ELECTRICAL CONDUCTION IN POLYIMIDE

by

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Abstract

Polyimides are a class of linear, high temperature, organic polymers which are widely used for electrical insulation. Although significant effort has been made to characterize and understand the electrical properties of polyimide (PI) and other insulating polymers, there is a large diversity among the reported results on conductivity and on the proposed mechanisms. There has been little quantitative agreement on the effects of impurities on the electrical properties.

The apparently poor reproducibility of electrical measurements often reported in PI and other polymers certainly contributes to the lack of a consensus on conductivity behavior and mechanisms. Whether the reproducibility problem is intrinsic to the material, due to the experimental methods used, or due to the unavoidable presence of mobile ionic impurities has not been clear. The somewhat uncritical adoption of conduction models which have proven successful in accounting for the electrical behavior in other classes of materials, but which may be inappropriate in these materials, has further obscured the analysis of the data. Finally, some portion of the reported non-reproducibility is likely to be due to a failure to faithfully reproduce the materials under study.

It is thought that mobile ionic impurities may play a key role in the electrical behavior of insulating polymers. Alkali ions are typically present in polymers in the range of 1-100 ppm. PI offers a new opportunity to study the effects of these impurities on the electrical behavior of polymers since a large supply of several different PIs, each with well controlled chemistry and purity, are commercially available.

The goals of this work are three-fold. First, reproducible measurement methodologies must be developed for PI and other related polymeric materials. The second goal of this work is to identify the role of mobile ionic impurities on the measured electrical properties of PI. To achieve this, the mobile ionic impurities in PI must first be qualitatively and quantitatively identified. The third goal of this work is to identify the intrinsic conduction mechanisms of PI. It is expected that these mechanisms would be typical of other similar polymeric materials but may differ significantly from those in inorganic insulators and semiconductors.

Electrical measurements have been made on electronics-grade PI films with a variety of electrode materials, including aluminum, gold and silicon dioxide on silicon. Charge versus time, and voltage, and current versus time, voltage, and temperature data has been collected under ramped and constant voltage in a controlled ambient. The PI films were dried before measurement. Controlled introduction of sodium ions has been used to evaluate the role of impurities on electrical conduction.

Controlled introduction of sodium into PI films has been used to identify sodium as a mobile species in the quasi-static charge-voltage measurement. The concentration of mobile sodium has been assayed in as-received electronics-grade PI. It has been demonstrated that sodium can be reversibly transferred between PI and silicon dioxide under bias at elevated temperatures. In the absence of an applied bias, sodium transfer between PI and silicon dioxide does not occur. The kinetics of sodium transport in the metal-PI-oxide-silicon structure at elevated temperatures has been shown to be consistent with a simple one-dimensional Fickian diffusion model, and the temperature dependent diffusion coefficient has been extracted.
Reversible measurement-history effects have been demonstrated in PI. A simple procedure which insures reproducible transient measurements has been developed. This procedure calls for a discharge of the sample at elevated temperatures before each measurement, thus removing any space-charge created by previous bias exposures.

History-free transient current measurements in Al-PI-Al structures at elevated temperatures are shown to have a characteristic peak, while the transient currents in Au-PI-Au structures do not. The transient peak is consistent with space-charge limited transient conduction. It is demonstrated that the transient current in metal-PI-metal structures increases roughly in proportion to the sodium concentration in the PI, although in samples with Al electrodes the total charge transported is much greater than can be accounted for by ion transport alone. In samples with Au electrodes, the total charge transported in the initial portion of the transient is comparable to the amount of sodium in the film.

These observations have been interpreted as follows: (1) In Al-PI-Al structures the transient current is dominated by a space-charge limited electron injection transient, modified by the presence of the mobile ionic impurities. Electron injection is permitted from Al to PI because Al has a low work function compared to Au. (2) A sodium ion/electron interaction enhances the effective PI conductivity. (3) In Au-PI-Au structures the transient current is dominated by ion redistribution, at least for short times.

A numerical simulation of ion transport and space-charge limited electron transients is given. In addition, the effect of space-charge due to mobile ions on the electron transients and error in apparent dielectric response due to ionic and electronic space-charge are considered.

Thesis Title: Electrical Conduction in Polyimide

Thesis Supervisor: Professor Stephen D. Senturia
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CHAPTER 1

Introduction

1.1. Goals and Scope of Thesis

Polyimides are a class of organic polymers which are widely used for electrical insulation, particularly in high-temperature and micro-electronic applications. Although significant effort has been made to characterize and understand the electrical properties of polyimide (PI) and other insulating polymers, there is a large diversity among the reported results on conductivity and on the proposed mechanisms. There has been little quantitative agreement on the effects of impurities on the electrical properties. On the other hand, the general behavior of PI in response to an applied voltage is similar even for different chemistries.

The apparently poor reproducibility of electrical measurements often reported in PI and other polymers certainly contributes to the lack of a consensus on conductivity behavior and mechanisms. Whether the reproducibility problem is intrinsic to the material, due to the experimental methods used, or due to the unavoidable presence of mobile ionic impurities has not been clear. The somewhat uncritical adoption of conduction models which have proven successful in accounting for the electrical behavior in other classes of materials, but which may be inappropriate in these materials, has further obscured the analysis of the data. Finally, some portion of the reported non-reproducibility is likely to be due to a failure to faithfully reproduce the materials under study.

It is thought that mobile ionic impurities may play a key role in the electrical behavior of insulating polymers. Alkali ions are typically present in polymers in the range of 1-100 ppm. The possibility that space-charge effects due to mobile ions may contribute to the
lack of reproducibility in polymers has been recognized by many researchers. Unfortunately, little quantitative work has been done in this area because it is more difficult to control the amount of impurities in organic materials than in inorganic materials.

This difficulty is mitigated somewhat in PI because the thermal stability of PI and its constituent monomers makes it possible to prepare relatively pure materials through the use of zone-refining techniques. Thus, PI offers a new opportunity to study the effects of these impurities on the electrical behavior of polymers since a large supply of several different PIs, each with well controlled chemistry and purity, are commercially available. The choice of these electronics-grade PIs for investigations has the clear advantage of making it easier to compare results from different workers.

The goals of this work are three-fold. First, reproducible measurement methodologies must be developed for PI and other related polymeric materials. This means a given measurement must be repeatable in two different senses: (1) the data from independently prepared samples must reproduce; (2) the data must reproduce when the measurement is repeated on a single sample. Also implied by the idea of a reproducible methodology is that all physical variables which influence the data must be identified and controlled.

The second goal of this work is to identify the role of mobile ionic impurities on the measured electrical properties of PI. To achieve this, the mobile ionic impurities in PI must first be qualitatively and quantitatively identified. Then, a controlled variation of the amount of impurities can be used to deduce the effect(s) of the impurities on the electrical properties of PI.
The third goal of this work is to identify the intrinsic conduction mechanisms of PI. It is expected that these mechanisms would be typical of other similar polymeric materials but may differ significantly from those in inorganic insulators and semiconductors. New conduction models or existing models with new modifications may be needed.

Electronic and ionic conduction in insulators are reviewed in the following section.

1.2. Conduction in Insulators

1.2.1. Band Model

The conventional model for electrical insulators is the wide band-gap model. In this view, electron states are delocalized throughout the solid, but occur only in allowed energy bands. These bands are separated by a forbidden gap where no delocalized electron states exist, although localized states may be found in the gap which arise from structural defects or impurities.

In the band model, the ground state of semiconductors and insulators are characterized by a filled valence band and empty conduction band. Since electron transport requires a partially filled band, the band model predicts that these materials have no conductivity in the ground state \( T = 0 \).

Electrons may be thermally excited from the valence band across the gap into the conduction band at finite temperatures. Such electrons can migrate under the influence of an applied electric field since the conduction band is only partially full. As the width of the forbidden gap is increased fewer electrons can be thermally excited into the conduction band, and conductivity falls. In the band model, insulators are distinguished from semiconductors simply by the width of the forbidden gap; the wider the gap, the more insulating the material.
1.2.2. Contact-limited Conduction

Electronic conduction in metal-insulator-metal systems can be either contact-limited and bulk-limited. Contact-limited conduction is reviewed here; bulk-limited conduction is reviewed in the following section.

If there is a potential barrier at the metal-insulator contact which blocks electron injection into the insulator and the film is too thick for electrons to tunnel from one electrode to the other, then the electronic current in a defect-free insulator is limited by the rate at which electrons can be thermally excited over the metal-insulator barrier. The Richardson saturation current at absolute temperature $T$ is given by

$$J = AT^2e^{-\frac{q\phi_0}{kT}}$$  \hspace{1cm} (1.1)

where $\phi_0$ is the interfacial potential barrier height and $A$ is the Richardson constant, typically 120 A/cm$^2$ [1]. Image forces due to the polarization of the electrode surface by electrons emitted into the insulator reduces the potential barrier by an amount proportional to the square root of the applied field. This is known as the Schottky effect, and the current is given by

$$J = AT^2e^{-\frac{q\phi_0}{kT}} e^{-\frac{\beta_S F^{1/2}}{kT}}$$ \hspace{1cm} (1.2)

where $\beta_S = \left(\frac{e^3}{16\pi \varepsilon}\right)^{1/2}$, $F$ is the electric field at the contact, $\varepsilon$ is the dielectric constant of the insulator, and $e$ is the electronic charge [1].

1.2.3. Bulk-limited Conduction

If the metal-insulator contact is ohmic, then a negative space-charge forms near the insulator. The maximum current that can flow in an insulator of thickness $d$ and dielectric constant $\varepsilon$ under an applied voltage $V_a$ is the space-charge limited current which is given by
\[ J = \frac{9}{8} e \mu_{\text{eff}} V_a \frac{a^2}{d^3} \]

where \( \mu_{\text{eff}} \) is the effective electron mobility in the insulator [2].

If the insulator has traps which immobilize electrons, then the effective electron mobility is reduced. If the electric field is strong enough, the interaction between Coulombic traps and the electric field can reduce the barrier height of the trap. This is called the Poole-Frenkel effect and is the bulk analog of the Schottky effect. The attenuation of the trap barrier is proportional to the square root of the electric field, so that the current is given by

\[ J = J_0 e^{-\frac{\beta_{\text{FF}} F^2}{kT}} \]

where \( \beta_{\text{FF}} = \left( \frac{e^3}{4\pi e} \right)^{\frac{1}{2}} \), and \( J_0 \) is the current in the absence of any field-induced barrier lowering [1].

1.2.4. Conduction in Molecular Solids

The band model has proven successful in predicting the behavior of many materials, but is most suited to covalently bonded crystals. Covalent bonds enhance electron delocalization throughout the periodic structure. However, there are significant questions about the validity of the band model in polymers. Band model calculations for crystalline polymers predict very narrow bands (= \( kT \)) separated by a wide gap (5-10eV) because small molecular orbital overlap [3]. Photo-emission studies in insulating polymers are consistent with the theoretical calculations. This means that a vanishingly small number of electrons are thermally excited into the conduction band. Moreover, electron transport in such narrow bands is strongly limited by scattering events, and the mean-free-path of an electron between scattering collisions may be less than the free-electron wavelength and the interatomic distance. Bloch-type, delocalized band states are not significant to electrical
atomic distance. Bloch-type, delocalized band states are not significant to electrical conduction in PI.

Polymers are molecular solids. These materials retain molecular identity in the solid state, and are characterized by strong intra-molecular and weak inter-molecular bonding, usually covalent. The lowest energy electronic states of the molecular solid are expected to be the same as those free molecule, but modified by the solid-state environment. Moreover, PI films possess a high degree of disorder. The resulting intrinsic charge states in PI are molecular ion states composed of local molecular orbitals of the monomer units, modified by polarization relaxations due to the solid-state environment [4].

In a covalent molecule, atomic valence electrons not in a bond orbital can be found in orbitals which may be delocalized over all or part of the molecule. If such an electron is removed, the resultant charged molecule is called a molecular ion. A molecular ion can also be formed by an additional electron. In aromatic PIs, the key monomer orbitals are the $\pi$ orbitals associated with the imide ring and with the phenyl rings. The imide ring is electron-withdrawing (acceptor-like), while the phenyl rings can be either electron-withdrawing or electron-donating.

The ionization energy of the molecule can be much lower in the solid than for the free molecule. The charged molecule can polarize neighboring neutral molecules reducing the total energy of the charged state (i.e. a polaron is formed). Thus, for molecular solids, the electronic states available for conduction may be localized on individual molecules, and electron transport may be by hopping from molecule to molecule. The hopping model does not depend on crystallinity. Positional disorder and thermal fluctuations (molecular motions) tend to spread out the distribution of localized states. Experimental evidence for this model has been found in the contact charge transfer studies on polyethylene terephthalate (PET) and other aromatic vinyl polymers by Fabish and Duke [4].
1.2.5. Ionic Conduction

Ionic conduction in insulators is thought to be a hopping process. Rate theory predicts that the current voltage relationship for ionic conduction will be given by

\[ J = J_0 \sinh \left( \frac{qV \lambda}{2kTd} \right) \] (1.5)

where \( \lambda \) is the ionic hopping length, and \( q \) is the ionic charge [5].

1.3. Summary of Polyimide Literature

The PI literature is reviewed in this section. Workers have studied a variety of materials under a wide range of conditions so that comparisons of results are not easily made. The focus here is on electronics-grade PIs, but many reports concern Kapton-PI films (Kapton is a registered DuPont trade name). Kapton, although based on the same basic chemistry as one of the commercially available electronics-grade PIs, differs from electronics-grade PI in several important aspects. In particular, the purity of Kapton is not as well controlled as in electronics-grade PI, and Kapton is processed differently.

1.3.1. Ionic Impurities in PI

There have been three methods reported for identifying the ionic impurities in PI films. Neutron activation analysis has been used to identify sodium, potassium, and chloride ions in Kapton films by Sacher [6]. Aqueous extraction of ions from Kapton films has also indicated the presence of sodium and potassium [7]. In addition, carboxylate and substituted ammonium ions are found by the aqueous extraction technique, but the extraction method may have contributed to their formation. Since chloride ions were not found by this method, but are found with neutron activation, suggests that they are not mobile in PI. An electrical method has been used to detect mobile sodium in electronics-grade PI deposited on silicon dioxide by Brown [8]. This latter method has served as the starting point for the work in this thesis.
1.3.2. Conduction Measurements in PI

Conduction in PI has received considerable attention [8-25]. A wide range of behaviors have been reported in response to an applied field, but some common features can be identified.

For low temperatures (20-120°C) a decaying polarization current of the form $t^{-n}$ where $n = 0.8$ has been reported by Hanscomb and Calderwood [9], Sacher [10], Sawa [11, 12], Sharma [13], Chang [14], and Smith [15, 16]. Reports of low temperature conduction measurements which have not identified this time dependent polarization current have been given by Rothman [17], Brown [8], Nevin [18], Schubert [19], and Yadlowski [20].

Currents which persist for long times have been reported at all temperatures, but there is little agreement on either voltage or temperature dependence. At low fields ($F < 10^5$ V/cm), most workers report ohmic behavior, but nonlinear behavior at low fields has been reported by Rothman [17], Schubert [19], and Yadlowski [20]. At higher fields exponential voltage dependence has been reported by Sawa [11, 12] and Sharma [13, 21], and square-root exponential voltage dependence has been reported by Brown [8], Nevin [18], Yadlowski [20], Hanscomb and Calderwood [9], Rothman [17], and Sessler [22]. Most workers report that the long-time current is temperature activated, but a wide range of activation energies (0.4-1.9 eV) have been reported [8, 11-18, 21, 22]. An increase in the activation energy at high temperatures has been reported by Chang [14], Sharma [13, 21], and Smith [15, 16].
1.3.3. Proposed Conduction Mechanisms in PI

Workers have tended to favor either protonic conduction [10-14, 21, 23-25], or electronic. Electronic conduction is often cited as either Schottky injection or Poole-Frenkel emission [8, 18, 20, 22], or hopping [9, 15, 16]. The distinction is usually made on the basis of fitting current voltage data to conductivity models. Unfortunately, the models do not make sufficiently distinct predictions to make a clear identification on this basis.

