DIELECTRIC PROPERTIES OF THIN INSULATING FILMS

by

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ABSTRACT

The dielectric polarization processes, conduction mechanisms and space charge effects occurring in tantalum / tantalum pentoxide / metal devices are investigated. The dielectric properties are analyzed on the basis of an ionic relaxation process with a nearly flat distribution of activation energies. This distribution leads to step response polarization currents following an inverse time law. The effect of an injected electronic space charge on the response of the device due to the removal of a step voltage is analyzed and results are given demonstrating this effect.

The devices used exhibit a rectification behaviour. For tantalum positive the currents follow a Schottky law and for tantalum negative, the bulk Poole-Frenkel law. Hysteresis effects are observed as well as the effects of a space charge on the Schottky law currents. On one sample, sufficiently high fields causes an increase in the conductance by a factor of \(10^3\) to \(10^5\). For this deformed sample, no hysteresis or rectification is observed and the currents follow a Schottky law for both polarities.

The validity of the ionic relaxation model is discussed in light of the observed dielectric losses at low temperatures. The experimental results indicate that an electronic rather than an ionic process could be responsible for the dielectric losses.
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o
A
A
a
α
β
D
E
C
C₀
Δ
Eₖ
Eₜ
Eᵥ
E_F
E_F₀
E_A
E_d
ε₀
ε'
ε''
εₛ
ε₁
f
G
I
J_P
J_sc

Angstroms
Richardson's constant
one-half distance between potential minima
slope of Shottky law
slope of Poole-Frenkel law
dielectric displacement
electric field
capacitance
capacitance of an air filled capacitor
ratio of free to trapped charge
conduction band energy
valence band energy
equilibrium fermi level
quasi fermi level
acceptor energy level
donor energy level
trap energy level
permittivity of air
real part of dielectric permittivity
imaginary part of dielectric permittivity
static permittivity
permittivity at high frequencies
Fermi-Dirac distribution function
distribution of activation energies
current
polarization current/unit area
space charge current/unit area
$J_L$ leakage current/unit area

$k = \varepsilon / \varepsilon_0$ = dielectric constant

$k$ Boltzmann's constant

$L$ thickness of film

$N_A$ acceptor state density/unit energy

$N_t$ trap density/unit energy

$N_d$ donor state density/unit energy

$n_c$ free electron density

$\nu_o$ attempt to escape frequency

$n_t$ trapped electron density

$n_t'$ trapped electron density/unit energy

$P$ polarization

$P_s$ static polarization

$Q$ charge/unit area

$q$ activation energy

$\sigma$ conductivity

$\sigma_o$ low field conductivity

$t$ time

$\tau$ relaxation time

$\tau_o$ constant = $1 / \nu_o$

$T$ temperature

$\mu$ mobility

$V$ volts

$\omega$ angular frequency

$T_c$ characteristic temperature

$\Theta$ electron affinity

$x$ distance through film

$x^*$ zero field point
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1. INTRODUCTION

The purpose of the work described in this thesis was to study the dielectric processes, the conductivity mechanisms and the effect of space charge on the external currents in thin insulating amorphous films.

Thin insulating amorphous films are used in several types of discrete electronic devices, e.g., the MOS field effect transistor, the thin film transistor, the electrolytic capacitor and the thin film capacitor. In monolithic silicon integrated circuits, insulating films are used for surface passivation and electrical insulation between the silicon and metal film interconnections, as well as for thin film capacitors and MOS field effect diodes and transistors.

Various factors enter into the choice of a thin film for a particular application, the most obvious being the electrical insulating properties of the film. For capacitor applications, a thin film, besides providing adequate insulation, should have sufficiently low dielectric losses and residual voltage effects. Residual voltages may be due to polarization processes with long decay times, or to electronic space charge effects. In MOS field effect transistors, such effects can cause drift in the device characteristics, in addition to effects due to sodium ion drift.

The films used in this study were anodic tantalum pentoxide. Device applications of these films include the electrolytic capacitor and thin film RC circuits.
The permittivity* was measured as a function of frequency and temperature using a conventional A.C. bridge. In addition, the loss (ε") measurements were extended to very low frequencies (0.01 Hz) by measuring the current response to a step voltage \(^{(1,9)}\). Since leakage currents may often be large enough to effectively cover up the polarization currents, the method used was to measure the currents upon removal of a voltage.

In addition to dielectric displacement currents, there may also be currents due to the decay of a trapped space charge. Accordingly, the charge and discharge transient currents were studied as a function of time and applied voltage, and various techniques were used to identify the transient current components.

Conduction currents through thin films are sometimes affected by the development of a space charge in the film \(^{(2,3)}\). The conductivity mechanism was investigated by measuring the steady state leakage currents as a function of voltage and temperature and relating the curves obtained to the absence or presence of a space charge as determined by the transient current measurements.

Chapter 2 is a review of the theories of the dielectric processes, conduction mechanisms and space charge effects in thin amorphous films. The experimental procedures are described in Chapter 3, and the results obtained are presented in Chapter 4. In Chapter 5 the results are discussed in the light of existing knowledge and the conclusions to be drawn from the work are given in Chapter 6.

* The dielectric properties are described by the frequency and temperature dependent complex dielectric permittivity,

\[
\varepsilon(\omega, T) = \varepsilon' (\omega, T) - j\varepsilon'' (\omega, T)
\]

where ε" is usually nearly independent of frequency for amorphous films.
2. THEORY

2.1 Dielectric Properties of Amorphous Films

A number of physical processes contribute to the polarization of ionic solids. Each process may be characterized by a particular characteristic frequency or range of characteristic frequencies, and responds to only those applied frequencies which are less than the characteristic frequency.

In a perfect ionic crystal, i.e., one which is free from all defects, it is usual to separate the polarization into electronic and ionic components. Electronic polarization, which is due to the displacement of electrons with respect to the ions, responds to the highest frequency and has a characteristic frequency in the optical or ultra-violet regions. Ionic (or atomic) polarization is due to the relative displacement of oppositely charged ions and has characteristic frequencies given by the lattice vibration frequencies, which are in the infra-red region. However, electronic and atomic polarization components cannot be completely separated as the ionic displacement induces an electronic displacement (ref. 4, P. 151).

In the case of a crystal which contains defects (e.g., impurity ions, lattice defects) there are additional polarization components due to processes associated with the defects. Examples of some processes are dipole orientation, ions moving between potential minima sites, electrons hopping or tunneling between localized impurity states, and orientation of impurity polar molecules (e.g., H₂O). Another type of process which can contribute to the low frequency losses involves the diffusion of ions up to and away from a barrier. Such interfacial polarization has, for example, been postulated to exist in electroluminescent phosphors. (5)
The polarization processes associated with defects are relaxation processes and have characteristic frequencies below the infra-red. These processes may be formally described by a superposition of Debye type processes\(^{(4)}\) with a distribution of relaxation times. A single Debye process is given by (Appendix I)

\[
\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{2-1}
\]

where

- \(\tau\) = relaxation time
- \(\varepsilon_s\) = static permittivity
- \(\varepsilon_\infty\) = permittivity at high frequencies
- \(\omega\) = applied angular frequency

Polarization processes in anodic Ta\(_2\)O\(_5\) films are complicated by the amorphous nature of the film. There is no long range order. The ionic lattice is aperiodic. It is reasonable to assume that the electronic displacements and elastic ion displacements are not essentially changed from those in regular crystals, except that in an amorphous substance there will be a spread in the characteristic frequencies so that, for example, a broader absorption band will be observable in the infra-red. Below infra-red frequencies, Ta\(_2\)O\(_5\) displays losses which are often almost independent of frequency over a very wide range of frequencies\(^{(7,8)}\). This situation requires a distribution of relaxation times of the form \(1/\tau\)\(^{(39)}\).

The fact that a \(1/\tau\) distribution gives losses independent of frequency can be easily shown. Setting equation (1-1) equal to equation (2-1) then

\[
\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2}
\]
Integrating over a $1/\tau$ distribution then

$$
\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{w \tau}{1 + \omega^2 \tau^2} \frac{d\tau}{\tau} = (\varepsilon_s - \varepsilon_\infty) \frac{\pi}{2} = \text{constant}
$$

This distribution of relaxation times may be produced by a variety of physical models, e.g., a Maxwell layer model (ref. 8, P. 161) with $\rho(x) = \rho_0 e^{x/L}$ where $\rho(x)$ = resistivity of the film, $L$ = thickness of the film, and $x$ = distance through the film; or models involving ions or electrons hopping between sites in the film.

The ionic relaxation model with a relatively flat distribution of activation energies has been claimed\(^{(6)}\) to adequately describe the frequency and temperature dependent permittivity of many amorphous insulators. The experimental results presented in this thesis will be discussed on the basis of this model. The ionic relaxation model gives an exponential approach to the steady state and thus can be described by the Debye equation (Appendix II). The relaxation time of this process is given by

$$
\tau = \frac{\tau_0}{2} e^{q/kT}
$$

where
- $q$ = activation energy or barrier height between potential minima
- $\tau_0$ = constant (inverse of jump frequency)
- $T$ = temperature in °K
- $k$ = Boltzmann's constant

Assuming an almost flat distribution of activation energies, $G(q)$, then the integration of the Debye equation over this distribution
(in Appendix III) gives
\[ \varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^{q_o} G(q) dq \]  \hspace{1cm} (2-3) 
\[ \varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \frac{\pi}{2} kT G(q_o) \]  \hspace{1cm} (2-4) 

where \( q_o \) is defined according to equation (2-2) as
\[ \frac{2\pi}{\omega} = \frac{q_o}{2} \frac{e^{q_o/kT}}{kT} \]  \hspace{1cm} (2-5) 

Equations (2-3) and (2-4), which were first derived by Gévers and Du Pré\(^{(6)}\), can be simply interpreted. In equation (2-3), only those processes with activation energies less than \( q_o \) respond to an applied frequency \( \omega \) where \( \omega \) is related to \( q_o \) by (2-5). In (2-4), losses occur only for those activation energies which have the characteristic angular frequency \( \omega \). (Note: from the relation in Equation (2-2), a flat distribution of activation energies \( G(q) \), corresponds to a \( 1/\tau \) distribution of relaxation times).

The polarization response to a step voltage for a nearly flat distribution of activation energies has also been calculated in Appendix III, and is
\[ J_p = (\varepsilon_s - \varepsilon_\infty) kT G(q') \frac{E}{t} \]  \hspace{1cm} (2-6) 

where \( J_p = \) polarization current/unit area
\( E = \) applied field step

and \( q' \) is defined according to equation (2-2) as
\[ \frac{t}{2} = \frac{q_o}{2} e^{q'/kT} \]  \hspace{1cm} (2-7) 

This definition of \( q' \) means that at some time \( t \), the polar-
ization current is dominated by a process with relaxation time \( \tau \) given by \( \tau = \frac{t}{2} \), which is equivalent to the activation energy \( q' \).

Equation (2-5) may be used to extend dielectric loss measurements to very low frequencies as follows:

Combining equations (2-5) and (2-4) gives

\[
\varepsilon''(\omega) = \frac{\pi}{2} \frac{J_{pt}}{E} \frac{G(q_o)}{G(q')} (2-8)
\]

The angular frequency \( \omega \) is determined by setting \( q' = q_o \) which gives

\[
\frac{2\pi}{\omega} = \frac{t}{2}
\]

Thus

\[
\varepsilon''(\omega) = \frac{\pi}{2} \frac{J_{pt}}{E} \quad \text{with} \quad \omega = \frac{4\pi}{t} (2-9)
\]

Measurements of polarization currents have been used by Hamon\(^{(9)}\) to extend loss measurements to frequencies less than 0.1 Hz. Excellent agreement was found between the measured values and those obtained by using a bridge at very low frequencies. The method of analysis used by Hamon, and later reviewed by Baird\(^{(1)}\) was to assume polarization currents of the form \( t^{-n} \) and then calculate what the losses would be at a corresponding frequency. The results are as given in Equation (2-9) so long as \( 0.3 < n < 1.2 \). In the present analysis (Appendix III), these numbers would correspond to how much the distribution \( G(q) \) would be allowed to vary before invalidating the assumptions used concerning the flatness of \( G(q) \).

