SPACE CHARGE AND HIGH FIELD EFFECTS
IN THIN AMORPHOUS FILMS

by

ABDEL HALIM MAHMOUD SHOUSHA

B.Sc., Cairo University, 1965
M.A.Sc., University of British Columbia, 1969

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Research Supervisor...............................

................................................

Members of the Committee.......................

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Members of the Department
of Electrical Engineering

THE UNIVERSITY OF BRITISH COLUMBIA

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Department of Elect. Eng.

The University of British Columbia
Vancouver 8, Canada

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ABSTRACT

The present thesis is concerned mainly with space charge and high field effects on the electrical properties of thin amorphous films.

A theory of space charge contribution to the polarization current in thin dielectric films is proposed. The transient current on short-circuiting a thin dielectric film is believed to consist of two components, one due to the dielectric polarization and the other due to trapped space charge. The space charge contribution is investigated using a model for a film containing distributed traps. Computed results seem to be consistent with experimental results on Ta/Ta$_2$O$_5$/Au diodes, so that space charge effects are more important at low preapplied fields. The applicability of step response techniques to determine low frequency dielectric losses is discussed and the effect of space charge on the dielectric losses is analysed.

The theory of thermoluminescence and thermally stimulated currents is extended to the case of traps with distributed binding energies to investigate the possibility of distinguishing between distributed and discrete trap levels. It seems possible to distinguish experimentally between distributed and discrete traps by using different doses of optical radiation to obtain initially different amounts of trapped charges, and by varying the frequency of optical excitation over a suitable frequency range to allow only certain energy levels to be occupied by excited electrons.

High field electronic conduction through very thin films sandwiched between two metal electrodes is analysed. In view of the fast tunneling time of electrons through very thin films, MIM structures can be used for microwave detection. It is shown that the maximum responsivity-bandwidth product of such detectors is obtained when they are biased at a voltage equal to the anode work function (in volts), and that the presence of invariant positive space charge
increases the magnitude of this maximum.

In considering high field switching in thin films of semiconducting glasses, it is suggested that Joule heating, which could account for the delay times observed experimentally, serves only to initiate an electronic switching mechanism. A model for current-controlled negative resistance due to space charge formation is proposed and its dc characteristics are computed. Carrier injection from the electrodes is taken to occur either by Schottky thermionic emission or a Fowler-Nordheim tunneling mechanism. The injected carriers develop space charge regions near the electrodes by impact ionization. The position dependent generation-recombination rate is discussed. The small ac signal equivalent circuit of the model is given. The formation of current filaments is analysed. Memory devices are discussed in terms of filament formation and phase change mechanisms due to excessive heating.

Filamentary breakdown has been observed in anodic films grown on Ta, Al, Nb and Ti. A detailed experimental study of film growth and the effects of growth conditions, film thickness, counterelectrodes and temperature on breakdown strength has been carried out. A possible mode of breakdown, in which breakdown can result from thermal effects following a non-destructive electron avalanche, is proposed and its limitations are pointed out. It is concluded that breakdown in thin anodic films would occur due to disruption of the chemical bonds as the applied field approaches the formation field. The product of the molecular dissociation and the presence of energetic electrons could start an accumulative process which might end with the formation of a highly conducting channel. The injected electrons, field distortion and thermal runaway could assist in the channel development. Once the channel is developed, the sample's stored energy starts to dissipate through the channel. The voltage collapse has been found experimentally to occur in a time of less than 200 nanoseconds.
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1. INTRODUCTION

1.1 General

Due to their importance in monolithic, hybrid and thin film integrated circuits, thin amorphous films have been a subject of extensive experimental and theoretical studies\textsuperscript{1-3} which have led to an understanding of their properties and much confidence in their use. Their applications in MOS field effect transistors, thin film transistors, switching devices, electrolytic and thin film capacitors and R-C distributed circuits are of increasing importance. A particular application may pose stringent requirements on the film properties, and consequently it may be required to optimize many of the film properties. The study of the properties and a better understanding of the physical processes involved are vital to the improvement of device characteristics and performance.

The performance of a film is greatly affected by its structural properties which in turn, depend on the material and the methods used for its preparation. Experimental analyses of noncrystalline films show clearly the existence of a short range order and equally clear the absence of a long range order in the atom distribution. However, these analyses cannot distinguish between the two essential structural models for amorphous materials\textsuperscript{4,5}. The continuous model assumes that the individual bonds are slightly disordered both in direction and in extension, but that the cumulative effect of this disorder is to produce a complete smearing out of the long range order. This model represents an idealized amorphous continuum which is statistically homogeneous everywhere. The other model considers the amorphous solids as a discontinuous arrangement of crystallites separated by intermediate regions which accommodate the misfits between the crystallites.
These two structural models are really only limiting cases among many models which may represent the actual structure. A unified model can explain all the experimental observations. In this model, the structure is not assumed to be quite uniform but has regions with more or less order on a scale much greater than that of interatomic spacing. In some cases crystallites may be more definite while in others the structure may be closer to a homogenous but irregular network. The transition from one extreme case to the other is gradual and it depends on the material used and preparation techniques.

Theoretical predictions of the energy band diagram and characteristics of amorphous materials differ according to the particular model used. However, since the basic features of the energy band diagram are determined primarily by the short range order, or more precisely by the actual bonds between atoms, the general features of the energy band diagram are preserved in the transition from the crystallite to amorphous states. The disappearance of long range order leads to a new concept, that of localized states. An electron in a localized state can be described as trapped. This means that the absence of long range order produces a high density of traps.

Fig. 1.1 Density of states in a noncrystalline semiconductor, the localized states are shown shaded. In (a) there is an energy gap; in (b) the energy gap disappears.
The energy band gap of amorphous materials either persists or it may be replaced by a minimum in the allowable density of states (pseudogap). For energies near the extremities of the free bands or in the pseudogap, the wave functions become localized and the mobility is much less than that in the free bands of a crystal, typically by some order of magnitude.

It should be stated that there are still many unsolved problems in the quantum theory of amorphous materials (some have recently been pointed out by Mott) and that there are many theoretical disagreements between different authors at the present time.

1.2 Scope of the Present Thesis

This thesis is concerned mainly with space charge and high field effects in thin amorphous films. In Chapter 2, a theory of space charge contribution to polarization currents is given, and the effect of the presence of space charge on dielectric losses is discussed. To investigate the possibility of distinguishing between distributed and discrete trap levels, the theory of thermoluminescence and thermally stimulated currents is extended to the case of traps with distributed binding energies (Chapter 3). In Chapter 4, high field emission and MIM Tunneling diodes as wave detectors are analysed. Chapter 5 deals with high field switching in thin amorphous films. The delay times are analysed in terms of sample self-heating while the switching mechanism is considered electronic in nature. A model for current-controlled negative resistance due to space charge formation is developed. The formation of current filaments and memory devices are discussed. In Chapter 6, detailed experimental and theoretical studies on breakdown in anodic oxide films are presented and a possible mechanism for breakdown is proposed. The main results and conclusions to be drawn from the present thesis are given in Chapter 7.
2. SPACE CHARGE CONTRIBUTION TO
THE POLARIZATION CURRENTS

2.1 Introduction

In considering the polarization processes\(^8,9\) in thin amorphous films, it is reasonable to assume that electronic and elastic ionic displacements* are not essentially changed from those in regular crystals, except that in amorphous films there will be a spread in the characteristic frequencies so that a broader absorption band will be observable in the ultraviolet and infrared range.

Below the infrared range, the polarization processes are relaxation type processes which involve the movement of ions and electrons between energy wells**. In accordance with the nature of amorphous films, the associated activation energies will differ for different ions. Even for a particular ion or electron the force field in which it travels will be rather irregular and accordingly the potential barrier height will vary from one point to another. Thus, one would expect a spread in the characteristic

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* Since electronic and ionic polarization cannot be completely separated because ionic displacement induces electronic displacement, it seems better to characterize polarization as either ultraviolet (solely electronic displacement) or infrared (both electronic and ionic displacement contribute)

** The further mechanism of orientation of molecules with permanent dipoles is unlikely to arise in amorphous films since it is improbable that molecular groups having permanent dipole moments could be incorporated in the film in such a way as to rotate with the field, though the motion of molecular chains may occur as postulated for glasses\(^11\).
frequencies. Another complication could arise from space charge formation (e.g., trap charging and discharging) which is a time dependent process and contributes to the polarization currents. The magnitude and character of the space charge polarization current is determined by the presence of electron traps. In amorphous films, the trap density is expected to be high and to strongly affect the measured polarization current.

Dielectric measurements on several amorphous dielectrics (e.g., SiO$_2$, Ta$_2$O$_5$, Al$_2$O$_3$) have shown that the dielectric constant, $\varepsilon'$, and the loss factor, $\tan \delta$, at room temperature are relatively independent of frequency in the audio range. Several models have been proposed to explain the near constancy of $\varepsilon'$ and $\tan \delta$. Young has used the Maxwell layer model in which there was an exponential dependence of the conductivity on distance into the dielectric film, but it is difficult to account for the required dependence of parameters on film thickness. It seems more likely that film dielectric properties are related to ion or electron hopping processes between energy wells. Argall and Jonscher have discussed electron hopping in relation to SiO films. Maserjian has analysed electron trap to conduction band transitions in connection with Nb$_2$O$_5$ anodic films. Gevers and DuPre have proposed a model, for a dielectric with uniform distribution of activation energies in which ions make field-assisted thermally-activated jumps between contiguous equilibrium sites separated by potential barriers, which has been shown to adequately describe the frequency and temperature dependences of $\varepsilon'$ and $\tan \delta$ of many amorphous dielectrics.

The step response can be related to the ac response by the Fourier transform, if linear dielectric theory applies. Transient measurements have
been used by Hamon\textsuperscript{19} to determine the dielectric losses at very low frequencies. Transient discharge currents observed experimentally typically follow a $1/t^n$ law (e.g., $n=1$ for Ta$_2$O$_5$ and SiO$_2$ films). They have been interpreted as due entirely to the step response of a linear dielectric\textsuperscript{21} or to electronic space charge\textsuperscript{20,22,23}. The polarization current for a linear dielectric is linearly dependent on the preapplied field, while space charge effects are expected to be nonlinear with the preapplied field. Thus, if space charge effects are present, the relaxation function $\phi(t)$ (i.e., the current $I(t)$ as a function of time on removing a unit step voltage) will be a non-linear function of the preapplied field. Thus as Pulfrey, Wilcox and Young\textsuperscript{14} noted, it should be possible to experimentally distinguish between the two possible models (linear dielectric model and electronic space charge model) by using the expected non-linearity in the relaxation function.

In a previous work\textsuperscript{24,25}, the high field electronic conduction for a model of an amorphous dielectric film containing traps with distributed binding energies, has been investigated. Such a model seems relevant to typical thin film dielectrics such as SiO$_2$ and Ta$_2$O$_5$ which are used in microelectronic devices. The injection of electrons at metal/film interface was taken to be governed by Schottky thermionic emission. The space charge density was taken as determined by the balance between detrapping due to the Poole-Frenkel effect and field independent trapping. It was noted that the steady state charge distribution of trapped electrons in this system was the appropriate starting point for an analysis of the effects of electronic space charge on the discharge current obtained by subsequently shorting a film previously held for sometime at constant applied field.

In this chapter, the contribution of both space charge and dielectric
polarization to the external discharge current and their consequence in determining the low frequency dielectric losses using step response measurements are investigated. Space charge effects on the small ac signal dielectric losses are also analysed.

2.2 Analysis of External Discharge Current

On shorting a metal/dielectric/metal structure previously held for some time at constant electric field, the electric field \( E(x,t) \) is taken as changing from \( E(x,-0) \) to \( E(x,+0) \) instantaneously (relative to the long discharge time) resulting in a sudden change in surface charge from \( Q(0,-0) \) to \( Q(0,+0) \). This sudden change will cause a current impulse \( A\delta(t) \) in the external circuit, i.e.,

\[
J_{\text{ext}}(t) = A\delta(t) + J(t)
\]

where

\( J(t) \) is the non impulsive part of \( J_{\text{ext}}(t) \) and \( \delta(t) \) is the dirac delta function.

The continuous discharge current density, \( J(t) \), is due to some long relaxation processes which are dielectric polarization processes and processes associated with the release of trapped space charge.

Fig. 2.1 Metal/amorphous film/metal structure during discharge. (a) Energy band diagram; (b) electric field distribution. Solid lines, negative space charge; broken lines, positive space charge.
Figs. 2.1-a and 2.1-b show an energy band diagram and electric field distribution for a film containing space charge with shorted dissimilar electrodes. Due to the presence of space charge we may find a point, $x^*$, where the field inside the film is zero. In this case, using Gauss' theorem, the time rate of change of the free charge per unit area on the cathode, assuming that the trapped charge density is much greater than the free charge density, is given by

$$\frac{dQ}{dt} = \frac{dD(0,t)}{dt}$$

$$= \frac{d}{dt} \left( \int_{x}^{0} e[N_o(x) - n_t(x,t)]dx + P(x^*,t) \right)$$

And by applying Leibnitz's rule for the differentiation of an integral, we obtain

$$\frac{dQ}{dt} = e[n_t(x^*,t) - N_o(x^*)] \frac{dx^*}{dt} + e \int_{0}^{x^*} \frac{\partial n_t(x,t)}{\partial t} dx + \frac{dP(x^*,t)}{dt}$$

(2.2)

where $D(0,t)$ is the electric displacement at the cathode, $n_t(x,t)$ is the trapped space charge density, $N_o(x)$ is the invariant positive space charge inside the film, $P(x,t)$ is the dielectric polarization and $e$ is the magnitude of the electronic charge.

The conduction current density inside the film at the metal/dielectric interface can be determined by using the current continuity equation

$$\int_{0}^{x^*} \frac{\partial J_{in}(x,t)}{\partial x} dx = e \int_{0}^{x^*} \frac{\partial (n_t(x,t) - N_o(x))}{\partial t} dx$$

Assuming that $J_{in}(x^*,t)$ is negligibly small (since the electric field at $x^*$ equals zero), the above relation reduces to
\[ J_{in}(0,t) = -e \int_0^t \frac{\partial n_t(x,t)}{\partial t} \, dx \]  \hspace{1cm} (2.3)

using Eqs. (2.2) and (2.3) and the continuity equation

\[ J(t) = \frac{dQ}{dt} + J_{in}(0,t) \]

the external discharge current \( J(t) \) can be given by

\[ J(t) = e[n_t(x*,t) - N_0(x*)] \frac{dx^*}{dt} + \frac{dP(x^*,t)}{dt} \]  \hspace{1cm} (2.4)

Thus one can write

\[ J(t) = J_{sc}(t) + J_p(t) \]  \hspace{1cm} (2.5)

where \( J_{sc} \) is the space charge contribution to the external current density and \( J_p \) is the contribution of dielectric polarization processes.

Eq. (2.4) has two limiting cases: first, when space charge density is negligibly small, Eq. (2.4) reduces to

\[ J(t) = J_p(t) = \frac{dP(t)}{dt} \]  \hspace{1cm} (2.6)

And for amorphous films, one can derive an expression for \( J_p \) using a dielectric polarization model with a uniform distribution of activation energies (Sec. 2.3).

Secondly, when space charge predominates, Eq. (2.4) becomes

\[ J(t) = J_{sc}(t) = e[n_t(x*,t) - N_0(x*)] \frac{dx^*}{dt} \]  \hspace{1cm} (2.7)

This case will be considered in some detail in Sec. 2.4.

### 2.3 Polarization Current of a Dielectric with a Uniform Distribution of Activation Energies

The dielectric polarization response to a step field for a model in which ions make field-assisted thermally-activated hops between adjacent equilibrium sites separated by a potential barrier of height \( q \) is given by

\[ J(t) = J_{sc}(t) = e[n_t(x*,t) - N_0(x*)] \frac{dx^*}{dt} \]
\[
\frac{dP}{dt} = \frac{1}{\tau} (P_s - P) \tag{2.8}
\]

where

\[
\tau = \frac{\tau_0}{2} \exp(q/kT) \tag{2.9}
\]

\(\tau_0\) is a constant equal to the inverse of the jump frequency

\(P_s\) is the static polarization

\(k\) is Boltzmann's constant

\(T\) is the temperature

When only one process with activation energy \(q\) is operative, and a sinusoidal field represented by \(E = \dot{E} \exp(j\omega t)\) is applied, the dielectric permittivity, \(\varepsilon(\omega)\), can be obtained by substituting

\[
P(\omega) = (\varepsilon(\omega) - \varepsilon_\infty) \dot{E} \exp(j\omega t)
\]

\[
P_s = (\varepsilon_s - \varepsilon_\infty) \dot{E} \exp(j\omega t)
\]

in Eq. (2.8), where \(\varepsilon_s\) and \(\varepsilon_\infty\) are the values of the dielectric permittivity at zero and infinite frequencies respectively. Thus, we get the Debye equation for the real, \(\varepsilon'(\omega)\), and the imaginary, \(\varepsilon''(\omega)\), components of the dielectric permittivity:

\[
\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{2.11}
\]

\[
\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{2.12}
\]

For amorphous films, the above situation of one site with single activation energy will not be valid and we have to consider many sites with suitable distribution of activation energies \(G(q)\) where

\[
\int_0^\infty G(q) dq = 1 \tag{2.13}
\]

Introducing a certain activation energy \(q_0\), being the value of \(q\) corresponding to the case \(\omega \tau = 1\), i.e.,
\[ \omega = \frac{2}{\tau_0} \exp\left(-\frac{q_0}{kT}\right) \]

Eqs. (2.11) and (2.12) become

\[ \varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q)}{1 + \exp\left(2\frac{q-q_0}{kT}\right)} \, dq \tag{2.14} \]

\[ \varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \frac{G(q) \exp\left(2\frac{q-q_0}{kT}\right)}{1 + \exp\left(2\frac{q-q_0}{kT}\right)} \, dq \tag{2.15} \]

The denominator in the integrand of Eq. (2.14) can be approximated to one for \( q < q_0 \) and to infinity for \( q > q_0 \). Thus, Eq. (2.14) reduces to

\[ \varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^{q_0} G(q) \, dq \tag{2.16} \]

Gevers and Dupré have showed that if a nearly flat distribution of activation energies \( G(q) \) is present in the dielectric then Eq. (2.15) reduces to

\[ \varepsilon''(\omega) = (\varepsilon_s - \varepsilon_\infty) \frac{n}{2} kT G(q_0) \tag{2.17} \]

The polarization current is given by

\[ J_P = \frac{dp}{dt} \tag{2.18} \]

Eqs. (2.8) and (2.18) for a single polarization process, give

\[ J_P = \frac{P_s}{\tau} e^{-t/\tau} \tag{2.19} \]

For a distribution of activation energies, one could write

\[ J_P = \frac{\int_0^\infty G(q) P_s e^{-t/\tau}}{\tau} \, dq \]

Using Eq. (2.9) we get

\[ J_P = P_s kT \int_0^\infty \frac{G(q) e^{-t/\tau}}{\tau^2} \, dt \tag{2.20} \]

Since \( G(q) \) is assumed nearly flat, it may be evaluated at the peak of \( e^{-t/\tau}/\tau^2 \), and taken outside the integral. Eq. (2.20) can be easily integrated to give
\[ J_p = \frac{kT G(q')}{t} P_s \]  
(2.21)

where

\[ q' = kT \ln(t/t_o) \]  
(2.22)

Thus, on removing a polarization field, i.e., \( E = E_o (1 - u(t)) \), the polarization current is given by

\[ J_p = \frac{kT G(q') (\varepsilon_s - \varepsilon_\infty)}{t} E_o \dot{u}(t) \]  
(2.23)

Combining Eqs. (2.17) and (2.23) gives

\[ J_p = \frac{2}{\pi} \frac{\varepsilon''(\omega)}{t} \frac{G(q')}{G(q_o)} E_o u(t) \]  
(2.24)

Again, making use of the assumed flat distribution of activation energies, Eq. (2.24) reduces to

\[ J_p = \frac{2}{\pi} \frac{\varepsilon''(\omega)}{t} E_o u(t) \]  
(2.25)

Thus, the polarization current of the above model follows a law with a linear dependence on the preapplied field.

2.4 Space Charge Polarization Current

2.4.1 Model and Basic Equations

A metal/dielectric film/metal sandwich may be represented by a one-dimensional model in which carriers of one type only, assumed here to be electrons, are considered. In view of the amorphous nature of the film, the trap concentration might be expected to be high in an energy range \( W \) below the conduction band edge. The trap density/unit energy is assumed to be

\[ N_{Wt} = A_t \exp(-\varepsilon_t/NkT) \]  
(2.26)

where \( \varepsilon_t \) is the trap energy measured downwards from the conduction band, and \( A_t \) and \( N \) are constants which define the shape of the distribution of traps with respect to energy.
In the ordinary derivation of the Poole-Frenkel equation, traps which exhibit a coulombic attraction with respect to current carriers (electrons in this case) are necessary\textsuperscript{27}. Thus traps are assumed to be neutral when occupied and positively charged when empty (i.e., they are donors). It seems clear that even with the use of the high frequency permittivity the Poole-Frenkel law (and the Schottky law) are based on no more than semiclassical treatments and are not to be expected to be accurate.

The idea of a simple coulombic force between electrons and either donor traps or metal is not more than a simple convenient approximation. Field enhanced release from acceptor levels (defined as levels which are neutral when emptied of an electron) may conveniently and probably just as accurately be described by the same Poole-Frenkel equation. The actual mixture of donor and acceptor traps is represented by introducing a variable parameter $N_A$, representing the space charge which would exist if all traps were donors and were fully ionized. By varying $N_A$ the range from all donors to all acceptors may be considered, with a corresponding variation in the concentration of electrons in the conduction band, and hence the conductivity, in electrically neutral dielectric.

The electric field distribution in the film is governed by Poisson's equation

\[ \frac{\partial E}{\partial x} = -\frac{e}{\varepsilon} [N_t (1-F(x,t)) - N_A - n_c(x,t)] \quad (2.27) \]

where $E$ is the electric field whose direction is the negative $x$ axis.

$F$ designates the occupation of the whole set of traps.

$n_c$ is the free carrier density.

Let $n_t(x)$ be the filled trap density at position $x$ and $N_0 = N_t - N_A$. 

thus Eq. (2.27) can be simplified to

\[
\frac{\partial E}{\partial x} = \frac{e}{\varepsilon}[n_c(x,t) + n_c(x,t) - N_o(x)] \tag{2.28}
\]

During the transient, the rate of change of charge density is related by the continuity equation

\[
\frac{\partial (n + n_c)}{\partial t} = \mu E \frac{\partial n}{\partial x} + \mu_n \frac{\partial E}{\partial x} - D \frac{\partial^2 n_c}{\partial x^2} \tag{2.29}
\]

where \(\mu\) is the carrier mobility, \(D\) is the diffusion constant.

The rate of change of trapped charge can be obtained from the difference between the rate of electron capture from the conduction band \(r_1\) and the rate of electron release from traps \(r_2\). Considering an infinitesimal range of trap energies between \(\epsilon_t\) and \(\epsilon_t + d\epsilon_t\), the expression for \(r_1\) and \(r_2\) can be written as

\[
r_1 = n_c N_t (1 - f_d) \sigma V_{th} d\epsilon_t \tag{2.30}
\]

where \(\sigma\) is the capture cross section.