1.3.4. Moisture in PI

Moisture uptake has been studied by Sacher [26], Malladi [27], and Denton [28]. The maximum amount of water absorbed ranges from 2 to 3% depending on the material. The dielectric constant is modified by the absorbed water, and the absorption of water is reversible.

Only Sacher [10, 24] and Smith [15, 16] specifically address the moisture content of PI during electrical measurement. Smith reports a marked increase in conduction when the PI is allowed to absorb water.

1.4. Summary of Thesis

Electrical measurements have been made on electronics-grade PI films with a variety of electrode materials, including aluminum, gold and silicon dioxide on silicon. Charge versus time, and voltage, and current versus time, voltage, and temperature data has been collected under ramped and constant voltage in a controlled ambient. The PI films were dried before measurement. Controlled introduction of sodium ions and absorbed water has been used to evaluate the role of impurities on electrical conduction.

Controlled introduction of sodium into PI films has been used to identify sodium as a mobile species in the quasi-static charge-voltage measurement first used on PI by Brown [8]. The concentration of mobile sodium has been assayed in as-received electronics-grade
PI. The amount of sodium detected with this method is in good agreement with the amount detected by other analytic methods [6, 7]. It has been demonstrated that sodium can be reversibly transferred between PI and silicon dioxide under bias at elevated temperatures. Nikolic [29] has extended this work to show that in the absence of an applied bias, sodium transfer between PI and silicon dioxide does not occur. The kinetics of sodium transport in the metal-PI-oxide-silicon structure at elevated temperatures has been shown to be consistent with a simple one-dimensional Fickian diffusion model, and the temperature dependent diffusion coefficient has been extracted.

Measurement-history effects have been demonstrated in PI. This apparent non-reproducibility has been shown to be to be worsened at elevated temperatures and higher ionic concentrations. A simple procedure which insures reproducible transient measurements has been developed. This procedure calls for a discharge of the sample at elevated temperatures before each measurement, thus removing any space-charge created by previous bias exposures.

History-free transient current measurements in Al-PI-Al structures at elevated temperatures are shown to have a characteristic peak, while the transient currents in Au-PI-Au structures do not. The transient peak is consistent with the space-charge limited transient conduction model of Manv and Rakayv [30]. It is demonstrated that the transient current in metal-PI-metal structures increases roughly in proportion to the sodium concentration in the PI, although in samples with Al electrodes the total charge transported is much greater than can be accounted for by ion transport alone. In samples with Au electrodes, the total charge transported in the initial portion of the transient is comparable to the amount of sodium in the film.

These observations have been interpreted as follows: (1) In Al-PI-Al structures the transient current is dominated by a space-charge limited electron injection transient,
modified by the presence of the mobile ionic impurities. Electron injection is permitted from Al to PI because Al has a low work function compared to Au. (2) A sodium ion/electron interaction enhances the effective PI conductivity. (3) In Au-PI-Au structures the transient current is dominated by ion redistribution for short times, and (4) at longer times, the effect of the ions accumulating at the cathode is to increase the cathode field, which in turn permits field-assisted electron tunneling from the Au into the PI.

Also reported are the results of Hershkowitz [31, 37], who found that the conduction current in Al-PI-Al structures at room temperature under a given voltage is proportional to the product of the amounts of water and sodium present in the film. This is interpreted as evidence that the current in PI at low temperatures is due to sodium drift. Solvation of the sodium ion by absorbed water increases the effective mobility of the ion.

A numerical simulation of ion transport and space-charge limited electron transients is given. In addition, the effect of space-charge due to mobile ions on the electron transients is considered.

1.5. Organization of Thesis

Polyimide chemistry, processing, and basic material properties are described in Chapter 2. In Chapter 3 the experimental methods used in this work are discussed. In particular, sample fabrication, sodium doping, moisture control, and electrical measurement techniques are described. The experimental results are divided into two parts based on sample structure. The data from metal-PI-oxide-silicon structures, used for mobile ion studies, are given in Chapter 4, and the transient current data from metal-PI-metal structures are given in Chapter 5. The results given in Chapter 4 have been published in the Journal of Electronic Materials [32], and the results in Chapter 5 have been published in the Proceedings of the Second International Polyimide Conference [33] and in the ACS Symposium Series [34], and have been presented at the 1988 IEEE Conference on Electrical
Insulation and Dielectric Phenomena [35]. In Chapter 6 several theoretical concepts used to analyze the transient current data from the metal-PI-metal structures are reviewed, including space-charge limited conduction, carrier hopping transport, the Lewis phonon-assisted hopping polarization theory [36], and metal-PI contacts. A numerical model for space-charge effects and simulated conduction transients are presented in Chapter 7. Some of the modeling results have been included in the ACS publication [34] and in a manuscript which has been submitted to the Proceedings of the Third International Polyimide Conference [37]. Finally, Chapter 8 discusses the implications of this work for the measurement of electrical properties of materials containing mobile ionic impurities.
CHAPTER 2

Polyimide

2.1. Introduction

Polyimide (PI) denotes a class of organic, linear, high-temperature, insulating polymers which have found wide application in microelectronics and other fields as an electrical insulator and structural component. It is commercially available in the form of a soluble precursor which can be cast into a thin film or can used as a matrix for fiber reinforced composites. After the precursor material has been applied, thermal curing results in an insoluble polymer which has unusually good thermal and chemical stability. For example, fully cured PI of the type used in microelectronics decomposes only above 500°C in vacuum and is immune to most solvents. This thermal stability and chemical resistance are important in microelectronic applications, where high temperatures and strong chemical processes are used in device fabrication. For structural applications, thermal stability and strength are highly desirable.

A broad range of PIs are commercially available. Soluble PIs (pre-imidized) have the advantage of lower shrinkage, but may not be as chemically resistant as thermally cured PI. Photosensitive PIs are also available. In these materials, incident radiation alternately generates or removes interchain crosslinks, thus modifying polymer solubility.

A general discussion of PI chemistry and processing is given in this chapter. First, the chemical structure of PIs is described. Next, the materials and processing used in this work are detailed. Finally, several non-electrical properties of PI are discussed.
2.2. Chemical Structure

2.2.1. Synthesis

PI chemistry is based on the cyclic imide group illustrated in Fig. 2.1. The first PI was synthesised in 1908 by heating of 4-aminophthalic anhydride, evolving water and forming PI (see Fig. 2.2) [38]. PIs may be formed with aliphatic or aromatic links in the main chain, although PIs with aromatic links generally have higher thermal stability.

A two-step polycondensation of aromatic PI was first developed and patented by DuPont in 1959 [39]. The first step, shown in Fig. 2.3a, is the condensation polymerization in a polar solvent of two monomeric components, a dianhydride and a diamine, to form polyamic acid (PAA). In Fig. 2.3, R and R' represent any of a number of aromatic groups, and Fig. 2.4 shows a list of commonly used aromatic dianhydrides and diamines. Table 2.1 lists commonly used solvents. Typically, the diamine first is dissolved in the solvent at room temperature. Subsequently, an equimolar amount of the dianhydride is slowly added

![Cyclic imide group](image)

**Figure 2.1:** Cyclic imide group is the basis of polyimide chemistry.
while stirring. The viscosity of the solution slowly increases as dianhydride is added. When a nearly equimolar amount of the dianhydride has been added the viscosity increases sharply [40].

The PAA is the soluble PI precursor, and yields transparent films when the solvent is evaporated. These films are elastic, but soften near 100°C. The density of PAA films is typically on the order of 1.3 gm/cm³. The degree of polymerization is typically about 100, and the molecular weight average is on the order of 20,000.
2.2.2. Imidization

The second step in the formation of PI is imidization, or cyclization, and is shown in Fig. 2.3b. This reaction may be effected either thermally or chemically. Thermal imidization begins to occur at 125°C. Once partially imidization occurs, further imidization of the PAA is mobility controlled since the polymer backbone becomes increasingly rigid as cure progresses.

Figure 2.3: (a) Step 1: Condensation of dianhydride and diamine to form polyamic acid (PAA). Various aromatic substituents R and R' are shown in Fig. 2.4. (b) Imidization or cyclization of PAA to form cured PI with attendant evolution of water.
Figure 2.4: Commonly used dianhydrides and diamines.
Table 2.1

Solvents used in PI Synthesis [40]

N,N-dimethylacetamide
N,N-dimethylformamide
N,N-diethylacetamide
N,N-dimethylmethoxyacetamide
N-methylcaprolactam
dimethyl sulfoxide
N-methyl 2-pyrrolidone
pyridine
dimethyl sulfone
N-acetyl-2-pyrrolidone

progresses. To insure complete imidization of the PAA, the material must be heated to temperatures above 250°C. Two water molecules are removed for each repeat unit. The closure of the imide ring results in a more rigid polymer and accounts for the thermal and chemical stability.

PI films are transparent and yellow, reddish-brown or colorless. The density of PI is on the order of 1.4 gm/cm³ but varies with imidization conditions.

2.2.3. Blends

The incorporation of flexible linkages in the monomeric units results in PIs with lower glass transition temperature and greater elasticity. Often, several PAA's are blended to achieve optimum film properties. For example, benzophenontetracarboxylic dianhydride (BTDA) - oxydianiline (ODA) is blended with BTDA - metaphenylenediamine (MPDA) because BTDA-MPDA alone is too rigid to form a satisfactory film. Here the oxygen linkage in ODA supplies additional flexibility.
2.2.4. Impurities

All organic polymers contain residual impurities from synthesis. For electronic applications, mobile ionic impurities are undesirable because electrical instabilities can result. In particular, Na and other alkali ions must not be introduced in Metal-Oxide-Silicon (MOS) devices since they are mobile in the silicon dioxide (SiO₂) at device operating temperatures. Mobile ions can cause threshold drift and create parasitic devices in MOS integrated circuits [41].

To minimize these impurities, electronics-grade PIs are prepared from monomers which have been zone-refined. This procedure, common in inorganic materials, is not often applied to organics because of thermal instabilities. The thermal stability of the aromatic monomers used for PI allows very pure materials to be prepared. Ionic impurities are typically reduced to the part per million level in electronics-grade PIs, while more conventional polymers contain at least 10-100 parts per million ionic impurities.

A major thrust of this work has been to identify and characterize mobile ionic species in PI films. The role of these ions on the apparent electrical properties of PI films has been examined in detail, as well as the possibility of ionic contamination in MOS devices which contain PI films. Controlled introduction of Na has been used to vary the impurity content of the films used in this work. Na-doping is described in Section 3.2.1.

2.3. Materials and Processing

2.3.1. Polyimides

In this work two PI chemistries supplied by DuPont have been used. Both PIs are received in the form of PAA in N-methyl-pyrrolidone (NMP) solution. The first material is a blend of two PI chemistries with different diamines: benzophenontetracarboxylic dianhydride with metaphenylenediamine and oxydianiline (BTDA-MPDA/ODA) known
commercially as DuPont Pyralin PI-2555. The second material is based on a pyromellitic
dianhydride with oxydianiline (PMDA-ODA) chemistry which is known as DuPont Pyralin
PI-2545. These chemistries are shown in Fig. 2.5.

2.3.2. Film Deposition

Thin PI films may be prepared either by spraying, by dipping, with a doctor blade, or
by spin-coating PAA solutions on a substrate. In this work spin-coating has been used

Figure 2.5: (a) BTDA-MPDA/ODA (b) PMDA-ODA
because it affords the greatest uniformity in the micron thickness range. PAA solutions are poured directly on the substrate to cover about 75% of the substrate. The substrate is then spun-up to 6000 rpm with an acceleration of 200 rpm/sec for 90 sec. Film thickness may be varied either by dilution of the PAA solution or by adjusting the spin speed. In this work, the as-received PAA solutions were diluted 5:1 with NMP which resulted in a one micron cured film per coat. One to six coats were used. Films were deposited in a glovebox purged with dry air to prevent particulate contamination and to keep the PAA dry.

2.3.3. Cure Cycle

After spin-coating, the PAA films are baked at 135°C for 10 min after each coat. This is called beta- or B-staging. Solvent removal and imidization begin here but are not completed at this temperature. Adhesion of the PAA films to the substrate and to each other is promoted by heating above the softening point which allows the PAA to flow.

After all the desired coats are deposited and B-staged, the rest of the solvent is removed and imidization is completed at 400°C in dry N₂ for one hour. The N₂ prevents oxidation of the film, carries away the evolved solvent and water, and prevents contamination of the furnace by laboratory air and particulates. In this work a tube furnace and quartz substrate boat were used. The boat was at room temperature when loaded with substrates and then inserted into the hot furnace. The thermal mass of the substrates and boat caused the film temperature to be ramped from room temperature to 400°C over a period of 15 min.
2.4. Polyimide Characteristics

2.4.1. Film Morphology

Thermally cured PI films have low crystallinity as measured by small angle x-ray scattering, although in-plane orientation of the polymer chains is observed in PMDA-ODA films cured on rigid substrates [42]. Anisotropic morphology has also been inferred from measurements of optical birefringence [43] and anisotropic diffusivity of water [44] in PI films. This anisotropy is presumably due to shrinkage during cure and differences in thermal expansion between PI and substrate.

2.4.2. Glass Transition Temperature

The glass transition temperature, $T_g$, of the BTDA-MPDA/ODA PI is about 325°C. The PMDA-ODA PI does not exhibit a well defined glass transition below 400°C. A $T_g$ above the highest cure temperature is not physically meaningful.
CHAPTER 3

Experimental Methods

3.1. Introduction

Two basic structures have been used in this work to measure the electrical response of polyimide (PI) films: Metal-Polyimide-Oxide-Silicon (MPOS) and Metal-Polyimide-Metal (MPM). The ionic response of PI was probed in the MPOS structures, exploiting the ionic conductivity of silicon dioxide. The response of the MPM structures included both ionic and electronic components. The approach, therefore, was to first quantify the ionic response in MPOS structures, and subsequently use that information to separate the electronic and ionic contributions to the MPM response. In some measurements the two structures were merged into a single sample to ensure that the PI processing was identical in the fabrication of both structures. Silicon wafer substrates were used for all structures.

Controlled introduction of Na into PI films was used to study the role of mobile ionic impurities on the electrical response of PI. Samples are described as either as-received or Na-doped. Ionic content of Na-doped films was measured using the charge-voltage method, first used by Brown on MPOS structures [8]. Aside from the preparation of the PAA solution, both doped and as-received sample were fabricated identically.

Comparison of the Na concentration measured with the charge-voltage method with the Na level computed from the Na-doping was used to identify Na as the mobile ionic species in the MPOS structures. The charge-voltage method was also used to assay the intrinsic Na concentration in as-received PI. The transfer of Na between PI and SiO₂ has been demonstrated with a combination of bias-temperature stressing and PI removal and

42
reapplication. The PI stripping was done with a room temperature chemical etch to prevent any Na redistribution during the PI-strip. Oxide Na levels were checked with the charge-voltage method after PI removal. Another PI film was deposited to verify the reversibility of the ion transfer with an opposite polarity bias-temperature stress. The possibility of Na transfer at elevated temperatures without applied bias was examined.

