended Poole Frenkel theory proposed in part IV of this thesis. The critical fitting parameters are indicated in the insert, and all others are found in Table X, page 145.
The $\beta$'s of the vacuum baked oxides show similar temperature behavior to the unheated samples (Figure 39), even though the room temperature value of $\beta$ lies closer to the $\gamma = 2$ line in this case. (*) - anodic bias, (o) - cathodic bias. To produce the solid curve shown, the ratio of $N_a/N_d$ was increased over that used in Figure 39 by a factor of $\frac{3}{3}$. 

$N_a/N_d = 3 \times 10^{-15}$

$\Phi_d = 1.75 \text{ eV}$
Figure 341 Y-β Behavior of Hydrogen Annealed Oxides

β's for the hydrogen annealed samples are plotted against reciprocal temperature. Values of θ and d can be chosen to fit the observed β at one temperature, but as in Figures 39 and 40, standard theory cannot fit all temperatures simultaneously. Even though β is much lower than what can be estimated from pre-anneal θ and d values, perhaps it is also exhibiting a transition from γ = 1 to γ = 2 conditions. If so, the appropriate fitting parameters are those indicated in the insert and in Table X.
3. SUMMARY OF RESULTS

The matter rests at an impasse. Standard Poole Frenkel conduction theory cannot be carried any further; however, the results which have been explained by the existing theory can be summarized thus far.

1) Current is distributed uniformly down to the scale of microns. Flaw dominated conduction is considered unlikely.

2) Current density and the nonlinearity coefficients depend upon insulator thickness in the manner predicted by the punch through Schottky barrier emission, hopping and Poole Frenkel conduction. In contrast, the predictions of imperfect insulator-metal Schottky barrier emission and Space Charge Limited Conduction (SCLC) were not upheld.

3) Independent measurements of $c$ and $d$, which permit the calculation of a theoretical $\beta$, show that "normal" Poole Frenkel conduction occurs in three different tantalum oxy-nitride compositions. Their compensation index is one, in line with the theory that nitrogen compensates the donor operative in the undoped films. The undoped film, on the other hand, showed a room temperature compensation index of 1.5, which is permitted by the theory of Yeargan and Taylor (184), but has not been reported prior to this work. It corresponds to a condition dominated by intermediately compensated donors, where neither partial

(126)
compensation nor uncompensated donor statistics can be applied. In both cases, Schottky conduction is ruled out.

Analysis of the J-V behavior of the nitrogen-doped devices also puts hopping conduction in an unfavourable light because the inferred hop lengths are much larger than what is normal for this conduction mechanism.

4) By vacuum baking the undoped sample, conductivity can be increased and its Poole Frenkel compensation index can be brought up to approximately 2. Under the Poole Frenkel model it is concluded that vacuum baking decreases the number of acceptors - possibly by removing water from the film. Hydrogen annealing, on the other hand, creates a new shallower donor - possibly related to oxygen vacancies. The magnitude nonlinearity coefficient, $\beta$, of the hydrogen annealed sample cannot be explained by the Poole Frenkel model on the basis of physical parameters measured before annealing. The hopping model, on the other hand, has no difficulty explaining the nonlinearity of the hydrogen annealed sample. It also implies that vacuum baking and hydrogen annealing increases the number of impurities (of a shallower energy depth in the case of the hydrogen annealed samples), causing the hop length to decrease and conductivity to increase.

5) Low field ohmic and a second "Poole Frenkel-like" conduction regime were found at very low field strengths. The only slightly rectifying nature of the ohmic behavior limits the magnitude of any postulated pre-existing internal field, such as
would result from contact metal work function differences. The shape of the low field ohmic region is correctly predicted by the Onsager-Poole Frenkel model.

6) The nature of the asymmetry in the high field region is such that the extrapolated peak in the activation energy vs $\sqrt{V}$ plots is shifted in the direction of the anodic polarity in both the unheated and vacuum baked samples. This supports result 4) that the vacuum baked and unheated samples differ in the number of donors and acceptors, not the type of donor. The hydrogen annealed samples were shown to have symmetric activation energy behavior.

7) Using the temperature dependences of the zero bias conductance and the voltage dependence of current density it was shown that the hopping models all predict conductances well below the observed values. This evidence, combined with the exceptionally large hop lengths, and the generally poor J-V fits lead to the dismissal of the hopping model.

8) Discrepancies were found in the inferred values of the physical parameters that make up $\beta$ estimated from temperature dependences, and field dependences. The standard Poole Frenkel model is unable to explain these results. An extension to the theory is proposed in the following section to resolve the difficulty.
1. EXTENSIONS TO THE THEORY

Introduction:

The analysis has shown that standard Poole Frenkel conduction theory has been successful in predicting the functional dependences of J-V data on such physical properties as thickness and dielectric constant. It has also been able to present a consistent picture with regards to the compensating effects of nitrogen doping and heat treatments. But two problems remain. The first, and the most disturbing problem is that one cannot use the standard Poole Frenkel theory to predict unique values for such physical parameters as $\gamma$, the compensation index, from both the $J(V)$ and the $J(T)$ data. This problem manifests itself most clearly in the temperature dependence of $\sigma$. It rises too steeply with decreasing temperature. The second problem is that the J-V data is asymmetric; cathodic currents exceed the anodic currents, but the Poole Frenkel model, being strictly a bulk phenomenon, has no provision for this effect. In this section, the Poole Frenkel conduction theory is extended to include explanations for both the anomalous J-V-T behavior and the asymmetry of current with respect to zero bias.
PART IV - DISCUSSION

2. INTERMEDIATELY COMPENSATED DONORS:

The anomalous J-V-T data, which gives us different estimates for the physical parameters depending on how the data is analysed, is the crux of the problem. Analysis at any one temperature gives reasonable estimates for all the disposable parameters in the Poole Frenkel conductivity expression. It is the attempt to analyse the behavior at all temperatures simultaneously that leads to the inconsistency. Therefore it is a valid question to ask if there really is a problem. Could the measurements be in error? The answer to this question is "not likely". Adequate calibration of temperature, current and voltage measuring devices, the strict use of controls to check for drift, and the fact that a large number of devices have been tested over a span of many fabrication runs limits the possibility for error. The possibility becomes even more remote when the literature is consulted. Similar anomalous J-V-T behavior has been reported, but not explained, by Jonscher (65) working with SiO$_x$, by Sinha and Smith (213) also working with SiO$_x$, by Brown et al (205) working with Si$_3$N$_x$, and by Meaudre and Meaudre (215) also in SiO$_x$. Temperature dependent dielectric constants and/or thickness have been suggested. However, the anomaly described in this thesis appears to be the furthest from theory yet seen. Therefore even the most generous estimates of temperature dependences in
and $d$ are simply insufficient to bring the data in line. Fortunately, these temperature dependences are not required to fully explain the $J-V$-$T$ data reported here and in the literature. In the first extension to the theory presented below, a simple model is derived from within the framework of the Poole Frenkel model to fit the $J-V-T$-behavior based on the existence of partly partially compensated donors within the Ta$_2$O$_5$.