\(V_{th}\) is the electron thermal velocity

\(f_d\) is the occupancy factor of a trap such that

\[
F(x) = \frac{\int_{\epsilon_t}^{\epsilon_t + d\epsilon_t} f_d N_t \, d\epsilon_t}{\int_0^{\epsilon_t + d\epsilon_t} N_t \, d\epsilon_t}
\]

The rate \(r_2\) depends upon the concentration of centres which are occupied by electrons and on the electron relaxation time \(\tau\). In the stated model \(\tau\) is given by an expression of the form

\[
\tau = \frac{1}{v} \exp((\epsilon_t - \Delta\epsilon_t)/kT) \tag{2.31}
\]

where \(v\) is the attempt to escape frequency

\(\Delta\epsilon_t\) represents the lowering of the trap barrier height assuming a Poole-Frenkel mechanism.
\[ \Delta \varepsilon_t = \beta_{PF} k T E^{1/2} \]

and

\[ \beta_{PF} = \frac{e}{kT} \sqrt{\frac{e}{\pi \varepsilon}} \]

It is then possible to write

\[ r_2 = N_{wt} f_D \exp\left(-\frac{\varepsilon_t}{kT}\right) \exp(\beta_{PF} E^{1/2}) d\varepsilon_t \] (2.32)

combining Eqs. (2.30) and (2.32), we get

\[ \frac{\partial \Delta n}{\partial t} = n_c N_{wt} (1-f_D) \delta v_{th} d\varepsilon - N_{wt} f_D \delta v_{th} d\varepsilon - N_{wt} f_D \exp\left(-\frac{\varepsilon_t}{kT}\right) \exp(\beta_{PF} E^{1/2}) d\varepsilon_t \] (2.33)

Assuming that most of the trapping takes place between the thermal equilibrium level \( \varepsilon_{fo} \) and quasi fermi level \( \varepsilon_{fn} \) such that \( f_D \) equals one over the energy range between \( \varepsilon_{fo} \) and \( \varepsilon_{fn} \) and equals zero elsewhere, and since \( \varepsilon_{fo} \gg NkT \), one may take \( \varepsilon_{fo} \) equal to infinity, and the integration of Eq. (2.33)

yields

\[ \frac{\partial n}{\partial t} = n_c \delta v_{th} [\int_0^{\infty} N_{wt} d\varepsilon_t - \int_{\varepsilon_{fn}}^{\infty} N_{wt} d\varepsilon_t] - \exp(\beta_{PF} E^{1/2}) \int_{\varepsilon_{fn}}^{\infty} N_{wt} \exp\left(-\frac{\varepsilon_t}{kT}\right) d\varepsilon_t \]

Substituting for \( N_{wt} \) form Eq. (2.26) the above equation reduces to

\[ \frac{\partial n}{\partial t} = n_c \delta v_{th} (N_t - n_t) - \frac{\nu N_t}{1+N} \frac{n_t}{N_t} \exp(\beta_{PF} E^{1/2}) \] (2.34)

We are now in position to solve Poisson's equation (Eq. (2.28)), thus giving an expression for the voltage drop across the film, namely

\[ \int_0^d E(x,t) dx = (\phi_2 - \phi_1)/e \] (2.35)

where \( \phi_1 \) and \( \phi_2 \) are the work functions of the two electrodes.

Finally the external space charge polarization current is given by

\[ J_{sc} (t) = e(n_t(x^*,t) - N_0(x^*)) \frac{dx^*}{dt} \] (2.36)
2.4.2 Normalized Equations

If the normalized variables

\[ x_n = x/d, \quad E_n = E/(\varepsilon N d), \quad \phi_n = \varepsilon (\phi_2 - \phi_1)/e^2 d^2 N_t \]

\[ n_{tn} = n_t/N_t, \quad n_{cn} = n_c/N_c, \quad N_{on} = N_o/N_t \]

\[ \sigma_n = \sigma v N_t (1+N)/\nu, \quad \mu_n = e\mu N_t (1+N)/\varepsilon \nu, \quad J_{scn} = J_{sc} (1+N)/\ve N_t d \]

are substituted in Eqs. (2.28) (2.29), (2.34), (2.35) and (2.36), we get

\[ \frac{\partial E_n}{\partial x_n} = n_{tn} + n_{cn} - N_{on} \quad (2.37) \]

\[ \frac{\partial n_{tn}}{\partial t_n} = \sigma_n n_{cn} (1-n_{tn}) - (n_{tn})^{1+N} \exp(C_1 E_n^{1/2}) \quad (2.38) \]

\[ - \frac{\partial (n_{tn} + n_{cn})}{\partial t_n} = \mu_n E_n \frac{\partial n_{cn}}{\partial x_n} + \mu_n n_{cn} (n_{tn} + n_{cn} - N_{on}) - c_2 \mu_n \frac{\partial^2 n_{cn}}{\partial x_n^2} \quad (2.39) \]

\[ \int_0^1 E_n \, dx_n = \phi_n \quad (2.40) \]

\[ J_{scn} = (n_{tn} (x*, t_n) - N_o (x_n)) \frac{dx_n}{dt_n} \quad (2.41) \]

where

\[ C_1 = \beta_{PP}(e N_t d/\varepsilon)^{1/2} \quad \text{and} \quad C_2 = \varepsilon D/(e\mu N_t d^2) \]

2.4.3 Method of Solution

Finite difference methods \cite{28,29} were used to solve the above equations. The partial differential equations are approximated by finite difference equations through the transformation scheme below. The values of a variable \( y(x,t) \) are then determined at a discrete mesh of points in \((x,t)\) space.
The derivatives of the quantity \( y(x,t) \) are approximated by

\[
\frac{\partial y(x,t)}{\partial x} = \frac{y(x+h,t) - y(x-h,t)}{2h}
\]

\[
\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{y(x+h,t) - 2y(x,t) + y(x-h,t)}{h^2}
\]

\[
\frac{\partial y(x,t)}{\partial t} = \frac{y(x,t+k) - y(x,t)}{K}
\]

Thus, Eq. (2.38) becomes

\[
n_{\text{tn}}(x,t+k) = n_{\text{tn}}(x,t) + k \sigma_n n_{\text{cn}}(x_n,t_n)[1-n_{\text{tn}}(x_n,t_n)] - k[n_{\text{tn}}(x_n,t_n)]^{1+N} \exp(c_1 \sqrt{E_n})
\]

Combining Eqs. (2.38) and (2.39), we get

\[
[n_{\text{tn}}(x_n,t_n)]^{1+N} \exp(c_1 \sqrt{E_n}) = n_{\text{cn}}(x_n-h,t_n)[ - \frac{\mu_n E_n(x_n,t_n)}{2h} - \frac{c_2 \mu_n}{2h}]
\]

\[
+ n_{\text{cn}}(x_n,t_n)[- \frac{1}{k} + \sigma_n (1-n_{\text{tn}}(x_n,t_n)) + \frac{2 \mu_n c_2}{h^2}]
\]

\[
+ \mu_n[n_{\text{tn}}(x_n,t_n)+n_{\text{cn}}(x_n,t_n)-N_{\text{on}}] + \frac{\mu_n E_n(x_n,t_n)}{2h} - \frac{c_2 \mu_n}{h^2}
\]

\[
+ n_{\text{cn}}(x_n+h,t_n)[\frac{\mu_n E_n(x_n,t_n)}{2h} - \frac{c_2 \mu_n}{h^2}]
\]

\[
+ n_{\text{cn}}(x_n,t_n+k)/K
\]

For high resistivity materials with high trap density, free carriers can be neglected with respect to trapped charges. Thus, Eq. (2.44) can be reduced to a system of linear equations whose matrix has all its elements equal to zero except those in the main diagonal and on the two adjacent diagonals. Such a system of equations can be solved for a known distribution of trapped charge to determine the free carrier concentration \( n_{\text{cn}}(x_n,t_n) \) without pivoting. Once \( n_{\text{tn}}(x_n,t_n) \) and \( n_{\text{cn}}(x_n,t_n) \) were determined Eq. (2.43)
was used to determine \( n(x_n, t_n + k) \). The field distribution \( E_n(x_n, t_n) \) was obtained by integrating Poisson's equation (Eq. (2.37)).

\[
E_n(x_n, t_n) = E_n(0, t_n) + \int_0^x (n_{tn} - N) \, dx
\]  

(2.45)

The integration was evaluated using Simpson's rule, and \( E_n(0, t_n) \) was determined from

\[
E_n(0, t_n) = \phi_n - \int_0^1 \int_0^n (n_{tn} - N) \, dx' \, dx
\]  

(2.46)

The zero field point was determined by interpolation and the external current is readily obtained using Eq. (2.41).

2.4.4 Results and Discussion

The distribution of trapped charge which builds up during the application of a dc electric field depends on the physical mechanisms involved. A possible distribution may be estimated using one of the various models for space charge limited electronic conduction. The distribution assumed in the present study is based on the model discussed in references 24 and 25.

Figs. 2.2 and 2.3 were computed for the case where all trapped charges were in excess of electrical neutrality. The computed results show that the external electronic currents obey, after some initial time, a \( 1/t^n \) law, i.e.,

\[
J_{sc} = K_{sc}/t^n
\]  

(2.47)

where \( n \) is a constant very close to one. The magnitude of \( K_{sc} \) depends on the initial spatial trapped charge distribution. However, for a given distribution but with different initial amount of trapped charge, \( K_{sc} \) tends to the same value (Fig. 2.2) since the spatial distributions tend to be the same (Fig. 2.4).
Fig. 2.2 Space charge polarization currents for exponential spatial distribution of trapped charges.

Fig. 2.3 The effect of capture cross section on space charge polarization current.
Fig. 2.4 Decay of trapped charges inside a film having constants of Fig. 2.2. Solid lines, \( C = 0.5 \); dotted lines, \( C = 0.2 \).

Fig. 2.5 Time dependence of trapped charges. Solid lines, computed for a film having constants of Fig. 2.2 with \( C = 0.2 \); broken lines computed for a film having constants of Fig. 2.3 with \( \sigma_n = 0.01 \).
The local spatial rate of release from traps may be approximated, in some stage of the discharge, by a 1/t law (Fig. 2.5). Such time dependence can be derived, under simplified conditions, using the present model. Eq. (2.38) neglecting \( \sigma_n \) and \( c_1 \), can be reduced to

\[
\frac{dn_n}{dt_n} = -(n_n(0))^{1+N}
\]

and thus

\[
n_n(t_n) = \frac{n_n(0)}{\sqrt{1+N \int_0^t n_n(0)}}
\] (2.48)

differentiating Eq. (2.48), and assuming \( N >> 1 \), we may get

\[
\frac{dn_n}{dt_n} = \frac{-(n_n(0))^{1+N}}{(1+N \int_0^t n_n(0))}
\] (2.49)

now if \( N t_n n_n(0) >> 1 \), Eq. (2.49) reduces to

\[
\frac{dn_n}{dt} = \frac{-n_n(0)}{N t}
\]

However, a local spatial rate of release from traps obeying a 1/t law does not necessarily result in an external current obeying the same law and the current may even be identically zero. To observe any external current the spatial distribution must vary with time (i.e., \( n_t(x,t) \neq n_1(x)n_2(t) \)) in such a way that the rate of change of the zero field point exists (Fig. 2.6).

Fig. 2.7 shows the time dependence of \( x^* \) and \( n_{tn}(x^*,t_n) \) for an exponential initial trapped charge distribution. The variation of \( n_{tn}(x^*,t_n) \) is small over a long time and may be considered constant in calculating the external current. The zero field point may be given by

\[
x^* = A \ln(t/t_0)
\] (2.50)

and thus

\[
\frac{dx^*}{dt} = \frac{A}{t}
\] (2.51)
Fig. 2.6 Variation of trapped charge density and field with position in a film having constants of Fig. 2.3 with $\sigma_n = 0.01$.

Fig. 2.7 Time dependence of $x^*$ and $n_t(x^*, t)$ for a film having constants of Fig. 2.2.
where $A$ and $t_0$ are constants. However, since there is no simple way to derive an expression for $x^*(t)$, which depends directly on the shape of the spatial distribution of trapped charges, it will be postulated that to have an external current obeying a $1/t$ law the zero field point must change its position logarithmically with time (Eq. (2.50)).

For the case where invariant positive space charge is present and the initial amount of trapped electrons is such that the net charge inside the film is positive, more electrons will be trapped to achieve neutrality and thus the zero field point will move towards the cathode (Fig. 2.8b). In this case, an almost time-independent external current will result (Fig. 2.8a).

The effect of some model parameters was studied. Computed results show that the external space charge currents increase with increase of capture cross section (Fig. 2.3), diffusion constant or inverse of carrier mobility (not shown in Fig. 2.3). As expected, the magnitude of external current depends on the difference between the two metal work functions (Fig. 2.9). These results can be explained in terms of the relative changes in the spatial trapped charge distribution. A slowly varying spatial distribution results in a low value for the rate of change of the zero field point and thus small external current. Different rates can result from differences in free carrier concentration. For higher carrier concentration, one would expect faster changes in the spatial distribution and thus higher currents.

In concluding this section, we postulate that space charge polarization currents can follow a $1/t$ law, i.e., $J_{sc} = K_{sc}/t$ and that $K_{sc}$ divided by preapplied field is a decreasing function of preapplied field.
Fig. 2.8 The effect of the presence of invariant positive space charge.
(a) Space charge polarization current; (b) variation of trapped charge density and field with distance inside film.

Fig. 2.9 The effect of metal work function on space charge polarization current.
2.5 Experimental Procedures and Results

2.5.1 Tantalum Preparation

Both single crystals and sputtered β tantalum on Corning 7059 glass substrates were used. The single crystals were electropolished in a bath of 90% (by volume) \(\text{H}_2\text{SO}_4\) (98% reagent) and 10% HF (48% reagent) using a current density of about 100 mA/cm\(^2\) for about 10 minutes. Sputtered tantalum samples were degreased by immersion in sulphuric acid saturated with potassium dichromate.

2.5.2 Anodization of Tantalum

a. Solution Anodization

Tantalum samples were anodized in 0.5% by volume sulphuric acid at room temperature first by applying a constant current density (0.5 mA/cm\(^2\)) until a predetermined voltage was reached. The terminal voltage was then left on the sample for periods up to 12 hours.

b. Plasma Anodization

Plasma anodization of a tantalum single crystal was carried out in a dc glow discharge in the apparatus described in Reference 30 at a sample temperature of 35°C and in the negative glow of the discharge. The oxygen pressure was 80 mtorr and anodization was carried out at constant current density.

The thickness of the grown film was estimated using the spectrophotometric method described in Reference 3 making no allowance for the difference in substrate.
2.5.3 Deposition of Counterelectrodes

Counterelectrodes of gold dots were evaporated using photo-etched beryllium copper masks and a shutter in a conventional bell jar system (Veeco 400) which employed a diffusion pump and liquid nitrogen trap. Typically, the background pressure inside the vacuum belljar was about $10^{-5}$ torr or better. 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. Diameters of evaporated dots were measured by a travelling microscope and their areas were estimated by using bridge measurements at 1000 Hz and assuming $\varepsilon_r = 27.6$ for solution-grown films and $\varepsilon_r = 18$ for plasma grown films.

2.5.4 Electrical Measurements

Step response currents were measured by using a Keithley type 417 high speed picoammeter (accuracy: $\pm 3\%$ full scale for all ranges except the lowest, which is $\pm 5\%$). A Moseley 7100 BM strip chart recorder, connected to the output of the Picoammeter, was used for mapping the current transient.

Capacitance and dissipation factors were measured in a 3 terminal connection using a GR 1615A capacitance bridge in the frequency range 100 Hz-100 kHz. The GR 1615A is a transformer arm ratio bridge with the following rated accuracies

$$C_{\text{meas}} = C + 2 \times 10^{-5} \frac{f}{\text{kHz}}\% + 2 \times 10^{-3}(C/\mu\text{f})(f/\text{kHz})^2\%;$$

$$D_{\text{meas}} = D + 0.1 \times (D_{\text{meas}})\% + 0.001$$

All measurements were carried out in air at room temperature with the sample inside a grounded, light tight metal box. Electrical contacts
to the electrodes were made by using gold plated beryllium-copper springs mounted on Kulicke and Soffa micromanipulators.

2.5.5 Experimental Results

To avoid the superposition of the transient current and the dc conduction current, the technique used was to measure the current upon removal of the applied electric field. The initial transient current, $A\delta(t)$, can be neglected for $t > 1$ sec. since the time constant of the measuring circuit is much less than 1 sec. (the sample capacitance was of the order of $10^3$ pf and the input resistance of the picoammeter used increases from $10^2\Omega$ in the $10^{-5}$A range to $10^{10}\Omega$ in the $10^{-13}$A range in the decade steps).

Fig. 2.10 shows the discharge currents as a function of time with the preapplied voltage as a parameter for a plasma grown film. The discharge currents can be approximated by

$$J(t) = \eta(E) E/t^n$$

(2.52)

where $\eta(E)$ is a proportionality constant and is a function of the preapplied field, $E$ is the average preapplied field ($= V/d$) and $n$ is a constant close to one.

The quantity $\eta(E)$ is independent of time and should not vary with the preapplied field if space charge is absent. Fig. 2.11 shows $\eta(E)$ for several films prepared by different procedures. The observed nonlinearity can be explained in terms of the presence of trapped space charge. The dotted curve in Fig. 2.11 was drawn for $\eta(E)$ given by

$$\eta(E) = 0.65 + 0.8/E$$

(2.53)

Now, if space charge polarization current is almost independent of preapplied field or, at least, increases less than linearly with preapplied field (Sec. 2.4), the second term in Eq. (2.53) may be attributed to the release of trapped charges while the first term could be due to the dielectric polarization processes.
**Fig. 2.10** Discharge currents versus time as a function of preapplied voltage. (Ta-positive).

**Fig. 2.11** Discharge currents as function of field for films prepared by different procedures (Ta-positive).
2.6 The Applicability of Step Response Method

2.6.1 Step Response Method

Step response measurements are often regarded as a suitable means for obtaining dielectric losses at very low frequencies (less than $10^{-2}$ Hz) at which ac bridge measurements are tedious or impractical. If linear response theory holds, then $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are linked to the relaxation function $\phi(t)$ as follows:

$$
\varepsilon'(\omega) = \frac{1}{C_o} \left[ C_{\infty} + \int_0^\infty \phi(t) \cos \omega t \, dt \right] \tag{2.54}
$$

$$
\varepsilon''(\omega) = \frac{1}{C_o} \left[ \frac{C}{\omega} + \int_0^\infty \phi(t) \sin \omega t \, dt \right] \tag{2.55}
$$

where

- $C_{\infty}$ is the capacitance of the sample at very high frequencies.
- $C_o$ is the capacitance of the electrodes when the sample is replaced by air.
- $G$ is the steady state dc conductance.

The relaxation function $\phi(t)$ for many materials at fixed temperature obeys the relation

$$
\phi(t) = A t^{-n} \tag{2.56}
$$

where $A$ and $n$ are constants. Using this expression for $\phi(t)$ in Eqs. (2.54) and (2.55), we may get

$$
\varepsilon'(\omega) = \frac{1}{C_o} \left[ C_{\infty} + A \omega^{n-1} \Gamma(1-n) \cos(1-n) \frac{\pi}{2} \right] 0 < n < 1 \tag{2.57}
$$

$$
\varepsilon''(\omega) = \frac{1}{C_o} \left[ \frac{C}{\omega} + A \omega^{n-1} (1-n) \cos \frac{n\pi}{2} \right] 0 < n < 2 \tag{2.58}
$$

The dielectric loss can be expressed in terms of the relaxation function at a particular time $t_i$ as

$$
\varepsilon''(\omega) = \frac{\phi(t_i)}{\omega C_o} + G/\omega C_o \tag{2.59}
$$
provided that $\omega$ and $t_i$ are related by
\[ \omega t_i = \left[ \Gamma(1-n) \cos(n\pi/2) \right]^{-1/n} \tag{2.60} \]

Hamon$^{13}$ has shown that the right hand side of Eq. (2.60) is almost independent of $n$ in the range $0.3 < n < 1.2$, having the mean value 0.63 with an accuracy of $\pm 3\%$, i.e.,
\[ \omega = 0.63/t_i \]

If discharge currents are considered, then the conduction current is zero and thus, Eq. (2.59) can be written as
\[ \varepsilon''(\omega) = \frac{J(0.63/\omega)}{\omega \varepsilon_0 \varepsilon'} \]
or
\[ \varepsilon''(\omega) = \frac{J(0.63/\omega)}{\omega \varepsilon_0 E} \tag{2.61} \]

Eq. (2.61) was used by Hamon for the rapid evaluation of loss factor at very low frequencies.

2.6.2 Space Charge Effects

In deriving the above equations, it has been assumed that the superposition principle holds. Thus, if space charges are present, the applicability of Hamon's method may be violated. Fig. 2.12.b shows the frequency dependence of $\varepsilon''$ for 1050 $\AA$ solution grown film on sputtered tantalum. The high frequency points are those obtained by direct ac bridge measurements while the low frequency points were calculated from step response measurements and Eq. (2.61). The equation of the solid line is given by
\[ \log_{10}(\varepsilon_0 \varepsilon''/\varepsilon) = 1.42 - 0.09 \log_{10}(\varepsilon/\text{Hz}) \]

The observed nonlinearity between the discharge current and pre-applied field results in field-dependent values for calculated dielectric
Fig. 2.12 Low frequency dielectric losses. (a) The effect of pre-applied field on the calculated dielectric losses using step response measurements, (b) comparison of bridge and step response results.
losses (Fig 2.12a). However, the dielectric losses become field-independent for relatively high fields and may be extrapolated from their high frequency values. The apparent applicability of step response procedures at high preapplied fields gives us more evidence that space charge polarization currents are only appreciable at low preapplied fields. It is to be noted, however, that the directly measured dielectric losses may be affected by the presence of a dc biasing voltage and their values may be significantly different from the small ac signal values.