Transient charge-time measurements on the MPOS structure have been used to estimate the characteristic dielectric relaxation time of PI and to measure the kinetics of ion motion in PI. Quasi-static capacitance measurements were used to establish an estimate of the screening length in PI at elevated temperatures. Further mobile ion analysis was done using current-temperature measurements in MPOS structures.

PI conduction has been characterized in the MPM structures. Moisture content, Na content, applied bias, temperature and electrode metals have been systematically varied. It is demonstrated that the control of all experimental variables, as well as the control of sample measurement-history, is critical to reproducing the transient currents. Measurement-history refers to the total, cumulative bias-temperature exposure of the sample. Methods for controlling this aspect of data collection are given.

Some of the experimental methods presented here have previously been reported: Na-doping (3.2.1), MPOS fabrication (3.2.2), PI removal (3.2.5), charge-voltage measurement (3.5), charge-time measurement (3.6), and screening length measurement techniques (3.7) have appeared in the Journal of Electronic Materials [32]; MPM fabrication (3.2.3), perforated electrode structure (3.3.3), and transient current measurement techniques (3.9.1-2) have also appeared in the Journal of Electronic Materials [16]; measurement-history effects (3.9.3) have been reported at the Second International Polyimide Conference [33] and at the 1985 Materials Research Society Conference [49]; and the history-free transient measurement techniques (3.9.4) will appear in an ACS Symposium Series Book [34].
3.2. Sample Fabrication

3.2.1. Na-doping

These Na-doping techniques have been reported by Neuhaus et al. in the Journal of Electronic Materials [32].

Device-grade PIs contain on the order of 1 ppm Na [7]. To investigate the role of these mobile ions on the electrical response of PI additional Na ions were introduced to some PI films. The dopant was dissolved in the PAA solvent. The doped solvent was then used to dilute the as-received PAA solution.

The fraction by weight of Na in a cured film is:

\[ f = \frac{m_{\text{Na}}}{M_{\text{cured PI}}} = \frac{23m}{(W/n)sM} \]  

(3.1)

where \( m \) is the mass of dopant added to the PAA solution, \( M \) is the mass of the PAA solution, \( s \) is the fraction of solids in the PAA solution, \((W/n)\) is the dopant formula weight per Na ion, and 23 is the atomic weight of Na. For a cured film of thickness \( d \) and density \( \rho \), the mass PI per unit area is \( d\rho \), and the number of Na ions per unit area, \( N_i \) is then:

\[ N_i = \frac{d\rho}{23}N_A f = (3.7 \times 10^{18}fd) \text{ ions/cm}^2 \]  

(3.2)

where \( N_A \) is Avogadro's number, \( \rho \) is 1.4 g/cm\(^3\). The mass dopant \( m \) to be added to \( M \) grams PAA solution to achieved \( N_i \) sodium ions per unit area in the cured film is:

\[ m = \frac{(W/n)sM}{d\rho N_A}N_i \]  

(3.3)

Na lauryl sulfate (NaLS) is used for Na-doping because it is soluble in the PAA solvent, NMP. The formula weight of NaLS per Na ion, \((W/n)\), is 288.
3.2.2. **Metal-Polyimide-Oxide-Silicon Structures**

These fabrication techniques have been reported by Neuhaus et. al. in the Journal of Electronic Materials [32].

The MPOS structures were fabricated on 2-inch <100> n-type silicon wafers. Fabrication of MPOS structures begins with a three stage cleaning of the silicon substrate, called the RCA clean. Table 3.1 outlines the procedure in detail. The first step of the RCA cleaning procedure oxidizes any organic contamination on the silicon in a strongly basic solution of ammonium hydroxide and hydrogen peroxide in water. After rinsing the substrate in deionized (DI) water, the second step strips the oxide from the silicon surface in hydrofluoric (HF) acid. Another DI water rinse precedes the third cleaning step which removes ionic contamination from the substrate in a strongly acidic solution of hydrochloric acid (HCl) and hydrogen peroxide. The substrates are rinsed a final time and dried by spinning.

---

**Table 3.1**

**RCA Clean**

Organic clean:
15 min 1:1:5 solution of \( \text{H}_2\text{O}_2 \), \( \text{NH}_4\text{OH} \) and \( \text{H}_2\text{O} \) at 90°C

Oxide strip:
dip in dilute HF

Ionic clean:
15 min 1:1:5 solution of \( \text{H}_2\text{O}_2 \), HCl and \( \text{H}_2\text{O} \) at 90°C

Each step is followed by rinse in deionized (DI) water.
A thermal oxide is grown on the silicon substrate in a tube furnace. Table 3.2 outlines the conditions used for oxidation. The oxidation tube must be cleaned with gaseous HCl/O₂ before substrates are loaded to prevent ionic contamination of the oxide. The oxides are grown in dry O₂, and are annealed, in situ, in N₂ at 1100°C for 10 min. A four hour oxidation at 1100°C results in a 3000 Å oxide. Special care must be taken to avoid contamination of the oxide by environmental sources. Passivation of the oxide takes place immediately after removal from the furnace, coating either with PI or metal. The latter case yields PI-free control samples to be used for characterization of the oxide film.

The PAA solutions are spin deposited at 6000 rpm for 90 sec in a glovebox purged with dry air. The films are B-staged at 135°C for 10 min before additional coats are deposited. Imidization is done at 400°C for one hour in N₂. Cured film thickness is measured with a Dektak stylus profilometer.

One micron of pure Al is deposited in an electron beam evaporator. The metal is photolithographically patterned into a ringed-dot structure with the center dot being 0.01 cm² in area. The oxide on the backside of the wafers is stripped in HF. To monitor the

---

**Table 3.2**

**Oxidation Conditions**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube clean</td>
<td>1 hour HCl/O₂ at 1100°C</td>
</tr>
<tr>
<td>Oxide growth</td>
<td>4 hours in dry O₂ at 1100°C</td>
</tr>
<tr>
<td>Anneal</td>
<td>10 min in N₂ at 1100°C</td>
</tr>
</tbody>
</table>
quality and Na concentration in the oxides, a control oxide in each fabrication batch was metalized without PI (MOS samples). These MOS samples were sintered in forming gas (20% H₂ in N₂) for 15 min at 450°C. The MPOS samples were not sintered.

A schematic cross-section of the MPOS structure is shown in Fig. 3.1.

Figure 3.1: Schematic cross-section of metal-polyimide-oxide-silicon (MPOS) structure.
3.2.3. Metal-Polyimide-Metal Structures

These fabrication techniques have been reported by Smith et. al. in the Journal of Electronic Materials [16].

The MPM structures, like the MPOS structures, were fabricated on silicon wafers. However, the silicon served only as a mechanical substrate in the MPM samples. The wafers are cleaned with the RCA procedure (see Table 3.1) before metal deposition. One micron of pure Al or 0.5 micron of pure Au was deposited in an electron beam evaporator.

Three to six coats of PI are spin-coated and cured as described in Section 3.2.2 above. The chance of a catastrophic defect causing a dead short in a single film sample with a large area electrode is nearly unity. Using multiple coats of PI effectively eliminates this problem.

Finally, an upper electrode, either Al or Au is used, is evaporated. Several electrode patterns are used. For low temperatures a large single guarded electrode is patterned photolithographically on each wafer. The area of this electrode is 5.1 cm$^2$, and it is perforated as described in Section 3.3.3 for moisture control. For high temperature measurements an array of small ringed-dot electrodes is used. The area of the center dot is 0.01 cm$^2$. No perforations are needed on the small electrodes. A small region of the PI film near the edge of the wafer was removed to permit direct electrical contact with the lower electrode.

A schematic cross-section of the MPM structure with the large, perforated electrode is shown in Fig. 3.2 [16].

3.2.4. Merged MPOS/MPM Structures

Ideally, both MPOS and MPM structures should be fabricated with a single PI film. Then, information about the PI film derived from one structure can be unequivocally
Figure 3.2: Schematic cross-section of the metal-polyimide-metal (MPM) structure with the large, perforated electrode [16].

applied to the PI of other structure. This has been effected with a merged MPOS/MPM structure.

The fabrication of the merged structure is identical to the MPOS structure with one additional step: a film of Al is evaporated on one half of the wafer over the oxide layer. A shadow mask is used to prevent Al coverage of the other half of the oxide. A schematic cross section of the merged sample is shown in Fig. 3.3.
3.2.5. Polyimide Removal

This PI removal technique has been reported by Neuhaus et. al. in the Journal of Electronic Materials [32].

To demonstrate Na transfer between PI and SiO₂, the PI of several MPOS samples has been stripped from the oxide after curing and metalization. The Al was stripped and the PI etched in hydrazine hydrate (85% in water) for 20 min at room temperature. After the PI etch the wafers were rinsed in DI water and dried. Either MOS or MPOS structures were fabricated on the remaining oxide.
3.3. Moisture Control

3.3.1. Review Denton’s Moisture Results

Denton [28] has shown by gravimetric methods that PI absorbs about 3% water by weight at 100% relative humidity (RH) at room temperature. The amount of water absorbed at lower RHs is linearly proportional to ambient RH. This absorption is highly reversible; nearly all of the absorbed water is removed when the PI film is exposed to a dry ambient without heating.

Denton has characterized the kinetics of the absorption transient for a variety of RHs, temperatures, film thicknesses, cure conditions, electrode structures and surface treatments. In electrode-free samples, the uptake/loss transients were fitted to a one-dimensional, Fickian diffusion model. The results show that absorbed water is transported by a simple diffusion mechanism. The diffusion constant varied slightly with cure conditions and temperature, but was on the order of $5 \times 10^{-9}$ cm$^2$/sec.

Denton also showed that weight change due to water uptake can be correlated with change in dielectric constant. MPM structures were used, and the dielectric constant was measured at 0.1 kHz. A Clausius-Mosotti analysis of the capacitance data indicated that the average dipole moment of the absorbed water is 0.9 that of free water. This suggests that the absorbed water is not bound to the PI and exists in micro-voids within the polymer. This is consistent with the observation that the water absorption is reversible.

3.3.2. Moisture Generator

A moisture generating system has been constructed by Mario [45] which can deliver air of constant dewpoint (DP). The DP can be adjusted between dry (-70°C) and saturated (ambient temperature). A schematic of the moisture generator is shown in Fig. 3.4. Dry air (or any gas) is supplied by a compressor with dryer or a gas cylinder. A set of needle
Figure 3.4: Schematic of the moisture generator system.
valves divide the gas flow into two streams. One stream is saturated with water by bubbling through DI water, the wet stream, and the other remains dry. The two streams pass through separate flow meters before being recombined and sent to the sample chamber. The sample chamber is described in Section 3.4. A portion of the moisture generator output is split off before the sample chamber to be sent through another flow meter and finally to a General Eastern Model 1200 cold-mirror condensation dewpoint hygrometer. The hygrometer uses an optical feedback loop to adjust the mirror to the DP temperature of the sample gas flow. The dewpoint hygrometer was calibrated at the General Eastern factory. The DP, along with the sample chamber temperature and pressure allows the RH of the sample chamber to be calculated.

With this apparatus, the RH of the sample chamber can be controlled between dry (< 0.01% RH @ -70°C DP) and 100% RH. The delivered flow has a DP stable to ± 1°C, which translates to an accuracy at room temperature of ± 2.6% at 40% RH and ± 0.7% at 10% RH.

3.3.3. Perforated Electrode Structure

Smith [16] has designed a perforated electrode structure suitable for low temperature electrical measurements of PI under controlled moisture conditions. Due to the low current densities on PI films, a large area electrode must be used. If not perforated, a large, continuous metal film can trap moisture in the PI. More precisely, a large electrode, together with the diffusion coefficient of water in PI, establish an unsatisfactorily long equilibration or diffusion time. This time can be estimated by:

\[ t_{eq} = \frac{x^2}{D} \]  

(3.4)

where \( x \) is the minimum diffusion length. For a one inch square electrode, and \( D = 5 \times 10^{-9} \) cm²/sec, \( t_{eq} > 10 \) years.
The perforated electrode consists of approximately 800 parallel metal strips, each strip being 25 μm wide and spaced 5 μm apart. The total area of the metal is 5.1 cm². The equilibration time for this electrode, with a 12.5 μm minimum diffusion length, is approximately 300 sec or 5 min.

3.4. Apparatus

All electrical measurements were made with the MPOS or MPM samples enclosed in an aluminum sample chamber on a Micromanipulator hot chuck (20-400°C). A Eurotherm Model 822 programmable temperature controller was used in conjunction with a Eurotherm Model 831 zero-crossing 5 Amp SCR power supply and a type K thermocouple attached to the hot chuck to regulate the sample temperature. The sample chamber and hot chuck were mounted on a Rucker and Kolls probe stand in a light-tight, electrostatically shielded enclosure. Electrical contact to the sample electrodes was made using cat-whisker type probe pins. Current and charge measurements were made with an HP4140 pA/DC Voltage source and Keithly 610C coulombmeter, respectively. Capacitance measurements were made with a GenRad Digibridge Model 1689. These instruments were interfaced to a HP-85B desktop computer using the IEEE-488 parallel bus. Guard rings were used to protect the measurement from surface currents.

Moisture controlled N₂ or air was delivered to the sample chamber via stainless steel tubing and was allowed to exit the chamber through the probe pin aperture. A slight positive pressure was maintained in the chamber to prevent uncontrolled laboratory air from entering.
3.5. Quasi-static Charge-Voltage Method

3.5.1. Mobile Ions in Dual-dielectric Systems

The conventional technique for determining mobile ion concentrations in MOS structures is the capacitance-voltage (C-V) method. Bias-temperature (B-T) stresses are used to shift the mobile ions in the dielectric and the concentration of these ions is inferred from the flat-band voltage shifts [46]. As noted by Brown [8], this method is unsatisfactory for dual-dielectric systems. Any difference in conductivity between the two dielectrics results in the formation of interfacial charge between the two materials. This charge leads to flat-band shifts as determined by C-V which are indistinguishable from the shift due to mobile ions alone.

3.5.2. Brown's Quasi-static Charge-Voltage Method

A technique which quantitatively measures the transport of Na in PI/SiO₂ systems has been reported by Brown [8], and subsequently by Neuhaus et. al. in the Journal of Electronic Materials [32]. The method consists of slowly ramping the electrode bias of an MPOS capacitor while measuring the charge passed as a function of bias. The measured charge is plotted against voltage with an arbitrary vertical origin. A typical charge-voltage (Q-V) plot for the MOS structure is shown in Fig. 3.5 [32].

The slope of the room temperature Q-V plot for the MOS structure in Fig. 3.5 reflects the voltage dependent, low-frequency MOS capacitance, equal to the oxide capacitance, \( C_oxide \), for voltages away from flat-band [46]. For this sample, the slope is 125 pF, corresponding to 2480 Å of SiO₂ (\( \varepsilon = 3.9 \)) and 0.01 cm² electrode area. At 200°C, the Q-V plot shows a step, \( \delta Q \). The linear portions have the same slope, \( C_oxide \). The step is attributed to the motion of mobile ionic impurities in the oxide. The mobile ion concentration, \( N_i \), is related to the step, \( \delta Q \), the electrode area, \( A \), and the charge per ion, \( q \), by:
Figure 3.5: Typical charge-voltage (Q-V) plot for the MOS structure [32].

\[ N_i = \frac{\delta Q}{qA} = (6.25 \times 10^{20}) \delta Q \text{ ions/cm}^2 \]  \hspace{1cm} (3.5)

where \( \delta Q \) is expressed in Coulombs. In Fig. 3.5 \( \delta Q \) is 1.2\( \times \)10\(^{-10} \) C, which corresponds to a mobile ion concentration of 7.5\( \times \)10\(^{10} \) ions/cm\(^2 \).