One way to explain the $J-V-T$ results is to find a smooth variation with temperature in $\gamma$, the only other parameter left in $\beta$ whose temperature independence has not been verified. Intuitively, it is not hard to understand why this can occur. The degree of compensation, and thus $\gamma$ must be a function of temperature because the ratio of ionized donors to ionized acceptors is not the same for all temperatures. When temperature is increased the number of ionized donors increases whereas the number of ionized acceptors remains the same since they were all ionized to begin with. Clearly then, the ratio of ionized donors to ionized acceptors increases with heating, making the insulator less "compensated". Thus $\gamma$ must increase from 1 to 2. This magnitude of change is sufficient to fit the observed values of $\beta$ in the results presented here.
A detailed analysis will be presented in this section to show that the transition between \( \gamma = 1 \) and \( \gamma = 2 \) conditions occurs gradually over the observed temperature range. Recall from Part II, pages 71-75 that \( \gamma \) arose from the relationship between the carrier density and the donor density. The starting assumption was charge neutrality. Free holes and unionized acceptors were neglected. This gave equation (107).

\[
n = -\frac{1}{2} \left( N_d + N_c' \right) + \frac{1}{4} \left( \left( N_c' + N_d \right)^2 + 4 N_c' (N_d - N_a) \right)^{\frac{1}{2}} \tag{107}
\]

where \( n \) = density of free electrons

\( N_d \) = density of donors

\( N_a \) = density of acceptors

\( N_c' = \frac{N_c \exp \left( \frac{-\zeta_d}{kT} \right)}{2} \)

\( N_c \) = conduction band density of states

\( \zeta_d \) = donor energy depth

Standard theory assumed that if \( N_d >> N_c' >> N_a \) (i.e. donors are uncompensated) then only the \( 4\cdot N_c' (N_d - N_a) \) term in equation (107) was retained, and therefore the carrier density became:

\[
n = \sqrt{\frac{N_d N_c'}{2}} \exp \left[ -\frac{\zeta_d}{2kT} \right] \tag{108}
\]

Thus \( \gamma = 2 \)

Similarly, if \( N_d >> N_a >> N_c' \) (i.e. donors are partially compensated) then it was possible to expand the square root to second order and cancel the two terms in \( (N_d + N_c') \).
PART IV - DISCUSSION

This left the expression:

\[ n = \frac{(N_d - N_a)}{2N_a} N_c \exp \left(-\frac{\xi_d}{kT}\right) \]  

Thus \( Y = 1 \)

In contrast, the analysis presented in this section is concerned with the situation where the donors are neither uncompensated nor partially compensated. In effect, the donors are intermediate compensated. Mathematically speaking, these conditions prevail when:

\[ 4N_c'(N_d - N_a) < (N_c' + N_a) < 40N_c'(N_d - N_a) \]

and thus neither of the simplifying assumptions used in the derivation of equation <108> and <118> is valid. When the donor and acceptor densities are in the intermediate compensated regime, the temperature dependence of the carrier density must be calculated directly from <107>.

In the computation of values of equation <107> care must be taken to ensure that round off error does not adversely affect accuracy. For example, if \((N_c' + N_a)^2\) is more than \(10^9\) times larger than \(4N_c'(N_d - N_a)\), then a formulation of equation <107> exactly as written will return an incorrect value of zero when executed on the Apple //e computer. This is due to the nine digit limit of accuracy. Under these particular circumstances \( n \) is the difference between two nearly equal numbers. Therefore the expansion of the square root employed in the derivation of

(133)
equation \(118\) is not only valid under certain circumstances, it is necessary to preserve accuracy. Happily, the range of impurity concentrations where the full formula must be used instead of the expanded form lies within the range where the computation of the full formula is accurate. A similar problem in the computation of equation \(107\) is the limited dynamic range of the computer. Only numbers in the range of \(10^{-38}\) to \(10^{+38}\) may be manipulated. This problem can be easily circumvented by factoring out a common multiple of, say, \(10^{10}\) from \(N_a\), \(N_d\), and \(N_c\) prior to calculation.

The behavior of this function over the temperature range used in the J-V-T experiment is shown in Figure \(42\) for a range of acceptor densities. Several features of the plot can be described.

1) For all donor to acceptor ratios greater than \(10^{21}\), a transition is made between two linear \(\ln(n)\) vs \(1/T\) curves differing in slope by approximately a factor of two. The high temperature portion corresponds to equation \(108\) with slope equal to \(\zeta_d/2k\), while the low temperature portion corresponds to equation \(118\) with slope equal to \(\zeta_d/k\).

2) The larger the acceptor density, the higher the temperature at which the transition begins.

3) An alternate choice of donor density simply displaces the curves vertically.

4) The donor to acceptor ratios may seem exceptionally large. Why should such a seemingly insignificant number of
Carrier density, as described by equation (107), page 72, is plotted here against reciprocal temperature with acceptor density as a parameter. The impurity densities and activation energies are indicated in the inset. They are the same as those used for fitting the unheated oxides.
acceptors be so important? In fact, the number of ionized donors and ionized acceptors are comparable. For example, for \( T = 300 \text{ K}, N_d^0 = 10^{24}, N_A = 10^9 \), and \( \epsilon_d = 1.75 \text{ eV} \), the number of ionized donors is only \( 5.1 \times 10^9 \), and thus the material is indeed partially compensated. If, on the other hand, \( \epsilon_d \) were only \( 0.5 \text{ eV} \), then the donor to acceptor ratio must be below 100 to exhibit a transition in this temperature range. In short, the deeper the donors are, the fewer acceptors needed to compensate them.

5) The acceptor activation energy has no influence on the form of the plot provided \( E_F - E_A \) is greater than \( 2kT \). This was contained in the assumption that the material was n-type, and therefore that all of the acceptors were ionized.

6) The calculation is only valid up to the point where \( E_d - E_p \) becomes less than \( 2kT \). This was contained in the assumed validity of the Boltzmann relationship between carrier density and donor activation energy. All of the calculations shown in this thesis have been verified to be within the range of Boltzmann statistics.

The temperature dependence of carrier concentration with differing donor to acceptor ratios shown here is nothing startling. Similar graphs can be found in the text "Semiconductor Statistics" by Blakemore (235), and Hall data showing experimental evidence of the transition can be found (236).
is new is the application to the Poole Frenkel situation.

In the Poole Frenkel situation both $\beta_{pf}$, the nonlinearity coefficient, and $K_{pf}$, the conductivity coefficient, are affected by the degree of compensation. The Poole Frenkel conductivity coefficient, $K_{pf}$, in either of the two asymptotic doping regimes is equal to:

$$K_{pf} = \mu_q n_0 (T)$$  \[132\]

where $n_0 (T)$ is the carrier concentration in the absence of Poole Frenkel barrier lowering.

Thus in previous applications of standard Poole Frenkel theory plots of $K_{pf}$ vs $1/T$ were presumed to be linear with slope equal to $\xi_d / \gamma k$. Data and predictions of standard theory are given in Figures 43-45. In both the vacuum baked and unheated examples the standard theory tends to overestimate $K_{pf}$ in the low temperature range. Under the model described here, the decrease in $K_{pf}$ below the values predicted by standard theory is due to the transition from uncompensated to partially compensated donor statistics as temperature decreases. It might be expected that these $K_{pf}$ plots should be identical to those of $n(T)$ in Figure 42 except for a vertical displacement to account for the $\mu q / d$ multiplicative factor. Although such a fit to the data (given in Figure 43 only) shows the desired drop at low temperatures, this curve also deviates from the observed data. The trouble is that $K_{pf}$ is not exactly as given in equation 132.
This graph shows the large variation in the observed $K_p$ values over the temperature range examined. Standard theory $P_f$ is unable to fit the low temperature $K$'s which fall below the prediction, a). The curve b) drawn for the same fitting parameters used for the $\beta$-T fit (Figure <39>, page 125) correctly predicts the deviation, and falls between the anodic (•) and cathodic (*) points. Neglect of the voltage dependence of compensation leads to the dashed curve c).
The $K_{PF}-T$ behavior of the vacuum baked samples show even more clearly the low temperature deviation from standard theory a). The predictions of the extended Poole Frenkel theory, b), using the fitting parameters from the $\beta-T$ curve, Figure 40, page 125 falls between the anodic (*) and cathodic (*) points. As in the previous figure, the error bars are the 95% Student's T intervals.
Although the β-T curves for the hydrogen annealed samples, (Figure 41, page 125) exhibited a change in slope suggestive of a change in compensation, no corresponding break in this curve is apparent. The solid line is the prediction based on the fitting parameters used in the β-T plots.
when intermediately compensated donors are present. Instead, $K_p f$ must be rigorously defined as $\mu q/d$ times the value of $n(T)$ extrapolated from the Poole Frenkel bias regime to zero bias, denoted $n_{ex}(T)$. Under either of the uncompensated or partially compensated conditions, $n_o(T)$ is equal to $n_{ex}(T)$. Under partly compensated conditions, however, they are not. To find $n_{ex}(T)$, values of equation (107) must be calculated for a series of voltages with $\zeta_d$ replaced with $\zeta_{do} - \Delta \zeta_d$. Recall that the magnitude of the one dimensional Poole Frenkel barrier lowering, $\Delta \zeta_d$, is related to the applied bias via equation (84) found on page 62, and repeated here for convenience:

$$\Delta \zeta_d = \sqrt{\frac{q V}{\pi \epsilon \epsilon_0 d}}$$

(84)