2.7. Space Charge Effects on the Small Ac Signal Dielectric Losses

The carrier transport equation and Poisson's equation can be written, neglecting diffusion, as

\[ J_c(x,t) = e\mu n_c(x,t)E(x,t) \]  \hspace{2cm} (2.62)

\[ J(t) = J_c(x,t) + \varepsilon_d \frac{\partial E(x,t)}{\partial t} \]  \hspace{2cm} (2.63)

\[ \frac{\partial E(x,t)}{\partial x} = \frac{e}{\varepsilon_d}[n_t(x,t) + n_c(x,t) - N_0(x)] \]  \hspace{2cm} (2.64)

\[ \int_0^d E(x,t)dx = V(t) \]  \hspace{2cm} (2.65)

where

- \( J_c \) and \( J \) are the conduction and the total current whose direction is the negative \( x \) axis.
- \( E \) is the electric field whose direction is the negative \( x \) axis.
- \( V \) is the total applied voltage including the difference between the two metal work functions.
- \( \varepsilon_d \) is the dielectric constant.
  \[ \varepsilon_d = \varepsilon'' - j\varepsilon' \]

For an applied ac small signal superimposed on a dc bias, i.e.,
\[ V(t) = V_o + \tilde{v} \exp(j\omega t) \quad \tilde{v} \ll V_o \]  

(2.66)

and making the conventional small ac signal approximations:

\[ y(x,t) = Y_o(x) + \tilde{y}(x) \exp(j\omega t) \]  

(2.67)

where \( y \) represents anyone of the above physical quantities, Eqs. (2.63), (2.64) and (2.65) reduce to

\[
\frac{\partial \tilde{e}(x)}{\partial x} = \frac{e}{\varepsilon_d} \left[ \tilde{n}_t + \tilde{n}_c \right] 
\]  

(2.69)

\[
\int_0^d \tilde{e}(x) dx = \tilde{v} 
\]  

(2.70)

Eq. (2.68) can be integrated to yield

\[
\int \frac{d}{d} \tilde{J}(x) dx = e\mu \left[ \int_0^d \tilde{n}_c E_0 dx + \int_0^d n_c \dot{\tilde{e}} dx + j\omega \varepsilon_d \tilde{v} \right] 
\]  

(2.71)

The variation in trapped charge density, \( \tilde{n}_t(x) \), can be determined from the equation governing the carrier release from traps. Eq. (2.34) can be written, neglecting \( c_1 \), as

\[
\frac{\partial n_t(x,t)}{\partial t} = n_c \sigma v_{th} (N_t - n_t) - \frac{N_t n_t}{1 + N} \]  

(2.72)

which, with the help of Eq. (2.67), gives

\[
\tilde{n}_t = \frac{\tilde{n} \sigma v_{th} (N_t - n_{to})}{\sigma v_{th} n_{co} + v(n_{to}/N)^N} + j\omega \]  

(2.73)

\[
\frac{\Delta}{\beta + j\omega} \tilde{n}_c 
\]  

where

\[
\alpha = \sigma v_{th} (N_t - n_{to}) 
\]  

and

\[
\beta = \sigma v_{th} n_{co} + v(n_{to}/N)^N 
\]
Thus, Poisson's equation becomes

\[
\frac{d\tilde{\varepsilon}}{dx} = \frac{e}{\varepsilon_d} [\tilde{n}_c + \frac{\tilde{n}_c}{\beta + j\omega}]
\]

\[
= \frac{e}{\varepsilon_d} \tilde{n}_c [1 + \frac{\alpha(\beta - j\omega)}{\beta^2 + \omega^2}]
\]

and thus,

\[
\tilde{\varepsilon}(x) = \frac{e}{\varepsilon_d} \int_0^x \tilde{n}_c [1 + \frac{\alpha(\beta - j\omega)}{\beta^2 + \omega^2}] \, dx
\]  

(2.75)

Eq. (2.71) can now be written as

\[
\tilde{J}_d = e\mu_0 \int_0^x \tilde{n}_c E_0 \, dx + \frac{e}{\varepsilon_d} \int_0^x \tilde{n}_c \int_0^x \tilde{n}_c (x') [1 + \frac{\alpha(\beta - j\omega)}{\beta^2 + \omega^2}] \, dx' \, dx
\]

\[
+ j\omega(\varepsilon'_d - j\varepsilon''_d) \tilde{\nu}
\]

\[
\lambda = j\omega(\varepsilon' - j\varepsilon'') \tilde{\nu}
\]

(2.76)

For the limiting cases where there is no phase difference between the different physical quantities, i.e., when the applied signal frequency tends to zero or infinity, the dielectric losses may be written as

\[
\varepsilon''(\omega) = \varepsilon''_d(\omega) + \frac{1}{\omega \tilde{\nu}} [e\mu_0 \int_0^x \tilde{n}_c E_0 \, dx + \frac{e\varepsilon'_d}{\varepsilon_d} \int_0^x \tilde{n}_c \int_0^x \tilde{n}_c (x') [1 + \frac{\alpha \beta}{\beta^2 + \omega^2}] \, dx' \, dx]
\]

(2.77)

The above equation shows clearly that the dielectric losses increase as the dc field and/or trapped charge density increase (Fig. 2.13). Further, the effect of trapped charge is frequency dependent and tends to zero as the frequency tends to infinity.
2.8 Discussion

Space charge contribution to polarization currents is mainly determined by the nature and magnitude of localized energy states inside the film which act as electron traps. Electron traps could be neutral, positively or negatively charged when unoccupied. Experimental studies on electronic conduction through thin amorphous films indicate that conduction currents may be governed by Poole-Frenkel mechanism. Thus, one would expect that most traps are charged type traps so that they would be able to exhibit the Poole-Frenkel mechanism. If this were true then current carriers would not get trapped when the applied field is sufficiently high, i.e., trapped charge density may decrease with increasing preapplied field. Even if the
present traps are neutral, there is an upper limit for trapped charge
density determined by the available traps inside the film. The present
computed space charge polarization currents show that these currents,
after some initial time, do not depend on the initial amount of trapped
charges since they relax to almost the same spatial distribution. If one or
the other of the above conclusions were true, it would be reasonable to
expect that the magnitude of space charge polarization current divided by
preapplied field should diminish as the preapplied field is increased, i.e.,

$$\lim_{E \to E_c} J_{sc} E \to 0$$

On the other hand, linear dielectric theory predicts a linear
dependence of dielectric polarization current on the preapplied field, i.e.,

$$\frac{J_p}{E} = \frac{K_p}{t}$$

The above discussion indicates that space charge currents can
constitute an appreciable part of the external discharge current when the
preapplied field is sufficiently low; and there is a critical field above
which the external current is mainly due to dielectric polarization
processes, i.e.,

$$J(t) = J_p + J_{sc} \quad E < E_c$$

while

$$J(t) = J_p \quad E > E_c$$

The observed nonlinear dependence on preapplied field of the external discharge
currents and the validity of step response procedures to determine low frequency
losses only at high preapplied fields gives us some evidence which confirms
the above conjecture.
3. TRAP DETECTION
THERMALLY STIMULATED CONDUCTIVITY AND LUMINESCENCE

3.1 Introduction

As pointed out in the previous chapter, the presence of traps is the main cause for the build up of space charge in dielectric films. The nature and density of traps depend on the film structure. Traps could be an intrinsic property of amorphous solids as discussed in Sec. 1.1. In addition, the presence of impurities and the nonstoichiometric composition of some thin films (especially compound materials) could introduce more trapping states. A trap density of the order of $10^{18}$ cm$^{-3}$ is not unexpected in thin amorphous films.

Traps in crystalline materials, due to impurities or defects, occupy one or more discrete energy levels in contrast to amorphous materials where one can have a continuum of energy levels. In each of these levels, the electron is trapped and unable to move unless it receives sufficient thermal energy to release it. Trapped electrons can not tunnel from one trap to another, otherwise the trapped electrons would have finite mobility. Mott has shown that, if two states are close enough together for tunneling, they split into two states which do not have the same energy. It would be interesting to be able to distinguish experimentally between distributed and localized trap levels.

One of the most common methods for determining electron trap parameters and trapping kinetics is the thermal glow method, including thermoluminescence and thermally stimulated current. In the glow method, the sample is excited by ultraviolet radiation at low temperature such that electrons in the valence band and bound states are excited to the conduction
band. The excited electrons may recombine with holes either directly or at recombination centers, or may become trapped. Then, if the sample is warmed up at constant heating rates, electrons will be expelled from traps into the conduction band. Once in the conduction band, the excess free electrons could result in an increase of sample electrical conductivity or, in the case of luminescent materials, the free electrons could reach luminescence centers at which they recombine radiatively. By postulating an appropriate model, expressions can be derived to determine trap parameters from the experimentally observed glow curves. Most models, if not all, have assumed one or more of the following assumptions: 36-38

1. Traps occupy a single energy level (i.e., monoenergetic traps)
2. Retrapping processes are neglected or, only the limiting cases of slow and fast retrapping are considered.
3. The rate of disappearance of electrons due to recombination may be described by a constant recombination time $\tau$.
4. The neutrality condition is preserved.

The purpose of the present chapter is to study the glow curves for a material containing electron traps with distributed binding energies, and thus to determine their basic features which can be utilized experimentally to identify trap distribution. To this end, the effects of different model parameters on the glow curves are investigated for both monoenergetic traps and exponentially distributed traps.

3.2 Basic Equations

Analysis similar to that given in Sec. 2.3, gives for the rate of change of trapped charge density the following relation:
\[
\frac{dn_t}{dt} = n_c s v_{th} \left[ \int_0^\infty N_{Wt} d\varepsilon_t - \int_{\varepsilon_{fn}}^\infty N_{Wt} d\varepsilon_t \right] - v_{fn} N_{Wt} \exp(-\varepsilon_t / kT) d\varepsilon_t, \tag{3.1}
\]

where

- \( n_c \) is the free electron density.
- \( n_t \) is the trap density unit energy.
- \( \varepsilon_t \) is the trap energy measured downwards from the conduction band.
- \( s \) is the capture cross section.
- \( v_{th} \) is the electron thermal velocity.
- \( v \) is the attempt to escape frequency.

The rate of change of free electrons, assuming a constant recombination time \( T \), may be written as

\[
\frac{dn_c}{dt} = \frac{n_c}{T} - \frac{dn_t}{dt} \tag{3.2}
\]

The solution of Eq. (3.2) is given by

\[
n_c = \int_0^t dt' \left[ \frac{dn_t}{dt'} \exp\left(\frac{t' - t}{\tau}\right) \right] - T \frac{dn_t}{dt} \tag{3.3}
\]

The approximation adopted in Eq. (3.3) is a good approximation whenever the recombination time is sufficiently short, such that \( dn_c / dt < n_c / \tau \).

The resultant conductivity, \( \sigma \), is given by

\[
\sigma = n_c e\mu \tag{3.4}
\]

Where \( e \) is the electronic charge and \( \mu \) is the electron mobility. Combining Eqs. (3.3) and (3.4), we get

\[
\sigma = -e\mu \tau \frac{dn_t}{dt} \tag{3.5}
\]

A similar equation has frequently been used for thermoluminescence intensity,

\[
I = -c \frac{dn_t}{dt} \tag{3.6}
\]
where $I$ is the thermoluminescence intensity and $c$ is a proportionality constant.

Define a new variable, $G$, given by

$$G = \sigma/e^{\mu t} \quad (3.7a)$$

or

$$G = I/c \quad (3.7b)$$

In the glow method, the temperature is usually increased linearly with time, i.e.,

$$T = T_0 + \beta t \quad (3.8a)$$

or

$$dT = \beta dt \quad (3.8b)$$

Eqs. (3.1), (3.3), (3.5 or 3.6) and (3.8) can be solved simultaneously to determine the shape of glow curves (i.e., $\sigma$ vs. $T$ or $I$ vs. $T$).

3.3 Analytical Solutions

3.3.1 Monoenergetic Traps

In this case, all present traps are located at a single energy level $\xi_t$ eV below the conduction band, i.e.,

$$N_{Wt} = N_t \delta(e_t - \xi_t) \quad (3.9)$$

where

- $N_t$ is the trap density
- $\delta$ is the Dirac delta function

Combining Eqs. (3.1), (3.3), (3.8) and (3.9), we get

$$\frac{dn'_t}{dt} = -\frac{\nu n'_t \exp(-\xi_t/kT)}{\beta 1 + \alpha(1-n'_t)} \quad (3.10)$$

where
\[ \text{n}_t' \text{ is the normalized trapped charge density} \]
\[ = \frac{n_t}{N_t} \]
\[ \alpha = \tau s V_{th} N_t \]

Eq. (3.10) can be solved analytically for some limiting cases.

a. **Slow Retrapping** (\( \alpha << 1 \))

Eq. (3.10) can thus be reduced to

\[
\frac{dn_t}{dt} = -\frac{\nu}{\beta} n_t \exp\left(-\frac{\xi_t}{kT}\right) \tag{3.11}
\]

The solution of the above equation is given by

\[
n_t(T) = n_t(T_0) \exp\left[-\int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(-\frac{\xi_t}{kT}\right) dt\right] \tag{3.12}
\]

and thus,

\[
\sigma = n_t(T_0) \tau e^\nu \exp\left[-\frac{\xi_t}{kT_0} \int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(-\frac{\xi_t}{kT}\right) dT\right] \tag{3.13}
\]

The maximum conductivity occurs where

\[
\exp\left(\frac{\xi_t}{kT_m}\right) = \frac{\nu kT_m^2}{\beta \xi_t} \tag{3.14}
\]

where \( T_m \) is the temperature at which conductivity is a maximum. It is assumed that \( \nu \) is temperature independent and that over the temperature span of the glow curve, the variation of \( \nu \) and \( \tau \) with temperature can be ignored.

b. **Partially Filled Traps and Fast Retrapping** (\( \frac{n_t'}{1-n_t'} = n_t'; \alpha >> 1 \))

The reduced form of Eq. (3.10) under the above conditions is

\[
\frac{dn_t}{dT} = -\frac{\nu}{\beta \alpha} n_t \exp\left(-\frac{\xi_t}{kT}\right) \tag{3.15}
\]

Eq. (3.15) is the same as Eq. (A3.11) if \( \nu \) in Eq. (A3.11) is replaced by \( \nu/\alpha \). Thus the maximum conductivity occurs when
The temperature at which conductivity is a maximum decreases as the ratio \( \nu/\alpha \) increases. This result is in agreement with computed results (Fig. 3.3).

### 3.3.2 Exponential Trap Distribution

In this case the trap density per unit energy is taken to be given by

\[
N_{\text{wt}} = A_t \exp(-\xi_t/kT_c) \tag{3.17}
\]

where \( A_t \) and \( T_c \) are constants which define the shape of the distribution of traps in energy. Substituting Eq. (3.17) in Eq. (3.1) and integrating, we get

\[
\frac{dn_t}{dT} = \frac{\nu N_t}{T} \exp\left(\frac{\nu T_c}{T}\right) \tag{3.18}
\]

Combining Eqs. (3.3), (3.8) and (3.18), we have

\[
\frac{dn_t'}{dT} = -\frac{\nu}{\beta} \frac{1+\frac{c}{T}}{(1+\frac{c}{T})(1+\alpha(1-n_t'))} \tag{3.19}
\]

This equation is best solved numerically.

### 3.3.3 Uniform Trap Distribution

In this case, the trap density per unit energy is taken to be given by

\[
N_{\text{wt}} = \frac{N}{W} [u(\xi_t) - u(\xi_t - W)] \tag{3.20}
\]

where \( W \) is the energy range below the conduction band where traps are uniformly distributed \((W>>kT)\)

\( u \) is the unit step function

Using Eq. (3.20), Eq. (3.1) becomes

\[
\frac{dn_t}{dt} = ncs V_{th} (N_t - n_t) - \frac{\nu kT}{W} \exp\left(-\frac{W}{kT} (1-\frac{n_t}{N_t})\right) \tag{3.21}
\]
combining Eqs. (3.3), (3.8) and (3.21), we get
\[
\frac{dn'_t}{dT} = \frac{\nu kT \exp(-\frac{W}{kT(1-n'_t)})}{\beta W(1 + \alpha(1-n'_t))}
\] (3.22)

Once \( n'_t \) becomes much less than unity, the rate of change of trapped charge
(and hence conductivity) becomes independent of the magnitude of trapped
charges.

Eqs. (3.10), (3.19) and (3.22) are nonlinear differential equations:
their general solutions have been computed on an IBM360/67 machine using
fourth order Runge Kutta numerical method.

3.4 Numerical Results and Discussion

Glow curves for a range of values of model parameters have been
computed and they are displayed graphically in Figs. 3.1 through 3.3.
However the absolute values of the solutions of the model equations depend
directly on the absolute values chosen for the disposable parameters. The
following features are common to all computed glow curves:

(1) Glow curves computed for both monoenergetic traps and exponentially
distributed traps attain a maximum at a temperature, \( T_m \), defined by the model
parameters. The computed curves for monoenergetic traps are more symmetrical
around \( T_m \) than those computed for exponentially distributed traps, also the
latter curves are wider than those computed for monoenergetic traps (Fig. 3.1).
This is to be expected. When a distribution of trap levels exists, rather
than a single level, the trapped electrons are permitted to vary with
temperature over a wider range of temperature.

(2) The temperature at which the maximum glow, \( G_m \), occurs as well as
its value depend on the energy distribution of traps (Fig. 3.1). As the
Fig. 3.1 Glow curves for different trap distributions, (a) monoenergetic traps; (b) exponential trap distribution.
trap energy $\xi_t$ or the characteristic temperature $T_c$ increases both $T_m$ as well as $1/G_m$ increase, and consequently the glow curves become wider.

(3) For a given set of model parameters, the area under the glow curve is proportional to the initial trapped charge, $n_t(T_o)$. However, the detailed shape of the glow curves is dependent on $n_t(T_o)$ except in a few cases, e.g., the case of monoenergetic traps with slow retrapping.

(4) It may be useful to note that, even though $T_m$ is almost independent of the initial magnitude of trapped charges in the case of monoenergetic traps, it changes considerably as the initial trapped charges in exponentially distributed traps change (Fig. 3.2).

(5) As retrapping processes become more significant, the maximum of the glow will shift to a higher temperature while the magnitude of the maximum will decrease, resulting in a wider curve. On the other hand, as retrapping becomes less important the glow curve will be completely defined by the recombination process (Fig. 3.3).

(6) The increase of the heating rate, $\beta$, has the effect of increasing the magnitude of the maximum glow and shifting the temperature at which the maximum occurs to a higher value.

The above features could enable us to differentiate experimentally between monoenergetic traps and traps distributed over a range of binding energies. Apart from the clear differences in glow curves for both cases, the following experiments may be useful to confirm the nature of the trap distribution:

(1) Different doses of optical radiation (i.e., different excitation times) can be used to obtain different initial trapped charges. Then the dependence of $T_m$ on the excitation time could be utilized to investigate the nature of the trap distribution.
Fig. 3.2 Effect of the initial amount of trapped charge density on the computed glow curves, (a) monoenergetic traps; (b) exponentially distributed traps.
Fig. 3.3 Effect of retrapping on the computed glow curves, (a) monoenergetic
(2) The frequency of optical excitation may be varied over a suitable range of frequencies to allow only certain energy levels, if present, to be occupied by excited electrons. The dependence of the magnitude of the maximum glow on the optical wavelength should decrease monotonically with increasing optical wavelength.

Finally, it should be pointed out that the presence of several glow peaks does not exclude the possibility of the presence of distributed traps. It may only indicate that the trap distribution does not follow a simple analytic relation but that it could contain several peaks at certain energy levels depending on the preparation technique.
4. HIGH FIELD EMISSION: TUNNELING AND SCHOTTKY CURRENTS
IN VERY THIN FILMS

4.1 Introduction

High field emission from the cathode can modify the conduction properties of a thin film sandwiched between two metal electrodes. In considering the electronic conduction, the bulk properties as well as the electrode emission properties should be considered. However, for very thin films (film thickness less than, say, 100 Å) the electronic conduction is mainly governed by the metal/film interface.

Current carriers are injected from the metal electrode by electron tunneling and/or thermionic emission. The primary criterion for distinguishing between tunneling and thermionic emission currents has been the temperature dependence of the measured conduction current. The temperature dependence of tunneling current is very weak compared to that of thermionic current, and it arises mainly from the variation of the available electrons for tunneling the variation in the barrier shape and the temperature variation of the film energy-momentum relationship.

In calculating Schottky thermionic currents, the optical dielectric constant should be used (an electron emitted with velocity of $10^5$ m/sec. will cover $10^2$ Å in $10^{-13}$ sec.). However, the appropriate dielectric constant for calculating tunneling currents seems to be different from the optical value. This is because the time of interaction between the electron and the potential barrier is sufficiently long such that the ions in the barrier can follow the passing electron through the transition. The interaction time decreases as the barrier width decreases. Thus, the appropriate dielectric constant for tunneling might be assumed to decrease as the electron energy
approaches the top of the barrier where its width is smaller. In this study, we will use the static dielectric constant for calculating the tunneling current (recalling that the major part of the tunneling current takes place around the Fermi level of the cathode) and the optical dielectric constant for Schottky thermionic emission.

The object of this chapter is to investigate the transition from tunneling currents to thermionic currents, the effect of the presence of space charge on tunneling currents and to determine the optimum biasing for a metal/very thin film/metal detector.

4.2 Formulation

The tunneling current density from one metal electrode to the other across a dielectric (or, semiconductor) film is given by

\[
J_{12} = \frac{4 \pi m e}{h^3} \int_0^\infty dE \cdot f(E_1) [1 - f(E_2)] \int_0^E T(E_x) dE_x
\]  

(4.1)

where

\[m\] is the electron mass.
\[e\] is the electron charge.
\[h\] is Planck's constant.

\[f(E)\] is the Fermi-Dirac function; \(E\) refers to the total electron energy.

\[E_1, E_2\] refer to the initial and final electron energies respectively.

\[T(E_x)\] is the transition probability; \(E_x\) refers to electron energy in the \(x\) direction.

\[E_1 = E - E_x\]

Using a similar expression for the current in the opposite direction, the net current density is the difference between the two expressions. Thus,
\[
J = \frac{4\pi me}{h^3} \int_0^\infty dE_1 [f(E_1) - f(E_2)] \int_0^E T(E_x) dE_x \tag{4.2}
\]

Substituting for the Fermi-Dirac function

\[
f(E_1) = \frac{1}{1 + \exp((E_f - E_1)/kT)}
\]

\[
f(E_2) = f(E_1 + eV) = \frac{1}{1 + \exp((E_f - E_1 - eV)/kT)}
\]

Eq. (4.2) reduces to

\[
J = \frac{4\pi me kT}{h^3} \int_0^E \ln \left[ \frac{1 + \exp((E_f - E_x)/kT)}{1 + \exp((E_f - E_x - eV)/kT)} \right] T(E_x) dE_x \tag{4.3}
\]

It is convenient to define a new energy parameter

\[
\epsilon = E_x - E_f
\]

Thus, Eq. (4.3) becomes

\[
J = \frac{A T}{k} \int_{E_f}^\epsilon \frac{1 + \exp(-\epsilon/kT)}{\ln \left[ \frac{1 + \exp(-\epsilon/kT)}{1 + \exp((-\epsilon + eV)/kT)} \right]} T(\epsilon) d\epsilon \tag{4.4}
\]

Where \( A = \frac{4\pi me k^2}{h^3} \)

\[= 120 \text{ amp/cm}^2 \text{ deg}^2\]

It should be noted that the above integral is not sensitive to the absolute value of \( E_f \) provided it is sufficiently high (few eV) since \( T(\epsilon) \) decreases rapidly with decreasing energy.

The current magnitude depends critically on the potential barrier in the film which determines the transmission probability. The transmission probability is obtained by matching the Bloch waves at the two metal/film interfaces. However, an approximate solution using the WKB method (for slowly varying potential barriers) gives

\[
T(\epsilon) = \exp \left[ -2 \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2} (\phi(x) - \epsilon)} \, dx \right] \quad (4.5)
\]
with \[ \phi(x) = \phi_c + ((\phi_a - \phi_c) - eV) \frac{x}{d} + \phi_{sc} + \phi_I \] (4.6)

where

- \( \phi_c \) and \( \phi_a \) are the cathode and anode work function respectively.
- \( d \) is the film thickness.
- \( \phi_{sc} \) is the contribution of any present space charge.
- \( \phi_I \) is the image force correction.

\[
= - \frac{e^2}{8\pi\varepsilon_0} \left[ \sum_{n=1}^{\infty} \frac{1}{n} \frac{nd}{(nd)^2-x^2} \right] + \frac{1}{\varepsilon_0} \frac{d^2}{x(d-x)} \] (4.7)

Nonstoichiometric films may contain unneutralized space charge, e.g., in the case of thin oxide films it seems reasonable to assume that near the substrate metal an incomplete oxidation process gives rise to a region where excess positive ions exist. Assuming that the charge decreases exponentially with the distance from the substrate metal, we may write

\[ \rho(x) = N \exp\left( - \frac{mx}{d} \right) \] (4.8)

where \( N \) and \( m \) are constants.