The quantitative accuracy of the Q-V method in MOS structures has been verified using the C-V method. The MOS structures were stressed with 10V for 20 min at 200°C. Only reversible, parallel shifts of the C-V plots were observed as a result of B-T stressing.
The magnitude and direction of the C-V shifts agreed with the positive mobile ion levels measured by the Q-V method to within 5%.

3.5.3. Typical Q-V Results for MPOS Structures

Fig. 3.6 shows typical Q-V plots for an MPOS (BTDA-MPDA/ODA) structure at room temperature and at 200°C [32]. At room temperature the plot is linear with a slope equal to combined PI-SiO$_2$ capacitance (25.7 pF in this example). At 200°C a large hysteresis is observed. If the voltage is ramped slowly enough, the linear parts of the MPOS

![Graph showing Q-V plots](image.png)

**Figure 3.6:** Typical Q-V plots for an MPOS (BTDA-MPDA/ODA) structure at room temperature and at 200°C. The vertical shift, $\delta Q$, gives the total mobile ionic charge in the PI-SiO$_2$ system. In this example $\delta Q$ is $4.9 \times 10^9$ C which corresponds to $4.0 \times 10^{12}$ ions/cm$^2$ [32].
Q-V plot have a slope that equals the oxide capacitance, $C_o$, to within 6 pF. At elevated temperatures the PI is conductive enough to allow the oxide capacitance to be quasi-statically charged in response to the voltage ramp. The vertical shift, $\delta Q$, gives the total mobile ionic charge in the PI-SiO$_2$ system. In this example $\delta Q$ is $4.9 \times 10^9$ C which corresponds to $4.0 \times 10^{12}$ ions/cm$^2$.

The Q-V method requires that the voltage be ramped slowly enough that the oxide capacitor is in quasi-static equilibrium with the applied voltage. This means that the linear portions of the Q-V plot must have slope $C_o$. If the Q-V plot does not realize linear portions, then the charge transport is not complete, and the voltage ramp must be slowed. The fastest acceptable ramp speed varies with temperature. At higher temperatures the PI is more conductive, so faster ramp speeds will maintain quasi-static equilibrium. In this example at 200°C, the voltage was ramped at 0.0005 V/sec.

3.6. Transient Charge-Time Measurements

3.6.1. Experimental Method

These measurement techniques have been reported by Neuhaus et. al. in the Journal of Electronic Materials [32].

The time dependence of the charge transport in the MPOS structures has been measured. The procedure is to apply a constant bias non-zero to the MPOS structure for a long enough time to establish equilibrium. Then, the voltage is stepped to a new constant voltage. There are two possibilities: unipolar step or bipolar step. After the voltage step the charged passed is measured as a function of time.
3.6.2. Typical Charge-Time Transients

Fig. 3.7 shows a typical unipolar charge-time (Q-t) transient for an MPOS (BTDA-MPDA/ODA) structure at 280°C going from -5V to -10V [32]. There is a relatively rapid transient of magnitude $Q_j$, which is given the product of the MPOS capacitance, $C_{MPOS}$, and the voltage change, $\Delta V$. This is followed by a slower transient saturating at $Q_o$, where $Q_o$ is given the product of the product of the oxide capacitance, $C_o$, and the voltage change, $\Delta V$. Note that the voltage step occurs at a time shortly after ($\approx 0.5$ sec) zero as indicated in Fig. 3.7. This artifact is due to a delay in the computer program which controls the apparatus.

![Figure 3.7: Typical unipolar charge-time (Q-t) transient for an MPOS (BTDA-MPDA/ODA) structure at 280°C going from -5V to -10V [32].](image-url)
Typical bipolar $Q$-$t$ transients for the same MPOS (BTDA-MPDA/ODA) structure at $280^\circ$C going from -5V to +5V and +5V to -5V are shown in Fig. 3.8 [32]. The observed time dependence differs for positive-going and negative-going transients. The transient saturates at a maximum charge $Q_m$. Experimentally, $\delta Q$, as measured by quasi-static $Q$-$V$, equals the difference ($Q_m - Q_i$), where $Q_i$ is given by the product of the voltage change and the oxide capacitance: $Q_i = \Delta V C_o$.

Thus, the intrinsic conduction in PI can be separated from the ionic response in the $Q$-$t$ measurement by using unipolar voltage steps (on only one side of zero volts) for which no ion transport across the oxide is expected. In initial step in the unipolar response is due

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**Figure 3.8:** Typical bipolar $Q$-$t$ transients for an MPOS (BTDA-MPDA/ODA) structure at $280^\circ$C going from -5V to +5V and +5V to -5V [32].
to the charging of the MPOS capacitance to the new bias. The subsequent response has approximately typical RC exponential behavior, reflecting the charging of the oxide capacitance through the PI.

The characteristic dielectric relaxation time can be extracted from these data. Since the polarization transient is not a pure exponential decay, a lumped-element R-C model with a single time constant is not precise. However, the MPOS response may still be characterized by a relaxation time, \( \tau_r \), which, for convenience, is taken to be the time at which the transient reaches the 1/e point, that is, the time to reach \( Q_\tau \) where

\[
Q_\tau = 0.63 (Q_o - Q_i) + Q_i
\]  

(3.6)

If the initial bias is not held long enough to establish equilibrium, the bipolar transient saturates at a charge is less than \( Q_m \). This effect is attributed to Na distributions not in equilibrium with the initial applied bias. Since Na responds slowly in the PI, the initial bias for the Q-t measurement must be applied for a long time. Typical Na equilibration times for a one micron film were one hour at 300°C and 24 hours at 200°C.

3.7. Screening Length Measurement

3.7.1. Experimental Method

These measurement techniques have been reported by Neuhaus et. al. in the Journal of Electronic Materials [32].

Fig 3.6 suggests that after several relaxation times, \( \tau_r \), there is no voltage drop across the PI. In order to test this interpretation a direct measure of the PI screening length has been made. Quasi-static current-voltage (i-v) measurements have been made with a slow voltage ramp (0.01 V/s at 300°C) on MPOS and MOS structures fabricated with identically prepared oxides. The effective capacitance is given by:
\[ C = \frac{i}{dV/dt} \]  

(3.7)

If the PI were totally field-free the quasi-static MOS and MPOS effective capacitances would be exactly equal. On the other hand, if the polarization charge were distributed over a finite distance within the PI, there would be a greater effective capacitor plate separation and lower effective quasi-static capacitance. The characteristic length of such a distribution of the polarization charge is called the quasi-static screening or Debye length [47]. The relation between the effective capacitance and the screening length, \( L_s \), is given by the series combination of the oxide capacitance, \( C_o \), and the effective PI capacitance:

\[ \frac{1}{C_{MPOS}} = \frac{1}{C_o} + \frac{L_s}{\varepsilon_p \varepsilon_o A} \]  

(3.8)

so that

\[ L_s = \varepsilon_p \varepsilon_o A \left[ \frac{1}{C_{MPOS}} - \frac{1}{C_o} \right] \]  

(3.9)

where \( \varepsilon_p \) is the relative dielectric constant of PI and \( \varepsilon_o \) is the permittivity of free space.

3.7.2. Typical Screening Length Results

The quasi-static capacitance of the MPOS (BTDA-MPDA/ODA) structure with at 300°C differed from that of an identically prepared MOS structure by 6± 1 pF out of 240 pF. Using Eqn. 3.9, this difference corresponds to a quasi-static screening length of 25 Å in the PI. Under quasi-static conditions at elevated temperatures, the PI is field-free except for a region on the order of 25 Å thick at its boundaries.

3.8. Chromatography

Two MPOS measurements have been described: charge-voltage under ramped voltage, and charge-time after voltage step. Both measurements are done at constant temperature. Another measurement is possible: charge (or current) - temperature under ramped tempera-
ture. This is a variation of the thermal stimulated discharge (TSD) method [48]. It is called ion chromatography because it affords a separation of ionic species which become mobile at different temperatures.

3.8.1. Experimental Method

The MPOS sample is subjected to a sequence of temperature ramps, from room temperature to 350°C at 20°C/min, under bias. The initial ramp under negative bias serves to collect all positive mobile ionic species in the PI. No data are collected during this ramp. After the ramp to 350°C, the sample is cooled to room temperature (25°C) while the negative bias is still applied. Next the bias is switched positive and the temperature ramp is started again. Current-temperature data are recorded. At the end of the ramp, the sample is cooled to room temperature, another temperature ramp is started, and current-temperature data are recorded once more, all without changing the applied bias.

The first current-temperature (I-T) data set contains ionic and electronic components, while the second I-T data set has only an electronic component. The difference of the two I-T data sets is computed, yielding the net ion transport. Table 3.3 summarizes the procedure.

3.8.2. Typical Results

Fig. 3.9 shows typical MPOS I-T data for BTDA-MPDA/ODA and PMDA-ODA PIs. The data from the first sweep show one or more peaks, while data from the second increases monotonically with temperature. The peak(s) is(are) attributed to the motion of ionic specie(s) in the PI-SiO$_2$ system. The transport of the second species (higher temperature) in the BTDA-MPDA/ODA material appears to be incomplete at the end of the temperature ramp.
Table 3.3

Chromatography Procedure

1. Initial Stressing
   a. Apply -10V to electrode
   b. Ramp to 350°C at 20°C/min
   c. Cool to 25°C with bias applied

2. First Sweep
   a. Apply + 10V
   b. Ramp to 350°C at 20°C/min
   c. Record I versus T
   d. Cool to 25°C with bias applied

3. Second Sweep
   a. Apply + 10V
   b. Ramp to 350°C at 20°C/min
   c. Record I versus T
   d. Cool to 25°C with bias applied

4. Subtract
   a. Subtract second sweep from first sweep to get net ion transport
Figure 3.9: Typical MPOS I-T data for BTDA-MPDA/ODA and PMDA-ODA polyimides.

3.9. Transient Currents

PI films are excellent insulators and pass only small current densities. Special low-current measurement techniques have been used. Moreover, in response to a fixed applied voltage at constant temperature, PI films exhibit complex transient currents over a period of at least hours, perhaps days. Since true steady-state conduction has not been observed in PI films within one million seconds, the approach taken in this work is to consider mainly transient phenomena. Quasi-steady-state measurements are briefly discussed in Section 3.10.
3.9.1. Experimental Method

These measurement techniques have been reported by Smith et. al, in the Journal of Electronic Materials [16].

The experimental procedure for MPM measurements was developed by Smith et. al [16]. The MPM sample is housed in a chamber with controlled N₂ ambient. The ambient RH is manually set with the moisture generating system described in Section 3.3.2. All measurements were made in a dry (< 0.01% RH) ambient unless another RH has been specified. To insure that the PI film was free of any absorbed water, the sample was initially heat-treated at 135°C for 30 min in the sample chamber under dry N₂ flow.

The upper electrode is connected to the picoammeter, while the guard ring is grounded. The applied bias is delivered to the lower electrode. After the bias has been applied, the current-time data are recorded. The picoammeter output ten current readings per sec. The data are passed through a digital filter to removed electrical noise. The filter simply averaged consecutive current values. The averaging period was chosen to give ten filtered data points per decade. Thus, the filtered data are equally spaced in log-time.

The bias was typically held for 10,000 sec, followed by an equal discharging period. Both charging and discharging currents were recorded. As discussed in Section 3.9.4, the discharging was performed either at the measurement temperature or at 370°C. After the discharge period another measurement was usually made at another temperature, voltage, or RH.

3.9.2. Typical Results

Fig. 3.10 shows a typical Al-PI-Al (BTDA-MPDA/ODA) conduction transient plotted against log current-log time axes [33]. The data were collected at 100°C, and the applied bias was 100V across a 3.3 μm thick PI film. The PI sample was not doped, i.e. 1 ppm Na,
Figure 3.10: Typical Al-PI-Al (BTDA-MPDA/ODA) conduction transient data plotted against log current-log time axes. C, D, and T represent charging, discharging and transport, respectively. The applied bias was 100V [33].

and the ambient was dry. The charging (C) and discharging (D) data are shown. The discharging current, of course, flows in the opposite direction relative to the charging current. The absolute value of the discharging current has been plotted. Also plotted in Fig. 3.10 is the difference (of the absolute values) of the charging and discharging currents (T for transport).
The PI response is typical of many polymers and insulators. For short times, the charging transient exhibits power-law behavior:

\[ I(t) = I_0 t^{-n(T)} \]  \hspace{1cm} (3.10)

where \( n(T) \) ranges between 0 and 1. For these data, \( n \) is approximately 0.8. For longer times, the charging transient response deviates from the power-law. The data in this regime fit no simple analytic expression.

Upon removal of the applied bias, the discharge transient obeys the same power-law as under bias during the entire observation period. In principle, the power-law behavior can not persist indefinitely. For very long discharge times, the current is observed to fall off faster than dictated by the power-law.

3.9.3. Measurement-History Effects

Measurement-history effects in transient measurements have been reported by Neuhaus et. al. at the Second International Polyimide Conference [33] and by Feit et. al. at the 1985 Materials Research Society Conference [49].

By the principle of superposition, it is expected that the procedure of equal charging/discharging times described above will insure that an individual measurement will not be affected by any previous measurements. This procedure has been widely used in the study of insulators. This has been observed to be incorrect. In other words, equal charging/discharging times modifies the sample so that cumulative bias-temperature history of the sample gives rise to non-reproducible transients. Two examples are given below.

Two sets of charging transients in Na-doped Al-PI-Al (BTDA-MPDA/ODA) samples provided by Dr. Zeev Feit are shown in Fig. 3.11 [49]. These data were recorded at 40°C in a dry ambient. The objective of these measurements was to establish the voltage dependence of the charging current. Charging transients were measured successively at 10, 20,
Figure 3.11: Example of measurement-history effects in Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures at 40°C [49]. Charging transients were measured successively at 10, 20, 35, 50, 70, and 100V. After each charging transient was recorded, the sample was discharged for 10,000 sec. The discharging data are not shown. After the first sequence was made (set a), the procedure was immediately repeated (b).
35, 50, 70, and 100V. After each charging transient was recorded, the sample was discharged for 10,000 sec, although the discharging data are not shown for clarity. After the first sequence was made (Fig. 3.11a), the procedure was immediately repeated (Fig. 3.11b). The variation between the two sets an example of a measurement-history effect. This effect is reversible. The original behavior is recovered after 30 days at room temperature.

Another example of a measurement-history effect is shown in Fig. 3.12. Here, a Na-doped Al-PI-A1 (BTDA-MPDA/ODA) sample is subjected to 100V at several temperatures. Again, the sample is discharged for a period equal to the charging time at the charging temperature. The temperatures used were 240, 285, 325, and 370°C. The charging transients in this temperature range have a very different time dependence than illustrated earlier: a peak is observed which moves to shorter times with higher temperature. However, when the temperature sequence is repeated the peak is no longer present and the current is approximately one order of magnitude lower than at first.