Note that values of $\epsilon$, d and $\epsilon_0$ must be assumed. The values used and the rationale behind their choice will be discussed shortly. Also note that this equation is not valid for very low electric field strengths where a full three dimensional approach is necessary. These effects, which only add a low field ohmic portion to the curves have been omitted to highlight the effect under study. Figure (46) gives a plot of the calculated carrier density as a function applied voltage. For conditions corresponding to the temperature range where the activation energy of carrier density exhibits a transition between $\gamma = 1$ and $\gamma = 2$ conditions, $ln(n) \ vs \ \sqrt{V}$ has two approximately straight segments with slopes differing by approximately a factor of two.
Carrier density, as described by equation <107>, page 72, is plotted against \( \sqrt{\text{voltage}} \) for a range of temperatures. The donor energy was chosen to 1.75 eV. The \( N_a \) to \( N_d \) ratio was \( 10^{-15} \). Note there are two nearly straight portions, corresponding to the two linear portions on the Poole Frenkel plots of J-V-T (Figures <35-37>, following page 122).
These curves are strongly reminiscent of the J-V-T plots of Figures 35-37 in the region where the one dimensional Poole Frenkel conduction formula is expected to hold. This also implies that for intermediate compensated conditions \( n_{ox}(T) \) (and thus the true \( K_{pf} \)) is larger than \( n_{o}(T) \) (and the incorrect \( K_{pf} \) that may be calculated from it).

The effect can be easily explained under the model of the intermediate compensated donor. As the electric field increases, and the donor levels begin to empty, the degree of compensation decreases, and thus the slope of \( \ln(n) \) vs \( \sqrt{V} \) curve must decrease from a value corresponding to \( \gamma = 1 \) to one appropriate to \( \gamma = 2 \). Evidently, \( \gamma \) which relates the slope of the \( \ln(n) \) (or \( \ln(J/V) \)) vs \( \sqrt{V} \) curve to the physical properties of the oxide and was previously thought to be constant for a given device, is not only temperature dependent, but also bias dependent! When the predicted \( K_{pf} \) is calculated using the \( n_{ox}(T) \) extrapolated from the same bias region as that over which the experimental Poole Frenkel coefficients were calculated, good agreement between theory and experiment is achieved for the unheated and vacuum baked samples. The fit to the hydrogen annealed data is significantly poorer. The values used are given in the captions, and are summarized in Table X at the end of this section, page 145.

In a similar fashion, the anomalous temperature dependence of \( \beta \) can be explained. Again, values of \( n(V,T) \) are generated for
PART IV - DISCUSSION

specific values of $N_d$, $N_a$, $\xi_{do}$, $c$, and $d$. Since $J/V$ is proportional to $n$, $\beta$ is equal to the slope of a $\ln(n)$ vs $\sqrt{V}$ curve. Then $\gamma$ can be calculated from its original definition: that is, $\gamma$ equals the ratio of the constant,

$$\frac{1}{kT} \sqrt{\frac{q^3}{e\varepsilon_0 \pi d}}$$

to $\beta$. Because it is dimensionless, results of the calculation have wider application when expressed in terms of $\gamma$. Its temperature behavior is shown in Figure <47>. The transition spans a temperature range of approximately 200°C. For a limited range of approximately 50° within that span, the function is nearly linear. Because $\beta$ changes so smoothly with temperature, activation energy plots will appear normal, but give completely erroneous results because the temperature dependence of $\gamma$ was inadvertently included. It is no surprise that $\xi_d$ calculated in this manner does not vary with voltage with the correct constant of proportionality. In a similar fashion, a $\beta$ vs $1/T$ curve constructed for that region would be accidentally linear with an anomalously high slope. $\beta$ rises too rapidly at low temperatures because $\gamma$ is also dropping. The solid curves shown on Figures <39-41> demonstrate that the model presented here not only fits the $K_{pf}$ temperature dependence, but also the temperature dependence of $\beta$ using the same fitting parameters. Also, an unambiguous value of $c$ which fits the entire temperature range may be calculated for the vacuum baked and unheated samples. This

(139)
Figure 47: Temperature Dependence of Compensation Index

The effective compensation index can be calculated from equation 107, page 72, for experimental bias conditions. Note that it varies smoothly over a range of 200°C from $\gamma = 1$ to $\gamma = 2$ conditions.
is $3.52 \pm 0.07$ (i.e. $\bar{n} = 1.87 \pm 0.04$) — consistent with earlier optical measurements. See Table VII, page 114.

The shape of the $\beta$ vs $1/T$ curves for the hydrogen annealed sample is similar to those of the unheated and vacuum baked samples even though corresponding break points in the $K_{pf}$ vs $1/T$ and $J/V$ vs $\sqrt{V}$ curves are not apparent. The anomalously low values of $\beta$ indicate that either $\epsilon$ or $d$ for these oxides are larger than what was determined in macroscopic optical measurements on unheated samples. Note that if $d$ were assumed to be unchanged, then the $\epsilon$ that fits the observed $\beta$-$T$ curves is $24 \pm 5$. This is equal to the static dielectric constant for Ta$_2$O$_5$ (157). Such agreement may be coincidental, or it may indicate that ionic Poole Frenkel conduction is taking place. Recall that for such a process Poole Frenkel like $J(V)$ behavior is observed except that $\beta$ then depends on the static dielectric constant (159-161). There is not enough data to decide what conduction process is most appropriate for these oxides.

The numerical values for the other parameters in equation (107) are arrived at in the following fashion:

1) Donor depth: The steepness of the $ln(K_{pf})$ vs $1/T$ plots and the width of the transition in the $\beta$ vs $1/T$ curves is a strong function of $\zeta_{do}$, so that this value can be estimated without knowledge of $N_a$ or $N_d$. An interactive fitting program was written to allow user directed variations in $\zeta_{do}$ (and all other
fitting parameters) and comparison of the sum of the residual errors between predictions and theory. Convergence to a satisfactory fit could be rapid with careful choice of seed values. The value attained in this manner for $\xi_{do}$ for both the vacuum baked and unheated samples is $1.75 \pm 0.05$ eV, and $1.40 \pm 0.05$ eV for the hydrogen annealed sample. An independent estimate of $\xi_{do}$ is readily attained from the temperature dependence of the low field ohmic region. In light of the model proposed here, it is apparent that over the temperatures used to calculate the ohmic region's activation energy, $\gamma \approx 2$. Therefore the energy depth of the level responsible for the ohmic conduction is $2 \times 0.36$ eV = $1.72 \pm 0.08$ eV for the vacuum baked and unheated samples and $1.4 \pm 1$ eV for the hydrogen annealed samples. The shallow level has been observed in Ta$_2$O$_5$ films by other researchers (69,237), but the deeper one is new. It is believed that the optimization process employed by this laboratory to produce tantalum pentoxide with larger than normal conductivity levels may have enhanced a naturally occurring, but usually low density level, or has introduced a new, impurity related level.

2) Donor to acceptor density ratio: The temperature of the transition point between the two straight line portions of the $n(T)$ and therefore the $K_{pf}(T)$ curves is a strong function of $N_d/N_a$. The value of $N_d$ merely shifts the $n$ curves vertically on such a plot. Once the transition temperature is identified, the
PART IV - DISCUSSION

ratio is read off a graph such as Figure 48, generated for a specific $d_0$.

3) Donor density: The value used is arbitrary. However, other researchers have applied a wide variety of analysis techniques to anodic $Ta_2O_5$ and have independently arrived at a doping concentration of $10^{24} m^{-3}$ even though the films differed in preparation, and conductivity behavior (31, 58, 59, 110, 137). This value may be universal for this material, for much the same reasons that amorphous semiconductors were thought to be intrinsically undopable (238). Impurities are simply tied up somewhere in the loose atomic structure where they are not electrically active.