The solution of Poisson's equation, when the substrate metal is biased negatively, gives

\[ \phi_{sc}(x) = - \frac{e^2Nd^2}{\varepsilon_0\varepsilon_r m} \left[ (1 - \exp(-\frac{mx}{d})) - \frac{x}{d} (1 - \exp(-m)) \right] \] (4.9)

while for positive substrate metals, the solution is

\[ \phi_{sc}(x) = - \frac{e^2Nd^2}{\varepsilon_0\varepsilon_r m} e^{-m} \left[ (1 - \exp(m \frac{x}{d})) - \frac{x}{d} (1 - \exp(m)) \right] \] (4.10)
Once the shape of the potential barrier is determined, the transmission probability can be calculated and the voltage-current characteristics of the tunnel diode may be obtained.

4.3 Transition from Tunneling Mechanism to Schottky Thermionic Emission

In evaluating tunneling currents, the upper integration limit in Eq. (4.4) should be the potential barrier maximum, $\varepsilon_m$. However, numerical calculations show that the major part of tunneling current takes place within a narrow energy range around the Fermi level of the cathode. On the other hand, Schottky thermionic emission occurs when electrons have sufficient kinetic energy to surmount the potential barrier rather than to tunnel through it. An expression for Schottky thermionic emission can be obtained by substituting $T(\varepsilon) = 1$ and assuming $\varepsilon >> kT$ in Eq. (4.4). Thus, we get

$$J_s = \frac{AT}{k} \int_{\varepsilon_m}^{\infty} \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon$$

$$= AT^2 \exp\left(-\frac{\phi_c}{kT}\right) \exp\left(\Delta\varepsilon/kT\right)$$

(4.11)

where $\Delta\varepsilon$ is the barrier height lowering. Eq. (4.11) shows that Schottky current is very sensitive to temperature variation in contrast to tunneling current which varies very slightly with temperature. Fig. 4.1 shows that the ratio $J_T/J_s$ increases as:

1. the ambient temperature decreases.
2. the applied voltage increases, except for very thin films and low applied voltages where the anode work functions could have pronounced effect.
Fig. 4.1 Transition from tunneling mechanism to Schottky thermionic emission
3. the magnitude of the positive space charge increases.

4. the cathode work function decreases (not shown in Fig. 4.1)

Thus the predominant process, whether it is tunneling or Schottky emission, depends on film parameters, applied voltage and ambient temperature. It is interesting to note that both processes could contribute equally to conduction current under certain conditions. The rest of this study will be concerned only with tunneling currents.

4.4 Space Charge Effect on Tunneling Currents

Fig. 4.2 shows the voltage-current characteristics of a film space charge-free and that of a film containing positive space charge. The main feature of the computed characteristics is that \( \frac{d^2 \ln I}{dV^2} \) changes sign as the applied voltage passes \( \phi_a /e \), i.e., when \( \phi(d) \) lies below the cathode Fermi level. It is worth noting that Fowler-Nordheim tunneling currents have a negative value for \( \frac{d^2 \ln I}{dV^2} \). Assuming that the tunneling current occurs at \( \varepsilon = 0 \) and that \( \phi(d) = 0 \) and neglecting space charge and image force effects, we get from Eq. (4.5)

\[
T(0) = \exp\left[-2 \int_0^d \frac{2m}{\hbar^2} \left[ \phi_c + \left( \phi_a - \phi_c \right) - eV \right] \frac{d^2 \ln I}{dV^2} \ dx \right]
\]

\[
= \exp\left[ -\frac{8\pi d\sqrt{2m}}{3\hbar} \frac{\phi_c}{\phi_a - \phi_c - eV} \right]
\]

If the available electrons for tunneling are almost constant, tunneling current, at high applied fields, might be proportional to the above quantity. The Fowler-Nordheim expression for tunneling at high fields is

\[
J_{FN} = \frac{e^2V^2}{8\pi\hbar^2\phi} \exp\left( - \frac{8\pi d\sqrt{2m}}{3\hbar} \frac{\phi_{3/2}}{V} \right)
\]

(4.12)
Fig. 4.2 Voltage-current characteristics of a MIM tunneling diode, the presence of positive space charge increases the current density.

Fig. 4.3 Potential barrier lowering as a function of the applied field.
The presence of the above mentioned inflection point leads to an interception between the forward and reversed V-I characteristics. The same features are applicable to films containing invariant space charge. However, the presence of positive space charge increases the current density for a given applied voltage since the positive space charge increases the potential barrier lowering.

The potential barrier lowering is presented in Fig. 4.3. It is related to the applied field by the relation

\[ \Delta \phi = \beta \sqrt{V/d} \]

where \( \beta \) is a constant depending on the film dielectric constant. The presence of space charge inside the film and the difference between the two metal work functions might change the magnitude of \( \beta \) and could cause an appreciable deviation from the above relation especially at low applied voltages.

4.5 Optimum Bias for MIM Detectors

Because of the nonlinear nature of the voltage-current characteristics of very thin dielectric (or, semiconductor) films sandwiched between two metal electrodes, MIM diodes can be used as wave detectors. The figure of merit, \( F \), for such detectors is usually taken to be the responsivity-bandwidth product, where the diode responsivity is defined as the detected voltage divided by the input power. In this section it will be shown that there is a bias voltage which gives maximum responsivity-bandwidth product. To avoid excessive computing time, in determining the small signal characteristics, the following procedure has been used. Around each biasing point, the already computed dc characteristics have been fitted to a power function using least
squares fitting:

\[ I(\bar{v}) = G\bar{v} + G_2\bar{v}^2 + G_3\bar{v}^3 \]

where \( \bar{v} \) is the small signal voltage measured from the biasing point. The computed results show that \( G_2/G \) is a maximum at the above mentioned inflection point (when the biasing voltage is \( \phi_a/e \)). This is true, since if

\[ \frac{d^2\ln I}{d\bar{v}^2} = 0 \]

then

\[ \frac{d\ln I}{d\bar{v}} = \frac{d^2I}{d\bar{v}^2} / \frac{dI}{d\bar{v}} = 2G_2/G \]

But \( \frac{d\ln I}{d\bar{v}} \) is a maximum (see Fig. A.2), hence \( G_2/G \) is a maximum.

The detected dc voltage across the diode, in response to \( v = v \sin \omega t \), is thus given by

\[ V_D = \frac{1}{2} \left( \frac{G_2}{G} \right) v^2 + \frac{4}{3\pi} \left( \frac{G_3}{G} \right) v^3 \]

and the responsivity-bandwidth product is given by

\[ F = \left( 2V_D/\sqrt{2}G \right) \times (G/2\pi C) \]

\[ = \frac{1}{C}\left[ \frac{1}{2\pi} \left( \frac{G_2}{G} \right) + \frac{4}{3\pi^2} \left( \frac{G_3}{G} \right) v \right] \]

where \( C \) is the detector capacitance. Fig. 4.4 shows the variation of the diode responsivity-bandwidth product as a function of the bias voltage. The highest value for the responsivity-bandwidth product occurs when the bias voltage is \( \phi_a/e \). This is because \( G_2/G \) is maximum at that bias. The presence of positive space charge increases the magnitude of the maximum, since the potential barrier height changes with applied voltage faster than that for space charge-free diodes.

It is worth noting that the discussed optimum bias is also applicable.
Fig. 4.4 Variation of the detector responsivity-bandwidth product as a function of the bias voltage.
for the case of heterodyning detectors. In this case, we should replace Eq. (4.13) by

\[ V_D = v_1 v_2 (G_2/G) \]  \hspace{1cm} (4.15)

where \( v_1 \) and \( v_2 \) are the magnitudes of the two applied signals. Thus, the same result follows.

4.6 Summary

The predominant conduction mechanism in very thin films, whether it is tunneling or Schottky emission, depends on film parameters, applied voltage and ambient temperature. In view of the fast tunneling time of electrons through very thin films, MIM structures can be used for microwave detection. It is shown that the maximum responsivity-bandwidth product of MIM detectors is obtained when they are biased at a voltage equal to the anode work function (in volts). The presence of invariant positive space charge increases the magnitude of this maximum.
5. HIGH FIELD SWITCHING
IN THIN AMORPHOUS FILMS

5.1 Introduction

Electrical instabilities have been observed in a large variety of thin amorphous films sandwiched between two metal electrodes. Most of those instabilities are of the current controlled negative resistivity (CCNR) type which have been observed in, e.g., NiO\textsuperscript{47}, Nb\textsubscript{2}O\textsubscript{5}\textsuperscript{48}, Ta\textsubscript{2}O\textsubscript{5}\textsuperscript{48}, TiO\textsubscript{2}\textsuperscript{49}, V\textsubscript{2}O\textsubscript{5}\textsuperscript{50,51}, Fe\textsubscript{3}O\textsubscript{4}\textsuperscript{52} and semiconducting glasses\textsuperscript{53-55}. The observed voltage-current characteristics suggest the four fold classification shown in Fig. 5.1\textsuperscript{56}.

![Fig. 5.1 Types of CCNR characteristics.](image-url)
(1) The Negative Resistance Device: Its V-I characteristic is retraceable and it shows an extended negative differential resistivity region.

(2) The Switching Device: It has no stable operating point between the original high resistance state and the conductive state to which the device switches at a threshold voltage $V_{th}$. The conductive state can be maintained only if the current is above the sustaining current $I_s$.

(3) and (4) The Negative Resistance Device with Memory and The Switching Device with Memory: They are similar to (1) and (2) respectively but with the difference that once the conducting state is established, it persists without noticeable decay. The high resistance state can be re-established by increasing the current above a certain value and switching it off rapidly.

The main experimental features of CCNR phenomena can be summarized:

(1) CCNR can occur in thin oxide films only if a forming process has been done. The forming process consists of passing a critical current ($\approx 0.1$ Amp/cm$^2$) in a pulsed or steady-state form. It is believed that considerable heating of the film and some irreversible changes, primarily solid-state diffusion of the metal electrodes in the film, occur at the interfaces with the metal electrodes.

(2) Conduction current through the amorphous film before switching (i.e., in the high resistance state) depends strongly on temperature and voltage and is proportional to the film cross sectional area. However, in the conductive state, the conduction current has been found to be independent of the film cross sectional area, the current is concentrated in narrow filaments.
(3) While the threshold voltage $V_{th}$ depends on sample thickness, the sustaining voltage $V_s$ is nearly constant for similarly prepared structures; the higher the dielectric constant the lower the value of $V_s$, suggesting an ionization process.

(4) White illumination increases the current, decreases the threshold voltage, but has no effect on the sustaining voltage.

(5) Infrared radiation has been observed during switching, e.g., vitreous $\text{As}_2\text{Te}_3 \cdot \text{As}_2\text{Se}_3$ at $78^\circ\text{K}$ shows a weak peak at 1.16 eV and a strong peak at 0.67 eV, the first peak is due to interband recombination and the stronger low energy peak may be due to the capture of carriers by recombination centers.

(6) The switching time $\tau_s$ (the time taken by the sample to undergo transition from the high resistance state to the conducting state) is of the order $10^{-9}$ sec. while the delay time $\tau_d$ (the time between the application of the voltage and the starting of the switching process) may be approximated by

$$\tau_d = A \exp(-BV)$$

where $\tau_d$ is approximately $10^{-6}$ sec. at $V = V_{th}$ and no switching appears possible below $V_{th}$ (i.e., $\tau_d = \infty$).

Several models have been proposed to explain CCNR in thin amorphous films. Some models have considered the phenomena to be essentially an electronic phenomenon, and the others considered it as a result of thermal effects. Double injection, tunnel injection through field-decreasing barrier, space charge formation, impact ionization, self-heating and filamentary conduction processes have been postulated as possible mechanisms responsible for CCNR characteristics. In this chapter, electrothermal
instabilities will be investigated and their limitations for describing CCNR observed in thin films will be pointed out. Sample self-heating could account for the observed delay times. However, it is believed that the switching process is an electronic process. Consequently, an electronic model is proposed. The small ac signal equivalent circuit of the model is given. Memory devices will be discussed in terms of filament formation and phase change mechanisms due to excessive heating.

5.2 Electrothermal Initiation of the Switching Mechanism

Pulse measurements, on an 0.8 μm thick layer of amorphous Te₀.₅₋₆As₀.₂Si₀.₁Ge₀.₂, show that the temperature of a switching device rises about 15°C above ambient before switching under static conditions. This temperature rise can be due to device self-heating which will now be discussed in some detail.

Whatever the true electronic process, or processes which initiate the CCNR characteristics are, they will determine the temperature and field conductivity dependences. The experimentally observed film conductivity is approximately of the form

\[ \sigma(E,T) = \sigma_0 \exp \left(\frac{-(\varepsilon - \beta E)}{2kT}\right) \]  

(5.1)

where \( E \) is the average applied field

\( k \) is Boltzmann's constant

\( T \) is the temperature

\( \sigma_0, \beta \) and \( \varepsilon \) are film constants

The exponential-dependence of conductivity on temperature could facilitate thermal heating. The sample temperature could eventually reach the critical temperature needed before switching takes place, provided the input power is
sufficiently higher than the heat losses from the sample surface

5.2.1 General Formulation

The sample self-heating process is essentially determined by the temperature dependence of the film conductivity and the associated feedback processes, namely: temperature rise, conductivity increase, current increase and higher power dissipation inside the film leading to temperature rise. Such a closed loop could produce an unstable situation in which the current density increases rapidly. Furthermore, whenever the film edges are kept at constant temperature (ambient temperature) the temperature rise will tend to be localized at some point inside the film. Thus the temperature need only increase in a localized area and this in turn will result in a shorter delay time and less energy will be required before switching takes place. The final steady state current will be limited by the energy loss from the sample, conductivity saturation and the external circuit.

The temperature distributions in the film can be expressed by the usual heat conduction equation

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (KVT) + P$$  \hspace{1cm} (5.2)

where \(P\) is the net power input per unit volume in the film and \(\rho, c, K\) refer to the film density, specific heat and thermal conductivity. If we assign a constant \(1/\lambda\) to the external thermal resistance of the sample, then the heat loss per unit volume per unit time can be written as

$$P_{\text{ext}} = \frac{1}{d} (T - T_0)$$  \hspace{1cm} (5.3)

where \(d\) is the film thickness and \(T_0\) is the ambient temperature. The electric power input is given by

$$P_i = \sigma(E,T)E^2$$  \hspace{1cm} (5.4)
Combining Eqs. (5.1), (5.4) yields the relevant equation which could describe CCNR phenomena. All the results presented have been obtained for cylindrical geometry with the current flowing along the z-axis and the cylinder wall maintained at the ambient temperature. It has been assumed that the film has no temperature gradient perpendicular to the electrical contacts and that the film thermal conductivity is temperature independent (or, its variation can be neglected compared to electrical conductivity variation). Thus the heat conduction equation can be written as

\[
\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = \frac{\lambda}{dK} (T - T_0) - \frac{E}{K} \frac{\partial}{\partial t} T + \frac{\partial C}{\partial t} \frac{\partial T}{\partial t}
\] (5.5)

with the boundary conditions

\[
\frac{\partial T}{\partial r} \mid_{r=0} = 0; \quad T(a,t) = T_0
\] (5.6)

and the initial condition

\[
T(r,0) = T_0 \quad \text{for} \quad -a \leq r \leq a
\] (5.7)

Eq. (5.5) is a non-linear partial differential equation whose general solution may be obtained using either an analogue or a digital computer. The discrete-space continuous-time analogue representation of Eq. (5.5) is shown in Fig. 5.2. The temperature distribution within the film could be obtained using the equivalent circuit shown, but the necessity of a separate non-linear function generator at each node creates a major problem. The results presented have been obtained an IBM 360/67 machine, using constants given in Table 5.1 (unless otherwise stated), which are intended to refer to chalcogenide glasses 53,55.
Fig. 5.2 Discrete-space continuous-time analogue representation of electrical heating of a thin film (electrical equivalent circuit for Eq. (5.5)).

Fig. 5.3 Computed voltage-current characteristics for a thin cylindrical structure.
TABLE 5.1. CONSTANTS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$5 \times 10^{-5}$</td>
<td>m,</td>
</tr>
<tr>
<td>$d$</td>
<td>$5 \times 10^{-7}$</td>
<td>m</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>$10^3$</td>
<td>$\Omega^{-1} \cdot m^{-1}$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>1</td>
<td>eV</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$4.3 \times 10^{-9}$</td>
<td>em</td>
</tr>
<tr>
<td>$K$</td>
<td>0.5</td>
<td>W m$^{-1} \cdot K^{-1}$</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>$10^6$</td>
<td>J kg$^{-1} \cdot K^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$5 \times 10^3$</td>
<td>W m$^{-2} \cdot K^{-1}$</td>
</tr>
</tbody>
</table>

Once the temperature distribution has been obtained, the total current, $I$, is given by

$$I = \int_0^a J(r) 2\pi r dr$$

(5.8)

or

$$I = \frac{2\pi V}{d} \int_0^a \sigma(r) r dr$$

(5.9)

where $J$ is the current density, $V$ is the applied voltage and $a$ is the film radius.

5.2.2. Static Characteristics

The static characteristics are governed by the equation

$$\frac{d^2T}{dr^2} + \frac{1}{r} \frac{dT}{dr} = \frac{\lambda}{dK} (T - T_o) - \frac{\sigma(E,T)}{K} E^2$$

(5.10)

The solution of Eq. (5.10) with the boundary conditions given by Eq. (5.6) has been obtained numerically using the 4th order Runge-Kutta method.

The computed results (Fig. 5.3) exhibit CCNR characteristics and a region where both current and voltage are decreasing while the sample is heating up. The current range where the voltage is triple-valued occurs when the current increase in the central region (the prospective filament) is less
than the current decrease in the low temperature region. This triple-valued region could account for the observed hysteresis in all switching devices.

Fig. 5.4 shows that the temperature distribution within the film is almost uniform until the onset of the electrical instability. Thus one could obtain an approximate expression for the threshold voltage by assuming \( \nabla^2 T = 0 \). The threshold field can be determined by equating the power input to the power loss and by equating their derivatives w.r.t. temperature, i.e.,

\[
\frac{\lambda}{d} (T_c - T_o) = \sigma_o \epsilon^2 \text{th} \exp((\beta E_{\text{th}} - \epsilon)/2kT_c) \tag{5.11}
\]

and

\[
\frac{\lambda}{d} = \sigma_o \frac{(\epsilon - \beta E_{\text{th}})}{2kT_c^2} E_{\text{th}}^2 \exp((\beta E_{\text{th}} - \epsilon)/2kT_c) \tag{5.12}
\]

Thus by dividing Eq. (5.11) by Eq. (5.12), we get

\[
\Delta T_c = (T_c - T_o) = \frac{2kT_c^2}{\epsilon - \beta E_{\text{th}}} \tag{5.13}
\]

but since \( \Delta T_c \) is always small (of the order of few tens of degrees centigrade), one may write

\[
\Delta T_c \approx \frac{2kT_o^2}{\epsilon - \beta E_{\text{th}}} \tag{5.14}
\]

The threshold field for switching can be obtained by substituting Eq. (5.14) in Eq. (5.11).

\[
E_{\text{th}} = \sqrt{\frac{\lambda \Delta T_c}{d \sigma(T_o) \epsilon}} \tag{5.15}
\]

where \( \sigma(T_o) = \sigma_o \exp((\beta E_{\text{th}} - \epsilon)/2kT_o) \), and

\[ e = 2.7182818 \]

Eq. (5.15) gives values for the threshold field very close to that obtained by solving the complete thermal conduction equation (Eq. (5.10)) whenever \( \lambda/d \) is sufficiently high such that the energy loss by radiation determines the threshold
Fig. 5.4 Current density and temperature distributions within the semiconducting film. The given distributions are those associated with points 1, 2, 3 shown in Fig. 5.3.

Fig. 5.5 Exact and approximate solutions for threshold field.
field. On the other hand, if \( \lambda/d \) is small, the temperature distribution within the sample affects the threshold field and it will be higher than that given by Eq. (5.15) Fig. 5.5. The computed results (Fig. 5.5) show that the threshold field becomes less dependent on \( \lambda/d \) as \( \lambda/d \) increases (i.e., as the film thickness or the radiation resistance decreases) and such dependence becomes even less as the ambient temperature decreases.

As the maximum temperature within the sample reaches its critical value, the temperature rate of increase will be very fast and the electronic conduction current will tend to concentrate in a narrow channel resulting in the so-called thermal channel. However, it should be noted that the maximum temperature will not increase indefinitely (otherwise breakdown occurs) but it will stabilize at some value determined by the external circuit and possibly by the associated electronic processes.

### 5.2.3 Delay Time

#### A. Square Wave Voltage

The electric energy dissipated in the sample during the delay time is used to heat up the sample which eventually reaches the critical temperature where switching can take place. The critical temperature rise is taken to be given by

\[
\Delta T_c = \frac{2kT_0}{\varepsilon - \beta E_b}
\]  

(5.16)

where \( E_b \) is the applied electric field.

Delay times were computed from Eq. (5.5) using finite difference methods (central differences for spatial derivatives and forward differences for time derivatives) and the critical condition given by Eq. (5.16). Fig. 5.6 shows that the computed delay times could be fitted to
\[ \tau_D = \tau_o(T_o) \exp\left( -\frac{V}{V_o(T_o)} \right) \] (5.17)

with \( \tau_o(300^\circ) = 4.5 \times 10^{-3} \) sec; and \( V_o(300^\circ) = 4.68 \) V, but the delay time starts to deviate considerably from the above relation as the applied field approaches the critical field.

An approximate expression for the delay time can be derived assuming a uniform temperature distribution (see Sec. 5.2.2) and an input power much greater than energy losses.

\[ \rho_c \frac{dT}{dt} = \sigma E^2_b \] (5.18)

The solution of the above equation follows as

\[ \tau_D = \frac{\rho c \alpha}{\sigma E^2_b} \left[ e^{\alpha/T} - Ei\left(\frac{\alpha}{T}\right) \right] \] (5.19)

where \( Ei \) is the exponential integral \( = - \int_{-\infty}^{\infty} \frac{e^{-x}}{x} \, dx \), and \( \alpha = (\epsilon - \beta E_b)/2k \).

A comparison between the results obtained from Eq. (5.19) with those obtained from Eq. (5.8) shows that the above approximate solution gives us almost an exact solution when the voltage pulse is relatively high (Fig. 5.7). Furthermore, if \( T_c \) is sufficiently small, Eq. (5.19) may be approximated as

\[ \tau_D = \frac{\rho c k T^2_o}{\alpha E^2_b} \exp\left( -\frac{\epsilon - \beta E_b}{2kT_o} \right) \] (5.20)

where \( \tau_o = \frac{\rho c E^2_b}{\alpha \sigma E_b^2} \exp\left( \frac{-\epsilon}{2kT_o} \right) \); \( V_o = (2kT_o)/\beta \).
Fig. 5.6 Computed delay time, critical temperature rise and electric energy needed for switching to occur versus applied voltage.

Fig. 5.7 Exact, ——, and approximate, ——, delay time as a function of applied voltage for different ambient temperature. The broken lines show the corresponding critical temperature rise.
The electric energy required before switching can take place is given by
\[ \epsilon_{nc} = \int_{0}^{\tau_D} IV \, dt \]
\[ = 2\pi E_d^2 \int_{0}^{\tau_D} \int_{a}^{a(r,t)} \sigma(r,t) \, rdr \, dt \]  \hspace{1cm} (5.21)

The computed results show that the required electrical energy is almost constant except when the applied field approaches the threshold value for switching.