2.2 Conduction in Thin Insulating Films

The leakage currents through thin insulating films may be due to movement of electrons, holes or ions.
For the particular film $\text{Ta}_2\text{O}_5$, experiments by Vermilyea\(^{(10)}\) and Standley & Maissel\(^{(11)}\) have been claimed to indicate that holes carry a negligible part of the current. Both Vermilyea and Standley and Maissel, using a Ta/$\text{Ta}_2\text{O}_5$/metal system found a rough correlation between metal work function and current magnitudes. Large currents were obtained for low work function metals, thus indicating hole injection is not an important factor in the conduction process. Vermilyea also arrived at a similar conclusion for the Ta/$\text{Ta}_2\text{O}_5$/electrolyte system.

$\text{Ta}_2\text{O}_5$ is grown anodically by placing a piece of tantalum in an electrolyte and applying a positive potential relative to another electrode. The film grows by ion movement and growth is appreciable only for fields of the order $6 \times 10^6$ v/cm. At fields much below this value the current is predominantly electronic in nature\(^{(10)}\), and film growth is negligible.

In the following review of conduction theories therefore, it will be assumed that the currents are electronic in nature. Some of the possible conductivity mechanisms include:

1. Schottky injection\(^{(13)}\)
2. Poole - Frenkel effect\(^{(14)}\)
3. Field emission or tunneling\(^{(15)}\)
4. Space charge limited\(^{(2, 16)}\)

The leakage current density may be limited by one or more of the above mechanisms acting simultaneously.

An energy level diagram for the metal/insulator/metal system with one rectifying and one ohmic contact appears in Figure\((2-1)\).\(^{(17)}\)

In this figure
\begin{align*}
\phi_1 \text{ and } \phi_2 &= \text{work functions of metals 1 and 2} \\
\Theta &= \text{electron affinity of the insulator} \\
E_c &= \text{conduction band edge} \\
E_v &= \text{valence band edge} \\
E_F^0 &= \text{equilibrium Fermi-level}
\end{align*}

This diagram is arrived at by using the principle that in equilibrium the Fermi level is the same throughout the system. If one considers the junction being made by bringing the metal and insulator into contact, then when the metal and insulator are widely separated nearly the total contact potential will fall across the separation distance. When brought into contact, the contact potential falls across the insulator. With two metal contacts and no space charge in the insulator, then the field in the insulator is given by \( \frac{\phi_1 - \phi_2}{L} \).

If there is sufficient free charge in the insulator then the contact potential may fall across space charge regions near the interfaces as shown in Figure (2-1). Electron depletion causes the bands to bend up, giving a rectifying contact. Electron accumulation bends the bands down, giving an ohmic contact. Surface states on the insulator can cause band bending before a metal contact is applied and can make the barrier height nearly independent of metal work function.

Referring to Figure (2-1), the ohmic contact at the metal 2 interface allows electrons to be drawn freely into the insulator under an applied field. At the metal 1 interface, conduction can take place only by the electrons either gaining enough thermal energy to pass over the barrier of height \( \phi_1 - \Theta \) or by tunnelling through the barrier.
Fig. 2-1  Energy level diagram of a metal/insulator/metal device

Fig. 2-2  Energy level diagram for tunnelling processes
2.2.1 **Schottky Injection**

Schottky injection is the field assisted thermal emission of electrons over a potential barrier. The current is given by (Appendix IV),

\[ J_L = A T^2 \exp\left(-\frac{\phi - \theta}{kT}\right) \exp \left(\frac{\alpha E(0)}{kT}\right) \]

(2-10)

where \( A = \) Richardson's constant \( \left(18\right) \)

\[ \alpha = \frac{e^3}{4\pi\varepsilon}, \quad \varepsilon = \text{high frequency dielectric permittivity} \]

\( E(0) = \) field at \( x = 0 \)

\( e = \) electronic charge.

Experimentally, the field \( E(0) \) at the interface cannot be obtained directly and so it is usually assumed that \( E(0) = \frac{V}{L} \) where \( V \) is the applied voltage. The high frequency dielectric constant is used, as an electron with sufficient energy to pass over the barrier will be moving very fast and the ions will not be able to respond to its motion.

2.2.2 **Poole-Frenkel Effect**

This is a bulk process in which the conductivity of the insulator is controlled by field-enhanced thermal emission from coulombic traps. The calculation of this effect is analogous to that of the Schottky law (Appendix IV). The conductivity is given by \( \left(25,35\right) \)

\[ \sigma^-(x) = \sigma_o \exp \left(\beta E^3(x)/kT\right) \]

(2-11)

where \( \sigma_o = \) low field conductivity, and \( \beta = 2\alpha \).

The leakage current is then given by
\[ J_L = \sigma(x)E(x) = \sigma_0 E(x) \exp \beta E(x)/kT \]  

(2-12)

As for the Schottky law, \( E(x) \) is usually assumed to be \( V/L \). This assumption is dubious because to observe a purely Poole-Frenkel effect would necessitate the condition of no barrier limitation on the current. Lack of any barrier limitation means that charge could be injected into the insulator with a consequent buildup of a space charge in excess of any equilibrium space charge due to contact potentials. The exact relationship between \( E(x) \) and the applied voltage then becomes complicated.

Frank and Simmons\(^{(3)}\) have computed \( \ln J - V^{1/2} \) curves for thin films where they have considered Schottky injection at a barrier, the barrier height modulated by a space charge in the bulk, and the bulk conductivity determined by the Poole-Frenkel effect on a single trapping level. At higher voltages their curves are asymptotic to the Schottky injection curve. At low voltages the effects of the space charge are more pronounced and the curves deviate from the Schottky law. A Poole-Frenkel characteristic, i.e., \( \ln J_L - V^{1/2} \) curve with slope given by \( \beta \), is not revealed at any time.

Linear \( \ln J_L - V^{1/2} \) plots have been observed with \( \text{Al}_2\text{O}_3 \)\(^{19}\), \( \text{SiO}_2 \)\(^{20,21,22}\), \( \text{ZnO} \)\(^{23}\), \( \text{Ta}_2\text{O}_5 \)\(^{12}\), and organic insulators\(^{24}\) with good agreement between the observed and calculated values of the slope

\[ \frac{d \ln J_L}{d E^{1/2}} = \frac{\alpha}{kT}. \]

However, some of these authors\(^{12,20,21,22}\) claim that the conduction was in fact bulk limited despite the observed Schottky value of \( \frac{d \ln J_L}{d E^{1/2}} \). A possible explanation for this was pointed out by Simmons\(^{25}\) and is discussed in Appendix IV.

2.2.3 Field Emission or Tunneling

The energy level diagram in Figure (2-2) shows several dif-
ferent tunnelling processes (Chynoweth\textsuperscript{(15)}). These are:

1. Tunnelling from metal to conduction band (Fowler-Nordheim effect\textsuperscript{(26)}).
2. Tunnelling from trap level into conduction band.
3. Tunnelling from valence band into conduction band.
4. Tunnelling from valence band into metal.

For insulators with a wide band gap process 3, known as the Zener effect, is negligible in comparison with processes 1 and 2. Process 4 is essentially hole tunnelling and is analogous to process 1. Accordingly only the first two processes will be considered here.

Similar expressions\textsuperscript{(15)} are obtained for both, namely,

\[ J_L = B E^n e^{-C \phi^{3/2}/E} \quad 1 < n < 2 \]  

where \( \phi \) = barrier height for 1 and trap depth for 2.

\( B, C \) = constants, nearly independent of temperature.

One tunnelling process which has not been included in the diagram is that from "metal to metal". Such a process requires films less than 100\( \text{Å} \) in thickness which is much thinner than those used in the present work.

Tunnel currents are relatively temperature independent. It has been observed\textsuperscript{(11,12)} for \( \text{Ta}_2\text{O}_5 \) that the leakage currents become less dependent on temperature as the temperature decreases. This indicates that tunnel currents at room temperature are masked by thermally produced currents. Mead's\textsuperscript{(12)} curves for \( \text{Ta}_2\text{O}_5 \) indicate a bulk tunnelling conduction process which he attributed to process 2.
2.2.4 Space Charge Limited Currents

It was pointed out by Mott and Gurney\(^{(27)}\) that it is theoretically possible to have a large amount of "space charge limited" current flowing through a thin insulating film. To make this possible, an ohmic contact and a trap free insulator are required. The ohmic contact insures a pool of electrons at the cathode, free to be drawn into the insulator by an applied field. For a perfect crystal, all the space charge will be free charge and the current is given by (Appendix VII)

\[
J_L = \frac{9}{8} \mu \varepsilon \frac{V^2}{L^2} \tag{2-14}
\]

where \(\mu\) = electron mobility.

Traps present in the crystal, or amorphous film will immobilize some of the carriers and the current will be reduced by a factor \(\Delta\) the ratio of free to total charge

\[
\Delta = \frac{n_c}{n_c + n_t} \sim \frac{n_c}{n_t} \tag{2-15}
\]

where \(n_c\) and \(n_t\) are the free and trapped charge densities, respectively.

For most insulators the trapped charge is usually much greater than the free charge.

Rose\(^{(2)}\), using a very simplified analysis, has calculated \(\Delta\) for a variety of trap distributions in the band gap. A single shallow trapping level leaves the \(V^2\) law of equation (2-14) unchanged, but lowers the current magnitude.

A uniform distribution of traps in the band gap gives a value
\[ \Delta \propto \frac{1}{V} e^{\gamma V} \quad \gamma = \text{constant} \quad (2-16) \]

Then
\[ J_L \propto \frac{V}{L} e^{\gamma V} \quad (2-17) \]

For a trap distribution of the form \( N_t \propto e^{E_t/kT_c} \) then
\[ J_L \propto V \left( \frac{T_c}{T} + 1 \right) \quad (2-18) \]

A characteristic similar to Equation (2-18) has been observed by Walker\(^{(28)}\) in Ta\(_2\)O\(_5\). Rose considered only the simplest conditions, i.e., no double injection, no recombination. When these effects are considered the J-V characteristics are quite different from above\(^{(16)}\).

Ohmic currents do not necessarily mean currents limited by the thermal production of free carriers in the bulk. A sufficiently small signal will give a linear J-V curve irrespective of the conduction mechanism.

Generally speaking, the most commonly observed conduction mechanism at room temperatures and high fields, in thin films, has been of the Schottky or Poole-Frenkel type. At high fields and very low temperatures tunnelling is observed and at low fields an ohmic characteristic is observed.

No mention has been made, so far, of the possible time dependence of the leakage currents. If the leakage currents were to depend in some manner on a space charge, and since the buildup of a space charge is time dependent, then the leakage currents would be time dependent. The equations derived so far are for the steady state, and possible transient effects are considered in the next section.
2.3 Space Charge Effects

As indicated previously, space charge regions may exist in a film due to contact potentials. Under an applied voltage, additional charge may be injected into the insulator and trapped. It is likely that an amorphous film has a high density of electronic traps, and that these traps will play an important role in the electronic processes occurring in the film.

An electronic trap is a localized state with an energy level such that the electrons commute between the trap and the conduction band. Such a state may be due to an impurity (i.e., doping in a semi-conductor) or a structural defect or simply the amorphous nature of some insulators.

It is often assumed that, for amorphous insulators, in the steady state most of any space charge resides in traps, and a negligible amount is free charge.

A space charge has a number of effects, namely:

1) The buildup of a space charge may result in an externally observed charging current \( J_{sc} \),
2) under short circuit conditions, an externally observed discharge current may be observed due to the decay of a trapped space charge,
3) the space charge may affect the leakage currents under both transient and steady state conditions,
4) the space charge may have an effect on the capacitance, dielectric losses and polarization currents.

Each of these possibilities will now be considered in detail.