4) Electron mobility: From the $K_{ph}(T)$ plots an estimate of electron mobility may be made (in the vacuum baked and unheated samples only, since the values of $d$ and $e$ are in question for the hydrogen annealed samples). The values calculated, which depend on the exact value of $N_d$, are on the order of $10^{-1} \text{cm}^2/\text{Vs}$ for all reasonable estimates (see Table X). They are fully consistent with electron propagation in the conduction band, and are in agreement with the results of Thomas (59).

The success of the model permits an interpretation of the observed J-V behavior in terms of impurities and their probable sources. To begin with, conduction in these films is now assured to be a bulk phenomenon. The sources of conduction electrons are

(142)
This graph recasts the data presented in figure <42>, after page 134 and <47> after page 139 to show the abrupt drop in $\gamma$ at a fixed temperature as acceptor density is increased. This feature facilitates the accurate determination of the donor to acceptor density ratio.
PART IV - DISCUSSION

partially ionized donors distributed throughout the oxide having an energy depth of 1.75 eV in unheated and vacuum baked samples. Conduction electrons (or ions) which dominate the hydrogen annealed samples have a different activation energy of 1.4 eV. This work has shown that under certain conditions compensating acceptors are also present. The identity of these donors and acceptors may be surmised by correlating the observed changes in the compensation index, $\gamma$, with the physical mechanisms by which the different process conditions change conductivity. Consider the undoped, unheated oxide. It exhibits a compensation index of around 1.5, and an intermediate conductivity coefficient, $K_{pf}$. After vacuum baking this oxide, $\gamma$ rises to 2, corresponding to uncompensated Poole Frenkel conditions, and $K_{pf}$ increases by an order of magnitude. Both observations may imply the loss of acceptors. It is proposed that the acceptor driven off in vacuum baking is water (or $\text{-OH}$), a well known impurity in anodic oxides formed in aqueous solutions. It was mentioned in the introduction that Krembs, working with tritiated water, estimated a density of $10^{24}$ m$^{-3}$ H atoms in anodized $\text{Ta}_2\text{O}_5$ (16), so there can be no doubt that this impurity is important.

Consider the unheated oxide once more. Now add nitrogen by reactively sputtering the parent tantalum. $K_{pf}$ drops dramatically and $\gamma$ falls to 1, corresponding to "complete" partial compensation. This can be accomplished by the addition of more acceptors, or the loss of donors. The expression of charge
neutrality makes both views equivalent. Nitrogen fits this role well. It may be introducing another acceptor in addition to water. However another hypothesis could be that the primary donor in Ta$_2$O$_5$ is an oxygen vacancy. As nitrogen replaces oxygen atoms in atomic arrangements that would normally lead to the creation of donors, the extra electrons become bound to the nitrogen instead of being excited to the conduction band. This would explain the drop in $K_p$ - there are fewer donors - and in $\gamma$ - the ratio of acceptor density to donor density rises. The changes observed in the hydrogen annealed samples point to large increases in the dielectric constant and/or oxide thickness. and a substantial increase in the carrier concentration. The reducing atmosphere used would increase the number of donors if these were oxygen vacancies (but the donors at 1.75 eV and 1.40 eV could not both be simple oxygen vacancies), or could be introducing hydrogen as an ionic charge carrier.
Table X - Summary of Poole-Frenkel Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unheated</th>
<th>Vacuum Baked</th>
<th>Hydrogen Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta_d$ (eV)</td>
<td>$1.75 \pm 0.05$</td>
<td>$1.75 \pm 0.05$</td>
<td>$1.4 \pm 1$</td>
</tr>
<tr>
<td>&amp; $1.72 \pm 0.03$</td>
<td>$1.72 \pm 0.02$</td>
<td>$1.41 \pm 0.08$</td>
<td></td>
</tr>
<tr>
<td>$\epsilon = n^2$</td>
<td>$3.61 \pm 0.07$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&amp; $3.58 \pm 0.03$</td>
<td>$3.47 \pm 0.03$</td>
<td>$(24 \pm 5)$</td>
<td></td>
</tr>
<tr>
<td>$d$ (nm)</td>
<td>$54.9 \pm 5$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$N_d^+ / N_a$</td>
<td>$3 \times 10^{-15}$</td>
<td>$1 \times 10^{-15}$</td>
<td>$3 \times 10^{-12}$</td>
</tr>
<tr>
<td>$N_d^a / N_a$</td>
<td>$2.1$</td>
<td>$5.1$</td>
<td>$1.9$</td>
</tr>
<tr>
<td>$\gamma_{280K}$</td>
<td>$1.5 \pm 1$</td>
<td>$1.84 \pm 0.09$</td>
<td>$(1.1 \pm 3)$</td>
</tr>
<tr>
<td>$\mu$ (m²/Vs)</td>
<td>$0.16$</td>
<td>$0.23$</td>
<td>$0.17$</td>
</tr>
</tbody>
</table>

Notes:
- $N_c = 10^{25} \text{m}^{-3}$ at 300 K with $T^{3/2}$ dependence is assumed
- Calculated from the slope of K-T data (Figures 43-45)
- Calculated from $\sigma_o - T$ data (Figure 32)
- Measured by ellipsometry
- Calculated from slope of $\beta - T$ data, $\gamma = 2$ (Figures 39-41)
- Parameter for best fit to K-T and $\beta - T$ (Figures 39-41 & 43-45)
- (Error in $\log(N_d^+ / N_a)$ is estimated to be $\pm 5$)
- Inferred from fitting parameters, for 300 K and zero bias
- Calculated from anodic $\beta$ and $\epsilon$ and $d$ given above
- Assuming $N_d = 10^{24} \text{m}^{-3}$, error in $\log(\mu)$ is estimated to be $\pm 5$
3. SPATIALLY NON-UNIFORM DONORS:

The preceding analysis is all for nought, if there is no explanation how a supposedly bulk conduction mechanism can be asymmetric: which $\beta$ does one use to fit the $\gamma(T)$ curves, and which $K_p\ell$ for the $n(T)$? In this section, an explanation, preserving the main tenets of Poole Frenkel conduction theory, is drawn from the J-V-T experiment and observations made by various researchers who have studied the physical and electrical properties of anodic $\text{Ta}_2\text{O}_5$. The first task, however, is to review what is known empirically about the asymmetry. Then the existing explanations will be explored, and their predictions compared to the data. And finally, a model which passes the test will be presented.

The term "asymmetry" needs a more precise definition than what has been used thus far. One figure of merit is the so-called rectification ratio, defined to be the ratio of current observed for a set "forward" voltage to that observed for that voltage applied in the "reverse" direction. In common practise, when the rectification ratio is between 1 and 10, the J-V behavior has been deemed to be symmetric. The films under study in this study might also qualify under that criterion: the rectification ratios observed are approximately 4 for the unheated samples, approximately 3 for the vacuum baked samples, and less than 2 for
the hydrogen annealed samples. In all three, the cathodic (i.e. tantalum negative bias) currents are greater than their anodic (tantalum positive bias) counterparts.

The next observation is that the rectification ratio is nearly constant throughout the Poole Frenkel regime - that is, a Poole Frenkel plot such as Figure 27, which is found after page 116, shows the curves for each polarity become parallel at higher voltages. Figures 19, following page 100, substantiates the observation over a wider range of voltage. Thus the major difference between polarities is in $K_p$, not $\beta$. Figures 43-45, found after page 135, of $K_p$ as a function of temperature show that the rectification ratio (as seen as the ratio of $K$(cathodic) to the $K$(anodic)) is also independent of temperature. This leads us to conclude that asymmetry cannot be due to a bias dependent activation energy; such a situation might arise if the potential wells around the donors showed a preferentially oriented distortion.

A corollary to the preceding observation is that $\beta$ tends to be the same for each polarity. As mentioned before, this is only approximately true. Differences of up to 10% have been observed, with the anodic $\beta$ being greater than the cathodic one (whereas the currents show the opposite trend). The large differences seen by Pulfrey, Wilcox and Young (13), a factor of two, is likely a manifestation of the Schottky to Poole Frenkel transition in the cathodic polarity. The variation of $\beta$ with T, shown in Figures
<39-41>, after page 125, show that in the case of a difference, the difference is greater at lower temperatures. It could be that the transition from $\gamma = 1$ to $\gamma = 2$ takes place at a lower temperature for the cathodic polarity. Unfortunately, there is no data to confirm that the $\delta$'s reconverge at even lower temperatures.