The presence of an external resistance would increase the device delay time. The delay time will continue to increase as the external series resistance increases (Fig. 5.8) and eventually reaching the critical condition would be impossible (i.e., \( \tau_D \rightarrow \infty \)). This occurs when the magnitude of the voltage across the device becomes less than the threshold voltage.

B. Sinusoidal Voltage

The basic features of ac switching of a switching device are given in Fig. 5.9, namely:

(1) The threshold field and the fractional delay time (\( \tau_D f \)) increase as the applied signal frequency increases.

(2) The electric energy required for switching is almost constant and is of the same order as that required in the case of pulse switching.

(3) The above mentioned quantities and the device cut-off frequency depend on the amplitude of the applied signal.

It should be noted that the above features are common to all voltage wave forms with finite rise time.
Fig. 5.8 The effect of external resistance on delay time.

Fig. 5.9 Ac switching characteristics: threshold voltage, delay time and electric energy needed for switching to occur. Applied voltage $V \sin 2\pi ft$. 
5.3 Switching Mechanism

The experimentally observed switching time in chalcogenide films is as low as $10^{-9}$ sec\textsuperscript{53} which cannot be accounted for by simple thermal runaway. It would require a much longer time and temperature in the current filament which could destroy the sample. In investigating chalcogenide glasses, Fritzsche\textsuperscript{56} has shown that it is not possible to find a value for the current filament cross sectional area which is small enough to permit a sizable temperature rise but at the same time large enough to yield the low value of resistance in the conductive state.

Furthermore, Eqs. (5.1) and (5.5) cannot represent stable dynamic operation which has been observed experimentally.\textsuperscript{52} Making the conventional small signal approximations:

\begin{align*}
E(x,t) &= E_b(x,t) + \tilde{e}(x,t), \\
\sigma(x,t) &= \sigma_b(x,t) + \tilde{\sigma}(x,t), \quad (5.22)
\end{align*}

and

\[ T(x,t) = T_b(x,t) + \tilde{T}(x,t), \]

Eq. (5.5) can be reduced to

\[ \nabla^2 \tilde{T} = \frac{\lambda}{dK} T - \frac{1}{K}(\beta E_b^2 + 2\sigma_b E_b \tilde{e}) + \frac{\rho_c}{K} \frac{\partial^2 T}{\partial t^2} \quad (5.23) \]

where $\tilde{e}$ is related to the external applied voltage $V_{ac}$ by

\[ \tilde{e} = (V_{ac} - 2\pi E_b R_s (\int_0^a \tilde{\sigma} rdr))/(d + 2\pi R_s \int_0^a \sigma_b rdr) \quad (5.24) \]

where $R_s$ represents the external series resistance. Considering the central part of the formed filament where $\nabla^2 T = 0$ and $\tilde{\sigma}$, according to Eq. (5.1), is given by

\[ \tilde{\sigma} = \frac{\epsilon - \beta E_b}{2 K T_b} \tilde{T} \quad (5.25) \]

Eq. (5.23) is thus reduced to

\[ \]
Neglecting the temperature dependence of \( \ddot{e} \), the solution of Eq. (5.26) is only stable if,

\[
\frac{\lambda}{d} \sigma_b \frac{a}{T_b^2} \frac{E_b^2}{T_b} = 2 \sigma_b E_b \ddot{e} \tag{5.27}
\]

But since this condition is not realizable, one would expect that for stable dynamic characteristics, the conduction mechanism should change so that thermal runaway may be avoided.

Thus, one can conclude that the switching mechanism and the processes responsible for the observed CCNR in thin chalcogenide semiconductor films are electronic in nature. However, it is believed that self-heating serves to initiate the electronic switching mechanism. Self-heating could initiate an electronic switching mechanism, e.g., by developing high field regions near the electrodes. Since the voltage, after the onset of electrothermal instability, is a decreasing function of the current density, the excess voltage is largest wherever the current density is largest (current density variation could be due to variations in the emissivity of the sample electrodes). A space charge region will develop resulting in higher fields at the electrodes. Another possibility could be a temperature gradient near the electrodes which may produce a electric field gradient so that higher fields exist at the electrodes. This, in turn, can enhance current carrier injection through the metal/film barrier. If the electric field inside the film is sufficiently high, carrier multiplication by impact ionization may occur and the film may show a CCNR characteristic which is electronic in nature.
5.4 Current Controlled Negative Differential Conductivity Due to Space Charge Barriers

5.4.1 Model and Basic Equations

A two carrier, one dimensional model may represent a metal/amorphous film/metal diode exhibiting CCNR characteristics. In the present model, entrance of current carriers from the cathode into the conduction band of the film is taken to be given by either Schottky thermionic emission or the Fowler-Nordheim tunneling mechanism (see Chapter 4), i.e.,

\[ J_n(0) = -A_n \exp(\frac{\beta \sqrt{E(0)}}{\epsilon}) \]  

(5.28)

or,

\[ J_n(0) = -A'_n \epsilon^2(0) \exp(-\frac{H}{E(0)}) \]

where

- \( J_n(0) \) is the electron current density at the cathode.
- \( E(0) \) is the electric field at the cathode.
- \( A_n \) and \( A'_n \) are constants.
- \( \beta_s \) is the Schottky slope

\[ \beta_s = \frac{e}{2kT \sqrt{\pi \epsilon}} \]

Injected carriers could undergo a multiplication process by impact ionization if the field inside the film is sufficiently high. Near the cathode the electrons, which have just tunneled through the barrier, are moving faster than in the body of the diode and so do not combine so easily with positive holes. That is why a concentration of positive charge builds up at the cathode before the rate of recombination balances the rate of generation. The steady state continuity equation can be written as

\[ \frac{1}{e} \nabla \cdot J_n = -(G - R) \]

(5.29)

\[ \frac{1}{e} \nabla \cdot J_p = G - R \]
where

\( J_n \) and \( J_p \) are the electron and the hole current density respectively.

\( G \) and \( R \) are the generation and recombination rate function respectively.

The electron-hole generation rate due to impact ionization is given by (see Reference 71 Chapter 2)

\[
G = \alpha_n n \mu_n + \alpha_p p \mu_p
\] (5.30)

where

\( n \) and \( p \) are the electron and hole density respectively.

\( \mu_n \) and \( \mu_p \) are the electron and hole mobility respectively.

\( \alpha_n/E \) is the electron ionization rate (= number of electron-hole pairs generated by an electron per unit distance travelled).

\( \alpha_p/E \) is the hole ionization rate.

\( \alpha_n \) and \( \alpha_p \) may be approximated by one of the following functions:

1. \( \alpha = \alpha_o (E/E_o)^m \)
2. \( \alpha = \alpha_o \exp(\beta E) \)
3. \( \alpha = \alpha_o \exp(-\beta/E)^m \) (5.31)

where \( \alpha_o, E_o, \beta \) and \( m \) are constants.

For the net generation-recombination rate, one may write

\[
G - R = U(E, n, p, x)
\]

However, for simplicity it will be assumed that

\[
U = G
\] or \[
U = 0 \] (5.32)

depending on the position inside the film.

The transport equations for \( J_n \), \( J_p \) are
\[ J_n = e \mu_n n E + e D_n \nabla n \]  
\[ J_p = e \mu_p p E - e D_p \nabla p \]  

(5.33)  

(5.34)

For steady state conditions, the total current density is

\[ J = J_n + J_p = \text{constant} \]

where \( D_n \) and \( D_p \) are the electron and hole diffusion constant respectively.

The electric field distribution inside the film can be determined from Poisson's equation

\[ \nabla \cdot E = \frac{\varepsilon}{\varepsilon} (p - n) \]  

(5.35)

and the voltage drop across the film is given by

\[ V = - \int_0^d E \, dx \]  

(5.36)

Eqs. (5.33), (5.34), and (5.35) can be combined to yield a nonlinear differential equation describing the electric field distribution inside the film. To derive such an equation, multiply Eq. (5.34) by \( 1/\delta \) (\( \delta = \mu_p / \mu_n = D_p / D_n \)) and subtract the result from Eq. (5.33). Thus, we get

\[ J_n - J_p /\delta = e D_n (\nabla n + \nabla p) - e \mu_n E (\nabla \cdot E) \]  

(5.37)

Similarly by adding Eqs. (5.33) and (5.34), we get

\[ J_n + J_p /\delta = -e D_n (\nabla \cdot E) + e \mu_n E (n + p) \]  

(5.38)

Now, for a one dimensional model, Eq. (5.37) upon integration gives

\[ \int_0^x (J_n - J_p /\delta) \, dx = e D_n (n + p) - \frac{e \mu_n}{2} E^2 + k' \]  

(5.39)

where \( k' \) is the integration constant

\[ = \frac{e \mu_n}{2} E^2(0) - e D_n (n(0) + p(0)) \]

Eliminating \( (n+p) \) from Eq. (5.39) by using Eq. (5.38) in one dimensional form, we get

\[ e D_n^2 \frac{d^2 E}{dx^2} + \mu_n k' E = \frac{e \mu_n^2}{2} E^3 + \mu_n E \int_0^x (J_n - J_p /\delta) \, dx - D_n (J_n + J_p /\delta) \]  

(5.40)
5.4.2 Normalized Equations

An alternative way of expressing the above equations results if the following normalized variables:

\[
\begin{align*}
J_{\text{nn}} &= \frac{J_n}{A_n}, \quad J_{\text{pn}} = -\frac{P_n}{A_n}; \quad x_n = \frac{x}{d} \\
\eta_n &= \frac{\sqrt{\frac{2}{\varepsilon_n} \frac{\mu_n d}{a_n}}}{e}, \quad \eta_p = \frac{\sqrt{\frac{2}{\varepsilon_n} \frac{\mu_n d}{a_n}}}{e} \\
E_n &= -E \frac{\mu_n e}{d A_n}, \quad V_n = V \frac{\mu_n e}{d A_n}
\end{align*}
\]

are substituted in Eqs. (5.28), (5.29) and (5.33)-(5.36). The modified equations are then given by

\[
J_{\text{nn}}(0) = \exp \left( \sqrt{\frac{C_2}{2}} E_n(0) \right) \tag{5.41}
\]

or

\[
J_{\text{nn}}(0) = E_n^2(0) \exp \left( -\frac{C_2}{2} E_n(0) \right)
\]

\[
\frac{dJ_{\text{nn}}}{dx_n} = U_n, \quad \frac{dJ_{\text{pn}}}{dx_n} = -U_n \tag{5.42}
\]

\[
J_{\text{nn}} = -C_1 \frac{d\eta_n}{dx_n} + E_n \eta_n \tag{5.43}
\]

\[
J_{\text{pn}}/\delta = C_1 \frac{d\eta_p}{dx_n} + E_n \eta_p \tag{5.44}
\]

\[
\frac{dE_n}{dx_n} = \eta_n - \eta_p \tag{5.45}
\]

\[
V_n = \int_0^1 E_n \, dx_n \tag{5.46}
\]

\[
C_1^2 \frac{d^2 E_n}{dx_n} + kE_n = \frac{E_n^2}{2} + E_n \int_0^x (J_{\text{nn}} - J_{\text{pn}}/\delta) \, dx - C_1 (J_{\text{nn}} + J_{\text{pn}}/\delta) \tag{5.47}
\]

where

\[
C_1 = \frac{D_n}{d} \frac{\varepsilon_n}{\mu_n \alpha A_n}
\]
For the no diffusion case, Eq. (5.47) becomes

$$E_n^2(x_n) = E_n^2(0) + 2 \int_0^x (J_n - J_p n / \delta) \, dx_n$$ \hspace{1cm} (5.48)$$

Eqs. (5.41) and (5.45)-(5.47) represent a general formulation of space charge current flow in a trap free film (or, when trap effects can be neglected) with blocking contacts and finite generation-recombination rate. The following computations are intended to show that the above model, under certain conditions, can exhibit CCNR characteristics.

### 5.4.3 Method of Solution

For a given generation-recombination rate function, the solution of the above equation could, in principle, be determined such that they satisfy the boundary conditions. To avoid excessive computing time, two relations may be derived to determine the total current density and the electric field at a point, \( x^* \), inside the film for given boundary conditions. Consider the diffusion free case: Eq. (5.48) may be written as (subscript \( n \) will be omitted)

$$\frac{d}{dx} (E \frac{dE}{dx}) = \frac{d}{dx} (J_n - J_p n / \delta)$$ \hspace{1cm} (5.49)$$

Multiplying Eq. (5.49) by \( 2 E \frac{dE}{dx} \) and integrating between \( x^* \) and general point \( x \), we get

$$\frac{dE}{dx} = (n - p) = \pm \frac{\sqrt{2}}{E} \sqrt{\frac{E(x^*)}{E(x)}} \left[ U(1 + 1/\delta) EdE + \frac{1}{2} (E \frac{dE}{dx})^2_{x=x^*} \right]$$ \hspace{1cm} (5.50)$$

where the sign determines the polarity of the net charge. Integrating once more, we have
\[ x^* = \pm \frac{\int E(x^*)}{E(0)} \sqrt{\frac{E(x^*)}{U(1+1/\delta)EdE + \frac{1}{2}(E\frac{dE}{dx})^2_{x=x^*}}} \]  

(5.51)

The total current density is given by

\[ J = J_n(0) + J_p(0) \]

\[ = 2J_n(0) + E(0)(P(0) - n(0)) \]

\[ = 2J_n(0) \pm \sqrt{\frac{\int E(x^*)}{E(0)} U(1+1/\delta)EdE + \frac{1}{2}(E\frac{dE}{dx})^2_{x=x^*}} \]  

(5.52)

For a given injected current from the cathode, \( J_n(0) \), (or, the electric field \( E(0) \)) and a boundary condition at the point \( x^* \), Eqs. (5.51) and (5.52) can be solved to determine the total current density and the electric field at \( x^* \). The electric field and charge distributions may then be determined to give the current-voltage characteristics.

### 5.4.4 Symmetrical Case

In this case, it is assumed that both electrons and holes have similar properties. The injected hole current at the anode is taken to be given either by Schottky thermionic emission or the Fowler-Nordheim tunneling process i.e.,

\[ J_p(l) = \exp(-C_2E(l)) \]  

(5.53)

or,

\[ J_p(l) = E^2(l) \exp(-C_2'/E(l)) \]

Due to symmetry, electrical neutrality will occur at the middle of the sample (i.e., \( x=0.5 \)). Thus if \( x^* \) is the point at which the neutral region begins, we have

\[ \frac{dE}{dx}|_{x^*} = 0 \]

Assuming \( \mu_n = \mu_p \) and \( \alpha_n = \alpha_p \), the generation-recombination rate may
be written as
\[
U = \frac{J}{E} f(E) \quad 0 \leq x < a; \quad a < x \leq 1
\]
\[
= 0 \quad \text{as} \quad x \leq 1-a
\]  
(5.54)

where \( f(E) \) has the same functional form of the ionization rate. For example, consider the case where
\[
f(E) = a \left( \frac{E}{E_o} \right)^m \quad E \geq E_o
\]
\[
= 0 \quad E < E_o
\]

Thus, Eqs. (5.51) and (5.52) reduce to
\[
x^* = \int_{E(0)}^{E(x^*)} \frac{E(x) \, dE}{k \sqrt{J} \left[ E^{m+1}(x) - E^{m+1}(x^*) \right]} 
\]  
(5.55)

\[
J = 2J_n(0) + k \sqrt{J} \left[ E^{m+1}(0) - E^{m+1}(x^*) \right] 
\]  
(5.56)

where
\[
k = \sqrt{\alpha/(m+1)E_o^m}
\]

Eq. (5.55) can be modified to yield for the current density
\[
J = \frac{B}{2} + \sqrt{\left( \frac{B}{2} \right)^2 - C}
\]

where
\[
B = 4 J_n(0) + k^2 \left( E^{m+1}(0) - E^{m+1}(x^*) \right)
\]
\[
C = 4 J_n^2(0)
\]

Eqs. (5.53), (5.55) and (5.56) have been solved simultaneously to determine \( J \), and \( E(x^*) \). The voltage drop across the sample can be determined after solving Poisson's equation. The computed \( V-I \) characteristics, for different boundary conditions and model parameters, are presented in Figs. 5.10 and 5.12. The details of computed CCNR characteristics clearly depend on the assumptions made. However, their basic features are in general agreement and will probably remain true for any reasonable assumptions concerning the physical mechanisms involved.
Fig. 5.10 Computed voltage-current characteristics: injected carriers are taken to be given by Schottky thermionic emission; $C_2 = 0.1$, $\alpha = 5$, $m = 8$, and $E_0 = 50$

Fig. 5.11 Field distribution within a film having constants of Fig. 5.10 with $a = 0.5$
Fig. 5.12 Computed voltage-current characteristics: injected carriers are taken to be given by the Fowler-Nordheim tunneling; $H=400$, $a=0.2$, $m=8$ and $E_0 = 50$

Fig. 5.13 Computed voltage-current characteristics; injected electrons are taken to be given by Schottky thermionic emission; $C_s=0.1$, $k=0.4$, $\beta=0.125$ and $E_0 = 50$
5.4.5 Asymmetrical Case

In this case, electrons and holes have different properties and the boundary conditions at the cathode and anode are different. Thus, the two electrodes will not be equidistant from the minimum field point. The position of the minimum field point depends on the true mechanisms involved. Since it is believed that thin films exhibiting CCNR contain a neutral region, it will be assumed that a charge neutrality region will occur in the space between \( x^* \) and the anode. The generation-recombination rate function may be written as

\[
U = \sqrt{\frac{\mu_n e d}{A_n}} \frac{J_\alpha n}{E} \frac{(1+\alpha p/\mu_n)}{(1+(\mu_p/\mu_n))}
\]

And if \( \mu_n \gg \mu_p \), the above relation may be approximated by

\[
U = \sqrt{\frac{\mu_n e d}{A_n}} \frac{J_\alpha n}{E} \]

Thus, we may write

\[
U = \frac{J}{E} f(E) \quad 0 \leq x < a
\]

\[
= 0 \quad \text{elsewhere}
\]

For the case where \( f(E) \) is given by

\[
f(E) = \alpha \exp(\beta E) \quad E \geq E_0
\]

\[
= 0 \quad E < E_0
\]

Eqs. (5.51) and (5.52) reduce to

\[
x^* = \int_{E(0)}^{E(x^*)} \frac{E(x) dE}{k \sqrt{\exp(E(x)) - \exp(\beta E(x^* - E(0))}}
\]

\[
J = 2J_n(0) + k \sqrt{\exp(\beta E(0)) - \exp(\beta E(x^*))}
\]

where

\[
k = \sqrt{(2(1 + 1/\delta)\alpha)/\beta}
\]
Fig. 5.13 shows the computed V-I characteristics using Eqs. (5.57) and (5.58). The injected electrons have been assumed to be given by Schottky thermionic emission. The constants used in computing Fig. 5.13 have been chosen to give characteristics similar to those obtained for the symmetrical case. However, one would expect that a major difference between this case and the symmetrical case would be a great reduction in the absolute value of the current density.

5.4.6 Discussion

It is believed\(^6\) that some physical processes responsible for CCNR characteristics in thin films are position dependent in addition to being field dependent. In the present model the generation-recombination rate is taken to be a position dependent process. However, other processes and film constants could be equally position dependent.

A model, for a film with blocking contacts and containing a position dependent generation-recombination rate, has been developed with the ability to exhibit CCNR characteristics. The computed results have the following features in agreement with experimental results:

(1) The threshold voltage depends greatly on the model parameters. Such dependence could explain the variation of \(V_{th}\) from sample to sample, because the generation-recombination rate could be sensitive to the preparation conditions.

(2) The sustaining voltage is almost constant and is related, in the present model, to the value of the electric field below which the generation rate is negligibly small.

(3) The reduction of the threshold voltage by white illumination
could be explained in terms of increasing the generation rate.

(4) Recombination radiation is to be expected since one of the basic mechanisms involved in the present model is the electron-hole recombination. Recombination processes could be interband recombination and/or through recombination centres.

5.4.7 Small Signal Equivalent Circuit

Spatial charge distribution obtained by using the present model (Fig. 5.11) suggests that a film could be divided into three distinct regions.

Regions one and three contain net positive and negative charge respectively, while region two is a neutral one.

Space charges density \( Q_1 \) and \( Q_2 \) are not linearly proportional to \( V_1 \) and \( V_3 \) and thus, it is more useful to define differential capacitances:

\[
C_{1d} = \frac{dQ_1}{dV_1} \quad (5.59)
\]

and

\[
C_{3d} = \frac{dQ_3}{dV_3} \quad (5.59)
\]

In the same way we define differential conductances

\[
G_{id} = \frac{dJ_i}{dV_i} \quad i = 1, 2, 3 \quad (5.60)
\]
now, if the applied voltage is a small ac signal superimposed on large dc bias, i.e.,

\[ V = V_0 + \tilde{v} \exp(j\omega t) \quad \tilde{v} \ll V_0 \]

the current modulation around its dc steady state \( J_0 \) has two components: One is in phase and the other out of phase with the applied ac signal. In region one, the two components are given by

\[
\begin{align*}
J_{1r} &= G_{1d} \tilde{v}_1 \\
J_{1q} &= \frac{dQ_1}{dt} = C_{1d} \frac{d\tilde{v}_1}{dt}
\end{align*}
\]

Similarly for region three

\[
\begin{align*}
J_{3r} &= G_{2d} \tilde{v}_3 \\
J_{3q} &= \frac{dQ_3}{dt} = C_{3d} \frac{d\tilde{v}_2}{dt}
\end{align*}
\]

while for region two, the capacitive component is given by

\[
J_{2q} = \frac{dD}{dt} = \frac{\varepsilon}{d_2} \frac{d\tilde{v}_2}{dt} = C \frac{d\tilde{v}_2}{dt}
\]

where

\[ C = \varepsilon / d_2 \]

which is generally small compared with \( C_{1d} \) or \( C_{2d} \). The resistive component is given by

\[ J_{2r} = G_{2d} \tilde{v}_2 \]

The above considerations lead to the small signal equivalent circuit shown in Fig. 5.14.
The equivalent series resistance and capacitance of the above circuit, neglecting C, are given by

\[
R_s = \frac{R_{13} + \omega^2 \tau_1^2 R_{3d} + \omega^2 \tau_3^2 R_{1d}}{1 + \omega^2 (\tau_1^2 + \tau_3^2) + \omega^4 \tau_1^2 \tau_3^2} + R_{2d}
\]  
(5.62)

\[
C_s^{-1} = \frac{\omega^2 (\tau_1 R_{1d} + \tau_3 R_{3d}) + \omega^4 \tau_1 \tau_3 (\tau_3 R_{1d} + \tau_1 R_{3d})}{1 + \omega^2 (\tau_1^2 + \tau_3^2) + \omega^4 \tau_1^2 \tau_3^2}
\]  
(5.63)

where

\[
\tau_1 = R_{1d} C_{1d}
\]
\[
\tau_3 = R_{3d} C_{3d}
\]
\[
\tau_{13} = R_{1d} + R_{3d}
\]
The series equivalent resistance tends to a constant value as the frequency tends to zero or infinity:

\[
\lim_{\omega \to 0} R_s(\omega) = R_{1d} + R_{2d} + R_{3d}
\]

(5.64)

\[
\lim_{\omega \to \infty} R_s(\omega) = R_{2d}
\]

(5.65)

and generally, we have

\[
R_s(0) \geq R_s(\omega) \geq R_s(\infty)
\]

(5.66)

The present model allows for a negative \( R_{2d} \) (see Fig. 3.11). Thus, the sample could exhibit NDC over a range of frequencies. The magnitude of the capacitance \( C \) will determine the upper frequency limit.