2.3.1 Buildup of a Space Charge

The total injected space charge in an insulator (per unit area) is given by
\[ \int_0^L (n_c(x,t) + n_t(x,t)) \, dx \]  

\[ J_{sc} = e \frac{d}{dt} \int_0^L (n_c(x,t) + n_t(x,t)) \, dx \]  

\( n_c \) and \( n_t \) are the free and trapped charge densities above the equilibrium values. The current density due to the buildup of a space charge is then

Any attempt to derive \( J_{sc} \) is complicated by the fact that an injecting contact limits the rate at which charge is injected, and the space charge buildup affects the values of the field at the injecting contact, thus the rate of injection.

The trapping kinetics also become very complicated when one considers the possibility of a distribution of trapping levels with varying capture cross sections, trap densities varying with distance through the insulator, effects of the field on the trapping kinetics, and different types of traps.

2.3.2 Decay of a Space Charge

In considering the externally observed current due to the decay of space charge in a metal/insulator/metal device a simplified model will be taken in which both barrier heights are equal and there is no space charge in the insulator at equilibrium.

**Fig. 2-3** Energy level diagram for model
\[ \Phi = \text{metal work function} \]
\[ \Theta = \text{electron affinity of insulator} \]
\[ E_F^0 = \text{equilibrium Fermi level} \]
\[ L = \text{width of insulator} \]
\[ E_C = \text{conduction band edge} \]
\[ E_V = \text{valence band edge} \]

The above assumptions necessarily restrict the value of the Fermi level \( E_F^0 \) to the range \( e(\Phi - \Theta) = E_C - E_F^0 \). It is assumed that a uniform distribution of trapping states through the band gap exists and that in equilibrium these are filled to about the Fermi level.

To achieve the assumed zero space charge it is necessary to postulate the existence of donor levels. Denoting the probability of occupation of a state by the Fermi factor \( f \), then the zero space charge density condition gives

\[
0 = e \int_{E_C}^{E_V} (1-f) N_d \, dE_d - e \int_{E_C}^{E_V} f \, N_t \, dE_t
\]

where
\[ N_d = \text{density of donor states per unit energy} \]
\[ N_t = \text{density of trapping states per unit energy} \]
\[ E_d = \text{energy level of donor state} \]
\[ E_t = \text{energy level of trapping state} \]

Under an applied voltage, it is assumed that electron injection takes place, and that the resultant negative space charge resides in the traps. At time \( t = 0 \), when a steady state is reached, the device is short circuited. Assuming no instantaneous change in the trapped space charge, then a redistribution of a positive charge on the plates takes place such that at a point \( x^* \) in the film the field is zero.
When an electron is released from a trap it will move under the influence of the space charge field, in a direction depending on which side of \( x^* \) it finds itself. In addition to the external current due to the space charge decay, there will be a depolarization current due to the ionic relaxation processes considered earlier. The polarization currents will be altered because of the altered field distribution in the insulator due to the space charge. As derived in Appendix V, the external current is given by

\[
J_{\text{ext}} = e n_t(x^*, t) \frac{dx^*}{dt} - \frac{\varepsilon_s - \varepsilon_{\infty}}{\varepsilon_s} e n_t(x^*, t) \frac{dx^*}{dt} \int_0^\infty e^{-t/\tau} G(q) dq - (\varepsilon_s - \varepsilon_{\infty}) kT G(q') \frac{E}{t} (x^*, t < 0) \tag{2-22}
\]

where

\[
E(x^*, t < 0) = -\frac{e}{\varepsilon_s} \int_0^{x^*} n_t(x, t < 0) dx + E(0, t < 0) \tag{2-23}
\]

The first term in (2-22) is due to space charge decay alone. The latter term is the depolarization current, slightly altered from equation (2-6). The second term is a mixture of both. The integration in the second term cannot be done unless the functional form of \( G(q) \) is known over the whole range of activation energies. However,
by integrating over a range of $q$ such that the relaxation times go from much less than $t$ to much greater than $t$, and assuming $G(q)$ is flat in this range, then

$$
\int_{Z_1}^{Z_2} e^{-t/Z} G(q) dq = -kT G(q) Ei(-t/Z_2)
$$

and $Ei(-\alpha)$ = exponential integral which is defined on the following page.

To determine $J_{ext}$ requires knowing the space charge density and the zero field point $x^*(t)$.

Neglecting any retrapping, the decay kinetics of $n_t^\xi$ are governed by

$$
\frac{dn_t^\xi}{dt} (x,t) = -\nu_0 n_t^\xi(x,t) \exp( (E_c - E_t)/kT )
$$

(2-24)

where $n_t^\xi(x,t)$ = space charge density/unit energy centered at $E_t$

$\nu_0$ = constant = jump frequency

Assuming a uniform density of traps in the band gap with their occupation governed by Fermi statistics then, as calculated in Appendix VI,

$$
n_t(x,t) = -kTN_t \left\{ Ei(-\nu_0 t \exp( (E_c-E_F^Q)/kT )) - e^{-\nu_0 t e^{-(E_c-E_F(x))/kT}} \right\} - Ei(-\nu_0 t (e^{-\nu_0 E_F^Q/kT} + e^{-(E_c-E_F(x))/kT}))
$$

(2-25)

where $E_F(x)$ is the quasi Fermi level at $t = Q$

and $Ei(-\alpha)$ is the exponential integral $= \int_{\alpha}^{\infty} \frac{e^{-\alpha} d\alpha}{\alpha}$
Some tabulated values for $E_i(-\alpha)$ are given below

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$-E_i(-\infty)$</th>
<th>$-e^{-\infty}E_1(-\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>0.01</td>
<td>4.04</td>
<td>4.08</td>
</tr>
<tr>
<td>0.10</td>
<td>1.82</td>
<td>2.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.22</td>
<td>0.60</td>
</tr>
<tr>
<td>10.0</td>
<td>$4.1 \times 10^{-6}$</td>
<td>0.09</td>
</tr>
</tbody>
</table>

It is evident that for large space charge densities such that

$$E_c - E_F^0 \gg E_c - E_F(x)$$

then $n_t(x,t)$ becomes nearly independent of $x$.

The zero field point $x^*$ is derived by using the short circuit condition. Thus,

$$V = 0 = - \int_{0}^{L} E(x,t)dx$$

Equations (2-25) and (2-26) are very difficult to solve, even by making very simplifying assumptions concerning $n_t(x,t)$. Thus, it is not clear what form the space charge discharge currents in Equation (2-22) will take.

Lindmayer (34) has claimed that a space charge will give a discharge current. His model was similar to that used here, except that he neglected the ionic polarization effects. Thus, from Equation (2-22), $J_{ext} = e n_t(x^*,t) \frac{dx^*}{dt}$ and from Equation (2-26), $0 = \int_{0}^{L} dx \int_{x^*}^{1} n_t dx$. He further assumed $E_F(x) \gg E_F^0$, thus making $n_t(x,t)$ independent of $x$.

From equation (2-26) this makes $x^*$ independent of $t$, and hence $J_{ext} = 0$, contrary to what Lindmayer concluded. What Lindmayer actually
calculated was \( \frac{dn}{dt} \) which from Equation (2-25) is proportional to \( \frac{1}{t} \). However, \( J_{ext} \) is not given by \( \frac{dn}{dt} \).

2.3.3 The Effect on Conduction Currents

The effect of space charge on the leakage currents has been covered in Section 2.2. Space charge affects the field distribution in the insulator and hence the leakage currents for any conduction mechanism. A space charge would also be expected to cause hysteresis in the J-V characteristic.

2.3.4 The Effect on Dielectric Properties

The effect of a space charge on the polarization of a dielectric was covered in Section 2.3.2. It is not clear how a space charge may effect the measured capacitance and losses in an insulating film. It is possible that losses may result from electrons hopping between trap sites in a manner similar to that considered for the ionic relaxation losses.
3. EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

Both bulk tantalum and tantalum sputtered onto glass slides* were tried. The bulk tantalum surface was prepared by cleaning in trichlorethylene and then chemically polishing.** Little success was achieved using the bulk tantalum, however, as most of the Ta/Ta$_2$O$_5$/metal devices constructed broke down at relatively low applied fields (5 x 10$^5$ V/cm). Microscope examination showed that sharp steps at the grain boundaries developed during the chemical polishing. An oxide would develop cracks at these sharp edges, thus leading to low breakdown voltages.

This difficulty was not present when using the sputtered tantalum films as they had a mirror surface as received and hence required no polishing. They could thus be used directly after a simple cleaning process.

The sputtered tantalum samples were degreased by immersion in sulphuric acid (96% Reagent) saturated with potassium dichromate. The metal surfaces cleaned by this treatment were hydrophilic, i.e., they could be wetted by a uniform thin film of water and would dry in a similar uniform manner. The samples were then rinsed in distilled water and mounted in a teflon holder for the anodization.

* Supplied by D. Mills, Northern Electric Research Laboratories Ottawa.

** Chemical polish was made up of 5 parts by volume 96% H$_2$SO$_4$, 2 parts 70% HNO$_3$, and 2 parts 48% HF.
An oxide is grown on tantalum by placing the metal in an electrolyte and applying a voltage to it which is positive with respect to another electrode (Platinum in this case). Oxide growth occurs by the movement of tantalum and oxygen ions, which at room temperatures requires fields in the film of the order $6 \times 10^6$ V/cm. The films used in this study were grown by applying a constant current until the desired thickness was reached (which is roughly proportional to the voltage applied to the cell during growth). The terminal voltage was then left on the sample for a number of hours so that weaker spots in the film would be allowed to grow thicker. Film thicknesses were kept below 1000 Å, as experiments by Vermilyea\textsuperscript{(10)} indicated that the conduction properties of thicker films were dominated by flaws.

Results are presented for three different samples. Sample 1 was anodized in 40% sulphuric acid at 100-105°C at approximately 25mA/cm\textsuperscript{2} to 30v. The sample was left at 30v. for two hours at which time the current had fallen to approximately 6μA/cm\textsuperscript{2}.
Sample 2 was anodized in 0.5% sulphuric acid at room temperature at approximately 22 ma/cm$^2$ to 30 volts. It was left on constant voltage for two hours at which time the current was about 5μa/cm$^2$. Some of this current may have been due to leakage between the electrolyte and the tantalum wire contact (see Fig. 3-1). For sample 3, the procedure was the same as for sample 2 except that the constant current used was 3 ma/cm$^2$.

Film thicknesses were measured using a model 14 Cary spectrophotometer and the curves on page 80 of reference 8.

3.2 Counterelectrodes

After the anodization was completed the films were rinsed in distilled water, air dried and placed in a Veeco vacuum system for evaporation of the counterelectrodes. Aluminum, gold and indium were used. The aluminum and gold wires were wound on tungsten helix wire and then cleaned in trichlorethylene using ultrasonic agitation. The indium was placed in a tantalum boat and cleaned in a similar fashion. The evaporation was carried out at approximately 10$^{-5}$ mm of Hg, and in all cases the evaporation was started before opening a shutter and exposing the oxide film to the source. The distance between source and film was approximately six inches. The masks used produced circular electrodes with diameters from 0.2 mm to 2 mm.

The aluminum counterelectrodes gave very unsatisfactory devices with low breakdown strength. Gold* and indium were found to give good rectifying contacts.

* Silcox and Maissel(33) found gold electrodes gave high breakdown strengths. They attributed this to a tendency of gold to bridge fine cracks in the oxide surface whereas aluminum tends to penetrate these cracks thus leading to low breakdown voltages.
The sample # 2 used in this work initially had aluminum electrodes. These were later removed with sulphuric and nitric acids and replaced by indium electrodes.

3.3 Experimental Setup

The earlier measurements were carried out in dry air with the sample mounted in an electrically screened sealed chamber (Fig. 3.3) which could be maintained at different temperatures in the range $80^\circ K$ to $400^\circ K$. Contact was made to the counterelectrode with a small gold probe. Efforts were made to minimize the contact pressure and no apparent damage to the film was observed due to the contact. Shielded, low noise cables were used for all connections. Connection points had to be fully shielded as the currents being measured were in the picoamp range.