Another observation: Even though the activation energies calculated in the experimental section cannot be directly related to the donor ionization energy, because the temperature dependence of $\gamma$ was unavoidably included in the calculation, its voltage dependence shown previously in Figure <38> after page 123, is representative. It is clear that the observed activation energy for a given cathodic voltage is less than that for the same size anodic voltage. The difference between the values is greater for the unheated samples than for the vacuum baked samples, whereas it is almost zero for the most highly symmetric hydrogen annealed samples. The first two sample types, which differ in rectification ratio, none the less have the same slope relating the square root of voltage to decrease in activation energy. Thus, any mechanism proposed to explain the asymmetry must not alter the voltage dependence of activation energy except for an offset in the square root of voltage.
PART IV - DISCUSSION

Previous Models for Asymmetry:

The predominant explanation used by other workers for asymmetry is the internal field resulting from metal work function differences (86, 209, 239). However, as discussed with the J-V-T experiment results, the fact that the ohmic component is non-rectifying, or slightly rectifying in the opposite sense to that seen in the Poole Frenkel regime clearly discounts this approach. A variation on the model could be that the internal fields arise only in the non-ohmic regime as a consequence of polarization or ionic drift. Ionic drift would be irreversible, and could be detected by comparison of J-V characteristics of devices with different biasing histories. This comparison has been made and no evidence of ionic drift was detected. Polarization on the other hand, is reversible for small voltages. It is field dependent, which would explain its appearance only at high fields. A polarity dependence, however, is difficult to justify.

In any case, the simple addition or subtraction of a voltage due to an internal field of any origin would fail to eliminate the apparent asymmetry for all current levels; the rectification ratio could not be constant at all currents as observed. Similarly, the activation energy plots versus the square root of voltage would be distorted by the addition of an internal field, not brought into coincidence.

To summarize, there is evidence that asymmetry is not due
to a simple internal field, arising from metal work function differences nor to ionic drift, nor from intrinsically distorted potential wells giving polarity dependent activation energies. Because the Poole Frenkel plots and the $C_d$ vs $\sqrt{V}$ are linear, the possible causes of asymmetry are limited to mechanisms which do not distort these relationships. The following proposal meets the criterion by applying the Poole Frenkel effect itself to a spatially non-uniform distribution of donors.

Consider the effect of Poole Frenkel barrier lowering on the non-uniform distribution of donors diagrammed in Figure (49). The donors are concentrated in the upper half of the anodic oxide adjacent to the chromium top metallization. As the field strength increases, the Fermi energy rises to maintain equilibrium. However, because there are more donors in the upper half of the oxide, the Fermi level moves further upwards in that half. The result is that the original electric field has been augmented by an internal field whose magnitude increases with the number of electrons added to the conduction band by Poole Frenkel barrier lowering.

A crude analysis is now offered to estimate the size of the effect proposed. It is necessary to solve Poisson's equation for a representative donor distribution. To start then:

$$\psi'' = \frac{-\rho}{\varepsilon \varepsilon_o}$$

where for uncompensated donors we have

$$\rho = q \sqrt{N_d(x)N} \exp \left[ \frac{-q \varepsilon_d}{2kT} \right] \exp \left[ \frac{1}{2kT} \sqrt{\frac{3}{\pi \varepsilon D}} \right]$$

(150)
Consider a Ta-Ta₂O₅-Cr device containing donors predominantly in the upper half of the insulator adjacent to the chromium.

At low bias, while the donors remained filled, there is no internal field. Nonpolar ohmic behavior would be observed.

Under sufficiently high cathodic bias, the charging of the donors causes $E_F$ to rise, but more so at $x = d$ than at $x = 0$. Therefore a potential $V_{in} = V_n(0) - V_n(d)$ is created.

Under anodic bias, however, the same mechanism works against the applied field and leads to a lower current flow.
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For brevity, write

\[ n = n_0(x) \exp\left[\frac{q\sqrt{\xi}}{kT}\right] \]

Furthermore, let \( n_0(x) = 0 \) for \( 0 < x < m \) - Region I
and \( n_0 \) for \( m < x < d \) - Region II

Therefore in Region I we have

\[ \psi''_I = 0 \]
\[ \psi'_I = c_1 \]
\[ \psi_I = c_1 x + c_2 \]

In Region II, we can write

\[ \psi''_II = -\frac{qN_0}{cc_0} \exp\left[\frac{q\sqrt{\xi}}{kT}\right] \]

To first order, let \( \xi(x) \) be nearly constant. This will be true in the case of small donor densities, and will be justified more generally by numerical analysis given later. Thus

\[ \psi'_II = -\frac{qN_0}{cc_0} \left[ \exp\left[\frac{q\sqrt{\xi}}{kT}\right] \right] x + b_1 \]
\[ \psi_{II} = -\frac{qN_0}{2cc_0} \left[ \exp\left[\frac{q\sqrt{\xi}}{kT}\right] \right]^2 + b_1 x + b_2 \]

The boundary conditions are such that

1) \( \psi_I(0) = 0 \), which sets \( c_2 = 0 \).
2) \( \psi_{II}(d) = -(V + V_{in}) \), which fixes \( b_2 \) with respect to \( b_1 \).
3) \( \psi'_I(m) = \psi_{II}'(m) \), which sets \( c_1 \) in terms of \( b_1 \).
4) \( \psi'_I(m) = \psi_{II}'(m) \), which sets \( c_1 \) with respect to \( b_1 \) and \( b_2 \).

\( (151) \)
The final solutions are given as:

\[
\psi_1 = -\left[\frac{V+V_{in}}{d}\right] - \frac{q}{\varepsilon \varepsilon_0} \frac{N_o}{\exp \left[\frac{a}{kT}\right]} \left[ x - \frac{(d^2 + m^2)}{2d} \right] x
\]

<141>

\[
\psi_{1'} = -\left[\frac{V+V_{in}}{d}\right] - \frac{q}{\varepsilon \varepsilon_0} \frac{N_o}{\exp \left[\frac{a}{kT}\right]} \left[ x - \frac{(d^2 + m^2)}{2d} \right] x
\]

<142>

\[
\psi_{1''} = -\left[\frac{V+V_{in}}{d}\right] - \frac{q}{\varepsilon \varepsilon_0} \frac{N_o}{\exp \left[\frac{a}{kT}\right]} \left[ x - \frac{(d^2 + m^2)}{2d} \right] x
\]

<143>

\[
\psi_{1'''} = -\left[\frac{V+V_{in}}{d}\right] - \frac{q}{\varepsilon \varepsilon_0} \frac{N_o}{\exp \left[\frac{a}{kT}\right]} \left[ x - \frac{(d^2 + m^2)}{2d} \right] x
\]

<144>

In both regions, the electric field which is equal to \( -\psi' \), is almost constant, being equal to the parallel plate value \( (V+V_{in})/d \), and a correction term. If we let \( N_d = 10^{24}/m^3 \), \( N_c = 10^{25}/m^3 \), \( N_o = 10^{9}/m^3 \), and \( \xi_d = 1.75 \) eV, the correction term can be calculated for a typical Ta<sub>2</sub>O<sub>5</sub> device at 10 V bias to be 10<sup>9</sup> times smaller than the constant term. Thus it is well justified to take \( \xi \) constant. The step function chosen here for the donor distribution is an extreme. For smoother \( n_o(x) \) distributions, the correction term will be even smaller.

The final step is to show how this result can lead to asymmetry. The result

\[
\xi = \frac{AV}{d}
\]

<145>

does not appear to offer any improvement over the "internal field" solution proposed by other researchers. Those models were
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unable to explain the coexistence of non-rectifying ohmic and asymmetric Poole Frenkel conduction regimes. Progress can be made, however, by examining the voltage dependence of $V_{in}$

By definition:

$$n = N_c \exp \left[ \frac{E - E_c}{kT} \right] = N_c \exp \left[ \frac{-q V_n(x)}{kT} \right]$$  \hspace{1cm} (146)$$

$$V_{in} = V_n(d) - V_n(0) = \frac{kT}{q} \ln \left[ \frac{n(d)}{n(0)} \right].$$  \hspace{1cm} (147)$$

Thus $V_{in}$ depends on the doping density at the end points only.