5.5 **Formation of Current Filaments Due to Radial Diffusion**

Ridley has shown that bulk diodes exhibiting CCNR characteristics form current filaments in an attempt to achieve electrical stability. Current filaments have been observed experimentally in thin film chalcogenide diodes. The filament shape depends on the actual mechanisms involved, e.g., Joule heating (Sec. 5.2), radial diffusion, radial drift due to radial field and space charge effects. The problem of filament formation is a difficult one and only an approximate analysis may be possible. In this section, an approximate treatment of current filament due to radial diffusion will be presented.

Eqs. (5.29) and (5.33)-(5.35) may be written in the normalized form as

\[
\nabla \cdot J_n = U
\]

(5.67)

\[
\nabla \cdot J_p = -U
\]

(5.68)
\[
J_n = -C'_1 \nabla n + En \tag{5.69}
\]
\[
J_p = C'_1 \nabla p + Ep \tag{5.70}
\]
\[
\nabla \cdot E = n - p \tag{5.71}
\]

Where \(C'_1\) is the radial diffusion constant, neglecting the longitudinal diffusion.

The above set of equations can be combined to yield a differential equation describing the current distribution in the radial direction (i.e., the filament shape). To obtain this equation, subtract Eq. (5.68) from Eq. (5.67) to get

\[
\nabla \cdot (J_n - J_p) = 2U
\]

Substituting from Eqs. (5.69) and (5.70) and assuming that \(J = (n+p)E\), we get

\[
-C'_1 \frac{\partial^2 J}{\partial E^2} + \nabla \cdot (E(n-p)) = 2U \tag{5.72}
\]

Now, if

\[
J = J(r)
\]

and

\[
E = E(x)
\]

and since

\[
\nabla = \nabla_x + \nabla_r
\]

we get

\[
\frac{\partial^2}{\partial x^2} \left( \frac{J}{E} \right) - \frac{\partial^2}{\partial r^2} \left( \frac{J}{E} \right) + \frac{1}{E} \frac{\partial^2}{\partial r^2} \left( J \right) = 2U \tag{5.73}
\]

Substituting Eq. (5.73) in Eq. (5.72), and integrating between the sample ends (i.e., 0.0 and 1.0) assuming that \(n(0) \ll p(0)\) and \(p(1) \ll n(1)\) and using Eq. (5.54) for \(U\), we get

\[
\frac{\partial^2}{\partial r^2} J + J \left[ \int_0^1 \frac{\partial^2}{\partial x^2} \left( \frac{1}{E} \right) dx + \frac{2}{C'_1} \left( \int_0^1 \left( f(E)/E \right) dx - 1 \right) / \int_0^1 \left( \frac{1}{E} \right) dx \right] = 0 \tag{5.74}
\]
Since the term inside the bracket could be a positive or negative quantity

we may write Eq. (5.74) as

\[
C_1 \nabla_r^2 J = \left( \frac{J}{\tau_-} - \frac{J}{\tau_+} \right)
\]

(5.75)

\[
\Delta \equiv -\frac{J}{\tau_-} \quad 0 < r < r_c
\]

(5.76a)

\[
\Delta \equiv \frac{J}{\tau_+} \quad \text{elsewhere}
\]

(5.76b)

To determine the filament shape, Eq. (3.74) may be solved with the boundary conditions

\[(\nabla_r J)_{r=0} = 0 \quad \text{and} \quad (\nabla_r J)_{r=\infty} = 0 \]

(5.77)

However, only approximate expressions for the functions involved may be determined. In the remaining part of this section, we will assume \(\tau_-^*\) and \(\tau_+^*\) are functions of the current density \(J\). Rectangular co-ordinates will be used.

Table 5.2 has been obtained for presumed current dependence of both \(\tau_-^*\) and \(\tau_+^*\). The complete filament shape could be determined by matching current densities and their derivatives at \(y = y_c\). Several features of current filaments are shown in Fig. 5.15 which has been computed for the case in which both \(\tau_-^*\) and \(\tau_+^*\) are constant. The current density distribution is given by

\[
J_x(y) = J_o \cos \left( y \sqrt{\frac{C_1}{18}} \right) \quad 0 \leq y \leq y_c
\]

\[
J_x(y) = \left( J_o / \sqrt{2} \right) \exp \left( \frac{(y_c - y)}{\sqrt{C_1^2}} \right) \quad \text{elsewhere}
\]

With

\[
\tan \left( y_c \sqrt{\frac{1}{18}} \right) = 1
\]
Solution of the equation
\[
\frac{d^2J}{dy^2} = -\frac{J}{C_1^\gamma} \quad \frac{dJ}{dy}_{y=0} = 0
\]

Solution of the equation
\[
\frac{d^2J}{dy^2} = \frac{J}{C_1^\gamma^*} \quad \frac{dJ}{dy}_{y=\infty} \to 0
\]

<table>
<thead>
<tr>
<th>(\tau^*)</th>
<th>Solution of the equation</th>
<th>Solution of the equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta)</td>
<td>(J(y) = J_o \cos(y/\sqrt{C_1^\beta}))</td>
<td>(J(y) = J_b \exp(-(y-y_c)/\sqrt{C_1^\beta}))</td>
</tr>
<tr>
<td>(\beta/J^M)</td>
<td>(J(y) = \frac{\sqrt{M/2+1}C_1^\beta}{\int_{J(y)}^{J_o} \frac{\sqrt{M+2}J}{J^M+2(y)} - \frac{\sqrt{M+2}}{J_o}} = y)</td>
<td>(J(y) = \frac{J_b}{[1+(y-y_c)J_b^M/2(M/\sqrt{(2M+4)C_1^\beta})]}^{2/M})</td>
</tr>
<tr>
<td>(\beta J/\exp(\alpha J))</td>
<td>(J(y) = J_o + \log_2(1+\sqrt{1-\exp(\alpha(J-J_o))}) - y/\sqrt{2\alpha C_1^\beta})</td>
<td>(\sec^{-1}(\exp(\frac{\alpha}{2}J_b)) - \sec^{-1}(\exp(\frac{\alpha}{2}J(y))) = \sqrt{\alpha/2C_1^\beta} (y-y_c))</td>
</tr>
</tbody>
</table>

\(\alpha, \beta\) and \(M\) are constants. \(J_o\) and \(J_b\) are the values of current densities at \(y=0\) and \(y=y_c\) respectively.

**TABLE 5.2 Analytical Expressions for Filament Shape**
It is apparent that the current density is almost constant around the filament centre and then drops rapidly to a diminishing value within a few characteristic lengths \((\sqrt{c_1\beta})\), and that the width of the current filament is proportional to the radial diffusion constant.

5.6 Memory State Formation

Experimental results indicate that a memory state can be realized by passing high current density through the sample in the low resistivity state so that a critical current density is exceeded. This critical current density depends on the composition, sample thickness, ambient temperature and perhaps other parameters.
In order to explain the memory state, which is stable under zero bias, Pearson has postulated some kind of semipermanent change in the sample structure. It seems reasonable to assume that the passage of high current, especially if the conduction current concentrates in a narrow filament, results in enough Joule heating to allow structural changes (e.g., phase separation or amorphous to crystalline transformation). If the new phases are of low resistivity and tend to form a continuous channel (in the position of the current filament) between the two metal electrodes, the low resistance channel that had been formed would be stable at zero bias. Thus, the conducting state will persist without noticeable decay.

The re-establishment of the high resistance state by passing a high current pulse in the memory state could be explained by postulating that the high pulse will result in fusion of some spots in the conducting channel that had been formed. Now, if the current ceases abruptly, these fused spots would be quenched to reinstate the amorphous high resistance state in the sample. On the other hand, if the current is decreased slowly, the slow cooling of the fused spots would result in recrystallization or phase separation to reform the continuous conducting channel and thus the sample would remain in the memory state.

Thus, memory switching could be considered as due to structural changes brought about by high electric fields and Joule heating in filaments.

5.7 Summary

Although sample self-heating could account for delay times observed experimentally, the fast switching in thin chalcogenide semiconductor films is believed to be electronic in nature. Thus, self-heating serves only to
initiate an electronic switching mechanism. A model for CCNR due to space charge formation is proposed. The injected current carriers could develop a space charge barrier near the electrode by impact ionization. The concept of position dependent generation-recombination rate is discussed. The position dependent processes could represent the actual physical situation. The computed results, using the proposed model, show many features which are in agreement with the experimental results, e.g., the dependence of threshold voltage on model parameters and the constancy of the sustaining voltage.

Conduction through diodes exhibiting CCNR characteristics is of the filamentary type. A differential equation is derived to describe the filament shape. The memory state can be explained in terms of a phase change mechanism due to excessive heating which could produce a highly conducting channel. To destroy the memory state, the conducting channel must be interrupted at some spot.
6. Filamentary Breakdown in Thin Anodic Films

6.1 Introduction

Dielectric breakdown could occur in thin anodic films before CCNR characteristics can be observed if the forming process described in Sec. 5.1 has not been performed. Dielectric breakdown is often classified as electric (intrinsic or avalanche) or thermal breakdown\textsuperscript{75,76}. This is a loose classification and it corresponds to the theoretical solutions of the problem of determining the breakdown strength. The breakdown event in thin films seems to occur in two stages, namely\textsuperscript{77}: (1) the establishment of a conducting channel between the electrodes and (2) the discharge of the sample's stored energy through this channel. The second stage can be explained in terms of the heating and evaporation of the dielectric and the associated counter electrodes, but the main problem is in identifying and interpreting the conducting channel formative processes. It seems probable that more than one process is operative in developing the conducting channel.

The principal theories of breakdown have concentrated only on the inception of breakdown. Experimental studies using samples with self-heating breakdown provide a better opportunity for understanding the destructive phase and a possibility of distinguishing between film electrical properties governed by weak spots or bulk conditions.

The present study is concerned mainly with the breakdown in thin oxide films prepared anodically. It is confirmed experimentally that filamentary conduction takes place just before the onset of breakdown, but it is rather difficult to identify the process responsible. Some of the possible physical processes (electron avalanche, collective electron, ionic transport and thermal runaway) are discussed. The conditions for thermal runaway of an
incomplete channel are investigated. The discharge of a channel is observed experimentally and the rate of voltage collapse is accounted for in terms of the sample capacitance discharging through the channel.

6.2 Electric Breakdown Theories

Electric breakdown theories are either of the avalanche or collective electron type. Collective electron theories assume that breakdown is intrinsic, i.e., independent of cathode material and sample thickness. They assume that breakdown occurs when the rate of gain of energy by conduction electrons from the applied field, $A$, is more than the rate of loss of energy, $B$, which may be due to electron-phonon interactions and, in an imperfect crystal, by collisions with trapped electrons and lattice defects, i.e.,

$$A(E, \epsilon, T_o) > B(\epsilon, T_o) \quad (6.1)$$

where

$E$ is the electric field.

$\epsilon$ is the electron energy.

$T_o$ is the ambient (lattice) temperature.

Thus no stable conduction electron distribution can exist when the electric field exceeds a critical value; and when this is exceeded the conduction electron density increases catastrophically. To be able to calculate the breakdown strength, a critical field strength criterion is needed. Fröhlich proposed that the critical field strength, $E_c$, is the highest at which balance is possible, i.e.,

$$A(E_c, I, T_o) = B(I, T_o) \quad (6.2)$$

where $I$ is the ionization energy. This is known as the high energy criterion in contrast to the low energy criterion proposed by von Hippel and developed by Callen. It identifies the electron energy $\epsilon$ of Eq. (6.1) with $\epsilon'$. 
that energy for which $B(e, T_o)$ is a maximum with respect to $e$. Thus, the critical field strength is given by

$$A(E_c, e', T_o) = B(e', T_o)$$

(6.3)

The high energy criterion yields values of electric strength equal to about 50% of the corresponding low energy values.

Avalanche theories assume that the loss of insulating properties is caused by a large increase in the number of conduction electrons sufficiently large to destroy the structure. The initiation of electron avalanche may be due to field emission, by quantum tunneling from valence to conduction band (Zener effect), or by collision ionization. The presence of space charge and cathode injection may affect the avalanche development. The single electron theory, or the forty generations theory, developed by Seitz has been used frequently for the interpretation of experimental results. It assumes that a single electron at the cathode starts an avalanche by impact ionization. Seitz determined the critical avalanche size at the anode considering the energy transfer to the lattice, and concluded that melting would result if the avalanche contained $10^{12}$ electrons, i.e., an electron must take part in about 40 ionizing collisions in traversing the specimen, irrespective of its thickness. The probability, $P$, that the electron energy increases from average energy, $e_{av}$, to the ionization energy, $e_I$, assuming no phonon scattering, is given by

$$P = \exp\left(-\frac{E_I}{e_{av}} \frac{1}{\tau} \left(\frac{dE}{dt}\right)^{-1} \frac{dE}{de}\right)$$

(6.4)

where $\tau$ is the mean time between two interactions. Since for an electron not undergoing collisions,

$$\frac{dE}{dt} = (2mc)^{1/2} \frac{eE}{m}$$

(6.5)
Eq. (6.4) can be reduced to

$$P = \exp(-H/E)$$  \hspace{1cm} (6.6)

where

$$H = \sqrt{\frac{m}{2e^2}} \int \frac{I_C}{\varepsilon_{av}} \frac{d\varepsilon}{\varepsilon^{1/2} \tau}$$  \hspace{1cm} (6.7)

and the electric field strength is given by

$$E_c = \frac{H}{\ln(d/E_c \mu \gamma)}$$  \hspace{1cm} (6.8)

where

- $d$ is the film thickness.
- $\mu$ is the average mobility.
- $\gamma$ is the critical number of generation ($\approx 40$).

The growth of the avalanche is a chance event, it depends on the probability $P_1$ of injection of electrons at the cathode and the probability $P_2$ of an avalanche growing in excess of the size required for destruction.

Thus, the statistical time lag is given by

$$T_s = (P_1 P_2)^{-1}$$  \hspace{1cm} (6.9)

which decreases rapidly when the applied field exceeds the critical field strength.

O'Dwyer\textsuperscript{79} calculated the field produced by positive charges left behind in the insulator by the electron avalanche. His calculations have shown that the field opposing the applied field would be $10^{13}$ V/m for a destructive avalanche containing $10^{12}$ electrons, spread over an area of about $10^{-9}$ m, while the dielectric breakdown occurs at about $10^8$ V/m. In an attempt to avoid such difficulty, O'Dwyer has developed a space charge modified field emission theory. The starting point of his theory is again Eq. (6.6) but he imposed the current continuity condition which results in a positive space
charge region near the cathode and thus a dependence of the dielectric strength on the sample thickness. It should be noted here, that the current continuity equation need not be sustained in the unidimensional configuration which O'Dwyer used, especially when a conducting channel is set up through the dielectric film.

The effect of cathode injection has been considered by Forlani and Minnaja. They assumed that the current injection at the cathode dielectric interface is governed by Fowler-Nordheim tunneling mechanism. The injected current, $I_c$, increases by collision ionization through the dielectric to a value at the anode, $I_a$, given by

$$I_A = I_c \exp \alpha(E)d$$  \hspace{1cm} (6.10)

$$= AE^2 \exp \left(-\frac{B\phi^{3/2}}{E} + \alpha(E)d\right)$$  \hspace{1cm} (6.11)

where

$\alpha(E)$ is the ionization rate.

$\phi$ is the cathode work function.

$A$ and $B$ are constants.

The critical field strength will be given by the zero of the exponent, i.e.,

$$E_c = \frac{B\phi^{3/2}}{\alpha(E)c}d$$  \hspace{1cm} (6.12)

And for the case where the field strength is so high that the lattice vibration has no effect on the process of collision ionization, the rate of collision ionization is thus the reciprocal of the distance travelled by a free electron in attaining energy $I$, i.e.,

$$\alpha(E) = \frac{eE}{I}$$  \hspace{1cm} (6.13)
And thus,

$$E_c = \frac{\sqrt{2} \sqrt{2} \pi m \hbar^2 d^{3/2}}{3 \hbar e^2} \quad (6.14)$$

Where \( \hbar \) is Planck's constant. A similar expression with different thickness dependence can be derived by taking the injection current to be governed by Schottky thermionic emission.

Finally, it should be pointed out that no one of the above theories seems to be able to account for, even qualitatively, the experimental results. Each theory disagrees with one or more of the observed dependences on experimental conditions and sample parameters such as sample thickness and ambient temperature dependence and possible electrode dependence of breakdown strength. It seems more probable that more than one of the above mechanisms is operative at a time, so that the actual mechanism is more complex and changes considerably with changes in the condition of the experiment.

6.3 Breakdown Tests: Experimental Procedure

6.3.1 Sample Preparation

Ta_2O_5, Al_2O_3, Nb_2O_5 and TiO_2 capacitors 2 mm in diameter were prepared by the techniques summarized in Table 6.1. To ensure self-healing breakdown the metal counterelectrode thickness was, in all cases, less than 1000 Å such that it evaporates at the breakdown sites before sample destruction occurs. Ta_2O_5 and Nb_2O_5 film thicknesses were estimated using a model 14-Cary spectrophotometer making no allowance for the difference in substrate. Al_2O_3 and TiO_2 film thicknesses were estimated from bridge measurements assuming \( \varepsilon_r = 8.8 \) for Al_2O_3 and \( \varepsilon_r = 50 \) for TiO_2. A Sloan angstrometer was used to estimate counter-electrode thickness.
<table>
<thead>
<tr>
<th></th>
<th>Ta/Ta$_2$O$_5$/M</th>
<th>Al/Al$_2$O$_3$/M</th>
<th>Nb/Nb$_2$O$_5$/M</th>
<th>Ti/TiO$_2$/M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Metal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Used metal</td>
<td>sputtered Ta Film</td>
<td>Evaporated Al Film*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Metal surface preparation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dielectric Film Growth</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Anodizing electrolyte</td>
<td>0.5%(by value)H$_2$SO$_4$</td>
<td>5%(by weight)H$_3$PO$_4$ solution concentrated with concentrated NH$_4$OH</td>
<td>0.5%(by volume)H$_2$SO$_4$</td>
<td>Saturated ammonium borate in ethylene glycol</td>
</tr>
<tr>
<td>4. current density</td>
<td>0.5 mA/cm$^2$</td>
<td>0.5 mA/cm$^2$</td>
<td>0.5 mA/cm$^2$</td>
<td>0.5 mA/cm$^2$</td>
</tr>
<tr>
<td>5. Final voltage is kept constant for</td>
<td>one hour</td>
<td>20 minutes</td>
<td>one hour</td>
<td>one hour</td>
</tr>
<tr>
<td><strong>Counterelectrodes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Counterelectrode preparation technique **</td>
<td>evaporated Au, Al, In</td>
<td>evaporated Au, Al</td>
<td>evaporated Au</td>
<td>evaporated Au</td>
</tr>
</tbody>
</table>

* Evaporation was carried out at 10$^{-5}$ torr or less using conventional belljar system Veeco (400)

** Counterelectrode areas were defined by using photoetched beryllium copper masks.

Table 6.1 Sample Preparation techniques
6.3.2 Electrical Measurements

Prebreakdown conduction currents were measured using a Keithley type 417 high speed picoammeter. Breakdown strength was measured using a ramp waveform from the sweep circuit of a Tektronix model 515A oscilloscope. The ramp rate was adjusted such that the applied electric field increased by about 0.5 MV/cm sec. When the breakdown event took place, the breakdown pulse generated by the abrupt change in the sample voltage was amplified, shaped and fed into the gate terminal of a silicon controlled rectifier (SCR) which, on triggering, short circuited the sample. The SCR remained in the high conductivity state until the applied voltage dropped to zero. Then another ramp was applied to the sample. Voltage collapse was observed during the breakdown event, on applying a single pulse generated by an HP model 214A pulse generator, with a Tektronix type 581 oscilloscope and photographed with Polaroid type 410 film.

Most measurements were carried out in air at room temperature with the sample in an electrically shielded dark chamber. For temperature dependence measurements, the temperature was controlled by placing the sample in a Statham SD6 oven which allowed for a temperature range between -40°C and 150°C.

6.4 Breakdown Tests: Experimental Results and Discussion

6.4.1 Prebreakdown Conduction

Dc conduction currents through amorphous dielectric films for electric fields in excess of 10^4 V/m often approximate to the form

\[ J = C \exp\left(-\frac{\phi - \beta E^{1/2}}{kT}\right) \]  \hspace{1cm} (6.15)

Where

- \( J \) is the current density.
- \( E \) is the average electric field.
- \( k \) is Boltzmann's constant.
- \( C, \phi \) and \( \beta \) are constants.
Figs. 6.1 and 6.2 show Schottky plots for Ta/Ta₂O₅/Au samples and the temperature dependence of the dc conduction current respectively. Even though these samples obey Eq. (6.15) up to field strengths close to the breakdown strength, the values of C, ϕ and β depend strongly on the applied field polarity. The observed rectification can be attributed to the relative ease of electron injection when the tantalum electrode is negative. Apart from the difference between the two metal work functions, the presence of ionized positive defects near the tantalum electrode, which can be due to excess tantalum ions at the metal oxide interface, may enhance current injection when the tantalum electrode is negative. The energy band diagram given in Fig. 6.3 shows clearly that the energy barrier at the cathode is lowered only when the positively charged defects are near the cathode.

The agreement between experimental results and Eq. (6.15) indicates that the conduction process is a thermally activated electronic process rather than an ionic process which, if present, would exhibit an exponential voltage-current characteristic.

Measurements of sample current versus ramp voltage (or, time) up to the point of the breakdown are shown in Fig. 6.4. Such currents are given by

\[ I = I_c + CV \frac{dv}{dt} \]  

(6.16)

Where

- \( I_c \) is the conduction current.
- \( C \) is the sample capacitance.
- \( V \) is the voltage.

For a ramp voltage, the charging current is constant while the conduction current varies with the voltage magnitude. Current rectification is again clear in Fig. 6.4; the ratio between the conduction current at the onset
Fig. 6.1 Schottky plot for Ta₂O₅ films

Fig. 6.2 Temperature dependence of conduction current: applied voltage = 25V; Film thickness (Ta₂O₅) = 1820 Å
Fig. 6.3 Energy band diagram for a metal/dielectric/metal showing the effect of a positive ion at a depth of a. The different barrier shapes are for different impact radius r (Ref. 81).

Fig. 6.4 Current-voltage characteristics of $a_0 Ta_2O_5$ film using an applied ramp voltage (film thickness = 2050 Å)
of breakdown when the tantalum electrode is negative to that when it is positive is about $10^3$. Fig. 6.4 also indicates that the transition to the breakdown condition occurs without a current precursor.

6.4.2 Filamentary Breakdown

The following experiments performed on self-healing samples were intended to demonstrate the existence of filamentary breakdown in anodic oxide films.

6.4.2.1 Optical Microscope Observations

By using self-healing samples a distinction can be made as to whether the destruction of a sample occurs over the whole of its area or in a narrow filamentary channel, since the thin metal electrode evaporates at the breakdown sites. Fig. 6.5 shows clearly that breakdown occurs over a localized site of the tested sample. Breakdown patterns as shown in Fig. 6.5 contain a central region of complete destruction of the three layers of the sample surrounded by a region of heavy, but lesser, damage. The area evaporated from the metal electrode was concentric with the central region and its spread depended on the metal film thickness.