These measurement history effects are apparently worsened at higher temperatures and with higher impurity levels. Non-reproducibility of electrical measurements is widely reported in the polymer literature [50]. Often researchers report that they measure each sample only once [51], or subject the sample to a particular thermal anneal [52] after each measurement. No general explanation of these effects has been given. The observation that impurity levels and temperature worsen measurement-history effects suggests that space-charge due to the redistribution of mobile ionic impurities may be partially responsible.
Figure 3.12: Example of measurement-history effects in Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures at elevated temperatures. Charging transients were measured successively at 240, 285, 325, and 370°C for 100V. After each charging transient was recorded, the sample was discharged for 10,000 sec before the temperature was increased. The discharging data are not shown. After the first sequence was made, the sample was cooled to 240°C and the procedure was repeated.
3.9.4. History-Free Transients

These measurement techniques have been reported by Neuhaus and Senturia at the 1988 Conference on Electrical Insulation and Dielectric Phenomena [35] and will appear in an ACS Symposium Series Book [34].

If space-charge gives rise to the measurement-history effects in polymers, then complete discharge of the sample after each measurement should give reproducible results. The equal charging/discharging time approach and the underlying superposition principle assume that the same physical mechanism governs both charging and discharging. If this were true, then it follows that both charging and discharging would proceed at the same rate. If, on the other hand, space-charge due to ionic redistribution gives rise to the history effects, then there is no a priori reason to expect that both charging and discharging should proceed at the same rate.

The following procedure has been found to yield reproducible, history-free transients. After each measurement the sample is heated to 370°C and allowed to discharge for 10,000 sec. Then the sample is cooled to the desired measurement temperature. To insure that the sample is completely discharged initially, this procedure is also performed before the first charging transient is recorded.

Fig. 3.13 shows three charging transients from the Al-PI-Al (BTDA-MPDA/ODA) sample used in the preceding example. The measurement temperature was 285°C and the applied bias was 50V for two measurements and -50V for the third. Before each measurement the sample has been heated to 370°C and discharged for 10,000 sec. The reproducibility is not perfect, but the transient is stable and repeatable. Presumably, the same result could be achieved at constant temperature with a very long discharge.
Figure 3.13: Example of history-free transients in Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures at 285°C. The applied bias was 50V for curves A and B, -50V for curve C. After each charging transient was recorded, the sample was discharged for 10,000 sec at 370°C. The discharging data are not shown.
3.9.5. Reverse Polarity Transients

There exists a considerable literature concerning a technique often referred to as the reverse polarity transient measurement [53-55]. The procedure is to subject a metal-insulator-metal structure to a fixed bias in order to polarize the insulator. After a suitable period of polarization, the polarity of the applied bias is suddenly reversed, and the resulting transient current is recorded.

This procedure has been used on Au-PI-Au structures. The samples were polarized with 20V applied bias for 10,000 sec. The bias was switched to -20V and the transient current was recorded. Fig. 3.14 shows a typical reverse polarity transient at 300°C in a Au-PI-Au (BTDA-MPDA/ODA) structure.

![Reverse Polarity Transients](image)

**Figure 3.14:** Typical reverse polarity transient in Au-PI-Au (BTDA-MPDA/ODA) structure at 300°C. The initial 20V bias was applied for 10,000 sec.
3.10. Quasi-steady-state Measurements

3.10.1. Experimental Method

An effort was made to characterize steady-state conduction in PI. In fact, only quasi-steady-state currents have been observed in PI films. At low temperatures (T < 200°C), the data show that true steady-state conduction is reached on a time scale weeks, or perhaps even longer. At elevated temperatures (T > 200°C), steady-state conduction is experimentally inaccessible because the PI is slowly but continually modified by the heat exposure.

At temperatures above 300°C the PI conduction current does not change rapidly with time after the bias has been applied for several thousand sec. This behavior can be exploited to estimate the voltage dependence of the steady-state conduction current at elevated temperatures. The following procedure has been used: the MPM sample was heated to 370°C and 1V was applied across the insulator. After 10,000 sec the 1V current was recorded. The voltage was stepped up to 65V in 1V increments, and the current was recorded after 1000 sec at each voltage. Then the bias was stepped back down to 1V in 1V steps, with the current recorded after 1000 sec at each voltage.

3.10.2. Typical Results

Typical current-voltage data are shown on log current-log voltage axes in Fig. 3.15 for an Al-PI-Al (BTDA-MPDA/ODA) sample. The currents for decreasing voltage are significantly less than for increasing voltages below 10V. This is attributed to the effect of mobile ion redistribution. When the bias is increasing, the mobile ions contribute a current component which adds to the steady-state conduction current, but when the bias is decreasing, the contribution due to mobile ions opposes the steady-state conduction current.
Figure 3.15: Typical quasi-steady-state log current-log voltage data for an Al-PI-Al (BTDA-MPDA/ODA) sample at 370°C.
CHAPTER 4

Measurements on Metal-Polyimide-Oxide-Silicon Structures

4.1. Introduction

In this chapter the results of the measurements on MPOS structures are given. These structures have been used to characterize the mobile ions in PI. First, Na is identified as being mobile in the PI-SiO\textsubscript{2} system at temperatures above 200°C by doping PI with Na. Then the number or concentration of Na in as-received PI is determined. In Section 4.3, it is shown that Na ions are reversibly and quantitatively transferred between PI and SiO\textsubscript{2} under an applied at elevated temperatures, but not in the absence of an applied bias. The work of Nikolich [29] on Na transfer between PI and SiO\textsubscript{2} during PI cure (without an applied bias) is also reported in Section 4.4 and extends the results of this thesis. The kinetics of Na transport in PI is shown to be consistent with a one dimensional Fickian diffusion model during the transfer from PI to SiO\textsubscript{2} in Section 4.4. Finally, in Section 4.5, a chromatographic technique is applied to the MPOS structure.

The MPOS results presented in this chapter, except for work of Nikolich on Na transfer during PI cure and the MPOS chromatography of Section 4.5, have been reported by Neuhaus et. al. in the Journal of Electronic Materials [32]. The work of Nikolich appears in a 1987 MIT Bachelor Thesis [29].

4.2. Mobile Ion Assay

4.2.1. Identify Na as Mobile Species

The identification of Na as the mobile species in the Q-V measurement of MPOS (BTDA-MPDA/ODA) structures was made with samples fabricated with PI doped with
NaLS at four levels: 1.2, 12, 120 and 1200 ppm. Mobile ion concentrations determined with the Q-V method in the Na-doped MPOS (BTDA-MPDA/ODA) structures are plotted against doping level in Fig. 4.1. The ideal line of slope one and the MOS mobile ion concentration are also shown. The experimental values agree with the doping levels to within 5% above the 1.2 ppm level. Since the PI supplier, DuPont, estimates the Na contamination level in this PI (BTDA-MPDA/ODA) to be one ppm [56], the deviation at very low doping levels is not unreasonable. This identifies Na as the mobile species in the Q-V measurement.

Figure 4.1: Mobile ion concentrations determined with the Q-V method in the Na-doped MPOS (BTDA-MPDA/ODA) structures are plotted against doping level. The ideal line of slope one and the MOS mobile ion concentration are also shown.
4.2.2. Na Assay in As-received PI

The intrinsic Na contamination level in PI (BTDA-MPDA/ODA) was measured with the Q-V method in MPOS structures fabricated with as-received (un-doped) PI (BTDA-MPDA/ODA). The results depended strongly on the PI handling procedures. The lowest Na level was found in PI which had been applied directly from the original plastic bottle. The measured 0.9 ppm is in good agreement with DuPont's estimate of one ppm. PI transferred to glass containers showed more Na, as high as 10 ppm. The background oxide Na contamination level was maintained at $1.0 \times 10^{10}$ ions/cm$^2$. Since 1.2 ppm corresponds to $4.5 \times 10^{12}$ ions/cm$^2$, which is more than two orders of magnitude above the MOS background, it is reasonable to assign PI as the source of these ions.

It has been shown that the amount of mobile ionic impurities in a PI sample can be determined by an electrical measurement, and that this measurement gives results which are consistent with other analytic techniques for determining ionic impurity levels. The next objective is to show that the interpretation of the Q-V hysteresis in terms of ion transfer between PI and SiO$_2$ is correct and to characterize the ion transport in the PI film.

4.3. Ion Transfer Between PI and SiO$_2$

4.3.1. Verify Q-V Interpretation with PI Removal

It has been asserted in the interpretation of the Q-V measurement that Na is reversibly transferred between PI and SiO$_2$ under bias at elevated temperatures. This interpretation has been explicitly verified with a series of MPOS (BTDA-MPDA/ODA) structures made with Na-doped PI. These were subjected to a + 5V B-T stress at 350°C for 30 min. The samples were cooled under bias, and then the PI was stripped, and MOS structures were made. The procedure is schematically indicated in Fig. 4.2. The Na levels measured in these oxides has been plotted against Na-doping level in Fig. 4.3. Again, the measured
Figure 4.2: Schematic of procedure used to verify transfer of Na from PI to SiO$_2$ under bias.
Na concentrations in the MOS structure agree to within 5% of the original PI doping levels for levels of 12 ppm and above. This proves that Na can be quantitatively transferred from PI to SiO₂ under bias and that the interpretation of the Q-V measurement in terms of Na transfer is correct.

This type of experiment was also used to demonstrate that Na in an oxide can be transferred to a PI film. After Na-doped MPOS (BTDA-MPDA/ODA) structures were subjected to a positive B-T stress cycle to introduce Na into the oxides at levels ranging from 8×10¹² to 4×10¹⁵ ions/cm², the Al and PI were stripped. Un-doped (BTDA-
MPODA/ODA) PI was then applied to the contaminated oxides, and more Al was evaporated. These MPOS structures were negatively stressed, and the second PI and Al films were removed. A final Al film was evaporated and patterned for Q-V measurements. This procedure is schematically indicated in Fig. 4.4, and Fig. 4.5 shows the results. The Na level in all negatively stressed samples was found to be $1.1 \times 10^{11}$ ions/cm$^2$, regardless of the intermediate oxide contamination levels. The source of this increased value, above the MOS control level of $1.0 \times 10^{11}$ ions/cm$^2$, was determined to be the PI removal, as described below.

Control oxides without PI (and $1.0 \times 10^{10}$ ions/cm$^2$) which were subjected to the PI strip procedure and metallized were also found to have Na contamination level of $1.1 \times 10^{11}$ ions/cm$^2$. Oxides with Na levels above $1.1 \times 10^{11}$ ions/cm$^2$ showed no change in Na levels as a result of the PI etch step. All processing other than this PI removal step maintained the MOS control Na level of $1.0 \times 10^{11}$ ions/cm$^2$.

These transfer experiments were repeated by Nikolich [29]. The results from the repeated experiments for positive B-T stress agreed with those reported here. The negative B-T stress results of Nikolich indicated a uniformly lower oxide Na concentration after PI removal. Nikolich observed an oxide contamination level of $2 \times 10^{10}$ ions/cm$^2$. This improvement is attributed to differences in the PI etch step. In this work, reagent-grade hydrazine hydrate was used with ordinary pyrex glassware, while Nikolich used ultra-low Na, electronics grade hydrazine hydrate in RCA cleaned quartz vessels.

4.3.2. Transfer Without Bias

It has been demonstrated in the previous section that Na can be reversibly, quantitatively transferred between PI and SiO$_2$ under B-T stressing. In this section the question of transfer without bias is addressed. The amount of Na transferred from PI to SiO$_2$ during PI
TRANSFER $\text{SiO}_2 \rightarrow \text{PI}$

- Contaminated Oxide From $+B-T-S$

- Apply Un-Doped PI, Then Evaporate Al

- Negative Bias-Temperature Stress

- Strip PI, Then Evaporate Al

Figure 4.4: Schematic of procedure used to verify transfer of Na from $\text{SiO}_2$ to PI under bias.
Figure 4.5: Na found in oxide after negative bias-temperature stress plotted against original oxide charge.

cure (at 400°C but in the absence of applied bias) was measured. As-received (0.9 ppm) and Na-doped (12, 120, 1200) PI (BTDA-MPDA/ODA) films were deposited on SiO₂ films and cured. After the final cure step of 400°C for one hour, the samples were removed from the PI cure furnace without controlling the rate of cooling. The PI was stripped and Al was deposited and patterned. The amount of Na measured in the oxides is plotted against PI Na level in Fig. 4.6. This series of PI removals introduced less contamination (approximately 3x10¹⁰ ions/cm²) than in the previously cited PI removal experiments of this work. Regardless of the amount of Na in the PI, the final oxides are "clean" at the level of the MOS control. It is reasonable to conclude that, at worst, only a small fraction of the Na in the PI is transferred to the SiO₂ during cure.
The data can be used to estimate an upper limit on the relative segregation of Na between SiO$_2$ and PI (BT: A-1-M)$^+$DA/ODA). Consider the sample originally doped to 1200 ppm (or 4.5x10$^{15}$ ions/cm$^2$). If after cure this amount of Na were uniformly distributed between SiO$_2$ and PI layers, then based on thicknesses, the residual Na in the oxide would be 8.1x10$^{14}$ ions/cm$^2$. Experimentally, it is found that only 2.8x10$^{10}$ ions/cm$^2$ remain in the oxide. Even if all of this amount were transferred from the PI (clearly, a worst case in view of the control level), then the fractional transfer to SiO$_2$ is at most 3.5x10$^{-5}$ of what would occur for a uniform distribution.
Nikolich has repeated this work with similar results [29]. These experiments have not determined if these results are due to a preferential segregation of Na to PI over SiO₂ during cure. Nikolich has shown that Na is not segregated to the PI during cure. In that work, Nikolich coated oxides with known Na contamination with PI (BTDA-MPDA/ODA) and subjected them to the PI cure cycle. The PI was stripped and MOS structures were prepared. Q-V measurements indicated that no Na was transferred from the oxide to the PI during cure.

In summary, PI removal and reapplication has been used in conjunction with B-T stressing to show that Na is reversibly and quantitatively transferred between PI and SiO₂ under bias at elevated temperatures. It has also been shown that Na transfer does not take place in the absence of an applied bias, even at elevated temperatures. Thus, the distribution of mobile Na in PI-SiO₂ structures can be experimentally controlled with an applied bias.

4.4. Ion Kinetics

4.4.1. Screening Length

The quasi-static screening length of PI (BTDA-MPDA/ODA), as determined from a comparison of the quasi-static capacitances of the MOS and MPOS structures at 300°C, is on the order of 25 Å. This means that if a constant bias is applied to a MPOS structure for a period of time, or if the bias applied to the MPOS structure is ramped very slowly, the PI is field-free except for a region on the order of 25 Å thick at its boundaries. This result is used in the next sub-section to interpret MPOS charge transients in terms of a diffusion model.
4.4.2. Diffusion Model for Interpretation of Transient Charge-Time Data

In Fig. 4.7 the temperature dependence of the relaxation time, \( \tau_r \), extracted from unipolar Q-t transients and of the characteristic times for ion transport extracted from negative-to-positive Q-t transients in MPOS (BTDA-MPDA/ODA) structures are compared. The characteristic time for ion transport has been conveniently chosen to be the time required for one half of the total ionic charge to appear in the Q-t measurement. It is clear that, for all temperatures measured, the dielectric relaxation occurs as much as one order of magnitude faster than ion transport.