The currents were measured using a Keithley 417 picoammeter in the following circuit.

![Current measurements circuit diagram](image)

Fig. 3-2 Current measurements circuit
The x-y recorder was used for mapping current transients. Later experiments were carried out in a different chamber (Fig. 3-4) which could be evacuated to about 300μ Hg. The temperature was controlled by placing the whole unit in a Statham SD6 oven which allowed for a temperature range -40°C to +150°C. Coaxial leads with teflon insulation were used in the circuit in Fig. 3-2 with this setup.

Capacitance and dielectric losses were measured on a General Radio 1615 - A transformer bridge in the three terminal mode (which eliminates capacitances between the leads and ground). The frequency range used was 100 Hz to 100 KHz with signal amplitudes between 10mv and 100 mv peak to peak. The measured values of capacitance and losses did not depend on the signal amplitude in this range. Measurements were extended to 500 KHz on one sample using a Boonton Model-75c capacitance bridge.

The circuit in Fig. 3-2 was checked for electrical leakage by removing the sample, applying a voltage greater than that used in the experiments and then ensuring that any resultant current was much smaller than the currents being measured in the experiments.

The specified accuracy of the picoammeter was ±3% for all ranges except the lowest, where it was ±5%. Thus except for current values less than 10⁻¹² amps, the overall accuracy of the measured values will be within ±5%.

The G.R. bridge accuracy is dependent on the measurement frequency and on the magnitude of capacitance being measured. Percent values are given in the results, where appropriate. The
Fig. 3-3 Test chamber for low temperature measurements

Fig. 3-4 Test chamber for measurements in vacuum
Boonton bridge accuracy also depends on the parameters of the sample being tested, and values are given where appropriate in the results.

3.4 Series Resistance

The measured values for the losses have to be corrected for series resistance due to contacts, lead resistance, etc. Correction for this can be most easily made using the series R-C model for the capacitor. Thus

\[
\tan \delta = \frac{R_L + R_s}{\omega C_s}
\]

where \( R_L \) is the extra series resistance due to leads, etc. Thus \( \tan \delta = (R_L + R_s) \omega C_s \) and it is a simple matter to determine the correct \( \tan \delta \) once \( R_L \) is known. \( R_L \) is more easily derived from the parallel R-C model.

\[
\tan \delta = \frac{R_L(1 + \omega^2 R_p^2 C_p^2) + R_p}{\omega R_p^2 C_p}
\]

At high frequencies

\[
\tan \delta = \omega R_L C_p
\]

A plot of \( \frac{\tan \delta}{\omega C_p} \) against \( 1/\omega \) extrapolated to infinite frequency gives \( R_L \). For materials with \( \tan < 0.1 \), \( C_S = C_p \) to within 1% and so \( \frac{\tan \delta}{\omega C_s} \) may be plotted against \( 1/\omega \).

The example illustrated below is for the bridge measurements on sample #3, electrode a, shown in Fig. 4-17.
Fig. 3-5 Series resistance example
4. RESULTS

4.1 Current Measurements

4.1.1 Charge and Discharge Currents

Figs. 4-1 to 4-4 are all concerned with the step response of a particular sample (#3) with a gold electrode "a" of area $3.62 \pm 0.05 \times 10^{-2} \text{ cm}^{-2}$. Film thickness was $644 \pm 5 \text{ Å}$. Measurements were carried out with the sample under a vacuum of 300 μHg. Previous to these measurements the sample had been annealed at $140 \pm 10^\circ\text{C}$ for approximately 40 hours. The sample was short circuited for approximately 8 hours before any measurements were made. Figs. 4-1 and 4-2 show the charging current densities as a function of time after applying step voltages of increasing magnitude. Polarities were alternated every one or two tests at the lower voltages. The straight lines drawn through the points for the lower voltages have a slope of $-0.90$. At the lowest voltages (0.25, 0.50, and 1.0v) the charging currents became too small to be measured after approximately 500 sec.

Figs. 4-3 and 4-4 show the discharge current densities as a function of time after removal of the applied voltages. The charging voltages were left on for at least 1000 sec., i.e. at least five times the length of time in which the discharge currents were observed. The lines have been drawn with a slope of $-0.90$ and the close fit between the points and the lines indicates the discharge currents can be represented by a law $J \propto t^{-0.90}$. Fig 4-5 shows the 2v Ta-positive discharge curve for four different gold electrodes, all on the same sample (#3). The lines are again drawn with a slope of $-0.90$. The four sets of points, roughly superimposed
Fig. 4-1  Charge currents for Ta- negative voltages
Fig. 4-2 Charge currents for Ta-positive voltages
Fig. 4-3 Discharge currents for Ta-negative voltages
Fig. 4-4: Discharge currents for Ta-positive voltages
on the lower line were taken at different stages in the annealing (i.e. from approximately 5 hours to 40 hours). The one upper set of points is for the same electrode as one of the lower set of points, but was taken prior to any annealing. Fig. 4-5 indicates that the results are reproducible for different electrodes on the same sample after the sample has been annealed. There does not appear to be a strong dependence on the annealing time.

4.1.2 Discharge Currents as a Function of Voltage

On the basis of the theory presented in section 2.1 for polarization currents, the deviation of $J_p$ from an exact $\frac{1}{t}$ law can be attributed to the distribution function $G(q)$ being not quite flat. According to equation (2-6), $J_p$ should be linear with voltage in the absence of a space charge. Thus, in Fig. 4-6, $\frac{J_t^{0.90}}{V}$ is plotted as a function of voltage where $J$ is taken from Figs. 4-3 and 4-4. The value of $J_t^{0.90}$ is obviously independent of time. The other three electrodes tested on this sample and referred to in Fig. 4-5 displayed a similar dependence of $\frac{J_t^{0.90}}{V}$ on $V$. The value of $\frac{J_t^{0.90}}{V}$ increased with increasing magnitude of Ta-negative voltages, went through a minimum at low Ta-positive voltages and then increased again at large Ta-positive voltages. Fig. 4-6 possibly indicates space charge effects. For purely polarization currents, than for a linear response, $\frac{J_t^{0.90}}{V}$ should be independent of $V$ and, if a polarization saturation phenomenon occurs, should be a decreasing function of $V$ (refer to equations II-8 and II-9). Thus the curve at low Ta-positive voltages in Fig. 4-6 may indicate a polarization saturation. The increasing portions of the curve may be due to a space charge decay current component or to an increased polarization current due to the effects
SAMPLE No3 GOLD ELECTRODES TESTED IN 300µ VACUUM
TEST VOLTAGE = 2.0 V Ta - POSITIVE

Fig. 4-5 Log J vs. log t for different electrodes on sample #3
Fig. 4-6 Discharge currents as a function of voltage – sample #3
of the space charge. Referring to equation 2-22, the space charge decay current is of the form \( n_t(x^*, t) \frac{dx^*}{dt} \). The polarization current characteristic is unchanged, though the magnitude of the current is changed (from \( V/L \) to \( E(x^*) \)). The fact that the discharge characteristic \( t^{-0.90} \) is the same for all voltages in Figs. 4-3 and 4-4 suggests the current is due only to one mechanism. The low voltage characteristic in Figs. 4-1 to 4-4 indicate a polarization current because the charge and discharge currents are equal and independent of polarity (up to 1 volt with a maximum deviation of 20% at \( t = 0 \) sec.). It can also be seen from Figs. 4-1 to 4-4 that discharge and charge currents are equal (for \( t \leq 10 \) sec.) for Ta- negative voltages = 2v and for Ta-positive voltages = 5v. This would seem to indicate polarization currents even though the discharge currents are of different magnitudes for opposite polarities at the same voltage.

Similar experiments to those above are now discussed for a different sample (#2) which had indium rather than gold electrodes. The film thickness was the same (644±5 Å) but this specimen was tested in dry air rather than in low vacuum and also was annealed at a maximum of 70°C. The results were considerably different from those for sample #3. Fig. 4-7 shows a plot of \( \frac{J_t^{1.0}}{V} \) vs. \( V \), analogous to the \( \frac{J_t^{0.90}}{V} \) plot in Fig. 4-6 for sample #3. \( t^{1.0} \) is used because figure 4-8 shows a slope of -1.0.

The curve decreases for both polarities and has a peak value about four times larger than that for sample #3. Three different electrodes on sample #2 gave similar curves. Fig. 4-8 shows the discharge current for the three electrodes for five volts Ta- positive. From equation (2-9), \( \frac{J_t}{V} \) is a measure of the losses at very low
Fig. 4-7 Discharge currents as a function of voltage - sample #2
SAMPLE No. 2 INDIUM ELECTRODES TESTED IN AIR
TEST VOLTAGE = 5V, TA - POSITIVE

ELECTRODE: a  b  c

\[
\frac{\delta \log J}{\delta \log t} = -1.0
\]

Fig. 4-8 Log J vs log t for different electrodes on sample #2
frequencies, assuming that $J$ is purely polarization current. The above results appear to show that sample #2 is three or four times as lossy as sample #3 at very low frequencies. However, at 1 KHz, the losses of the three electrodes on sample #2 varied between $\tan \delta = 0.0046$ and $\tan \delta = 0.0052$ while the four electrodes on sample #3 had losses varying between $\tan \delta = 0.0061$ and $\tan \delta = 0.0081$. The step response behaviour of sample #2, as demonstrated in Fig. 4-7 could not be satisfactorily explained. Some other samples tested during the course of the investigation showed a similar lack of correlation between the bridge measurements and the step response measurements. Data for these other samples is listed below and a single point for each sample is plotted in Fig. 4-7 to show the scatter. The plotted values have been corrected for the different film thicknesses.

1. Film formed to 100v on bulk Ta in 0.5% $\text{H}_2\text{SO}_4$, at 4 ma/cm$^2$, Al electrodes, $\tan \delta$(1 KHz) = 0.028, tested in air. At 5v. Ta- positive, $\frac{J_t}{V} = 3.3 \times 10^{-9}$ coul./cm.$^2$ volt.

2. Film formed to 50v on bulk Ta in 0.5% $\text{H}_2\text{SO}_4$ at 10 ma/cm$^2$. Al electrodes, $\tan \delta$(1 KHz) = 0.008, tested in air. At 3v Ta- positive, $\frac{J_t}{V} = 2 \times 10^{-9}$ coul./cm.$^2$ volt.

3. Film formed to 40v on bulk Ta in 0.5% $\text{H}_3\text{PO}_4$ at 22 ma/cm$^2$. Gold electrodes, $\tan \delta = 0.01$ tested in air. At 2v Ta- positive, $\frac{J_t}{V} = 2 \times 10^{-9}$ coul./cm.$^2$ volt.

4. Film formed on bulk Ta to 40v in 40% $\text{H}_2\text{SO}_4$ at 85°C at 20 ma/cm$^2$. Indium electrodes, $\tan \delta = 0.005$; tested in air. At 5v Ta- positive, $\frac{J_t}{V} = 2 \times 10^{-9}$ coul./cm.$^2$ volt.
Since gold electrodes appear to give better results, it may be that some of the poor results obtained with the other electrode materials were due to oxide deposited on the film when the electrode materials were evaporated. However it is not exactly clear why this should lead to a different step response. The use of gold electrodes appears to eliminate the problem.

4.1.3 D.C. Conduction Currents

Fig. 4-9 is a Schottky plot \( \log J_L \ vs \ (V/T)^{1/2} \) of the conduction currents. The leakage current \( J_L \) was estimated from Figs. 4-1 and 4-2 by extrapolating to larger times the lines drawn through the measured points. The higher voltages in Fig. 4-9 are not drawn in Figs. 4-1 and 4-2. The straight lines drawn and labeled \( \alpha/kT \) and \( \beta/kT \) correspond to the calculated values of the Schottky and Poole-Frenkel slopes respectively. These were calculated from equations 2-10 and 2-11 using a dielectric constant of 5. The Ta- positive voltage curve appears similar to those observed by Mead\(^{(12)}\) and to the curves calculated by Frank and Simmons\(^{(3)}\). Namely, at higher voltages the curve is asymptotic to the Schottky slope. The change in slope at 5v may correspond to when charge injection occurs. From Fig. 4-6, 5v Ta- positive is at the minimum in the curve and may correspond to when space charge effects begin to show up in the Ta- positive discharge curves.