Single channel breakdown can be observed only when the measuring circuit time constant is larger than the duration of the breakdown event, virtually no energy is supplied by the external circuit. On the other hand destruction over a larger area than that of a single channel can be observed if the voltage source is allowed to supply energy to the sample during breakdown. This breakdown is possibly triggered by a single channel breakdown. As Klein and Gafni noted in their studies on silicon oxide films, there may be two modes of propagation. In the first mode (Fig. 6.6A) single channel breakdowns occur at adjacent sites because the temperature rise and mechanical damage at the
Fig. 6.5 Typical single channel breakdowns (2.5 μm/div)

(A)

Fig. 6.6 Extended breakdown patterns (10 μm/div)

(B)
previous site aid the breakdown at the new site when sufficient energy is supplied from the supply. In the second mode (Fig. 6.6B), an arc destroys the upper electrode, the arc burning for as long as the supply can maintain it.

6.4.2.2 Observation of Voltage Collapse

The possibility that a sample can be recharged after the occurrence of breakdown events is another indication that breakdown is a filamentary type. This can easily be observed on an oscilloscope.

Typical voltage-time oscillograms on the application of single rectangular pulses are presented in Fig. 6.7 for one sample. These oscillograms show clearly that the rate of breakdown occurrence increases with increasing pulse magnitude and that all breakdown events start when the voltage magnitude across the sample reaches a well defined voltage, $V_b$, confirming that the observed breakdown strength is that of the bulk dielectric rather than of weak spots. It also shows that breakdown terminates at another defined voltage, $V_{\text{min}}$, (for possible explanation see Sec. 6.6.2). Thus, the energy dissipated in each breakdown event is given by

$$\varepsilon = \frac{1}{2} C(V_b^2 - V_{\text{min}}^2)$$  \hspace{1cm} (6.17)$$

provided that no energy is supplied by the external source.

The voltage waveform on a single breakdown event is shown in Fig. 6.8. The oscillogram shows that the transition from prebreakdown to breakdown conduction occurs without any current precursors. The current density at the onset of breakdown is as high as $10^6$ Amp/cm$^2$ and it starts to decrease as the threshold for the cessation of breakdown is approached. It was found that, in all cases, the voltage collapse takes place in a time period less than 200 nanoseconds.
Fig. 6.7 Voltage waveform across a sample. The number of breakdown events increase as the magnitude of the applied pulse increases. Horizontal scale $10^{-5}$ sec/div and vertical scale 15 V/div.

Fig. 6.8 Voltage collapse on single breakdown event. Horizontal scale $2 \times 10^{-7}$ sec/div and vertical scale 15 V/div.
6.4.2.3 Possible Physical Mechanisms for Channel Formation

In view of the facts that breakdown occurs at localized spots, that the rate of occurrence increases with increasing applied voltage and that thermal breakdown can not account for fast breakdown events in the case of high resistivity materials (Sec. 6.5), the breakdown must be associated with electric processes which can concentrate the conduction current into a narrow filament. The concentration of power dissipation within a narrow region could lead to instantaneous breakdown or, at least initiate a thermal runaway which would eventually lead to a breakdown event. Some of the possible electric processes responsible for channel formation will now be discussed.

(a) Electronic Avalanche

The formative processes could be an electronic avalanche, sustained possibly by field emission or Schottky emission at the cathode/dielectric film interface. Due to variations in the electron emissivity at the cathode, it seems probable that one particular site will eventually dominate so that a channel of high conductance will be formed. If the electronic avalanche is not sufficient to cause instantaneous breakdown, it could nevertheless result in a temperature increase of a few hundred degrees centigrade in the channel. A simple analysis based on the assumption that the channel is a uniform cylinder of cross-sectional area $A_c$ and that no heat conducts away from the channel, gives for the temperature rise $\Delta T$ the following relation

$$\Delta T = T_1 - T_0 = \frac{neE}{c\rho A_c}$$

(6.18)

where $n$ is the number of electrons in the avalanche, $c$ and $\rho$ are the film specific heat and density respectively. This temperature rise could initiate thermal runaway and breakdown would occur after a delay time $\tau_D$ which would depend on sample and channel parameters.
(b) **CCNR Characteristics**

Any diode exhibiting CCNR characteristics tends to form a current filament in an attempt to reach electrical stability. The excessive Joule heating in the channel could initiate a breakdown event (Chapter 5).

(c) **Molecular Dissociation**

A high applied field approaching the formation field could disrupt the chemical bonds between film constituents. The product of dissociation at a starting point will help in forming the channel: the produced ions can cause field distortion and the presence of energetic ions and electrons could break more bonds and thus, the accumulative process could finally set up a conducting channel between the two electrodes. The channel temperature will depend on the total charge passed and the heat produced due to the breaking of chemical bonds.

(d) **Localized Defects**

In order to show that the presence of a defect inside the film may lead to a highly conducting channel, consider Fig. 6.9 in which D represents a defect, presumably of low resistivity.

![Diagram](a)

![Diagram](b)

**Fig. 6.9** Channel development due to a localized defect.
The concentration of conduction current in the weak spot can expand the low resistance region by Joule heating (Fig. 6.9b). The breakdown would occur when the maximum temperature in the channel reaches some critical value.

6.4.3 Breakdown Strength of Ta$_2$O$_5$ Films

The breakdown voltage, $V_b$, is defined as the average breakdown voltage measured as outlined in Sec. 6.3.2, after removing all weak spots in the film. The breakdown field strength, $E_b$, is then given by

$$E_b = V_b/d$$

(6.19)

6.4.3.1 Thickness Dependence of Breakdown Strength

The knowledge of the thickness dependence of breakdown strength could be of considerable importance in determining the breakdown mechanism, however it does not enable a definite conclusion to be drawn, e.g., intrinsic and impulse breakdown should be thickness independent while avalanche and steady state thermal breakdown would be dependent on thickness.

Experimental results presented in Fig. 6.10 show that Ta/Ta$_2$O$_5$/Au samples could withstand a field strength very close to the formation field when the tantalum electrode is positive. This gives an average breakdown strength, almost independent of dielectric film thickness, of the order of 5.2 MV/cm. When the SCR circuit was removed and the applied field was allowed to increase a few percent above the measured strength, a destructive breakdown was observed in all cases. The fact that breakdown strength is almost the same as the formation field suggests a possible existence of a relation between the breakdown mechanism and ionic transport. On the other hand, cathodic breakdown strength (i.e., when the tantalum electrode is negative)
Fig. 6.10 Thickness dependence of breakdown strength.

Fig. 6.11 Breakdown dependence on pulse width.
is also almost independent of dielectric film thickness but it drops to an average value of the order of 3.1 MV/cm. This result, similar to the rectification phenomena discussed in Sec. 6.4.1 can be explained in terms of the presence of positive charged defects near the tantalum electrode whose presence, in addition to enhancing current injection, could reduce the electric field strength from a high value at the tantalum/dielectric film interface (presumably, close to the formation field) to a lower value in the bulk such that the average field is appreciably lower than the maximum field strength inside the film. If this were true, one would expect that breakdown events would start near the tantalum electrode where the electric field is a maximum.

6.4.3.2 Breakdown Dependence on Pulse Width

The breakdown strength of Ta/Ta2O5/Au samples was also determined by applying pulses of fixed width while increasing the voltage magnitude until breakdown took place. The breakdown events were observed oscillographically. Voltage pulses were generated by a HP model 214A pulse generator which enables the generation of a single pulse each time. Fig. 6.11 shows the breakdown voltages for different pulse durations. The decrease of breakdown strength with the pulse duration can be attributed to space charge formation, near the tantalum electrode, whose density can be argued to increase with pulse duration, resulting in a decrease of breakdown strength (assuming that the formed charge is positive due to the removal of electrons from neutral defects). It is interesting to note that the cathodic breakdown strength increases more than the anodic breakdown strength. This suggests that the formation of positive space charge is more important when the tantalum electrode is biased negatively.
When many breakdowns are observed on a sample by applying a long pulse or a dc voltage, the pulse duration, \( \tau_p \), can be identified with the mean interval between breakdown events, \( \tau_D \), as

\[
\tau_p = \tau_D = \frac{1}{R}
\]  

(6.20)

where \( R \) is the breakdown rate which decreases with decreasing voltage magnitude, and the delay time, \( \tau_D \), could possibly be of the order of minutes or even hours (Sec. 6.5).

### 6.4.3.3 Temperature Dependence of Breakdown Strength

The average breakdown strength measured by the ramp method as a function of the ambient temperature, controlled by a Statham SC6 oven, is presented in Fig. 6.12. The experimental results can be fitted to

\[
E_b = A \exp(\Delta V/kT)
\]  

(6.21)

Where

- \( T \) is the ambient temperature.
- \( k \) is Boltzmann's constant.
- \( A \) and \( \Delta V \) are constants.

\( \Delta V \) was found to be about 0.04 eV when the tantalum electrode was negative and about 0.024 eV when it was positive.

Temperature dependence similar to that given by Eq. (6.21) can be derived using a model proposed by Fröhlich for an amorphous dielectric containing traps over an energy range equal to 2\( \Delta V \) below the conduction band. Fröhlich assumed that the free and trapped electrons are strongly coupled by interelectronic collisions and that energy is lost to lattice vibrations both by free and trapped electrons. Energy is gained only by the free electrons and the breakdown strength is that at which a definite limited electronic
Fig. 6.12 Temperature dependence of breakdown strength (film thickness = 2050 Å)

Fig. 6.13 Breakdown dependence on the formation current density.
temperature is no longer possible. Frohlich assumed that $\Delta V \gg kT$ and $\Delta V$ should be polarity independent: both these assumptions are inconsistent with the present experimental results.

The observed temperature dependence may be explained in terms of the ease of ionic motion as the temperature increases, and if the ionic motion is the initiating mechanism for breakdown, one would expect a decrease of breakdown strength as temperature increases.

6.4.3.4 Breakdown Dependence on the Formation Current Density

From the study of growth kinetics of thin anodic films (Appendix 2), it is known that film thickness depends on the final voltage and the current density, i.e., the electric field required to grow a film depends on the current density. Such a dependence is given by

$$D = \frac{BV}{kT \ln(J/J_o)}$$

(6.22)

where

$J$ is the current density.

$V$ is the final voltage.

$J_o$ and $B$ are constants.

Fig. 6.13 shows the breakdown strength of several films grown on tantalum sputtered films to a final voltage of 100 volts using different current densities. Though each film grows at a different field strength, all prepared films can withstand the forming field required for low current density growth (a few $\mu$Amp/cm$^2$). This result, in agreement with the results given in Appendix 2, indicates that some relaxation processes in the film structure take place after removing the formation voltage in such a way that the prepared films have, sometime after their preparation, almost similar characteristics which are independent of the formation current density.
6.4.4 Breakdown Dependence on Dielectric Constant

Breakdown dependence on both dielectric constant and melting point is presented in Fig. 6.14 for four different dielectrics grown anodically on Al, Ta, Nb and Ti as base metals. Even though it seems that there is no clear relation between breakdown strength and the melting point, the breakdown strength decreases as the dielectric constant increases, i.e.,

$$E_b = F(1/\varepsilon_r)$$

where $F$ is an appropriate function. Young has recently derived a relation between ionic conduction and dielectric constant:

$$B \propto \varepsilon_r (\varepsilon_r - n^2)/n^2$$

(6.23)

where $n$ is the refractive index. Thus, the potential barrier for ionic motion decreases with increasing dielectric constant resulting in a lower breakdown strength.

The above discussion confirms that there is a possible relation between ionic motion and breakdown mechanism. Thus, one may conclude that the initiating mechanism for breakdown could be the ionic motion, but it is not excluded that thermal runaway may occur at some stages of the breakdown process.

6.4.5 Electrode Effects

The metal electrode has manifold effects on the breakdown strength of dielectric films. Some metals are more likely to penetrate into microfissures in the dielectric film during vacuum deposition. Thus, if thick counter-electrodes (i.e., the samples are not self-healing) are used the dielectric breakdown strength will depend on the nature of the present microfissures and it will be lower than the true bulk breakdown strength. Even if all weak spots and microfissures are removed from the dielectric film, the thermal properties...
Breakdown dependence on dielectric constant and melting point (dielectrics are $\text{Al}_2\text{O}_3$, $\text{Ta}_2\text{O}_5$, $\text{Nb}_2\text{O}_5$ and $\text{TiO}_5$).

Electrode effect on breakdown strength. (Metals used are Au, Al and In).
of the counterelectrode metal could possibly influence the breakdown strength especially if thermal runaway took place at some stage of the breakdown process. Furthermore, the field emitting properties of the metal electrode, especially its work function, will determine the injected current density when it acts as a cathode and this in turn could affect the breakdown strength.

Fig. 6.15 shows the breakdown strength of Ta/Ta₂O₅/metal samples using three different metals for the counterelectrode. Though the cathodic breakdown strength does not depend on the metal counterelectrode, the anodic breakdown does. It seems reasonable to assume that the field emitting properties of the metal counterelectrode are responsible for the observed increase in breakdown strength as the metal work function increases.

6.5 On the Possibility of Thermal Breakdown

Thermal breakdown is often thought to occur over the whole sample, i.e., complete sample destruction would occur on breakdown event. Klein suggested that distinction can be made between thermal and electric breakdown on the basis of whether the destruction of a sample occurs over the whole of its area or in a narrow filamentary channel. However, it was suggested that complete sample destruction is merely a result of the test circuit used and can, by suitable circuit design, be prevented from taking place. Furthermore, when total destruction is allowed to occur it does so through a series of consecutive breakdowns, each of which is localized and similar to single-channel breakdowns that occur during electric breakdown. Further evidence was drawn for the non-thermal nature of these single-channel breakdown from measurements which indicated that the transition to breakdown conduction occurred very rapidly without a current precursor, and that the breakdown voltage threshold was not very sensitive to temperature or to pre-breakdown conductance.
Further evidence cited was that the light emission during breakdown had the arc spectrum of excited species derived from the insulator and electrode material, i.e., this luminescence was from the final destructive phase of breakdown when a plasma exists in some region of the sample. The purpose of this section is to show that, even though destruction may be of a filamentary nature it is still possible that breakdown could result from thermal effects.

Due to variations in electron emissivity at the cathode/dielectric interface and the possible occurrence of any of the processes discussed in Sec. 6.4.2, it seems probable that a particular site will eventually dominate forming a high conducting channel between the two metal electrodes. An electronic charge will be associated with the development of such a channel and it could possibly raise the channel temperature from the ambient temperature, $T_0$, to a higher temperature, $T_1$. The initial temperature rise, $\Delta T = (T_1 - T_0)$, depends on the true mechanisms involved. If the initial temperature rise is sufficiently high such that the voltage collapse across the sample would occur instantaneously, the breakdown would be termed electric in type. On the other hand, if the initial temperature rise in the channel was not sufficient to cause breakdown, it may be possible that a thermal runaway process could start that would eventually lead to sample destruction. Such breakdown would then be termed thermal in nature. A model is presented below that exhibits those latter characteristics.

6.5.1 Basic Equations

The passage of an electronic charge raises the temperature of its channel to a value depending on the magnitude of the electronic charge and on the applied field. The temperature rise could be appropriate to start thermal runaway within the channel while the rest of the sample remains at the ambient
temperature, \( T_0 \). The temperature distribution within the dielectric film is
governed by the heat conduction equation \(^6^9\).

The electric input power per unit volume to the sample is given by
\[
p_L = \sigma(E,T)E^2
\]
where \( \sigma \) is the electric conductivity of the film and \( E \) is the applied field.

Various forms for \( \sigma(E,T) \) have been considered in formulating breakdown theories\(^7^5\): the following equation is applicable to thin amorphous films subject to high applied fields when either Schottky emission or a Poole-Frenkel mechanism governs the electronic conduction
\[
\sigma(E,T) = \sigma_0 \exp((-E^{1/2} - \psi)/kT) \tag{6.24}
\]
where \( \sigma_0, \beta, \psi \) are the temperature-independent constants for the material and \( k \) is Boltzmann's constant. When the current is controlled by some mechanism involving a combination of the Schottky and Poole-Frenkel effects, the field and temperature conductivity dependencies become more complicated\(^2^5\).

The dielectric film is considered to be cylindrical with the hot channel symmetrical around the Z-axis. Approximations similar to those used in Sec. 5.2, reduce the heat conduction equation to
\[
\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} = \frac{\lambda}{\kappa}(T-T_0) - \frac{\sigma E^2}{K} + \rho c \frac{\partial T}{\partial t} \tag{6.25}
\]
where \( 1/\lambda \) is the external thermal resistance of the sample and \( \rho, c, K \) refer to the film density, specific heat and thermal conductivity respectively.

The above equation has been solved numerically to investigate the growth of the current filament and the breakdown delay time, \( \tau_d \), defined as the time required for the hottest point in the channel to reach a critical temperature, \( T_m \), which is taken as the dielectric melting point.
6.5.2 Results and Discussion

It is assumed that breakdown will occur if the input power is sufficiently high that despite the heat loss from the hot channel the central position of the channel can be raised to a critical temperature. The delay time, \( \tau_d \), between the initial avalanche and the onset of breakdown will depend on the film parameters, the applied field, and in the present model, on the initial temperature rise and other channel parameters.

The growth of the conducting channel has been investigated numerically using Eq. (6.25) in the finite difference form (central differences for spatial derivatives and forward differences for time derivative). A plausible form for the initial temperature distribution would seem to be given by

\[
T(r,0) = T_0 + \Delta T/(1+\exp((r-r_c)/\delta))
\]

(6.26)

where \( \Delta T \), \( r_c \) and \( \delta \) are constants.

Fig. 6.16 shows how the channel current and the temperature of the hottest point (\( T(0,t) \)) change with time for different initial temperatures. The culmination of any breakdown process is a catastrophic increase in temperature over some region of the sample. However, sample current need not increase catastrophically. The current flowing through the sample can be thought of as consisting of a component \( I_c \) flowing through the high conductivity channel and a component \( I_r \) flowing through the remainder of the sample which is at a low temperature and therefore presents a higher resistivity region.

\[
I_T = I_c + I_r
\]

\[
= 2\pi \int_c^\infty J_c(r)rdr + J_rA_r
\]

(6.27)

Now, if the channel area is small compared with the sample area the contribution
Fig. 6.16 Thermal runaway: channel current and maximum temperature variation versus time. (Constants used are $\lambda/d = 10^2$, $\sigma_0 = 10^{-6}$, $\rho_C = 4 \times 10^{-6}$, $\phi = 0.6$ eV, $\beta/k = 0.2$ eV, $K = 0.5$, $r_c = 20\AA$, $\delta = 5\AA$. Unless otherwise stated, M.K.S. units are used).
of $I_c$ to $I_T$ will be small. Hence, $I_T$ will tend to some limiting value governed mainly by the current in the low conductivity region. On the other hand, as the channel area increases $I_c$ will tend to dominate and thus

$$I_T = I_c$$

Thus, it is only for large values of the channel radius that $I_T$ increases rapidly. Practically, breakdown events are encountered which are not associated with catastrophic increase of current.

The results showed that the effective channel radius decreases with the passage of time. This suggests that the rate of heat loss from the channel edges exceeds that from the central portion of the channel. However, it would be expected that for a thin film the heat loss normal to the surface would tend to be more important than the radial flow parallel to the surface. In fact, it turns out that a good approximation to the delay times ($\tau_d$ model) computed from the above model may be obtained by calculating $T(t)$ at $r = 0$ from

$$\frac{dT}{dt} = P_i - P_L$$

i.e., by putting $(V^2 T)_{r=0} = 0$ provided the channel radius is not too small. When the channel radius becomes so small that the radial heat conduction can seriously affect the maximum temperature in the channel, then the delay time to breakdown will increase, resulting in high percentage error. Also, it follows that for a given initial temperature rise ($T(0,0)$) there is a lower limit for the channel radius $r_c$ below which the proposed mechanism may not be possible because the input power can be dissipated non-destructively. This limiting value of channel radius depends inversely on the initial temperature rise since as the latter increases so does the channel electrical conductivity and hence, the power input.
The delay time to breakdown, shown in Fig. 6.17, has been computed by the Runge-Kutta method, using the approximation $v^2T = 0$. For the range of parameters considered relevant to dielectric films (e.g., $\text{Ta}_2\text{O}_5$ films have $\rho\sigma^{-1} = 10^{13} - 10^{14}$ V$^2$ sec$^{-2}$ m$^{-2}$ K$^{-1}$) the delay time is of the order of one second. That breakdown can actually take place after the elapse of times of this duration can be seen, e.g., from the data of Klein and Burstein$^90$ for vapor-grown $\text{SiO}_2$ thin films. For breakdown to occur in much shorter times the initial temperature rise must increase so that $T(0,0)$ tends to the critical temperature $T_m$, under which circumstances the breakdown would be no longer classed as thermal. Klein and Burstein realized this in their pulsed applied voltage experiments and found it necessary to call the breakdowns on short pulses electric. Further data from Klein$^77$, this time for the dc breakdown of $\text{Al/anodic Al}_2\text{O}_3/Au$ structures shows that $\tau_d$'s as long as 100 seconds are possible at room temperatures. As would be expected, the time delay to breakdown decreased with raising of either the applied voltage (i.e., input power) or the ambient temperature.

An interesting consequence of the present model is that the breakdown could occur at lower applied fields provided a suitable temperature rise in a channel occurs. The required field may be obtained by equating the power input to the power loss. Assuming the latter to be given by $P_x$, i.e., again neglecting $v^2T$, we get

$$E^2 \exp((\beta E^{1/2} - \psi)/kT) = \frac{\lambda}{\rho\sigma_0} (T-T_0) \quad (6.29)$$

As $P_x$ increases exponentially with $T$ and $P_x$ linearly with $T$, Eq. (6.29) could be satisfied at two points. For the purpose of calculating the breakdown field it is necessary to consider only the condition when the derivative of the input power is equal or faster than that of power loss, i.e.,
Fig. 6.17 Variation of delay time to breakdown with the initial temperature rise for different power inputs.

Fig. 6.18 Variation of critical field with the initial channel temperature rise for different power losses.
\[ E^2 \left( \frac{\psi}{k} - \frac{8E^{1/2}}{k} \right) \exp\left( (\beta E^{1/2} - \psi)/kT \right) \geq \frac{\lambda}{d\sigma_0} T^2 \tag{6.30} \]

Fig. 6.18 shows the critical field as a function of initial temperature rise for different values of \( \lambda/d\sigma_0 \). As expected, the computed results show that the critical field decreases with increasing initial temperature rise. However, it should be noted that the probability of an avalanche occurring at low applied field is very small.

In conclusion of this section, thermal runaway can follow a non-destructive electric process which sets up a highly conducting channel between the electrodes and thus the breakdown can occur in a narrow channel, demonstrating that complete sample destruction does not have to result before a breakdown event can be classed as thermal. Current runaway may not be observed when the channel is sufficiently small and breakdown can occur at fields lower than the normally accepted breakdown strength provided the initial temperature rise caused by the avalanche is sufficiently high. For typical constants of dielectric films of current interest, the present model can only account for delay times of the order of seconds; for much shorter delay times the breakdown is presumably electric in nature.

6.6 Breakdown Mechanism

The study of successive breakdown events on applying a rectangular pulse of suitable magnitude (Fig. 6.13) suggests that the breakdown process consists of two successive stages. First a conducting channel between the metal electrodes is developed, and then the sample's stored energy is discharged through the formed channel. Both stages will now be discussed in some detail.
6.6.1 **Stage I: Formation of a Conducting Channel**

The first few breakdown events which are observed to occur at field strength less than the average breakdown strength can be started at some defects in the prepared sample as discussed in Sec. 6.4.2. The breakdown strength measured after removing all weak spots should be that of the bulk dielectric.