![Graph showing temperature dependence of PI (BTDA-MPDA/ODA) dielectric relaxation time and characteristic times for ion transport in MPOS system.](image)

**Figure 4.7:** Temperature dependence of PI (BTDA-MPDA/ODA) dielectric relaxation time and characteristic times for ion transport in MPOS system.
A diffusion model for Na transport in PI and SiO₂ may be surmised from these observations: (1) the bulk of the PI film is field-free, and (2) positive-going Q-t measurements are proportional to \( t^{1/2} \). When a bias is applied to an MPOS structure under quasi-static conditions at elevated temperature, there is an electric field in the oxide and none in the PI. If the bias is negative there is an oxide field that drives any mobile Na in the oxide into the PI. Within the PI there is no field, so the Na redistributes by diffusion only until a uniform equilibrium distribution is reached. When the bias is switched positive, there is a period on the order of \( \tau_e \) during which the PI-SiO₂ interface charges, but after several relaxations times the PI is again field-free. Only a small fraction of the Na in the PI has had sufficient time to migrate to the oxide during this polarization interval. Once the SiO₂ interface is charged, the oxide field allows a net flux of Na to emerge from the PI and all of these ions are collected at the Si-SiO₂ interface. When the PI is completely depleted of Na the transport ceases and a new equilibrium is reached. If the bias is now switched to negative, the Na is quickly swept across the oxide and into the PI. The rate limiting mechanism in the positive-going transient is the diffusion of Na in PI, while in the opposite direction it is drift across the oxide.

The observed time dependence of charge emerging from the PI in positive-going Q-t transient was compared with a theoretical model of classical, one-dimensional diffusion. In one dimension, Fick's law is:

\[
\frac{\partial U(x,t)}{\partial t} = D \frac{\partial^2 U(x,t)}{\partial x^2}
\]  

(4.1)

where \( D \) is the diffusion coefficient and \( U(x,t) \) is the concentration as a function of position, \( x \), and time, \( t \). The boundaries of the PI film are the metal interface (\( x=0 \)) and at the SiO₂ interface (\( x=d \)). The initial distribution of Na is uniform, \( U_0 \). For \( t>0 \) the surface concentration at \( x=d \) is forced to zero by the oxide field. The distribution of Na in the PI for \( t>0 \) is given by [57]:
\[ U(x,t) = \frac{4U_0}{\pi} \sum_n \left[ \frac{-1}{2n+1} \exp \left( -\frac{D(2n+1)^2\pi^2 t}{4d^2} \right) \cos \left( \frac{(2n+1)^2\pi x}{4d^2} \right) \right] \] (4.2)

This may be integrated over the PI thickness to give the Na in the PI as a function of time. The charge passed in the external circuit as a function of time is given by:

\[ Q(t) = U_0 dA \left[ 1 - \sum_n \left( \frac{8}{(2n+1)^2\pi^2} \exp \left( -\frac{D(2n+1)^2\pi^2 t}{4d^2} \right) \right) \right] \] (4.3)

where \( A \) is the electrode area. This function is proportional to \( t^{1/2} \) for short times and saturates at \( Q(\infty) = U_0 dA \).

The theoretical diffusion model fits the MPOS (BTDA-MPDA/ODA) experimental data well, as shown in Fig. 4.8. The fit was made as follows. The origin of the Q-t transient is shifted to \( (Q_1, t_0) \), where \( t_0 \) is the time the bias applied to the MPOS structure was changed, and \( Q_1 \) is the change in charge due to the voltage step on the oxide capacitance, \( C_O \), so that \( Q_1 = \Delta V C_O \) (see Section 3.6.2). The time at which half of the Na has emerged from the film is denoted \( t_{1/2} \). When the expression for \( Q(t) \) is evaluated at \( t = t_{1/2} \), the following expression is found for \( t_{1/2} \) and \( D \):

\[ \frac{(Dt_{1/2})^{1/2}}{d} = \frac{\pi}{16} \] (4.4)

By evaluating \( t_{1/2} \), an estimate of \( D \) can be obtained.

The small differences between the experimental and calculated curves in Fig. 4.8 suggest that the assumed boundary conditions may be overly idealized. Also neglected in this model is the field-assisted ion transport during the time the PI is not field-free. Nevertheless, the dominant mechanism is simple one-dimensional diffusion, and the extraction of the diffusion coefficient of Na in PI is straightforward.
4.4.3. Experimental Results: Kinetics of Na Transfer

Transient Q-t measurements were made on MPOS (BTDA-MPDA/ODA) structures with Na-doped PI as well as as-received PI. The diffusion model was fitted to these data. The extracted diffusion coefficient within a given PI cure batch was found to be independent of the initial Na concentrations which ranged over three orders of magnitude, 1 to 1200 ppm. No differences were observed in the extracted diffusion coefficient between intrinsic and extrinsic Na samples. Agreement between results on different batches was not as good and is attributed to an apparent dependence of the Na diffusion coefficient on cure conditions. For example, Denton [28] has reported a dependence of moisture diffusion rate with final cure temperature. This dependence has not been systematically studied.
The extracted diffusion coefficient is independent of the bias used in the Q-t measurement if the bias used is great enough to produce a strong field (> 5x10^5 V/cm) in the oxide. If the applied bias is too small, it is possible for the ionic space-charge to cause field neutralization.

The temperature dependence of the diffusion coefficient from a single cure batch was examined. Assuming an Arrhenius behavior in the temperature dependence, Fig. 4.9 shows an activation energy of 1.9 eV and a prefactor of 2x10^9 cm^2/sec.

Figure 4.9: Temperature dependence of Na diffusion coefficient extracted from fit of diffusion model to MPOS (BTDA-MPDA/O DA) charge transients.
These results serve to characterize Na ion transport in PI films. It has been shown that under quasi-static bias conditions Na moves via a diffusion mechanism, and the diffusion coefficient of Na has been extracted. This is based on the observation that the PI is mainly field-free under quasi-static bias conditions. This result, however, can be translated to situations where is is a non-zero electric field in the PI with the aid of the Einstein relation which relates the diffusivity of a species to its mobility in the presence of an electric field. This is used in Chapters 6 and 7 where Na transport is modeled in MPM structures subjected to an applied bias.

4.5. Chromatography

Fig. 3.10 shows the chromatography data for two PIs: BTDA-MPDA/ODA and PMDA-ODA. Two peaks are visible in the BTDA-MPDA/ODA data although the high temperature peak appears to be incomplete at the end of the temperature ramp. The charge transported in the low temperature (300°C) peak has been calculated by integrating the BTDA-MPDA/ODA current. The amount of charge is $4.5 \times 10^{12}$ ions/cm$^2$ which is 12.5% greater than measured by Q-V in the same material.

The high temperature (near 350°C) peak in the BTDA-MPDA/ODA is attributed to potassium. Potassium has a lower mobility in PI and SiO$_2$ presumably due to a larger ionic radius. The charge under the second peak was not computed because it appears to be incomplete. Potassium has been detected at the ppm level by neutron activation analysis [7].

The PMDA-CDA data in Fig. 3.10 can not be clearly resolved into two peaks as in BTDA-MPDA/ODA. The charge transported in this sample corresponds to $2.4 \times 10^{13}$ ions/cm$^2$. 
Fig. 4.10 shows the chromatography data from some MPOS samples prepared by IBM in conjunction with the work of Denton et. al. [58]. The IBM fabrication process is proprietary and therefore has not been fully disclosed. The detailed differences in materials and processing are not known, but the IBM samples are made with a DuPont supplied, electronics-grade PI with an ionic impurity concentration comparable to the PI used in this work. The IBM fabrication sequence does include processing steps not done at MIT, including different metallization and plasma etching of the PI.

**Figure 4.10:** Chromatography data from MPOS samples prepared by IBM [58].
The data from the IBM sample appears to have three peaks: at 150°C, 240°C, and at 325°C. The two higher temperature peaks are not well resolved. The charge associated with both is $4.3 \times 10^{13}$ ions/cm². This is approximately ten times the charge associated with the 300°C peak in the MIT sample. The charge associated with the lower peak is $1.6 \times 10^{13}$ ions/cm². The low temperature peak is stable and reproducible. The origin of this low temperature peak is thought to be related to the plasma etch exposure, although this phenomenon could not be induced in MIT prepared samples by plasma exposure.

The chromatography method is a simple technique which unambiguously demonstrates differences between MPOS samples prepared at MIT and at IEM and can be useful as a process diagnostic tool to examine processing induced contamination.
CHAPTER 5

Measurements on Metal-Polyimide-Metal Structures

5.1. Introduction

The discussion of the results of measurements of MPM structures is divided into four sections: equal charging/discharging time measurements, history-free measurements, measurements under moist conditions, and quasi-steady-state measurements. The experimental methods were described in Sections 3.9.1, and 3.9.4, 3.3, and 3.10, respectively. In the low temperature range, the transient conduction is divided into reversible polarization and non-reversible transport as described in Section 3.9.2. The adjectives reversible and non-reversible refer only to the time dependence of the transient under charging and discharging conditions.

All results reported here have been reproduced in two ways: sample-to-sample, and repetition on a single sample. As described in Section 3.9.1, samples were heat-treated to remove absorbed water, and current data were passed through a digital filter to remove electrical noise. Except for Section 5.4, all MPM data are collected under dry conditions.

A large portion of the low temperature data has been provided by Dr. Zeev Feit [59]. In addition, Frank W. Smith III [15] has provided low temperature data for MPM structures made with PMDA-ODA PI for comparison with the BTDA-MPDA/ODA PI. The data presented in Section 5.4 has been excerpted from the Bachelor Theses of David R. Pehlke [60] and of Gerald B. Hershkowitz [31]. The MPM samples used by Feit, Smith, Pehlke, and Hershkowitz were fabricated as described in Sections 2.3 and 3.2.3.
5.2. Equal Charging/Discharging Time Measurements

5.2.1. Charging and Discharging Transients

Some results presented in this section have been reported earlier: low temperature PMDA-ODA data has been reported in the Journal of Electronic Materials by Smith et. al. [16]; some of the low temperature BTDA-MPDA/ODA data has been reported at the 1985 Materials Research Conference by Feit et. al. [49]; and the high temperature BTDA-MPDA/ODA data has been reported at the Second International Polyimide Conference by Neuhaus et. al. [33].

Typical Al-P1-A1 (BTDA-MPDA/ODA) charging and discharging data were shown in Fig. 3.11 for 100°C, 35V applied bias across a 3.3 μm thick PI film. Data collected at 40°C are shown in Fig. 5.1 for 20V applied bias across 3.3 μm [59]. At temperatures below 200°C, MPM charging and discharging transients exhibit approximately mirror image time dependences and can be approximated by a power-law of the form \( I(t) = I_0 t^{-n(T)} \) in a limited time range. At longer times, the two curves diverge and the charging curve tends to flatten out, and the discharging curve tends to fall off faster then dictated by the power law. The two currents diverge at earlier times with higher temperatures. At 40°C the charging and discharging transients diverge at approximately 1000 sec, while above 200°C they diverge before one sec.

Currents of this form have been observed in other insulating polymers such as polyethylene terephthalate [61], polyvinylchloride [62], polystyrene [63], polymethyl methacrylate [63], polypropylene [64], polyvinylidene fluoride [65], and polyethylene naphthalate [66], and in inorganic materials with low conductivity such as silicon at low temperatures [67].
Figure 5.1: Typical Al-PI-Al (BTDA-MPDA/ODA) charging and discharging data at 40°C for 20V applied bias across 3.3 μm [59].

The charging current is analyzed in terms of two components. The first is revealed directly in the discharge current, and is modeled as a reversible bulk polarization. The polarization current has a weak temperature dependence, and tends to zero for long times. The second component can be approximated as a transport current which persists in time. The transport current increases strongly with temperature, and dominates the charging current at higher temperatures and/or at long times.
The term transport may be misleading, since the transport current may include any conduction mechanism which does not exhibit mirror image discharge. Ion migration under bias, for example, can be thought of as a polarization process, yet would be separated into the transport component by the procedure described here. In this work, transport current is defined as the difference between the absolute values of the charging and discharging currents, while polarization is taken to be the absolute value of the discharging current.

5.2.2. Reproducibility and Polarity Independence

The reproducibility of transient measurements on Al-PI-Al (BTDA-MPDA/ODA) samples prepared in different batches is illustrated in Fig. 5.2. Here two 40°C discharge transients are shown [59]. The PI films were 3.3 μm thick. The samples had previously been charged with an applied voltage of 10V for 10,000 sec. The data reproduce well over five decades of current magnitude for the entire period of measurement.

The transient currents in Al-PI-Al structures are independent of the polarity of the applied bias. Fig. 5.3 shows the charging transients for +20V and -20V at 40°C in an Al-PI-Al sample with 6.6 μm of PMDA-ODA PI measured by Smith [15].

5.2.3. Thickness Dependence

Al-PI-Al (BTDA-MPDA/ODA) samples with three and six coats of PI were prepared. The cured PI thicknesses were 3.3 μm and 6.6 μm, respectively. The charging currents in these samples were compared at constant average electric field strength, i.e. 35V across 3.3 μm and 70V across 6.6 μm. The results, shown in Fig. 5.4, indicate that for a given field strength, the transient current is independent of film thickness or the applied voltage [59].
Figure 5.2: Reproducibility of transient measurements on Al-PI-Al (BTDA-MPDA/ODA) samples prepared in different batches [59].
Figure 5.3: Charging transients for +20V and -20V at 40°C in an Al-PI-Al (PMDA-ODA) sample with 6.6 μm film thickness measured by Smith [15].
Figure 5.4: Transient currents in Al-PI-Al (BTDA-MPDA/ODA) samples of different thicknesses at constant average electric field: 70V across 3.3 μm and 35V across 6.6 μm [59].

5.2.4. Polarization Current

Charging and discharging currents on Al-PI-Al (BTDA-MPDA/ODA) samples are shown for voltages between 10 and 100V at 40°C in Figs. 5.5a and 5.5b, respectively (provided by Dr. Zeev Feit [59]). The PI thickness was 3.3 μm, so the resulting electric fields ranged from $3 \times 10^4$ to $3 \times 10^5$ V/cm. The transport component of the charging current will be discussed in Section 5.2.5. The discharging currents follow approximately the same power-law for all voltages, but a slight bending of the curves is observed at long times. The curves are displaced parallel to each other with increasing voltage.
Figure 5.5: (a) Charging and (b) discharging currents on Al-PI-Al (BTDA-MPDA/ODA) samples for voltages between 10 and 100V at 40°C. Film thickness was 3.3 μm [59].
The curvature of the discharging currents can be understood by the superposition argument of Lewis [68]. In response to the applied voltage, the charging current, \( I_c(t) \), flows for 10,000 sec. After this, the sample is grounded and the discharging current, \( I_d(t) \), flows. This grounding of the sample can be considered as the superposition of the previously applied bias (say 10V) with the application of equal bias of opposite polarity (-10V). If \( t=0 \) is defined as the time the sample is grounded, after having been charged for a time \( t_c \), then the total discharging current in the sample can be considered as the sum of the original charging current, \( I_c(t + t_c) \), plus the charging current, \( I_c(t) \), that flows in response to the application of the -10V. The two currents, \( I_c(t + t_c) \) and \( I_c(t) \) are of opposite sign because the applied voltages, +10V and -10V respectively, are of opposite sign.

Symbolically

\[
I_d(t) = I_c(t + t_c) + I_c(t)
\]  

(5.1)

with

\[
I_c(t + t_c) = I_0(t + t_c)^{-n}
\]  

(5.2)

and

\[
I_c(t) = -I_0t^{-n}
\]  

(5.3)

The same \( I_0 \) and \( n \) are used for both expressions because the polarization component of the charging and discharging currents is symmetric.