It was noticed that sufficiently high voltages (from 10 - 15 volts of either polarity) caused a change in the properties of sample #3. Such changes are called "deformation" in the literature. The conductance of the sample increased by an amount depending on the magnitude of the applied voltage. This is illustrated in Fig. 4-10 which is for sample #3, electrode C of area
SAMPLE No 3 ELECTRODE "a"

- $T_a$ - NEGATIVE
- $T_a$ - POSITIVE

Fig. 4-9 Leakage current as a function of field - sample #2
Fig. 4-10 Leakage current as a function of field - sample #3
Fig. 4-11 Temperature dependence of leakage currents

$T_a / T_{a_2} O_5 / INDIUM$

SAMPLE No 2 ELECTRODE "b"

$O - 7.5 V T_a \text{ POSITIVE}$  
$O - 5.0 V T_a \text{ NEGATIVE}$

$0.82 \text{ ev}$  
$0.64 \text{ ev}$

$log_{10} (I / I \text{ amp} / cm^2)$

$\frac{1}{k} \times 10^3 x_{\circ K}$

3 3.5 4.5
Fig. 4-12 Leakage currents as a function of field - sample #2
3.50 ± 0.05 x 10^{-2} \text{ cm}^2$, measurements being taken with the sample in a 300\(\mu\) vacuum. Fig. 4-10 shows the J-V characteristic for a film deformed to a high degree. Before the film was deformed, the leakage currents were the same order of magnitude as those in Fig. 4-9 i.e. a factor of between $10^3$ to $10^5$ smaller than in the deformed film. Also the rectification behaviour disappears and hysteresis effects were reduced. The straight line drawn in Fig. 4-10 is the calculated Schottky slope.

Steady state leakage currents were measured as a function of temperature and voltage on sample #2, electrode b (area $4.25 ± 0.10 \times 10^{-3}$ cm$^2$) to determine the activation energy of the conduction process. Fig. 4-11 is a plot of log $J_L$ vs. $1/T$ where the measurements were taken for decreasing temperatures. The activation energy is determined from equation 2-10 for a Schottky process and from a similar equation with $\alpha$ replaced by $\beta$ for a Poole-Frenkel process. Fig. 4-12 is a Schottky plot of the leakage currents with the drawn lines corresponding to the calculated Schottky and Poole-Frenkel slopes as before. The reasonable fit between the points and the lines justifies calculating the activation energies shown in Fig. 4-11 by using the theoretical values of $\alpha$ and $\beta$ for the Ta- positive and Ta- negative currents respectively. The Ta- positive voltage activation energy was 0.64 ev. and the Ta- negative voltage activation energy 0.82 ev.

4.2 Bridge Measurements

4.2.1 Capacitance and Loss Measurements

Fig. 4-13 is a plot of capacitance and losses vs. frequency for sample #3, gold electrode b of area $6.3 \pm 0.2 \times 10^{-4}$ cm$^2$. 
Fig. 4-13 Frequency dependence of $C_0K'$ and $C_0K''$ at $295^\circ K$
The plotted values are $\text{CoK}'' = C \tan \phi$ and $\text{CoK}'$ where $K' - jK''$ is the complex dielectric constant and $C$ is the capacitance of the air filled capacitor. The G.R. bridge values for $\text{CoK}'$ are specified to be accurate to 0.01% for $f \leq 10$ KHz and to 0.2% at 100 KHz. $\text{CoK}''$ is accurate to 0.1%. The Boonton bridge measurements of $\text{CoK}'$ are specified to be accurate to 0.25% + 0.2pf and $\text{CoK}''$ is accurate to only 10%. The difference in the loss measurements shown for the two bridges is about 10%. The values of $\text{CoK}'$ above 100 KHz have been corrected for series resistance in the leads, connections etc., and approximate corrections have been made for lead inductances using the tables provided with the Boonton bridge. The decrease in $\text{CoK}''$ at frequencies less than 500 KHz was unusual as for most samples tested the losses continued to increase at low frequencies. A small electrode was required for these high frequency measurements as the Boonton can measure a maximum capacitance of only 1000 pf (without range-extending external capacitors).

For sample #3, measurements in a 300μ vacuum on two gold electrodes of area $3.5 \times 10^{-2} \text{cm}^2$ gave a value of $K' = 25.9 \pm 0.8$. Two gold electrodes of area $4.9 \times 10^{-3} \text{cm}^2$ gave a value of $K' = 26.5$ to 27.1 ± .8. The previous history of this sample included annealing at temperatures up to 140°C in vacuum. In general, it was found that capacitance and loss values tended to decrease with time for a freshly prepared sample. Once the samples had been shorted for about a day, the observed values of the capacitance would change less than 0.3% over a period of 2-15 days. Putting a sample in a vacuum (300μ) would cause a drop of about 0.5% in $\text{CoK}'$ and from 7-15% in $\text{CoK}''$ in a few minutes, and then a slow decrease as mentioned
above. Heating a sample and then cooling it would result in the same effect as short circuiting the sample for a day. This procedure was carried out on most samples.

4.2.2 Temperature Dependence of Capacitance and Losses

Fig. 4-14 shows a hysteresis effect in the values of $C_0$ and $C_0$ when a sample is heated. This figure is for sample 1, of thickness $718 \pm 5$ A with a gold counterelectrode of area $4 \times 10^{-3}$ cm$^2$. Measurements were made at 1 KHz in dry air. A similar effect was observed for all samples, though in most cases not so pronounced. The very rapid increase in $C_0$ and $C_0$ as the temperature was increased slightly may have been a special feature with this sample due to its previous history, in that immediately prior to this experiment, fields up to $3.5 \times 10^6$ v/cm with Ta- positive, had been applied to the sample. The losses are plotted as $C_0$, because according to equation 2-4, this can be interpreted as a plot of the distribution function $G(q)$. At the point marked "steady state" the sample was held at constant temperature for three hours and $C_0$ and $C_0$ changed less than 0.4% and 1.5% respectively in this interval. The sample was then slowly cooled to liquid nitrogen temperatures.

Fig. 4-15 shows the temperature dependence of $C_0$ and $C_0$ of sample 2 electrode a between $295^\circ K$ and $85^\circ K$ at 1 KHz, in dry air. The area of the indium electrode was $3.7 \pm 0.1 \times 10^{-3}$ cm$^2$. This figure, as did Fig. 4-14, demonstrated that below a certain temperature (approximately $250^\circ K$ here) the losses became linear with temperature. If the losses are due to the ionic relaxation process considered in section 2.1 then according to equation (2-4) the distribution $G(q)$ is flat over this lower range of activation
Fig. 4-14 Temperature dependence of $C_K'$ and $C_K''$ - sample #1
Fig. 4-15 Temperature dependence of $C'_0 K'$ and $C''_0 K''$ - sample #2
SAMPLE No2 ELECTRODE "a"
Ta/Ta₂O₅/ INDIUM

T = 82 °K

Fig. 4-16 Frequency dependence of CₒK' and CₒK'' at 82 °K
energies. Fig. 4-16 shows the frequency dependence of \( \text{CoK}' \) and \( \text{CoK}'' \) of the same sample at 82\(^\circ\)K. The losses are more independent of frequency than the losses at room temperature. This would be expected, as Fig. 4-15 shows that the distribution \( G(q) \) is not flat near room temperature. The value of \( K' \) calculated at 1 KHz and at room temperature was 24.3 \( \pm \) 0.8 to 24.1 \( \pm \) 0.8. The \( \pm \) 0.8 error is due mainly to uncertainty in the area of the electrode. This sample had been heated to a maximum of about 70\(^\circ\)C in its history.

An estimate of the activation energy of the loss processes may be accurately obtained from the results in Fig. 4-15. Applying equation III-10 and neglecting \( \frac{dE}{dT} \) (as was done by Géver's and Du Pré) gives \( \ln \frac{4\pi}{\omega \tau_0} = 34.8 \pm 1.5 \). Therefore the activation energies are \( q = 0.25 \pm .01 \) ev. at 85\(^\circ\)K and 0.88 \( \pm \) .05 ev. at 295\(^\circ\)K. By extrapolating the curves in Fig. 4-15 to 0\(^\circ\)K, then from equation (2-3) the intercept of \( \text{CoK}' \) at \( T = 0^\circ K \) gives \( \text{CoK}_0 \). The result is that \( K_\infty > 0.9K' \) where \( K' \) is taken at 295\(^\circ\)K. Thus the polarization processes with characteristic frequencies below the infrared contribute less than 10\% to the polarization of the dielectric.

4.2.3 Comparison of Bridge and Step Response Values for the Loss

Fig. 4-17 is a plot of the dielectric losses for sample #3, gold electrode \( a \), obtained by both bridge measurements and step response measurements, as a function of the relaxation time. For the bridge measurements, the relaxation time \( \tau \) is given by \( 2\pi/\omega \) and for the step response measurements, equation 2-9 was used with \( \tau = t/2 \). The step response values were taken from the one
SAMPLE No 3 ELECTRODE "a"
Ta/Ta$_2$O$_5$/GOLD

$T=297^\circ K$

- BRIDGE MEASUREMENTS $\tau = \frac{1}{f}$
- STEP RESPONSE $\tau = \frac{t}{2}$

Fig. 4-17 Dielectric losses vs. relaxation time
volt anodic curve in Fig. 4-4. The smooth joining of the two sets of points indicates that the currents measured at one volt were polarization currents. The bridge measurements in Fig. 4-17 have been corrected for series resistance due to the leads, etc. The deviations in the points at 60 KHz and 100 KHz may be due to small inaccuracies in determining the series resistance. The dielectric losses could not be calculated accurately, for example, as at 100 KHz the true series resistance accounted for less than 20% of the measured losses.

To obtain a complete curve of the losses vs. relaxation time in Fig. 4-17 would require either measuring the losses at very low frequencies, or measuring the polarization currents at very short times, or by using a temperature sweep technique. The latter method was attempted. Fig. 4-18 shows $C_0^\prime$ and $C_0^\prime\prime$ as a function of temperature between 300 K and 365 K. To relate a temperature change to a frequency change, the constant $Z_o$ is needed in equation 2-5, $q_o = kT \ln \frac{4\pi}{\omega Z_o}$. Using equation III-10 as before then $Z_o$ may be determined from Fig. 4-18. This procedure was not too successful as the results indicated an apparently temperature dependent value of $Z_o$. Taking $C_0^\prime$ to be linearly dependent on temperature, then, in order to have $Z_o$ constant, $C_0^\prime\prime$ must be independent of temperature. This is not the case as shown in Fig. 4-18. Using the largest value of $Z_o$, however, the calculated values for the losses did fall roughly on the line joining the two sets of points in Fig. 4-17.
Figure 4-18: Temperature dependence of $C_0K'$ and $C_0K''$ - sample #3
5. DISCUSSION

5.1 Step Response Measurements

Measurements of low frequency dielectric losses using a step response technique are complicated by space charge effects and polarization saturation effects. The theoretical analysis in section 2.3.2 showed how a space charge decay may contribute to the externally observed discharge currents and how it may affect the current due to dielectric polarization. The results shown in Fig. 4-6 indicate a space charge effect. A polarization saturation phenomenon might be expected at the fields used here, as can be seen by comparing equations II-8 and II-9. Fig. 4-6 displays what might be such an effect. Thus, to measure low frequency dielectric losses accurately requires using sufficiently low fields if saturation phenomenon are to be avoided and a rectifying contact to reduce any charge injection.