To calculate the magnitude of $V_{in}$, we cannot use the simple distribution used in the first example because $n(0)=0$ has certain unpleasant consequences in a logarithmic expression. It is also unphysical. If nothing else there is the intrinsic carrier concentration due to thermal excitation across the gap. Only in the purest semiconductor crystals are intrinsic conditions attained. Therefore it is probable in amorphous Ta$_2$O$_5$ that there are other sources of carriers with a total density of $n_i$. Let us assume that they are traps which do not experience Poole Frenkel barrier lowering. Therefore $n(x)$ has the form

$$n(x) = n_i \quad \text{for} \quad 0 < x < m$$

$$= n_i + n_0 \exp \left[ \frac{a \sqrt{\xi}}{kT} \right] \quad \text{for} \quad m < x < d$$  \hspace{1cm} (148)$$

Thus

$$V_{in} = \frac{kT}{q} \ln \left[ \frac{n_i + n_0 \exp \left[ \frac{a \sqrt{\xi}}{kT} \right]}{n_i} \right].$$  \hspace{1cm} (149)$$

for all biases wherein the one dimensional Poole Frenkel formula

(153)
PART IV - DISCUSSION

is valid, and at very high bias

\[ V_{\text{in}} \approx \frac{kT}{q} \ln \left( \frac{n_o}{n_i} \right) + \frac{n}{q} \xi \]  

Since no zero bias current leakage due to \( n_i \) in excess of what the Onsager model predicts for low bias Poole Frenkel behavior was observed, the upper limit on \( n_o/n_i \) can be estimated to be 0.1. This implies that at this limit \( V_{\text{in}} \) at zero bias is .002 V, and thus would not be observable. At a higher voltage, say 5 V, these same numbers give \( V_{\text{in}} \approx .20 \) V. Thus the difference in electric field for the forward and reverse directions is 8%.

Continuing to use representative values for the Poole Frenkel coefficients, a rectification ratio of 1.5 is calculated, in good agreement with observation. Because \( V_{\text{in}} \) increases with bias, the rectification ratio is nearly constant, as observed. The model also predicts the observation of a slightly larger anodic \( \beta \), because the relative magnitudes of \( V \) to \( V_{\text{in}} \) increases slowly at high bias.

The calculations just described are approximate, because there is a finite coupling between \( V_{\text{in}} \) and \( \xi \). \( V_{\text{in}} \) depends on the number of carriers, which depends on the electric field, which depends on \( V_{\text{in}} \). In addition, we used the assumption that \( \xi \) was constant, to prove \( \xi \) was constant in the preliminary example. An exact numerical analysis was performed to verify these results. The technique, known as a finite difference method, is in wide spread use in semiconductor device modelling (240). A potential
distribution is calculated by an iterative procedure which proceeds from an approximate solution to an arbitrarily exact solution of Poisson's equation for potential. The first step is to divide the device into a finite number of segments. The potential at each point is written as a function of the conditions at adjacent points. For example, to find the local carrier density from a given emission enhancement formula such as the Onsager equation (93b), found on page 65, the electric field is estimated to be the difference in potential between the two adjacent points, divided by twice the mesh spacing. M such expressions are written out, where M is the total number of interior mesh points. A Taylor expansion is then employed to write each equation in terms of the most recent estimate of the potential at that point, plus a small error term in the potential. The expressions used in this thesis are necessarily different than those used for diodes, transistors, and the like, which are published in the literature and form the foundation of such modelling programs as MINIMOS, and SPICE (241). Because Poole Frenkel barrier lowering links carrier density to the derivative of potential, and not potential itself as in diodes, new finite difference expressions were needed. These are given in Appendix I. The M linear equations for the M error terms are solved simultaneously by a Gauss-Seidel algorithm, executed on an Apple IIe. For each iteration, the new potential estimate is calculated from the sum of the previous one, and the error terms.

(155)
Convergence for a mesh spacing of 1 nm, and a tolerance in the potential of 0.01% was fast; usually within 5 passes. An outline of the algorithm is also given in Appendix I.

The results of these exact calculations are given in Figure 50. It is clear that the asymmetry is of the correct magnitude and varies with bias in the expected manner.

The implications of this model to the interpretation of the J-V-T behavior of the three types of samples are these: The donors responsible for conduction in the case of the unheated samples are more predominantly located in the upper portions of the oxide than in the vacuum baked samples; whereas the hydrogen annealed samples conduct by virtue of a different donor uniformly distributed throughout the oxide. It has already been suggested that there is sufficient justification for proposing nonuniform distribution of impurities in the anodic oxides. While asymmetry has been reported even when care is taken to exclude electrolyte incorporation, the knowledge that anodization proceeds from the center, leaving a demarcation that is detected by TEM and ellipsometric techniques, leaves open to doubt that anodic films are ever homogeneous. The work presented here is the first self consistent model to explain how such a distribution affects J-V-T behavior.
Figure 50. Calculated J-V Plots for Nonuniform Donor Distribution

Results of numerical calculations using the algorithm outlined in the appendix are shown here. For a ratio of $n_i/n_0$ of 10, and a $\beta$ of 3.45, J-V behavior is predicted that shows nonpolar ohmic behavior near zero bias, and asymmetric Poole Frenkel behavior for larger bias. The rectification ratio is nearly constant in this latter region, with a value of 1.4.
4. CONCLUSIONS:

The nonlinear conductivity exhibited by anodic oxides of tantalum and tantalum nitride has been explained in terms of an extended Poole Frenkel conduction model. Evaluation of the current density for electric fields up to $10^8$ V/m as a function of the physical properties of the films under investigation has verified the predictions of the theory. Specifically, the following predicted relationships were confirmed:

- $J-V$ as a function of device area ($4 \, \mu m^2$ to $>1000 \, \mu m^2$)
- $J-V$ as a function of device thickness ($40$ nm to $65$ nm)
- $J-V$ as a function of dielectric function ($2.99$ to $3.61$)

In the process of confirming Poole Frenkel conduction theory, the five main alternative conduction models, space charge limited conduction, polaron and variable range hopping conduction, and the punch through and imperfect insulator Schottky barrier models, were conclusively ruled out.

The $J-V$ behavior for temperatures between $-55^\circ C$ and $145^\circ C$, wherein conductivity varied by over eight orders of magnitude, was also fitted to a new extended Poole Frenkel model. The $J-V-T$ behavior, which would appear to be anomalous under the pre-existing Poole Frenkel theories, has been shown by the analysis presented here to be due to an intermediately compensated donor density. This analysis was also able to explain the appearance of a second Poole Frenkel region occurring at low
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bias levels. Both effects are related to the change in compensation as temperature is raised, or donors are ionized by increasing electric fields. Similar unexplained J-V-T anomalies have been reported in the literature.

The often observed asymmetry in anodic film devices such as the ones studied in this work was shown to be due to a spatially non-uniform distribution of the dominant Poole-Frenkel donors. Numerical analysis has quantified this effect, in good agreement with observation. This explanation is significantly better than previous attempts in that the predicted rectification ratio is only slightly dependent on current, as observed; activation energy plots are not distorted; and non-rectifying ohmic components at low field levels are permitted.

The extended theory has permitted the interpretation of the J-V behavior of anodic oxides processed under a variety of conditions. Nitrogen doping of the parent tantalum film has been shown to increase compensation by either introducing acceptors or reducing the donor density. Vacuum baking appears to remove an acceptor, probably due to water. Hydrogen annealing generates a shallow donor (1.4 eV) in sufficient numbers to dominate the deeper one (1.75 eV) seen in the unheated and vacuum baked films. Both heat treatments smooth out the spatial distribution of the donors, although some nonuniformity remains after vacuum baking.
APPENDIX

Appendix I: The Finite Difference Algorithm for Nonuniform Distribution of Poole Frenkel Donors

Consider an insulator with two impurity levels:

1) a trap like level, evenly distributed with a density of $n_1$, that does not experience Poole Frenkel barrier lowering.
2) a donor level, located in the outer section of the insulator with a density of $n_0$ at zero bias.