Combining the above expressions:

\[
I_d(t) = -I_0t^{-n} \left[ 1 - \left( 1 + \frac{t_c}{t} \right)^{-n} \right]
\]  

(5.4)
This result can be examined in three limiting cases:

1. Short discharging times, \( t < t_c \).

\[
I_d(t) = -I_0 t^{-n}
\]  
(5.5)

2. Intermediate discharging times, \( t \approx t_c \).

\[
I_d(t) = -I_0 t^{-n} (1 - \frac{1}{2}) = -\frac{I_0}{2} t^{-n}
\]  
(5.6)

3. Long discharging times, \( t > t_c \).

\[
I_d(t) = 0
\]  
(5.7)

These results account for the behavior observed in Figs. 5.1 and 5.5b. For short times, the discharging current is a power-law that is the mirror image of the charging current. For times within an order of magnitude of \( t_c \), the discharging currents begin to deviate, as the discharging current approaches a current that is less than the magnitude of the charging current at the same time. In Figs. 5.1 and 5.5b the discharging measurements are stopped at \( t = t_c = 10,000 \) sec. However, Fig 5.6 shows the discharging current up until 10,000 sec for a Al-PI-Al (BTDA-MPDA/ODA) sample which had been charged for only 250 sec at 23°C [59]. The discharging current rapidly tends to zero as the discharge time exceeds the charging time as predicted above.

The influence of the charging process on the observed discharging current is one example of what are called history or memory effects in the polymer literature. The history effect arises because a previous experiment can influence the results of the current experiment. These effects occur for both polarization and transport experiments and make attention to the sample measurement history critical to achieving reproducible data. See Section 3.9.3.
Since the polarization current changes with time, it is necessary to compare the variation of this current isochronally (at fixed times). To the extent that the polarization is an ideal power law, different isochrones simply scale in time.

The isochronal voltage dependence of the BTDA-MPDA/ODA polarization (discharge) current was examined at 40 and 100°C. The polarization current at 10,000 sec and 40°C is plotted against applied voltage in Fig. 5.7 and at 1000 sec and 100°C in Fig. 5.8.
Figure 5.7: Ohmic I-V behavior of the BTDA-MPDA/ODA polarization current at 40°C. Isochronal data collected at 10,000 sec, and the film was 3.3 μm thick [59].
Figure 5.8: Ohmic I-V behavior of BTDA-MPDA/ODA polarization current at 100°C. Isochronal data collected at 10,000 sec, and the film was 3.3 μm thick [59].

The polarization current is linear in the applied voltage. Ohmic polarization behavior has also been observed in PMDA-ODA PI by Smith [15].

The charging and discharging currents in Al-PI-Al (PMDA-ODA) structure at temperatures between 23 and 120°C in 20° intervals, provided by Smith [16], are shown in Figs. 5.9a and 5.9b, respectively. The charging and discharging currents in Al-PI-Al (BTDA-MPDA/ODA) structure in the temperature range of 25 to 220°C in 40° intervals, provided by Dr. Zeev Feit [59], are shown in Figs. 5.10a and 5.10b, respectively. The
Figure 5.9: (a) Charging and (b) discharging currents in Al-PI-Al (PMDA-ODA) structure at temperatures between 23 and 120°C in 20° intervals, provided by Smith [16]. Film thickness was 3.3 μm.
Figure 5.10: (a) Charging and (b) discharging currents in Al-PI-Al (BTDA-MPDA/ODA) structure in the temperature range of 25 to 220°C in 40° intervals, provided by Dr. Zeev Feit [59]. Film thickness was 6.6 μm.
PMDA-ODA PI was 3.3 μm, and the BTDA-MPDA/ODA PI was 6.6 μm. The charging voltaging for both data sets was 35V. The charging time for the PMDA-ODA data was 16,000 sec, and the BTDA-MPDA/ODA sample was charged for 10,000 sec, except at 25°C, where the charging time was 50,000 sec.

The PMDA-ODA polarization current shown in Fig 5.9b tends to follow a power law, \( I = I_0e^{-n} \), over the temperature range shown, but the index \( n \) varies with temperature. The value of \( n \) changes monotonically from 0.8 at 23°C to approximately 0.6 at 120°C. The curvature of the discharging current observed for long times can be accounted for by the Lewis argument presented above. The polarization current versus time plots appear to intersect at one point; approximately 100 sec. The polarization current is not strongly temperature dependent in the temperature range shown.

The temperature dependence of the BTDA-MPDA/ODA discharge currents, shown in Fig. 5.10b, follows the same trend as PMDA-ODA results (23-120°C) between 25 and 100°C: weak temperature dependence with monotonically increasing power-law index \( n \). At 25°C \( n \) has the value 0.86. Above 100°C, however, the discharging current deviates from the simple power-law behavior. At 140°C, the discharge current curves upward at approximately 100 sec, and at 200°C, the discharging current has a significantly lower power-law index of \( n \approx 0.48 \) up until 1000 sec, followed by a relatively sharp downward curvature.

The deviations from the ideal power-law behavior at the higher temperatures are attributed to measurement-history effects. As described in Section 3.9.3, history effects are apparently worsened at elevated temperatures, and the separation of polarization and transport currents fails in this regime. In other words, the observed deviations from the power-law behavior during discharge at elevated temperatures indicates that the measured discharging current is no longer identical to the polarization current.
The polarization current was also investigated as a function of the ionic impurity concentration in the PI film. The results of this experiment are given in Section 5.2.6.

5.2.5. Transport Current

The BTDA-MPDA/ODA transport component at various voltages extracted from the 40°C data shown in Fig. 5.5a and 5.5b has been plotted in Fig. 5.11. The transport current has more noise than either the charging or discharging current because the subtraction

![Figure 5.11: BTDA-MPDA/ODA transport component at various voltages extracted from the 40°C data shown in Fig. 5.5a and 5.5b [59].](image-url)
procedure induces greater uncertainty due to interpolation of the measured data. In addition, it appears that the transport current is more sensitive to history effects than is the polarization. The isochronal transport data shown in the next several figures has been extracted by averaging the three transport current data points nearest the time of interest.

The isochronal variation of the BTDA-MPDA/ODA transport current with applied bias has been plotted in Figs. 5.12 and 5.13 for 10,000 sec at 40°C and 1000 sec at 100°C, respectively. Both plots reveal a linear current-voltage relationship.

The PMDA-ODA transport component extracted from the 35V data at various temperatures shown in Figs. 5.9a and 5.9b has been plotted in Fig 5.14 [15], and the BTDA-MPDA/ODA transport component extracted from the 35V data at various temperatures shown in Figs. 5.10a and 5.10b has been plotted in Fig 5.15 [59]. The calculated difference between the charging and discharging currents increases and becomes flatter at higher temperatures. At high enough temperatures the transport current becomes comparable in magnitude to the polarization current. The transport current is not, however, constant in the reported time and temperature ranges. In the following sections, it is demonstrated that the transport current is strongly dependent on both the concentration of ionic impurities and sample measurement-history.

At temperatures above 200°C, the charging and discharging currents are no longer mirror images of each other. Fig. 5.16 shows charging and discharging transients at 215°C for 35V applied bias across 1 μm of the BTDA-MPDA/ODA PI with Al electrodes. The charging current is approximately one order of magnitude greater than the discharging current at t = 1 sec, and the two currents have very different time dependences. At approximately 150 sec the discharging current reverses polarity. The calculated transport current lies virtually on top of the charging current, and the distinction between charging and transport currents vanishes.
Figure 5.12: Isochronal variation of the BTDA-MPDA/ODA transport current with applied bias for 10,000 sec at 40°C [59].
Figure 5.13: Isochronal variation of the BTDA-MPDA/ODA transport current with applied bias for 1000 sec at 100°C, respectively [59].
Figure 5.14: PMDA-ODA transport component extracted from the 35V data at various temperatures shown in Figs. 5.9a and 5.9b [15].
Figure 5.15: BTDA-MPDA/ODA transport component extracted from the 35V data at various temperatures shown in Figs. 5.10a and 5.10b [59].
Figure 5.16: Charging and discharging transients in Al-PI-Al (BTDA-MPDA/ODA) structures at 215°C. The applied bias was 35V, and the film thickness was 1 μm.

Fig. 5.17 shows 60,000 sec charging transients under 35V applied voltage across a 1 μm BTDA-MPDA/ODA PI film with Al electrodes in the temperature range 190 to 370°C. Again, the transient current exhibits a complex time dependence, and does not reach steady-state. Transport current densities measured at 35V across 3.3 μm thick PI films with Al electrodes between 60 and 340°C in 40°C intervals are shown in Fig. 5.18 [33]. Two electrodes sizes were used, as indicated in the figure. The large, perforated electrode was used at low temperatures, while the small, solid electrode was used at higher temperatures.
Figure 5.17: Charging transients in Al-PI-Al (BTDA-MPDA/ODA) structure in the temperature range 190 to 370°C. The applied bias was 35V, and the film thickness was 1 μm.
Figure 5.18: Transport current densities in Al-P1-Al (BTDA-MPDA/ODA) structures measured at 35V between 60 and 340°C in 40°C intervals. Film thickness was 3.3 μm [33].
The current densities were computed by dividing the calculated transport current by the electrode area. The reasonable agreement between the data where both size electrodes were used, at 180 and 220°C, indicates that the transport current density is independent of electrode area. It should be noted that any possible history effects have not been accounted for in these data.

The shapes of the transients suggest three temperature regimes: room temperature up to 180°C, 180 to 220°C, and above 220°C. In the middle temperature range, the transport currents are relatively flat, while in the low range, a break in the curve is seen between 10 and 100 sec. Above 220°C, the transport current is not monotonic. A broad peak is observed which moves to shorter times at higher temperatures. The 340°C transient increases slightly after 1000 sec.

The isochronal variation of the transport current density with temperature is shown in Fig. 5.19 as an Arrhenius plot of effective PI resistivity. The effective resistivity, $\rho_{ef}$, is calculated from the sample thickness, $d$, applied average electric field, $\frac{V}{d}$, and transport current density at 10,000 sec, $\frac{I_t(10,000)}{A}$, according to:

$$
\frac{I_t}{A} = \frac{1}{\rho_{ef}} \frac{V}{d}
$$

(5.8)

where $A$ is the electrode area. This procedure assumes that the transport current is ohmic at high temperatures. This assumption is not rigorously correct. Transport current data for the PMDA-ODA PI has been included in Fig. 5.19. The low temperature data has been supplied for BTDA-MPDA/ODA by Feit [59] and for PMDA-ODA by Smith [15].
Figure 5.19: The isochronal variation of the transport current density with temperature as an Arrhenius plot of effective PI resistivity [16].
The transport current in the BTDA-MPDA/ODA PI is temperature activated with an activation energy of 0.6 eV below approximately 225°C, and an activation energy of 2.1 eV above this temperature. In the PMDA-ODA, the activation energy is 0.5 eV below 200°C, and 1.5 eV above this temperature.

This apparent increase in activation energy is consistent with the previously published data of Sawa [11] and Chang [14] and arises from transient effects. Since the transient proceeds more slowly at lower temperatures, the isochronal temperature data tends to probe different regimes of the transient. At temperatures above the breakpoint, the transient is largely completed; below the breakpoint, the transient is still in progress. Moreover, the temperature of the breakpoint depends directly on the particular choice of isochronal time.

This behavior reflects the difficulty of isochronal analysis of temperature dependent transient phenomena. Ideally, transient data taken at different temperatures should be compared, not isochronally, but at a fixed degree of completion. Caution must be exercised when interpreting isochronal data because the distinction between different mechanisms may be obscured.

5.2.6. Effect of Na-doping

The role of mobile ionic impurities on the electrical properties of PI has been investigated with the controlled introduction of sodium as described in Section 3.2.1. Transient currents in Al-PI-Al (BTDA-MPDA/ODA) structures prepared with Na-doped and as-received PI have been compared. The Na-doped PI contained 10-100 ppm Na by weight, while the as-received PI contained approximately 1 ppm. Na concentrations were determined with the Q-V method on MPOS structures as described in Sections 3.5.2 and 3.5.3. The Q-V results are given in Sections 4.1.1 and 4.1.2.
Polarization current is independent of the ionic impurity level, as shown in Fig 5.20, which compares discharge data in as-received and 100 ppm Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures at 40°C [49]. The charging voltage was 35V, and the PI films were 3.3 μm thick. The difference between the two currents is less than 10% over the entire transient for an increase in mobile ion concentration of two orders of magnitude.

Figure 5.20: Polarization current in as-received and 100 ppm Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures at 40°C [49]. Film thickness was 3.3 μm.
The transport current at various temperatures in 25 ppm Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures is shown in Fig. 5.21 for 35V applied across a 3.3 μm film. This figure is to be compared with 5.18 which shows transport current in 1 ppm as-received PI under the same field strength and similar temperatures. The undoped 40°C transient from Fig. 5.18 is reproduced in Fig. 5.21 for comparison. As noted above, no correction for any possible history effects has been made. It will be shown in Section 5.3 that the shape of the transients plotted in Figs 5.18 and 5.21 are not typical of history-free transients.

At a given temperature and time, the transport current in doped films is greater than in undoped films. The three temperature regimes described in Fig. 5.18 persist in the doped transients, but the behavior is not exactly the same. Below 100°C the curves break near 10 sec. At longer times the low temperature currents appear to be constant, but actually they are increasing slightly, as clearly seen in the 100°C data. Between 180 and 240°C the transport currents in doped PI are relatively flat. Above 240°C, the transient peak is well defined, and the current increases after 1000 sec in the 360°C data.

5.3. History-free Transients

History-free transient BTDA-MPDA/ODA PI data has been reported by Neuhaus et al in a ACS Symposium Book [34], at the 1988 IEEE Conference on Electrical Insulation and Dielectric Phenomena [35], and at the Third International Polyimide Conference [37].

Examples of measurement-history effects have been given in Section 3.8.3. In particular, an individual transient shown in Figs. 5.19 or 5.21 can not be reproduced with the equal charging/discharging time method unless the exact measurement-history is also reproduced. Evidently the sample is not fully discharged between measurements. A procedure which does give reproducible transient measurements has been described in Section 3.8.4. The difference in the new procedure is simply to discharge the Al-PI-Al (BTDA-MPDA/ODA) sample at 370°C for 10,000 sec before each transient is recorded. The
Figure 5.21: Transport current at various temperatures in 25 ppm Na-doped Al-PI-Al (BTDA-MPDA/ODA) structures for 35V applied across a 3.3 μm film [33].
resulting transients are called *history-free* because they do not vary with the measurement sequence. The choice of 370°C as the discharge temperature implicitly assumes that the sample has been charged only at temperatures well below 370°C. Obviously a higher discharge temperature can be used to increase the measurement range.

The development of this methodology is important because it permits useful comparisons between different experimental sequences to be made. Without history-free data, no useful analysis can be made.

### 5.3.1. Temperature Dependence

History-free charging transients at temperatures between 150 and 330°C in 30°C intervals are shown in Fig. 5.22 for an un-doped Al-PI-Al (BTDA-MPDA/ODA) structure [34]. The applied bias was 100V, and the PI film was 3.3 μm thick. Transient data of this type has not been previously reported in PI. The transient exhibits a well defined peak above 180°C. (At 180°C there is an indication of a peak beyond 10,000 sec.) The time of the peak decreases with increasing temperature. At 210°C the peak occurs at approximately 2000 sec, and at 300°C the peak is at 10 sec. Before the peak, the current is approximately constant. In the equal charging/discharging time data shown in Fig. 5.18, the peaks are visible only above 260°C and are much broader than those seen in the history-free data.