Cherki et al.\(^{(7)}\) carried out frequency response and step response experiments on a Ta/Ta\(_2\)O\(_5\)/gold device with results slightly different from those reported here. Their measured currents followed an exact \(\frac{1}{t}\) law at temperatures from 4\(^0\)K to 295\(^0\)K, were polarity independent and were linear with field up to \(5 \times 10^5\) V/cm (which corresponds to about 3 volts in Fig. 4-5). The losses were frequency independent over the same temperature range. In this range of fields they observed no space charge or polarization saturation effects. The results in this work indicated frequency-independent losses below about 250\(^0\)K. At 295\(^0\)K the losses were not quite independent of frequency. Dreiner\(^{(29)}\), using a Ta/Ta\(_2\)O\(_5\)/electrolyte system, observed \(\frac{1}{t}\) law discharge currents linear with a Ta-
fields up to $2 \times 10^6$ v/cm. Above this field the discharge currents increased more rapidly with field. It is not clear why a saturation phenomena does not appear in Dreiner's and Cherki's results. It is also not clear why Cherki et al. did not observe a space charge effect for Ta- negative voltages. Possibly their sample preparation technique resulted in the Ta/Ta$_2$O$_5$ barrier of their devices being higher than the barriers of the devices used in this work. However since no details of their sample preparation technique were given a comparison is not possible.

5.2 D.C. Conduction Currents

The investigation of d.c. electronic conduction was difficult because of marked time dependence of the currents. For sample #2 at high Ta- positive voltages the currents were still drifting slowly after twelve hours. The Ta- negative currents tended to go through a minimum at between 1 and 30 minutes after applying the voltage, and then slowly increased. Plotted values as in Fig. 4-12 were taken at the minimum current level. The transient charging currents shown in Fig. 4-1 and 4-2 for the larger voltages are much larger than can be accounted for by polarization currents. They are probably due to either one or both of two effects; 1) The transient is due to a space charge buildup according to equation (2-20), or 2) the current is due to space charge modulated leakage currents, which may be given by an equation like (2-10) where the field $E(0)$ is controlled by the development of a space charge.

The results in Fig. 4-9 and 4-12 indicate a Schottky process for Ta- positive voltage and a Poole-Frenkel process for Ta- negative voltage. In Fig. 4-9 the Ta- positive currents at the lower voltages
are less than predicted by the Schottky law due to a space charge. The curve has been drawn with a sudden change between three and five volts, since Fig. 4-6 appears to indicate that space charge develops in this interval. The asymmetry in conduction processes is marked by a pronounced rectification characteristic.

The activation energies for the conduction currents noted in Fig. 4-11 are considerably higher than those reported by Mead (12) (i.e. 0.4 ev). However if Mead's results were for a deformed film then it is probably meaningless to compare values. Cherki et al. (32) using a Ta/Ta₂O₅ electrolyte system, reported a value of 0.72 ev for Ta- positive currents, which is higher than the 0.64 ev reported here. If these values are due to the metal/oxide and electrolyte/oxide interfaces, it would be expected that they be different.

Sample #3 was the only one which deformed at higher voltages. Deformation commenced at about 10 - 15 volts of either polarity. The results shown in Fig. 4-10 for a highly deformed film are similar to the curves published by Mead (12) for a Ta/Ta₂O₅/Au device. That is, there is little or no rectification, the currents obey a Schottky law, and the currents are about the same order of magnitude for the same field. Thus it seems possible that Mead's results were for a deformed film. He reported that he could not get reproducible results due to drift.

Such deformations of oxide films due to an applied field have been reported previously (30,31). It is a necessary condition for observing the negative resistance displayed by thin films (31). To observe a differential negative resistance, researchers speak of applying a "forming" voltage to the film which causes a large increase in film conductivity. The processes occurring in the films when they are deformed are not fully understood.
5.3 **Comparison of Samples #2 and #3**

Samples #2 and #3 were prepared under identical conditions except for different formation current densities but displayed considerably different properties. Voltages up to 25 volts Ta- positive could be applied to sample #2 without causing breakdown or any deformation whereas 10-15 volts Ta- negative was sufficient to cause breakdown. Sample #3 would breakdown at about 15 volts Ta- positive and 10-15 volts negative and before breaking down would be considerably deformed, as already described. The step response behaviour of the two films also gave differing results; that is, the step response of sample #2 could not be correlated with the losses as measured with a bridge. The dielectric constant of sample #3 was higher than that of sample #2. These differences could a priori be attributed to: the different electrode metals, the different formation current density, or the different history of the samples and experimental conditions. (i.e. sample #2 was measured in air, sample #3 in vacuum). It is probable that the first and third reasons are the most important. The high temperature annealing of sample #3 may have altered the stoichiometry of the oxide. Experiments by Smythe et al.\(^{(36)}\) have indicated that annealing causes an increase in the capacitance, which may explain the difference in $K'$ noted here. The deformation properties of sample #3 may also be caused by the vacuum annealing. Hickmott\(^{(37)}\) has noted that negative conductivity (i.e. deformation) is achieved more easily under vacuum, though this is not a necessary condition. Schwartz et al.\(^{(38)}\), using Ta/Ta$_2$O$_5$/Au devices, noted that the presence of water vapour caused highly asymmetric breakdown characteristics. After vacuum-baking their samples, the Ta- positive breakdown
voltage had decreased to approximately the same as the Ta-negative breakdown voltage. This perhaps explains why sample #2 here showed such high Ta-positive breakdown strength when compared with sample #3.

As mentioned previously, no satisfactory reason could be found for the different step response results.

5.4 Frequency and Temperature Dependence of the Dielectric Properties

Fig. 4-13 shows that the losses CoK" become flat at 500 KHz. This would be expected if the sample had a temperature behaviour similar to that shown in Fig. 4-15. From equation (2-5), an increase in frequency has the same effect as a decrease in temperature, and according to Figs. 4-14 and 4-15 the losses become flat as the temperature decreases.

The reason for the rapid increase of CoK' and CoK" with an increase in temperature, as shown in Fig. 4-14, is not clear. It may be due to a process involving the release of electrons from traps or to some process in which the temperature increase causes a change in the number of polarizable particles. The latter possibility may also explain the apparent nonconstant value of \( \tau_0 \) determined from Fig. 4-18. If the losses are due to ions not bound to any particular site in the film, then the number of such "interstitial" ions could be temperature dependent. The analysis in Appendix II considered only a fixed number of polarizable particles.

It was noticed that by heating some samples, and then cooling them, the losses could be reduced by as much as 50%. A similar effect was noticed after simply shorting a freshly prepared sample for a long time. Under vacuum conditions, the losses decreased rapidly at first and then slowly, as above. This drift in the loss
values may be due to two effects: 1) If the losses are due to "interstitial" ions, then the losses will decrease as these ions are trapped in lattice sites. Annealing at high temperatures will speed the process. This argument is supported by the dependence of the losses on formation current density and on time after ceasing formation (reference (8), p. 163). 2) If the losses are due to absorbed impurities such as water then the losses will decrease as the film is "dried". Experiments by Schwartz and Gresh (38) have indicated that the presence of water vapour can cause large increases in the losses in Ta\(_2\)O\(_5\).

The strong temperature dependence of the dielectric losses is indicative of an activation energy process. Cherki et al. (7) measured losses down to 4.2\(^0\)K on a Ta\(_2\)O\(_5\) specimen, where they found the distribution of activation energies to be flat. However their results indicate that the distribution has a different value at 4.2\(^0\)K than at 77\(^0\)K and at 295\(^0\)K. From equation (2-4), a measure of the distribution \(G(q)\) is given by \(\frac{C_0K''}{T}\). From Cherki's paper then, at 295\(^0\)K, \(\frac{C_0K''}{T} = 0.0407\) pf/\(^0\)K, at 77\(^0\)K, \(\frac{C_0K''}{T} = 0.0403\) pf/\(^0\)K and at 4.2\(^0\)K, \(\frac{C_0K''}{T} = 0.35\) pf/\(^0\)K. Their distribution is flat from 295\(^0\)K to 77\(^0\)K whereas that shown in Figs. 4-14 and 4-15 is flat from approximately 250\(^0\) to 80\(^0\)K. It is possible to calculate the activation energies of the processes occurring at 4.2\(^0\)K in the paper of Cherki et al. Using equation III-10 and their values of \(C_0K'\) and \(C_0K''\) between 295\(^0\) and 77\(^0\)K, then \(\ln \frac{4\pi}{\omega \varepsilon_0} = 31.3\). From \(q = kT \ln \frac{4\pi}{\omega \varepsilon_0}\), then \(q = 0.011\) ev at 4.2\(^0\)K.

5.5 The Ionic Relaxation Model

It seems improbable that ions with very low binding energies are the cause of the losses at 4.2\(^0\)K, since, if such shallow levels
existed, then at room temperatures the ions would be free to move until trapped. Cooling the films would result in there being no ions in the shallow levels. If at room temperature the ions were not trapped, then ionic conduction would occur at low fields. This perhaps suggests that the losses may be due to an electronic process, such as electrons hopping between impurity states at higher temperatures and perhaps tunneling at low temperatures. Cherki's results show that CoK" becomes much less temperature dependent below 77°K, perhaps indicating a tunneling process. One further fact which conflicts with an ionic loss process is that the activation energy of the bulk electronic conduction currents (~ 0.82 ev) is about the same as the activation energy of the losses at room temperature (~ 0.88 ev). If the losses were ionic, then the conduction should be also.

A possible model for an electronic process would be an exponential trap distribution in the bandgap of the form \( N_t \propto \exp\left(\frac{E-E_t}{kT}\right) \). Above the Fermi level, the trap occupation would be given by a Boltzmann distribution, \( \exp\left(\frac{E_t-E_F}{kT}\right) \). Thus the number of electrons at a particular trap level will be independent of that trap level, which is essentially the same situation as was assumed in calculating the ionic relaxation losses.

The rather large activation energy (0.88 ev) of the losses at room temperature suggests a reason for the apparent increase in the distribution near room temperature shown in Figs. 4-14, 4-15 and 4-18. At these activation energies, some ion movement may be expected and so the losses could be composed of an electronic component and an additional ionic component. The analysis presented in Appendix III would have to be modified to account for the changing number of polarizable particles.
6. CONCLUSIONS

In studying the properties of a Ta/Ta$_2$O$_5$/metal device, the dielectric losses were found to be nearly independent of frequency over a very wide range of frequencies. The strong temperature dependence of the losses indicated an activation energy type process. Bridge measurements at temperatures below 250°K indicated that the distribution of activation energies became flat between approximately 0.25 ev and 0.75 ev. Measurements at 500 KHz at room temperature also showed the losses becoming frequency independent, as indicated by the low temperature measurements.

The theory suggested that space charge effects will show up in the discharge current transients after removal of an applied voltage. The effects were observed experimentally and were found to be polarity dependent; that is, different barrier heights at the metal/oxide interfaces either facilitated or inhibited charge injection into the insulator. The space charge can cause a discharge current due to the decay of the space charge and can cause a change in the magnitude of the polarization currents. The experiments indicated that the main effect of the space charge was to alter the polarization current magnitude.

A polarization saturation effect was observed in the step response experiments when the space charge effects were reduced by using a rectifying contact. The polarization saturation effect and the space charge effects must be taken into consideration when measuring the low frequency dielectric losses by a step response technique.
The losses were found to be very dependent on the sample history. For example, an annealing process reduced the losses by as much as 50% in some cases.

The conduction currents were found to be time dependent, which was attributed to the development of a space charge. The Ta-positive currents obeyed a Schottky law and the Ta-negative currents obeyed a Poole-Frenkel law. This asymmetry in conduction mechanisms was marked by a pronounced rectification characteristic. The Schottky law currents showed theoretically predicted space charge effects, and the onset of these space charge effects was correlated with the presence of space charge as indicated in the step response experiments. On one sample tested, high voltages caused a deformation of the film, characterized by an increased conductance. For these deformed films, the rectification behaviour disappears and the currents follow a Schottky law.

The activation energy of the bulk electronic conduction currents was found to be about the same as that calculated for the ionic relaxation losses at room temperature. This fact, coupled with the observed high losses at low temperatures, indicates that the losses may be due to an electronic process rather than an ionic process. If the losses were due to ions, then an ionic conduction current would be expected.