If all other sources of carriers are assumed to be much smaller than these two, Poisson's equation may be solved approximately as follows:

\begin{equation}
\text{given: } n = n_1 \quad \text{for } 0 < x < m \quad (151)
\end{equation}

\begin{equation}
 n = n_1 + n_0 \exp\left(\frac{\sqrt{\xi}}{kT}\right) \quad \text{for } m < x < d \quad (152)
\end{equation}

where $\alpha$ is a constant defined in equation (84), page 62.

$\xi$ is the electric field.

then for $0 < x < m$

\begin{equation}
\psi I = -\frac{q}{\varepsilon \varepsilon_0} n_1 \quad (153)
\end{equation}

\begin{equation}
\psi = -\left(\frac{V_{in} + V}{d}\right) + \frac{q}{2\varepsilon \varepsilon_0} \left( n_1(d - 2x) + n_0 \exp\left(\frac{\sqrt{\xi}}{kT}\right) \left( d - \frac{m^2}{d} - 2m \right) \right) \quad (154)
\end{equation}

\begin{equation}
\psi = -\left(\frac{V_{in} + V}{d}\right)x + \frac{q}{2\varepsilon \varepsilon_0} \left( n_1(dx - x^2) + n_0 \exp\left(\frac{\sqrt{\xi}}{kT}\right) \left( d - \frac{m^2}{d} - 2m \right)x \right) \quad (155)
\end{equation}
Similarly for \( m < x < d \)

\[
\psi'' = \frac{-q}{\varepsilon \varepsilon_0} \left[ n_1 + n_0 \exp \left( \frac{\alpha \zeta}{kT} \right) \right] <156>
\]

\[
\psi' = \left( \frac{V_{in} + V}{d} \right) + \frac{q}{2\varepsilon \varepsilon_0} \left[ n_1 (d-2x) + n_0 \exp \left( \frac{\alpha \zeta}{kT} \right) (d - \frac{m^2}{d} - 2x) \right] <157>
\]

\[
\psi'' = \left( \frac{V_{in} + V}{d} \right)x + \frac{q}{2\varepsilon \varepsilon_0} \left[ n_1 (dx-x^2) + n_0 \exp \left( \frac{\alpha \zeta}{kT} \right) (d - \frac{m^2}{d} - x) \right] <158>
\]

These results are approximate; to arrive at analytical solutions, \( \zeta \) was assumed to be nearly constant in the integration steps, when, in fact, the above results demonstrate that \( \zeta - \psi' \) does have a small \( x \) dependence. This \( x \) dependence represents a small error term which can be evaluated by a finite difference algorithm. The central premise of such a technique is that the carrier concentration at any given point in the device is specified by the local potential distribution, i.e.

\[
n_{II} (x) = n_1 + n_0 \exp \left[ \frac{\alpha \zeta(x)}{kT} \right]
\]

\[
\left( n_1 + n_0 \right) \exp \left( \frac{-q}{kT} \left( \psi''_{II} (x-6x) - \psi''_{II} (x+6x) \right)}{20x} \right) <159>
\]

In the limit \( \delta x \to 0 \)

\[
(160)
\]
APPENDIX

Using the approximate \( \Psi' \), given in equations \( <154> \) and \( <157> \), we may replace equation \( <152> \) with the more accurate equation \( <159> \) for the carrier distribution. This may lead in turn to a more accurate expression for \( \Psi(x) \), but this step can no longer be done analytically.

To show how \( \Psi(x) \) is obtained from the modified \( p(x) \) distribution, it is usually convenient to change notation at this point. For simplicity, it is customary to divide the device into \( M+2 \) segments, and then specify the potential at each of the \( M \) interior mesh points. In this example the mesh points are equally spaced, with a separation \( h \), but this need not be so in every case. Thus for an arbitrary point \( N \):

\[
\Psi''(N) = \frac{\Psi'(N^+) - \Psi'(N^-)}{h} \\
= \frac{1}{h} \left( \frac{\Psi(N+1) - \Psi(N)}{h} - \frac{\Psi(N) - \Psi(N-1)}{h} \right) \\
= \frac{\Psi(N-1) - 2\Psi(N) + \Psi(N+1)}{h^2} \tag{<160>}
\]

In addition, \( \Psi \) may be expressed as a Taylor expansion, i.e.

\[
\Psi(N) = \Psi^0(N) + \delta \Psi(N) \tag{<161>}
\]
APPENDIX

So that combining \(153\), \(156\), \(160\) and \(161\), we have:

for \(0 < x < m\)

\[
\delta \psi(N-1) - \delta \psi(N) + \delta \psi(N+1) = C(N)
\]

\[
= \frac{-q_{n_{A}} h^2}{\epsilon r_{o}} \left[ \sigma_{1} + n_{o} \exp \left( \frac{\sigma_{1}}{kT} \right) \right] - \psi^{o}(N-1) + 2\psi^{o}(N) - \psi^{o}(N+1) \tag{162}
\]

and for \(m < x < d\)

\[
\delta \psi(N-1) - \delta \psi(N) + \delta \psi(N+1) = C(N)
\]

\[
= \frac{-q_{h^2}}{\epsilon r_{o}} \left[ \sigma_{1} + n_{o} \exp \left( \frac{\sigma_{1}}{kT} \right) \right] - \psi^{o}(N-1) + 2\psi^{o}(N) - \psi^{o}(N+1) \tag{163}
\]

There are \(M\) such expressions, one for each of the \(M\) interior mesh points. The two end points are invariant: \(\psi(0) = 0\), and \(\psi(M+1) = V + V_{in}\). These form a tridiagonal system of linear equations:

\[
\begin{array}{cccccc}
-2 & 1 & 0 & 0 & \cdots & 0 \\
1 & -2 & 1 & 0 & & \\
0 & 1 & -2 & 1 & & \\
\vdots & & & \ddots & \ddots & \ddots \\
0 & 0 & 1 & -2 & & \delta \psi(M) \\
\end{array}
\begin{array}{c}
\delta \psi(1) \\
C(1) \\
\vdots \\
\delta \psi(M) \\
C(M) \\
\end{array}
= \begin{array}{c}
\delta \\
\end{array} \tag{164}
\]

The unknowns to be found by solving these equations are the error terms in \(\psi\). Once the \(\delta \psi(n)\)'s are found, the present guess for \(\psi^{k}\) is improved by:

\[
(162)
\]
\[ v^k(N) = v^{k-1}(N) + \delta v(N) \]  \hfill (165)

New \( C(N) \)'s are calculated, and the process is repeated until the \( \delta v(N) \)'s are arbitrarily small. Figure (51) gives a flowchart of the program.

The algorithm used to solve the equations (164) is the Gauss-Seidel method (242). This is an exact method which is particularly useful for solving sparse matrices (i.e., possessing few off diagonal elements) such as (164). This property also reduces the memory needs, and thus brings the problem within the capabilities of an Apple //e. The method is outlined for a general \( 3 \times 3 \) matrix as follows:

Consider:
\[ a_1x + b_1y + c_1z = d_1 \]
\[ a_2x + b_2y + c_2z = d_2 \]
\[ a_3x + b_3y + c_3z = d_3 \]

If \( y \) and \( z \) can be given estimated values \( y_0 \) and \( z_0 \), then
\[ x_1 = \frac{d_1 - b_1y_0 - c_1z_0}{a_1} \]  \hfill (169)

Using this estimate of \( x \), a better guess for \( y \) may be made:
\[ y_1 = \frac{d_2 - a_2x_1 - c_2z_0}{b_2} \]  \hfill (170)
Figure 51: Flowchart for the Finite Difference Algorithm

INPUT PARAMETERS

MAKE 1st GUESS AT $\psi(N)$
(equations 155 and 158)

CALCULATE $n(N)$ from $\psi'(N)$
(equation 159)

SET UP MATRIX OF LINEAR EQUATIONS
(equations 162 and 163)