The study presented in Sec. 6.5 shows that thermal breakdown through a narrow channel in high resistivity materials would occur after appreciable delay times and it can not generally account for the observed much shorter delay times. The independence of breakdown strength on film thickness excludes the possibility that the avalanche processes are the channel forming processes. The breakdown strength dependence on the metal counterelectrode excludes the possibility of being a completely intrinsic breakdown.

In view of the facts that there is a strong dependence of breakdown strength on film dielectric constants and that anodic breakdown occurs at a field strength very close to the forming field, it may be reasonable to propose that the breakdown would be initiated by disruption in the chemical bonds as the applied field approaches the forming field. The product of molecular dissociation and the presence of energetic electrons could start an accumulative process which may form a highly conductive channel. The injected electrons, field distortion and thermal runaway could assist in the channel development.

Cathodic breakdown could be due to the same process except that the presence of positively charged defects near the base metal causes a
distortion in the electric field distribution with its highest value near the cathode. Thus, any molecular dissociation will start near the cathode while the average field is less than the forming field. Furthermore, the dissociation processes are greatly assisted by the higher injected current density at the cathode/dielectric interface. The higher sensitivity of cathodic breakdown strength on ambient temperature and pulse width can be attributed to the sensitivity of space charge development under the different conditions.

6.6.2 Stage II: Discharge of Sample's Stored Energy

As the conducting channel is completely developed, i.e., has attained the breakdown conditions, the sample's stored energy begins to dissipate in the channel. During the discharge, the sample can be represented by its capacitance, C, (assuming that it does not vary during the discharge since the channel area is a small portion of the sample area) in parallel with the channel resistance, R(t), which varies with time. Thus, the equivalent discharge circuit can be represented as shown below, where $V_s$ is the applied voltage and $R_s$ is the series limiting resistance.
The voltage across the sample, \( V(t) \), is thus given by

\[
V(t) = R(t)\left[\frac{V_s - V(t)}{R_s} - C \frac{dV(t)}{dt}\right] \quad (6.31)
\]

and the energy dissipated in the channel is given by

\[
\varepsilon(t) = \int_0^t P(t)dt = \int_0^t \frac{V^2(t)}{R(t)}dt \quad (6.32)
\]

This energy must be equated with the heat needed for material evaporation, the heat lost by radiation, the heat producing temperature increase around the breakdown spot and the heat gained by the oxidation of the electrodes, i.e.,

\[
\varepsilon(t) = \varepsilon_e + \varepsilon_r + \varepsilon_s - \varepsilon_o \quad (6.33)
\]

The radiation losses are negligible and so is oxidation. Conduction losses were estimated by considering the short time temperature transients in the material adjacent to the evaporated electrode and these were found to be a few percent of the heat energy required for material evaporation. Thus, if \( q_e \) is the latent heat of vaporization of a given sample per unit area, one may write

\[
\varepsilon(t) = q_e [A_c(0) - A_c(t)] \quad (6.34)
\]

Where \( A_c(t) \) is the cross sectional area of the channel at time \( t \) after starting the discharge. The channel resistance at time \( t \) is given by

\[
R(t) = \rho \frac{d}{A_c(t)}
\]

Thus, Eq. (6.34) can be written as

\[
\varepsilon(t) = q_e \rho d\left[\frac{1}{R(0)} - \frac{1}{R(t)}\right]
\]

\[
\approx \lambda R^{-1}(0)\left[1 - \frac{R(0)}{R(t)}\right] \quad (6.35)
\]

where
\( \rho \) is the channel resistivity.

\( \lambda \) is a sample constant.

\[ q_e \rho d \]

Fig. 6.19 Computed voltage collapse and channel resistance during the discharge.

The voltage collapse across the sample, \( V(t) \), and the channel resistance, \( R(t) \), can be obtained by solving Eqs. (6.31) and (6.35). The computed example (Fig. 6.19) shows that the voltage collapse occurs in a fraction of a microsecond and that the rate of voltage decay decreases as the voltage across the sample (or the sample's stored energy) becomes sufficiently low. These features are in good agreement with the experimental results (Sec. 6.4.2). After the channel resistance becomes sufficiently high (i.e., a main part of the channel has been evaporated), the sample will be charged again from the external source until another breakdown event takes place.
7. CONCLUSIONS

Space charge and high field effects on some electrical properties of thin amorphous films have been investigated.

A theory of space charge contribution to polarization currents in thin dielectric films has been proposed. The external discharge current on short circuiting a thin film capacitor is believed to consist of two components, one due to dielectric polarization and the other due to trapped space charge. The space charge contribution has been investigated using a model for a film containing traps whose densities vary exponentially with their binding energies. The effects of diffusion, metal work function and the presence of positive space charge have been considered. The computed space charge polarization currents follow a $1/t$ law when trapped electrons are in excess of electrical neutrality. A time-independent current is possible when there is a positive space charge. The current magnitude is almost independent of the initial amount of trapped charge in contrast to the linear dielectric polarization current which varies linearly with the preapplied field. Experimental results on Ta/Ta$_2$O$_5$/Au diodes seem to be consistent with the present model, so that space charge effects are more important at low preapplied fields. This result is also confirmed by the apparent applicability of step response procedures at high preapplied fields.

The theory of thermoluminescence and thermally stimulated currents has been extended to the case of traps with distributed binding energies to investigate the possibility of distinguishing between distributed and discrete trap levels. The results show that it should be possible to distinguish experimentally between both cases. Apart from the clear differences in glow curves,
the following experiments may be useful to confirm the nature of the trap distribution: (1) different doses of optical radiation could be used to obtain different amounts of trapped charges; (2) the frequency of optical excitation could be varied over a suitable range of frequencies to allow certain energy levels to be occupied by excited electrons.

The predominant high field emission mechanism from a metal electrode can be either tunneling or Schottky thermionic emission, depending on film parameters, applied voltage and ambient temperature. In view of the fast tunneling time of electron through very thin films, MIM structures could be used for microwave detection. The dc and ac tunneling characteristics of such detectors have been analysed. The results show that a bias equal to the anode work function (in volts) gives the maximum responsivity-bandwidth product of MIM detectors, and that the presence of invariant positive space charge increases the magnitude of this maximum.

High field switching in thin amorphous films is considered to be an electronic process. However, sample self-heating, which could account for the delay times observed experimentally, precedes the switching event and serves to trigger it. The delay time, due to Joule heating, has been shown to depend exponentially on the applied voltage, i.e., $\tau_D \propto \exp(-V/V_o)$. A model for CCNR due to space charge barriers has been developed. Carrier injection has been taken to occur either by Fowler-Nordheim tunneling or Schottky thermionic emission. Injected carriers could undergo a multiplication process by impact ionization until a balance between generation and recombination rates is achieved. The concept of position dependent generation-recombination rates was discussed. The computed results show many features which are in agreement with experimental results, e.g., the dependence of threshold voltage
on model parameters and the constancy of the sustaining voltage. The small ac equivalent circuit of the proposed model has been given. The formation of current filaments, to achieve electrical stability, has been formulated in terms of radial diffusion processes. Memory state formation was attributed to phase change processes due to excessive heating.

Filamentary breakdown has been observed in anodic oxide films grown on Ta, Al, Nb and Ti. All prepared samples were able to withstand field strengths of the order of the forming field required for low current density growth (a few μAmp/cm²) when the base metal was biased positively but only about 0.6-0.7 of the forming field when the base metal was biased negative. This difference may be attributed to the presence of positive charged defects, presumably excess metal ions, near the base metal. The breakdown strength has been found to be independent of the anodizing current density, provided the measurements are taken some time after the end of the growth process. The strong dependence of breakdown strength on the film dielectric constant gives further evidence for the existence of a relation between ionic motion and breakdown process. The metal counterelectrode has been found to affect the cathodic breakdown strength and not the anodic breakdown strength. This can be explained in terms of the differences between work functions which in turn affect the injected current density at the cathode/dielectric film interface. The observed breakdown events appear to consist of two successive stages, namely: (1) The formation of a highly conducting channel in dielectric films: the forming could be initiated by disruption of the chemical bonds under the high applied field. The ions produced can cause field distortion and the presence of energetic ions and electrons can break more bonds. The development of the channel is achieved
through successive ionic dissociation assisted by the products of previous
dissociation, energetic electrons, field distortion and thermal runaway.

(2) The discharge of the sample's stored energy through the formed channel:
This can be explained in terms of heating and evaporation of the dielectric
film and the associated metal counterelectrode. The voltage collapse has
been found experimentally to occur in a time of less than 200 nanoseconds.
APPENDIX 1. **CALCULATION OF RELAXATION TIME SPECTRA**  
IN AMORPHOUS FILMS

Most relaxation processes in amorphous films can not be described by an exponential function with single relaxation time. Two approaches to a phenomenological description can therefore be taken:\(^9^2\): (1) writing of an explicit nonexponential function to describe the time variation of a given property or, (2) describing the behaviour by a sum of simple exponential terms, reaching an integral in the limit. The latter approach is the most common one. A procedure to calculate the relaxation time spectra from a given experimental data will now be discussed.

Let \(N(\tau)\, d\tau\) be the contribution to an arbitrary thermally activated property \(S\) of a group of processes having relaxation times in the range \(d\tau\) around \(\tau\). The total contribution of all present processes, if the superposition principle holds, will then be given by

\[
S_S - S_\infty = \int_0^\infty N(\tau) \, d\tau \tag{A1.1}
\]

where

- \(S_S\) is the static value of \(S\)
- \(S_\infty\) is the instantaneous value of \(S\)

The time dependence of the response, \(R(t)\), associated with \(S\) due to the application of a field \(E(t)\) may be written as

\[
R(t) = S_\infty E(t) + \int_0^t h(T)E(t-T) \, dT \tag{A1.2}
\]

Where

- \(h(T)\) is the decay function due to all processes present

\[
= \int_0^\infty e^{-T/\tau} \, N(\tau) \, d\tau/\tau \tag{A1.3}
\]

But if

\[
h(T) = 0 \quad \text{for} \quad T < 0
\]
Eq. (A1.2) may be written as

\[ R(t) = S \int E(t) + \int_0^\infty h(T)E(t-T)dT \]  \tag{A1.4}

In periodic fields, \( E(t) \) may be expressed as

\[ E(t) = \tilde{e} \exp(j\omega t) \]  \tag{A1.5}

Substituting Eq. (A1.5) in Eq. (A1.4), we get for the real and imaginary part of \( S(\omega) \):

\[ S'(\omega) = S_\infty + \int_0^\infty h(T) \cos \omega T dT \]  \tag{A1.6a}

\[ S''(\omega) = \int_0^\infty h(T) \sin \omega T dT \]  \tag{A1.6b}

with

\[ S(\omega) = s'(\omega) - j S''(\omega) \]  \tag{A1.6c}

Substituting for \( h(T) \) from Eq. (A1.3) we get

\[ S'(\omega) = S_\infty + \int_0^\infty \frac{N(\tau)}{1+\omega^2 \tau^2} d\tau \]  \tag{A1.7a}

\[ S''(\omega) = \int_0^\infty \frac{\omega N(\tau)}{1+\omega^2 \tau^2} d\tau \]  \tag{A1.7b}

The functional form of \( N(\tau) \) could be determined using Eqs. (A1.6) and (A1.3). Taking inverse Fourier transform of Eq. (A1.6a), we get

\[ h(T) = \frac{2}{\pi} \int_0^\infty (S'(\omega) - S_\infty) \cos \omega T d\omega \]  \tag{A1.8}

substituting \( \nu = \frac{1}{\tau} \) in Eq. (A1.3), we have

\[ h(T) = \int_0^\infty e^{-\nu T} \left( N(1/\nu)/\nu \right) d\nu \]

which is a Laplace transform. Taking the inverse transform, we get for \( N(\tau) \)

\[ N(\tau) = \frac{1}{2\pi j} \left[ \int_{-\infty}^{\infty} h(T) e^{\nu T} dT \right]_{\nu=1/\tau} \]  \tag{A1.9}

It is possible, in principle, to determine the functional form of \( N(\tau) \) from the experimental data using Eqs. (A1.8) and (A1.9) successively. An alternative procedure is to assume the form of \( N(\tau) \) which describes the physical situation, and then to make a check between the calculated and the measured values of the property in question.
APPENDIX 2. GROWTH AND IONIC CONDUCTIVITY OF Ta₂O₅ FILMS

Ionic conduction in thin anodic films can be investigated using a small ac signal superimposed on the dc voltage. Ac measurements can be considered the most general measuring technique in which steady state and transient measurements are only two special cases. In this Appendix, growth and ionic conductivity of Ta₂O₅ films will be investigated briefly using ac measurements.

A2.1 Theories of Ionic Conduction

Various theories have been developed to describe ionic conduction in solids. The most important of these are (for a detailed discussion see References 3, 86, 94):

(a) The classical theory of ionic conduction.
(b) Frenkel defect theory.
(c) The channel model.
(d) The dielectric polarization theory.

Experimentally and theoretically dc ionic conduction currents can be described by the expression

\[ J = J_0 \exp(-W(E)) \]  

(A2.1)

The functional form of \( W(E) \) depends on the theory used. The above theories give for \( W(E) \) the following expressions respectively

(a) \[ W(E) = (W - q a E)/kT \]  

(A2.2)
(b) \[ W(E) = ((W + W')/2 - q (a + a')/2)/kT \]  

(A2.3)
(c) \[ W(E) = (W - \gamma E^{1/2})/kT \]  

(A2.4)
(d) \[ W(E) = W - \alpha E_e - \beta E_e^2 \]  

(A2.5)
where

\[ W \text{ and } a \] are the activation energy at zero field and the half jump distance of a defect.

\[ W' \text{ and } a' \] are the activation energy at zero field and the half jump distance for the production of a Frenkel defect.

\[ q \] is the charge on the ions.

\[ E_e = E + \frac{p}{\varepsilon_0} \] is the effective field

\[ p \] is the total polarization

\[ \alpha, \beta, \gamma \text{ and } \delta \] are constants.

A2.2 Sample Preparation

Tantalum samples were cut from Fansteel capacitor grade metal sheet and were about 0.9x0.4x0.12 cm\(^3\) with a tab. Tantalum surfaces were chemically polished in an \(\text{H}_2\text{SO}_4, \text{HNO}_3\) and HF solution (5:2:1.5 by volume). The working areas were defined using either epoxy resin or black wax. The cathode was a large platinized platinum electrode in the form of a cylinder surrounding the sample. The cell was immersed in a thermostatted bath of water and glycerol (temperature control better than \(\pm 0.2^\circ\text{C}\)). Samples were anodized in 0.2 N sulphuric acid at room temperature using a constant current supply.

A2.3 Measurements

Film growth was studied using small ac signals\(^95,96\). Two current components, one in phase and the other out of phase with the ac voltage across the cell were monitored using two lock in amplifiers (model HR8) incorporated in the circuit shown in Fig. A2.1. The dc formation current was supplied
to the circuit from a constant current supply via a toggle switch $S_1$ which also opened relay $S_2$. The ac signal to the cell was provided by an oscillator (Wavetek 111) via an isolating transformer and voltage divider. Lock in amplifiers were used in the external mode with the amplified voltage across the cell as their reference signal. The phase angle was adjusted to be $0^\circ$ for one amplifier and $90^\circ$ for the other. The outputs of the two amplifiers were monitored by the two channels of a Moseley 7100 BM recorder.

Fig. A2.1 Circuit employing lock in amplifiers to measure the film impedance during film growth

Film thicknesses were determined from the minima in the specular reflectivity as a function of wavelength using a Cary double beam spectrophotometer. Curves given on page 80 Reference 3 were used to obtain film
thickness making no allowance for the difference in the substrate.

A2.4 Small Signal Film Impedance

A dielectric film may be represented by a capacitance, \( C_p \), in parallel with a resistance, \( R_p \). Both components could be frequency dependent. During the film growth, the presence of a dc ionic current contributes to both \( C_p \) and \( R_p \) by changing the film susceptibility and conductivity. Thus, their values could be different from those measured without a dc ionic current. The parallel representation and its equivalent series representation are given in Fig. A2.2, where \( R_{\text{ext}} \) represent any external resistance, e.g., the electrolyte resistance, and \( R_0 \) is the resistance across which the lock in amplifier measured the voltage drop.

![Parallel and series equivalent circuits](image)

Fig. A2.2 Parallel and series equivalent circuits.

The normalized ac voltage measured by the lock-in amplifier, using the series equivalent circuit, is given by

\[
\frac{V_i}{V_o} = \frac{1}{1 + \left( \frac{f_s}{f} \right)^2}
\]
The resistive and capacitive components are given by

\[
\frac{v_o}{v_i}(\theta) = \frac{\omega^2 C_s^2 R_s (R_{ext} + r_s) + jwC_s R_s}{1 + \omega^2 C_s^2 (R_{ext} + r_s)^2}
\]  \( \text{(A2.6)} \)

\[
v_{nr} \triangleq \frac{v_o}{v_i}(0) = \frac{\omega^2 C_s^2 R_s (R_{ext} + r_s)}{1 + \omega^2 C_s^2 (R_{ext} + r_s)^2}
\]  \( \text{(A2.7a)} \)

\[
v_{nc} \triangleq \frac{v_o}{v_i}(90) = \frac{\omega C_s R_s}{1 + \omega^2 C_s^2 (R_{ext} + r_s)^2}
\]  \( \text{(A2.7b)} \)

The values of the film capacitance and resistance may be obtained from the relations

\[
C_s = v_{nc} \frac{v_{nr}}{\omega R_s}
\]  \( \text{(A2.8a)} \)

and

\[
r_s = \frac{1}{\omega C_s} \left( v_{nr} \right) - R_{ext}
\]  \( \text{(A2.8b)} \)

The external resistance is determined from the zero intercept of the total series resistance versus \( 1/\omega \) as \( \omega \) goes to infinity. The parallel equivalent components \( R_p \) and \( C_p \) can be obtained by the conversion

\[
C_p = \frac{C_s}{(1 + \frac{1}{\omega C_s^2 r_s^2})}
\]  \( \text{(A2.9a)} \)

\[
R_p = r_s (1 + \frac{1}{\omega C_s^2 r_s^2})
\]  \( \text{(A2.9b)} \)

A2.5 Experimental Results and Discussion

The measured values of \( 1/C_p \) and \( R_p \) during film growth are given in Fig. A2.3. The ac signal frequency was 100 Hz and its amplitude was 15 mV. The result can be approximated to
Fig. A2.3 Dependence of film resistance and capacitance on the charge passed during anodization.

Fig. A2.4 Log$_{10}$ J-E characteristics of grown films (tafel plot).
\[ \frac{1}{C_p} = k_1 q \]  \hspace{1cm} (A2.10) \\

and \\

\[ R_p = k_2 t \]  \hspace{1cm} (A2.11) \\

where \( k_1 \) and \( k_2 \) are constants, almost independent of the current density. Their values are \( 20 \pm 1 \) Coulomb\(^{-1}\) microfarad\(^{-1}\) and \( 28 \pm 1 \) ohm sec\(^{-1}\) respectively. Relation (A2.10), with the help of Faraday's law \((\text{d}Q)\), shows that the film dielectric constant is independent of the current density while relation (A2.11) indicates that film conductivity during anodization is proportional to the current density, i.e., \\

\[ \sigma = k_3 J \]  \hspace{1cm} (A2.12) \\

Such a dependence can be obtained by differentiating relation (A2.1), \( k_3 \) and \( W(E) \) are related by \\

\[ k_3 = - \frac{dW(E)}{dE} \]

As discussed in Sec. A2.4, the measured values of \( C_p \) and \( R_p \) have contributions from both dielectric properties and ionic conduction of the dielectric film. To estimate the dielectric contribution only, i.e., if the effect of the ionic current vanishes, \( C_p \) and \( R_p \) should be measured sometime after removing the ionic current. The time period must be sufficient to allow the mobile ionic carriers to relax into lattice sites leading to a decrease in their concentration in the film, and thus, a decrease in the ionic conductivity. \( C_p \) and \( R_p \) were measured about 15 hours after removing the ionic current. Even though no difference could be detected in the value of film capacitance, the film resistance increased to a much higher value Fig. A2.5 and it can be attributed only to the dielectric losses.

The film thickness is proportional to the amount of charge passed across the oxide electrolyte during the growth time (Faraday's law) Thus,
Fig. A2.5 Film resistance dependence on the forming current density

Fig. A2.6 Frequency dependence of ionic conductivity
the final thickness depends on both the final values of ionic current density and the applied voltage. Different films were grown up to forty volts using constant current densities. Assuming that the electric field does not depend on film thickness, its value was estimated by dividing the final voltage by the final film thickness measured by the spectrophotometric method. The tafel plot of the prepared films is given in Fig. A2.4. As a first approximation, it can be fitted to

\[ J = J_0 \exp(\beta E) \]  
(A2.13)

with

\[ J_0 = 4.3 \times 10^{-18} \text{ Amp cm}^{-2} \text{ and } \beta = 5.4 \times 10^{-6} \text{ V}^{-1} \text{ cm} \]

It has been known that, if the potential changes suddenly from a steady state value \( V_1 \) to another value \( V_2 \) giving a change of field from \( V_1/d \) to \( V_2/d \), the ionic current changes suddenly to some new value and then gradually reaches the steady state value. This means that the value of \( \beta \) depends on the rate of change of the applied signal and we may define

\[ \beta_s \overset{\text{s}}{\overset{\text{Lim}}{\rightarrow}} \lim_{\frac{dE}{dt} \rightarrow 0} \frac{\Delta \ln J}{\Delta E} \]  
(A2.14a)

\[ \beta_i \overset{\text{i}}{\overset{\text{Lim}}{\rightarrow}} \lim_{\frac{dE}{dt} \rightarrow \infty} \frac{\Delta \ln J}{\Delta E} \]  
(A2.14b)

Fig. A2.6 shows the frequency dependence of \( k_3 \) for a film grown using current density of 0.1 mAmp/cm².

The observed frequency dependence of ac ionic conductivity could be explained in terms of relaxation processes involving ionic motion over potential barriers. (e.g., creation and annihilation of Frenkel defects).
These processes should be thermally-activated processes whose relaxation times can be expressed in Arrhenius form

\[ \tau = \tau_o \exp(W(E)/kT) \]

where \( W \) is the field dependent activation energy and \( \tau_o \) is an appropriate constant.

For amorphous films, one would expect a spread in the values of \( \tau \) which can arise from a distribution in either \( \tau_o \) or \( W \), or both simultaneously.

For every relaxation process, there is an upper limit for the signal frequency above which the process cannot respond to the applied signal. Now if the frequency is sufficiently high, then only those processes which can be considered as instantaneous processes (i.e., \( \tau \to 0 \)) will contribute to the measured conductivity which can be related to \( \beta_i \) through the relation

\[ \lim_{\omega \to \infty} \sigma(\omega) = \sigma_i = J\beta_i \quad (A2.15a) \]

On the other hand, if the frequency is sufficiently low to enable all the present processes to contribute to the measured conductivity, one can write

\[ \lim_{\omega \to 0} \sigma(\omega) = \sigma_s = J\beta_s \quad (A2.15b) \]

Relations (A2.15a) and (A2.15b) are in agreement with the experimental results presented.
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