One of the objectives of future work on these films should be to determine what causes the large increase in film conductance, observed in some samples, when a large enough voltage is applied. Such changes in film properties can be detrimental in device applications.
APPENDIX I

Debye Equation

The polarization response to a step field for a relaxation process is (ref. 4, p. 72)

$$\frac{dP}{dt} = \frac{1}{\zeta} (P_s - P)$$  \hspace{1cm} (I-1)

where $P =$ polarization for the process with relaxation time $\zeta$

$P_s =$ static polarization

Integrating I-1 from $t = 0$ gives

$$P(t) = P_s (1 - e^{-t/\zeta})$$  \hspace{1cm} (I-2)

Considering $D = \varepsilon E = \varepsilon_0 E + P$, then, at frequencies higher than those at which the relaxation processes will respond,

$$\varepsilon_\infty E = \varepsilon_0 E + P_\infty$$  \hspace{1cm} (I-3)

At intermediate frequencies

$$\varepsilon(\omega) E = \varepsilon_0 E + P_\infty + P(\omega)$$  \hspace{1cm} (I-4)

and at very low frequencies such that all processes follow the field exactly (i.e. $\omega = 0$)

$$\varepsilon_s E = \varepsilon_0 E + P_\infty + P_s$$  \hspace{1cm} (I-5)

where $P_s$ is the static polarization due only to the relaxation processes.

Letting $E$ be sinusoidal, i.e. $E = E_0 e^{j\omega t}$, then subtracting I-3 from I-4 and I-5 gives

$$P(\omega) = (\varepsilon(\omega) - \varepsilon_\infty) E_0 e^{j\omega t}$$  \hspace{1cm} (I-6)

and

$$P_s = (\varepsilon_s - \varepsilon_\infty) E_0 e^{j\omega t}$$  \hspace{1cm} (I-7)

Substituting I-6 and I-7 into I-1 gives

$$j\omega(\varepsilon(\omega) - \varepsilon_\infty) = \frac{1}{\zeta} (\varepsilon_s - \varepsilon_\infty) - (\varepsilon(\omega) - \varepsilon_\infty)$$  \hspace{1cm} (I-8)

which, when solved for $\varepsilon(\omega)$, gives the Debye equation

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega \zeta}$$  \hspace{1cm} (I-9)
APPENDIX II

Ionic Relaxation Model

A charged particle is assumed to possess two equilibrium positions a distance $2a$ apart, separated by a potential barrier of height $q$.

![Ionic relaxation model](image)

Assuming $q \ll kT$, then, in thermal equilibrium, only a fraction of the particles, given by the Boltzmann factor $e^{-q/kT}$, will have enough energy at any given time to go over the barrier. Application of a field raises the barrier for particles in position 2 by $eaE$ and lowers it by the same amount for particles in position 1. Letting $\nu_0$ be the frequency of oscillation (i.e. attempt to escape frequency) of the particle, then, under an applied field, the probability per second for a particle transfer from 1 to 2 is

$$\omega_{12} = \nu_0 e^{-q/(kT)}$$

and from 2 to 1 is

$$\omega_{21} = \nu_0 e^{-(q-eaE)/kT}$$

If at any instant of time there are $N_1$ particles at 1 and $N_2$ at 2, the rates of change of $N_1$ and $N_2$ are given (assuming the particles are independent of each other) by

$$\frac{dN_1}{dt} = -N_1 \omega_{12} + N_2 \omega_{21}$$

$$\frac{dN_2}{dt} = N_1 \omega_{12} - N_2 \omega_{21}$$

The total number of particles is fixed

$$N = N_1 + N_2$$
Subtracting II-3 from II-4 and using II-5 gives
\[ \frac{d}{dt} (N_2 - N_1) = -\left(\omega_{12} + \omega_{21}\right)(N_2 - N_1) + (\omega_{12} - \omega_{21})N \quad \text{II-6} \]

Assuming that at \( t=0, N_1 = N_2 \), then
\[ N_2 - N_1 = \frac{N(\omega_{12} - \omega_{21})}{\omega_{12} + \omega_{21}} (1 - e^{-t(\omega_{12} + \omega_{21})}) \quad \text{II-7} \]

The induced polarization is proportional to \( N_2 - N_1 \) and thus approaches the steady state exponentially. The static polarization (i.e. at \( t=\infty \)) is proportional to
\[ \frac{e\alpha E}{kT} - \frac{-e\alpha E}{kT} \quad \text{II-8} \]
and for low fields is usually approximated by
\[ \frac{e\alpha E}{kT} \quad \text{II-9} \]

The relaxation time \( \tau \) of the process for low fields is given by
\[ \frac{1}{\omega_{12} + \omega_{21}} \]
That is
\[ \tau = \frac{1}{2\nu_0} e^q/kT \quad \text{II-10} \]

Equation II-7 can be written in the same form as I-2. That is
\[ P = P_s \left(1 - e^{-t/\tau}\right) \]

Throughout the above analysis, the vector nature of \( \vec{\alpha} \) and \( \vec{E} \) has been neglected. When \( \vec{\alpha} \) and \( \vec{E} \) are not parallel then \( \vec{\alpha} \cdot \vec{E} \) should replace \( \alpha E \) in all the above expressions.
APPENDIX III

Dielectric Response for a Uniform Distribution of Activation Energies

A nearly uniform distribution of activation energies, as considered in Appendix II, is assumed. The distribution, \( G(q) \), is normalized

\[
G(q) dq = 1 \quad \text{III-1}
\]

The Debye equation, separated into real and imaginary parts, is integrated over this distribution where the relaxation time, \( \tau \), of the process is given by equation II-10. Thus from equations 1-1 and 2-1

\[
\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q) dq}{1 + \omega^2 \tau^2} \quad \text{III-2}
\]

\[
\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q) \omega \tau dq}{1 + \omega^2 \tau^2} \quad \text{III-3}
\]

Defining an activation energy \( q_o \) corresponding to a relaxation time \( \tau = \frac{2\pi}{\omega} \), then, from equation II-10

\[
\frac{2\pi}{\omega} = \frac{\tau_o}{2} \varepsilon q_o / kT \quad \text{III-4}
\]

where \( \tau_o = 1/\nu_o \)

Substituting equations II-4 and II-10 into III-2 gives

\[
\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q) dq}{1 + (2\pi)^2 \exp^2 (q-q_o)/kT} \quad \text{III-5}
\]

The denominator in the integrand is of the form shown in Fig. (III-1). This curve can be approximated to that of the dotted line, giving

\[
\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty G(q) dq \quad \text{III-6}
\]

Similarly, equation III-3 is

\[
\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q) 2\pi \exp (q-q_o)/kT dq}{1 + (2\pi)^2 \exp 2(q-q_o)/kT} \quad \text{III-7}
\]
Fig. III-1 Approximation of Debye equation - real part

The integrand appears as in Fig. III-2

Fig. III-2 Approximation of Debye equation - imaginary part

Assuming that $G(q)$ is flat enough so that it doesn't change much in the region centered at $q_0$, then $G(q)$ may be evaluated at $q_0$ and taken outside the integral. Thus

$$
\varepsilon'' = (\varepsilon_S - \varepsilon_\infty) \frac{\pi}{2} \cdot kT \cdot G(q_0)
$$

III-8

Two experimentally useful relations can be derived from equations
III-6 and III-8, namely
\[ \frac{\partial \varepsilon'}{\partial \ln \omega} = -\frac{2}{\pi} \varepsilon'' \] III-9

and
\[ \frac{\partial \varepsilon'}{\partial T} = \varepsilon'' \frac{2}{T} \ln \frac{4\pi}{\omega \tau_0} + \frac{\partial \varepsilon''}{\partial T} \] III-10

where a temperature independent static permittivity has been assumed in III-10.

The above equations, first derived by Gevers and Du Pré\(^{(6)}\), may be extended to include step response.

The displacement current density is given by
\[ J_p = \frac{dD}{dt} \] III-11

which becomes, for a fixed field,
\[ J_p = \frac{dP}{dt} \] III-12

For a step applied at t=0, then, from equation I-2,
\[ J_p = P_s \frac{e^{-t/\tau}}{\tau} \] III-13

Integrating equation III-13 for distribution of activation energies G(q), and using II-10, then
\[ J_p = P_s kT \int_0^\infty G(q) \frac{e^{-t/\tau}}{\tau^2} \] III-14

The integrand appears as in Fig. III-3

---

**Fig. III-3** Step response curve
Assuming the $G(q)$ changes very little over the range of activation energies which span the major part of the above curve, then $G(q)$ may be evaluated at the peak (i.e. $\tau = \tau^* = \frac{t}{2} = \frac{\tau_0}{2} e^{q'/kT}$) and taken outside the integral.

Thus

$$J_p = P \frac{kT}{t} G(q')$$

where

$$q' = kT \ln \frac{t}{\tau_0}$$
APPENDIX IV

Schottky Law, Poole-Frenkel Effect, and Simmons' Defect Model

1) Schottky Effect

The maximum number of electrons per second approaching a barrier with energies high enough to get over the barrier, or what would be the saturation current density in the absence of a field is given by the Richardson-Dushman equation (18).

\[ J_L = AT^2 e^{-\frac{(\phi - \Theta)}{kT}} \]  

where \( \phi - \Theta \) = barrier height as in Fig. 2-1

\( A \) = Richardson's constant

The Schottky effect is the field lowering of the metal/insulator barrier and is calculated by considering the "image force" associated with an electron leaving a metal surface.

\[ \text{Fig. IV-1 Image force in Schottky effect} \]

Under an applied field \( E \), the potential of an electron passing over the barrier is

\[ \psi = \frac{-e^2}{16\pi \varepsilon x} - eEx + (\phi - \Theta) \]  

where \( \varepsilon \) = high frequency permittivity.

A potential maxima occurs when \( \frac{d\psi}{dx} = 0 \)

Then from IV-2, the maxima, \( x_m \) is

\[ x_m = \left( \frac{e}{16\pi \varepsilon E} \right)^{\frac{1}{2}} \]  

The potential at the maxima is from IV-2

\[ \psi(x_m) = (\phi - \Theta) - \left( \frac{e^3}{4\pi \varepsilon} \right)^{\frac{1}{2}} E^2 \]

\[ = (\phi - \Theta) - \alpha E^{\frac{1}{2}} \]  

IV-4
The barrier height is lowered by \( \propto E_F^2 \) as shown in Fig. IV-2.

**Fig. IV-2** Barrier lowering due to Schottky effect

2) Poole-Frenkel Effect

This is analogous to the Schottky effect, except that the coulombic attractive force is supplied by a trapping center, rather than an image force. Thus only particular kinds of defects will show a Poole-Frenkel effect; i.e. one that has a charge when empty. The electron and the positively charged trap are separated by a distance \( x \) rather than the \( 2x \) shown in Fig. IV-1. Carrying through the calculation as before results in the trap barrier being lowered by the amount \( \beta E_F^2(x) \) where \( \beta = 2\alpha \).

Calculation of the conductivity requires assuming some defect structure for the insulator. Mark and Hartman[35] proposed acceptor and donor levels with partial ionization of the donors:

\[
\begin{align*}
\text{Electron energy levels} &:
E_C, E_d, E_F, E_a, E_V \\
\text{Energy levels} &:
E_d = \text{donor energy level} \\
E_a = \text{acceptor level} \\
N_a = \text{acceptor state density} \\
N_d = \text{donor state density}
\end{align*}
\]

**Fig. IV-3** Insulator defect structure

Assuming that most of the ionized donor electrons reside in the acceptor levels, then

\[
N_a \left( \frac{1}{1 + \exp(-(E_F - E_a)/kT)} \right) = N_d \left( 1 - \frac{1}{1 + \exp(-(E_F - E_d)/kT)} \right)
\]
which, for \( N_d > N_a \) gives

\[ E_F = E_d + kT \ln \frac{N_d - N_a}{N_a} \tag{IV-5} \]

The conductivity is given by

\[ \sigma^- = n_c e \mu = N_c e \mu \exp \left( \frac{E_c - E_p}{kT} \right) \tag{IV-6} \]

where \( N_c = \) constant

\( \mu = \) electron mobility

The Poole-Frenkel effect will operate on the donor centers (which are positively charged when empty) to give a conductivity

\[ \sigma^-(x) = \sigma_o \exp \beta \frac{E_P^\beta(x)}{kT} \tag{IV-7} \]

where

\[ \sigma_o = N_c e \mu \left( \frac{N_d - N_a}{N_a} \right) \exp \left( \frac{E_c - E_d}{kT} \right) \tag{IV-8} \]

Simmons\(^{25}\) has proposed a defect structure in which the Poole-Frenkel effect displays a Schottky characteristic.