SOLVE FOR $\partial\psi(N)$
(equation 164, Gauss-Seidel method)

REVISE $\psi(N)$
(equation 165)

IF $|\partial\psi(N)| < \text{TOLERANCE}$ THEN END, ELSE
\[ z_1 = \frac{d_3 - a_3 x_1 - b_3 y_1}{c_3} \]  
\[ \quad \text{\{171\}} \]

With these \( x \), \( y \), and \( z \) estimates, new estimates are made using the general formulae for the \( k \)th iteration:

\[ x_k = \frac{d_1 - b_1 y_{k-1} - c_1 z_{k-1}}{a_1} \]  
\[ \quad \text{\{172\}} \]

\[ y_k = \frac{d_2 - a_2 x_{k-1} - c_2 z_{k-1}}{b_2} \]  
\[ \quad \text{\{173\}} \]

\[ z_k = \frac{d_3 - a_3 x_{k-1} - b_3 y_{k-1}}{c_3} \]  
\[ \quad \text{\{174\}} \]

Convergence is assured if the diagonal element, the so-called pivot point, is larger than the sum of all others in that column. Therefore, row interchanges are employed to produce this condition. A second technique to reduce instability is point relaxation, whereby each new \( x_k \) is generated from a weighted average of \( x_{k-1} \) and the value produced by equation \{172\}. Convergence is determined by examining the size of the change in values between the last two iterations.
REFERENCES

(1) L. Young, ANODIC OXIDE FILMS (Academic Press, London and New
York, 1961)

(2) S.R. Morrison, ELECTROCHEMISTRY AT SEMICONDUCTOR AND OXIDIZED

(3) Reference (1), page 90

(4) W.D. Westwood, N. Waterhouse and P.S. Wilcox, TANTALUM THIN

(5) J.P.S. Pringle, "A Very Precise Sectioning Method for
Measuring Concentration Profiles in Anodic Tantalum Oxide", Journal Electrochemical Society, 119 (1972) 482-491

(6) J.G. Simmons, "Conduction in Thin Dielectric Films", J.Phys.D:
Appl.Phys., 4 (1971) 615-620

(7) M. Lampert and P. Mark, CURRENT INJECTION IN SOLIDS, (Academic

(8) H.K. Henisch and J.C. Manfacier, "Macroscopic Aspects of

(9) L.I. Maisel and R. Glanig, HANDBOOK OF THIN FILM TECHNOLOGY,

(10) H. Birey, "Thickness Dependence of the Dielectric Constant

(11) M.W. Jones and D.M. Hughes, "Electrical Conduction in Anodic

(12) A.K. Jonscher and P.A. Walley, "Electrical Conduction in

(13) F. Nazar and M. Atiq, "High-Field Conduction Mechanism Changes

(14) D.M. Smyth, G.A. Shinn, and T.B. Tripp, "Heat Treatment of
Anodic Oxide Films on Tantalum, I", Journal Electrochemical
Society, 110 (1963) 1264-1276

(165)
REFERENCES


(166)
REFERENCES


(33) Reference (4), pages 76-84


(35) Reference (4), page 317


(38) P.K. Reddy and S.R. Jawalekar, "Improved Properties of TaH-Ta2OxNy-Al Capacitors", Thin Solid Films, 64 (1979) 71-76

(39) Reference (4), chapter 3, pages 96-200


(167)
REFERENCES


(44) J.M. Sanz and S. Hofmann, "Quantitative Evaluation of AES Depth Profiles of Thin Anodic Oxide Films (Ta₂O₅/Ta, Nb₂O₅/Nb)", Surface and Interface Analysis, 5 (1983) 210-216


(48) Reference (1), page 193

(49) Reference (4), page 260

(50) Reference (4), chapter 6, pages 289-405


REFERENCES

(55) T.Kallfass and E.Lueder, "High Voltage Thin Film Transistors Manufactured with Photolithography and with Ta_2O_5 as the Gate Oxide", Thin Solid Films, 61 (1979) 259-264


REFERENCES

(68) V.Kadary and N.Klein, "Electrical Breakdown During the Anodic Growth of Tantalum Pentoxide", Journal Electrochemical Society, 127 (1980) 139-151


(77) M.Hacskaylo, "A Relationship Between the Schottky Emission Mechanism and the Energy Bands of Thin Film Metal-Insulator-Metal Configuration", J.Appl.Phys., 35 (1964) 2943-2947


(79) S.Namba et al., Rika Gaku Kenkusho Hokoku, 40 (1964) 92-106 (as quoted in (78))

(80) C.A.Mead in BASIC PROBLEMS IN THIN FILM PHYSICS, R.Neidermayer and H.Mayer (eds) (Vandenhoek and Reephecht, Gottingen, 1966) (as quoted in 65)


(170)
REFERENCES


(84) M.Stuart, "Conduction in Silicon Oxide Films", British J.Appl.Phys., 18 (1967) 1637-1640


REFERENCES

(96) Reference (95), pages 25-27

(97) Reference (95), chapter 14

(98) Reference (95), pages 116-121


(100) J. Lindmayer, "Current Transients in Insulators", J. Appl. Phys., 36 (1965) 196-201


(105) E. Sciri and R. Chabicovsky, "Conduction Phenomena in Nb-Nb_2O_5-Au Thin Film, Structures Fabricated by Various Techniques", Vacuum, 27 (1975) 299-304


(172)
REFERENCES


(111) Reference (47), pages 39-43


(123) Reference (47), pages 50-52

(124) Reference (47), page 21

(173)
REFERENCES


(126) N.F.Mott, "Conduction in Glasses Containing Transition Metal Ions", J.Noncrystalline Solids, 1 (1968) 1-17


(174)
REFERENCES


(141) J.E. Fike, "ac Conductivity of Scandium Oxide and a New Hopping Model for Conductivity", Phys. Rev. B, 6 (1972) 1572-1580


(144) M. Meaudre, and R. Meaudre, "AC Conductivity in RF Sputtered SiO₂ Films" Phil. Mag. B, 40 (1979) 401-410


REFERENCES


(156) A.G.Hilmes, DEEP IMPURITIES IN SEMICONDUCTORS, (Wiley Interscience, New York, 1973) 3

(157) Reference (4), page 378

(158) Reference (1), Chapter 7


(164) R.M.Hill, "Poole Frenkel Conduction in Amorphous Solids", Phil. Mag., 23 (1971) 59-86


(166) L.Onsager, "Initial Recombination of Ions", Phys.Rev., 54 (1938) 554-557

(176)
REFERENCES


(172) P.C.Arnett and N.Klein, "Poole Frenkel Conduction and the Neutral Trap", J.Appl.Phys., 46 (1975) 1399-1400


(177)
REFERENCES


(190) W. G. Trodden, as quoted in Reference (65)


(192) C. J. Miner, Bell-Northern Research internal report, Feb. 1979


(178)
REFERENCES


(199) J. Robertson, "Electronic Structure of Amorphous Semiconductors", Advances in Physics, 32 (1983) 361-452


(202) Reference (72), page 44

(203) N. Klein, private communications, Summer 1981


REFERENCES


REFERENCES


(231) S.Kumagi and L.Young, "Ellipsometric Investigation of the Optical Properties of Anodic Oxide Films on Tantalum", Journal Electrochemical Society, 111 (1964) 1411-1416


(234) Reference [4], page 293

(235) J.S.Blakemore, SEMICONDUCTOR STATISTICS, (Pergamon Press, 1962)


(181)
REFERENCES


(239) H.Ekrut and A.Hahn, "Polarity Dependent Tunneling Conductance of Ta/Ta_2O_5/Ag Junctions", J.Appl.Phys., 51 (1980) 1686-1691

(240) M.Kurata, NUMERICAL ANALYSIS FOR SEMICONDUCTOR DEVICES, (Lexington Books, Lexington, Massachusetts, 1979)

(241) G.Tarr, course notes for "Surface Controlled Semiconductor Devices" given by the Department of Electrical Engineering, Carleton University, Winter 1983

(242) A.Miller, BASIC PROGRAMS FOR SCIENTISTS AND ENGINEERS, (Sybex, Berkeley, 1981) 106