---

Figure IV-4 Simmons' Defect Model

He assumes that most of the ionized donor electrons reside in the shallow trapping level. Thus

\[ N_d \left( 1 - \frac{1}{1 + \exp \left( (E_F - E_d)/kT \right)} \right) = \frac{N_t}{1 + \exp \left( (E_F - E_t)/kT \right)} \]
\[ N_d \exp\left(\frac{E_F - E_d}{kT}\right) \approx N_t \exp\left(\frac{E_F - E_t}{kT}\right) \]

Thus
\[ E_F = \frac{1}{2}(E_d + E_t) + \frac{1}{2}kT \ln \frac{N_d}{N_t} \quad \text{IV-9} \]

Substituting this into equation IV-6, and allowing for the lowering of the donor barrier by the Poole-Frenkel effect then
\[ \sigma^-(x) = \sigma_o \exp \frac{E^-(x)}{kT} = \sigma_o \exp \frac{E^3(x)}{kT} \quad \text{IV-10} \]

where
\[ \sigma_o = N_c e\mu \left(\frac{N_d}{N_t}\right)^\frac{1}{2} \exp\left(-E_c - \frac{1}{2}(E_d + E_t)\right)/kT \quad \text{IV-11} \]
Zero Field Point and Calculation of Space Charge Decay Currents

It can be simply shown that when there is a trapped negative space charge in the film and the sample is short circuited, the field is zero at some point \( x^* \) in the film (see Fig. 2-4).

Poisson's equation in one dimension is

\[
\frac{dE(x)}{dx} = -\frac{\varepsilon}{\varepsilon} n_t(x)
\]

where \( n_t(x) \) = trapped space charge density.

Integrating from \( x = 0 \), then

\[
E(x) = E(0) - \int_0^x n_t(x) \, dx
\]

From the short circuit condition \( V = 0 \), then

\[
V = -\int_0^L E(x) \, dx = \frac{\varepsilon}{\varepsilon} \int_0^L dx \int_0^x n_t(x) \, dx = E(0) \cdot L = 0
\]

Therefore

\[
E(0) = \frac{\varepsilon}{\varepsilon} \int_0^L dx \int_0^x n_t(x) \, dx > 0
\]

Now it need only be shown that \( E(L) < 0 \) and thus the field will have to be zero at some point \( x^* \) where \( 0 < x^* < L \).

Since \( \int_0^x n_t(x) \, dx \) is an increasing function of \( x \) then

\[
\int_0^L \int_0^x n_t(x) \, dx < L \int_0^L n_t(x) \, dx
\]

From (V-2)

\[
E(L) = E(0) - \frac{\varepsilon}{\varepsilon} \int_0^L n_t(x) \, dx
\]

From equation V-4 and V-5

\[
E(0) < \frac{\varepsilon}{\varepsilon} \int_0^L n_t(x) \, dx
\]

Therefore, from V-6 \( E(L) < 0 \) . QED.

In calculating the space charge discharge currents, the polarization effects of the space charge will be considered. Referring to Fig. 2-5, \( Q_1 \) and \( Q_2 \) are the free charges per unit area on the plates.
Then
\[ \frac{dQ_1}{dt} = J_{\text{ext.}} - J(0) \quad \text{V-7} \]
where \( J(0) \) is the current density at the metal/insulator interface. This current will be due to electrons being released from traps and being swept to the electrode by the space charge field. \( Q_1 \) is given by the displacement vector.
\[ Q_1 = D(0) = \varepsilon_0 E(0) + P(0) \quad \text{V-8} \]
D is related to the space charge by
\[ \nabla \cdot D = -en_t(x, t) \quad \text{V-9} \]
Integrating in one dimension gives
\[ D(x, t) = -e \int_{x^*}^{x} n_t(x, t) dx + P(x^*, t) \quad \text{V-10} \]
where \( D(x^*, t) = P(x^*, t) \) because \( E(x^*, t) = 0 \). The polarization at the zero field point may not be zero because of the polarization caused by fields applied before short circuiting the sample (i.e. \( t < 0 \)). Considering the polarization mechanism discussed in section (2.1) then
\[ P(x^*, t) = P_s(x^*) \int_0^{\infty} e^{-t/x} G(q) dq \quad \text{V-11} \]
where
\[ P_s(x^*) = (\varepsilon_s - \varepsilon_\infty) E(x^*, t < 0) \quad \text{V-12} \]
\( E(x^*, t < 0) \) refers to the static field at \( x^* \) before short circuiting the sample and is given by
\[ E(x^*, t < 0) = \frac{-e}{\varepsilon_s} \int_{x^*}^{\infty} n_t(x, t < 0) dx + E(0, t < 0) \quad \text{V-13} \]
To determine \( J(0) \) in equation V-7, the continuity equation is used. Neglecting recombination (i.e. when an electron is released from a trap it does not get retrapped) then
\[ \frac{dJ(x, t)}{dx} = e \frac{dn_t}{dt} (x, t) \quad \text{V-14} \]
Thus
Thus

\[ J(x,t) = e \int_{x^*}^{x} \frac{d n_t(x,t)}{d t} \, dx \]  

V-15

where

\[ J(x^*, t) = 0 \quad \text{as} \quad E(x^*, t) = 0 \]

From equations V-7 and V-8

\[ J_{\text{ext}} = \frac{d}{d t} D(0) + J(0) \]

Substituting for \( D(0) \) and \( J(0) \) from equations V-10 and V-15 and using V-11 and V-12 then

\[ J_{\text{ext}} = e n_t(x^*, t) \frac{d x^*}{d t} - (\varepsilon_s - \varepsilon_\infty) G(q') \frac{E(x^*, t < 0) kT}{t} \]

\[ - \frac{(\varepsilon_s - \varepsilon_\infty)}{\varepsilon_s} \quad e n_t(x^*, t) \frac{d x^*}{d t} \int_0^\infty \frac{e^{-t/q}}{q} G(q) dq \]  

V-16
APPENDIX VI

Calculation of Zero Field Point and Space Charge Density

The decay of a trapped space charge, neglecting recombination is given by

\[ \frac{dn_t'(x,t)}{dt} = -\nu_0 n_t'(x,t) \exp \left( \frac{E_c - E_t}{kT} \right) \]  

where \( n_t'(x,t) \) is the space charge density/unit energy, centered at an energy level \( E_t \) and \( \nu_0 \) = jump frequency.

Integrating from zero time, then

\[ n_t'(x,t) = n_t'(x,0) e^{-t/\tau(E_t)} \]  

where

\[ \tau(E_t) = \frac{1}{\nu_0} \exp \left( \frac{E_c - E_t}{kT} \right) \]  

Assuming that at \( t = 0 \) the steady state charge distribution \( n_t'(x,0) \) through the band gap can be given by Fermi-Dirac statistics, then

\[ n_t(x,t) = N_t \int_{E_F}^{E_c} \frac{e^{-t/\tau}}{1 + \exp \left( \frac{E_f(x) - E_t}{kT} \right)} \, dE_t \]  

where \( N_t = \) trap density/unit energy

\( E_f(x) = \) quasi-fermi-level

The integration is carried out only above the equilibrium fermi level as this is the region in which the injected space charge resides.

Letting \( a = \exp \left( \frac{E_f(x) - E_c}{kT} \right) \) then

\[ n_t(x,t) = -N_t kT \int_{\frac{t}{\tau(E_t)}}^{\frac{t}{\tau(E_t)}} \frac{e^{-t/\tau}}{\tau(1+a/\nu_0)} \, d\tau \]  

where

\[ \tau(E_t) = \frac{1}{\nu_0} \exp \left( \frac{E_c - E_t}{kT} \right) \]
\[ n_t(x,t) = kTN_t \left\{ Ei\left(-t/\tau\right) - e^{\nu_0 t} \frac{E_F(x) - E_c}{kT} Ei\left(-t/\tau - \frac{\nu_0 t}{a}\right) \right\}^{1/\nu_0} \]

where \( Ei(-\alpha) \) is the exponential integral given by
\[
Ei(-\alpha) = \int_{\alpha}^{\infty} \frac{e^{-\alpha}}{\alpha} d\alpha
\]

Assuming \( E_c/kT \gg E_F(x)/kT \) then
\[ n_t(x,t) = -kTN_t \left\{ Ei\left(-\nu_0 t \left( E_c - E_F^0 \right)/kT \right) - \nu_0 t \ e^{-(E_c - E_F(x))/kT} Ei\left(-\nu_0 t \left( E_c - E_F^0 \right)/kT + e^{-(E_c - E_F(x))/kT} \right) \right\}^{1/\nu_0} \]

The zero field point, \( x^* \), is derived using the short circuit condition, \( V = 0 \).

Thus
\[ V = 0 = -\int_{0}^{L} E(x,t) dx \]

\( E(x,t) \) is given by
\[ E(x,t) = \frac{1}{\varepsilon_0} \left( D(x,t) - P(x,t) \right) \]

where \( D(x,t) \) is given by equation VI-10.

\( P(x,t) \) may be divided into components due to the decay of polarization for fields applied before short circuiting (i.e. Appendix III), the build up of polarization of the type considered in Appendix III due to the space charge field, and to the high frequency polarization component due to the space charge field. Thus
\[
P(x,t) = (\varepsilon_s - \varepsilon_\infty) \ E(x, t < 0) \int_{0}^{\infty} e^{-t/\tau} \ G(q) dq + (\varepsilon_s - \varepsilon_\infty) \ E(x, t) \int_{0}^{\infty} (1 - e^{-t/\tau}) \ G(q) dq + (\varepsilon_\infty - \varepsilon_0) \ E(x,t) \]

\( E(x,t) \) may be determined in terms of \( n_t(x,t) \) from VI-10 and VI-9, using VI-11, VI-12, VI-13 and VI-2, however, it gets very complicated.
and no attempt has been made to derive the time dependence of $x^*$. If it is assumed there is no polarization due to ion movement then equation VI-8 has the simple form

$$0 = \int_0^L dx \int_{x'}^{x} n_t(x,t)dx \quad \text{VI-11}$$
APPENDIX VII

Space Charge Limited Currents

Neglecting diffusion effects, the current density is given by

\[ J_L = n_c e \mu E \]  \hspace{1cm} (VII-1)

where \( n_c \) = free electron density
\( \mu \) = electron mobility

For a perfect crystal, the net charge in the insulator will be free charge and from Poisson's equation

\[ \frac{dE}{dx}(x) = -\frac{e}{\varepsilon} n_c(x) \]  \hspace{1cm} (VII-2)

Thus

\[ J_L = -\varepsilon \mu E(x) \frac{dE(x)}{dx} \]  \hspace{1cm} (VII-3)

Integrating from \( x = 0 \) and assuming \( E(0) = 0 \) then

\[ J_L x = -\frac{\varepsilon \mu}{2} E^2(x) \]  \hspace{1cm} (VII-4)

Thus

\[ V = \int_{0}^{L} E(x)dx = 2/3 \left( \frac{-2J_L}{\mu \varepsilon} \right)^{1/2} L^{3/2} \]  \hspace{1cm} (VII-5)

and

\[ J_L = -\frac{9}{8} \mu \varepsilon \frac{V^2}{L^3} \]  \hspace{1cm} (VII-6)
REFERENCES