### 5.3.2. Voltage Dependence

The variation of the history-free charging transient with applied bias in un-doped Al-PI-Al (BTDA-MPDA/ODA) structures at 300°C is shown in Fig. 5.23 [34]. The peak moves to shorter times with increasing voltage. At 10V the peak is at 100 sec, and the peak is at 10 sec at 100V. Similar results are obtained in a 30 ppm Na-doped film as shown in Fig. 5.24 [34].
Figure 5.22: History-free charging transients at temperatures between 150 and 330°C in 30°C intervals for an un-doped Al-PI-Al (BTDA-MPDA/ODA) structure. The applied bias was 100V, and the PI film was 3.3 μm thick. Before each transient, the sample was discharged at 370°C for 10,000 sec [34].
Figure 5.23: Variation of the history-free charging transient with applied bias in undoped Al-PI-Al (BTDA-MPDA/ODA) structures at 300°C [34]. Film thickness was 3.3 μm.
5.3.3. Effect of Na-doping

The role of the ionic impurities in history-free transient currents is shown more clearly in Fig. 5.25 which reproduces the 10 and 100 V data from Figs. 5.23 and 5.24 (1 ppm Na as-received and 30 ppm Na-doped). The two samples are identical except for Na concentrations. At a given voltage the transient current increases roughly in proportion to the Na ion concentration in the film. In addition, the peak moves to a later time at the higher Na level.
Figure 5.25: Comparison of history-free transient currents in 1 ppm Na as-received and 30 ppm Na-doped BTDA-MPDA/ODA PI at 10 and 100V data from Figs. 5.23 and 5.24 [34]. Arrows indicate the times at which the total charge transported equals the charge associated with the Na ions.

The charge under the current-time curves has been calculated by numerical integration of the transient and compared to the amount of charge due to Na ions. In Fig. 5.25 the time at which the charge transported equals the Na charge is indicated by the arrows. At long times the total charge transported is much greater than the Na charge. This means that the increase in current in Na-doped films can not be simply due to the transport of the Na ions. The total charge transported is greater than can be accounted for by an ionic
mechanism alone, thus electrons (or holes) must carry at least part of the current. Fig. 5.25 shows that the electronic current is modulated by the ionic impurity concentration.

This data suggests that in PI samples with Al electrodes, there is an electronic conduction mechanism. Moreover, there is an interaction between electrons and mobile ionic impurities. The existence of an electronic conduction mechanism in PI has been rejected by several authors [7-11, 18, 20-22], but has been suggested by others [5, 6, 12, 13, 17, 19].

5.3.4. Effect of Electrode Metal

History-free transients have been recorded for Au-PI-Au structures. Fig. 5.26 shows history-free charging currents at various temperatures in as-received Au-PI-Au (BTDA-MPDA/ODA) structures measured at 20V [37]. Fig. 5.27 shows history-free charging currents at various temperatures in 20 ppm Na-doped Au-PI-Au (BTDA-MPDA/ODA) structures measured at 27V [37]. The history-free currents in Au-PI-Au structures exhibit no peak as observed in Al-PI-Al structures. Instead the transients are relatively flat. The history-free transients in Au-PI-AU structures are polarity independent.

Fig. 5.28 compares charging currents at 300°C in as-received BTDA-MPDA/ODA PI under 100V applied voltage for Al-PI-Al and Al-PI-Au structures [37]. The charging currents in Al-PI-Al structures are polarity independent, and only one polarity transient is shown for these samples. The Al-PI-Au structure is not polarity independent and both the Al-cathode and Au-cathode polarities are shown. A transient peak is observed only in the Al-PI-Al and Al-PI-Au Al-cathode polarity curves. No peak is observed when the cathode is Au.
Figure 5.26: History-free charging currents at various temperatures in as-received Au-PI-Au (BTDA-MPDA/ODA) structures measured at 20V [37]. Arrows indicate the times at which the total charge transported equals the charge associated with the Na ions.
Figure 5.27: History-free charging currents at various temperatures in 20 ppm Na-doped Au-PI-Au (BTDA-MPDA/ODA) structures measured at 20V [37]. Arrows indicate the times at which the total charge transported equals the charge associated with the Na ions.
Figure 5.28: History-free charging currents at 300°C in as-received BTDA-MPDA/ODA PI under 100V applied voltage for Al-PI-Al and Al-PI-Au structures [37]. Currents in Al-PI-Al structures are polarity independent, but not in Al-PI-Au structures.

These results also suggest that the peak in the transient current is due to electron injection at the Al-cathode. Since the work function of Al (4.3 eV) is smaller than that of Au (5.1 eV), one expects the Al-PI contact to be a better electron injector than the Au-PI contact.

Analysis of the total charge transported in the transients suggests that ionic redistribution in Au-PI-Au (BTDA-MPDA/ODA) structures is responsible for the initial portion of
the transient. This is indicated by the arrows in Figs. 5.26 and 5.27 which show the times at which the total charge transported equals the charge associated with the Na ions. Consistent with this hypothesis is the observation that the initial current of the history-free transients in the Au-PI-Au structures at a given temperature is roughly proportional to the Na concentration.

After the initial portion of the transient and the Na ions have polarized, a smaller current persists, suggesting the existence of another conduction mechanism in the Au-PI-Au structures. This subsequent current is much greater in the Na-doped samples which suggests that ionic polarization may enhance field-assisted injection at the electrodes.

5.4. Currents in Moist Films

Moisture is known to increase conductivity in PI films [10, 24, 15, 16]. Fig. 5.29 shows charging transients in a PMDA-ODA PI at two relative humidities (RH): dry and 14% RH [16]. The applied voltage was 35V across 3.3 μm, and the temperature was 50°C. PI absorbs water in proportion to the ambient RH as described in Section 3.2. The current at 10,000 sec is increased by more than one order of magnitude by the presence of the absorbed water.

The effect of water in transient conduction in the BTDA-MPDA/ODA PI was studied by Pehlke [60]. Pehlke found that the PI polarization current increased slightly with absorbed water, and that the increase was mainly in the power-law pre-factor, \( I_0 \). The functional dependence of \( I_0 \) on the amount of absorbed water was too weak to be unambiguously characterized. Pehlke also observed an increase in transport current with absorbed water, and that the transport current varied more strongly with RH than with temperature. Specifically, for a constant dew point ambient the transport current decreased with an increase in temperature because of the corresponding decrease in RH. Pehlke reported a strong dependence of the transport current on the Na concentration in the film.
The effect of ionic impurities in conjunction with absorbed water on transient conduction in PI has been further studied by Hershkowitz [31]. Hershkowitz found that the isochronal transport current in PI at given temperature, voltage, and thickness varies in proportion to the product of the Na concentration, [Na], and amount of absorbed water, RH. This result is shown in Fig. 5.30 for 10 and 35V at 40°C [31]. Three Na levels were used; un-doped ($2.0 \times 10^{13}$ ions/cm$^2$), $9.2 \times 10^{13}$, and $1.6 \times 10^{14}$ ions/cm$^2$. A total of eight different
Figure 5.30: Isochronal (1000 sec) transport current in Al-PI-Al (BTDA-MPDA/ODA) plotted against the product of ambient RH and Na concentration for 10 and 35V at 40°C [31]. Film thickness was 2.5 μm.

RHs were used between dry and 32%RH. The Al-PI-Al (BTDA-MPDA/ODA) samples were all 2.5 μm thick.

The interpretation of the data in Fig. 5.30 is that at low temperatures the transport current is due to the transport of mobile ionic impurities, and this transport is facilitated by the presence of absorbed water. Presumably the water serves to increase the mobility of the ions in the PI film.
This result is inconsistent with the possibility of protonic conduction suggested by several authors [7-11, 18, 20-22]. If protonic conduction were significant then the current would be expected to be proportional to the sum of ionic and water concentrations. Thus, the observed interaction between absorbed moisture and mobile ionic impurities suggests that the dominant conduction mechanisms in PI are mobile ion transport and electronic conduction (see Section 5.3.4).

5.5. Quasi-steady-state Measurements

The quasi-steady-state voltage dependence of Al-PI-Al (BTDA-MPDA/ODA) structures at 370°C was shown in Fig. 3.15. This data show that the current is approximately ohmic at voltages below 10V. Above 10V the current is super-linear in the applied voltage. The slope of the log-log plot above 10V is approximately 1.5. These observations are not inconsistent with the theory of space-charge limited conduction presented in Section 6.5.2.

The similarity between predicted steady-state space-charge limited voltage dependence and the observed quasi-steady-state voltage dependence of Al-PI-Al (BTDA-MPDA/ODA) structures, along with the shape of the history-free current transient (see Sections 5.3.1 and 6.5.3) and the total charge transported during the transients (see Section 5.3.3) are used to conclude that space-charge limited conduction of injected electrons is the dominant conduction mechanism in PI with low work function electrodes (Al).
CHAPTER 6

Theoretical Considerations

6.1. Introduction

In this chapter several theoretical concepts used in analyzing the DC transient data from MPM structures are reviewed. In Section 6.2 general relationships between charges, electric fields and currents in insulators are developed. The Lewis theory [36] of power-law polarization and the theory of space-charge limited transient conduction are reviewed in Sections 6.3 and 6.4, respectively. A formalism due to Iwamoto [69] for hopping conduction is reviewed in Section 6.5. Finally, in Section 6.6 metal-polymer contacts are discussed.

The goal is formulate a general PI conduction theory. Such a theory must account for the observed (1) low temperature polarization and transport currents, (2) high temperature transient currents, and (3) measurement-history effects. Charge transport in PI is modeled with a hopping mechanism. The high temperature transient in Al-cathode samples is modeled as space-charge limited injected electron transients, while in Au-cathode samples electron injection does not occur. At lower temperatures, the power-law polarization is attributed to limit-range electron hopping. Redistribution of ionic impurities and electronic space-charge give rise to measurement-history effects. Low temperature transport currents are attributed to ion transport.

Parallel plate geometry is considered. The one-dimensional metal-PI-metal system is shown in Fig. 6.1. The PI is a film of thickness $d$. The bias $V_a$ is applied to the left-hand electrode, M1, at $x=0$ and the right-hand electrode, M2, at $x=d$ is maintained at ground potential.
6.2. Charges, Electric Fields, and Currents in Insulators

We are interested in the distributions of charge, electric field, and current as functions of time, bias, temperature, etc. Two fundamental equations for $\rho(x,t)$, $F(x,t)$ and $J(x,t)$ are applied.

**Continuity of electric charge:** For each species of charge carrier, $k$:

$$\frac{\partial \rho_k}{\partial t} + \frac{\partial J_k}{\partial x} = 0$$

(6.1)

where $\rho_k$ and $J_k$ are the charge and current densities of the $k$th species, respectively.

**Poisson's equation:** For the total charge density, $\rho_t=\sum_k \rho_k$,

$$\frac{\partial F}{\partial x} = \frac{\rho_t}{\varepsilon_0}$$

(6.2)
where $F$ is the electric field strength. This is one of Maxwell's equations and is always valid if all charges are included in $\rho_i$. In Section 6.2.2 another form of Poisson's equation, more appropriate for polarizable materials, is developed.

The electric field, $F(x,t)$, can be developed from the electric potential, $\psi(x,t)$, where

$$F = -\frac{\partial \psi}{\partial x}$$  \hspace{1cm} (6.3)

Since the potentials of the electrodes are known, integration of this expression to get a constraint on $F(x,t)$.

$$\int_{x=0}^{x=d} F(x) \, dx = \left[ \psi(d) - \psi(0) \right] = V_a$$  \hspace{1cm} (6.4)

6.2.1. The Ideal Insulator

The ideal insulator has no components able to respond to the applied field. Since no realistic materials have this property, we can imagine the electrodes as being separated by a vacuum gap. This region is entirely neutral, i.e. $\rho_i(x,t) = 0$. From Poisson's equation

$$\frac{\partial F}{\partial x} = \frac{\rho_i}{\varepsilon_0} = 0$$  \hspace{1cm} (6.5)

implying

$$F(x) = F^{\text{vac}} = \text{constant}$$  \hspace{1cm} (6.6)

From the constraint on $F$ due to $V_a$

$$V_a = \int_0^d F \, dx = dF^{\text{vac}} \quad \text{and, so} \quad F^{\text{vac}} = \frac{V_a}{d}$$  \hspace{1cm} (6.7)

The situation is depicted in Fig. 6.2. If $V_a > 0$ then $F^{\text{vac}} > 0$. This means that a positive charge would tend to move to the right.
Figure 6.2: Electric potential, electric field, and space-charge within an ideal metal-insulator-metal system when $V_a$ is the applied bias. The ideal insulator (vacuum gap) has no components able to respond to the applied field.

The electrodes and insulating gap form a capacitor able to store charge. Although there are no charges within the vacuum, there are equal and opposite charges on the electrodes due to the applied bias. From integrating Poisson's equation across the electrode-
insulator interface, the charge per unit area on the electrode, $Q_{m}^{\text{vac}}$, is

$$Q_{m}^{\text{vac}} = \varepsilon_0 F_{\text{vac}} \cdot \mathbf{n}$$ (6.8)

where $F_{\text{vac}} \cdot \mathbf{n}$ is the dot product of the electric field vector, $F_{\text{vac}}$, and the inward, unit, normal vector, $\mathbf{n}$. In one dimension there are only two possible vector directions, so $F$ may be written as the signed, scalar quantity $F$. Then, $F \cdot \mathbf{n} = F$ at $x=0$, and $F \cdot \mathbf{n} = -F$ at $x=d$. The sign difference is due to the directions of inward normals at the two electrodes. The charge on the electrode at $x=0$, $Q_{0}^{\text{vac}}$, and the charge on the other electrode, $Q_{d}^{\text{vac}}$, are given by

$$Q_{0}^{\text{vac}} = -Q_{d}^{\text{vac}} = \varepsilon_0 F_{\text{vac}}$$ (6.9)

The capacitance per unit area is

$$C_{\text{vac}} = \frac{|Q_{m}^{\text{vac}}|}{V_a} = \frac{\varepsilon_0}{d}$$ (6.10)

6.2.2. Dielectric Polarization

When the vacuum gap is filled with an insulating material, the applied field tends to redistribute the component charges of the material. In this section the effects of molecular polarization on the electric field and electrode charge are considered. Molecular polarization has three components: electronic polarization, atomic polarization, and molecular dipole orientation. Only the static response to the applied field is considered, neglecting any time required to establish the polarization.

Dielectric polarization is due the material's atomic or molecular components forming microscopic dipoles along the applied field. Uniform, isotropic dielectric polarization $P$ dipole moment per volume results in a surface charge of $- P \cdot \mathbf{n}$ charges/area at the insulator-metal interface. (Again, $\mathbf{n}$ is the inward normal unit vector). These charges are called bound charges as opposed to ordinary free charges because they remain bound to their own atom or molecule. This charge is denoted by $\sigma_b$ in Fig. 6.3.
The bound charge at the dielectric surface induces an additional charge in the adjacent electrode, equal and opposite to the bound charge. This means that the electrodes can store more charge per applied volt.

\[ Q_m = Q_m^{\text{vac}} + P \cdot n = \left[ \varepsilon_0 F^{\text{vac}} + P \right] \cdot n \]

Here, a plus sign is used because the electrode charge is opposite the bound charge. The two electrodes still store equal and opposite charge: \( Q_0 = -Q_d \). The ratio of charge stored with dielectric to that stored without is the relative dielectric constant,

\[ \varepsilon_r = \frac{C}{C^{\text{vac}}} = \frac{Q_m}{Q_m^{\text{vac}}} \]

In linear, isotropic, homogeneous dielectrics it is found that \( P = \varepsilon_0 \chi F \), where \( \chi \) is the dimensionless dielectric susceptibility. Because \( F \) and \( P \) have the same direction, \( \chi > 0 \). From Eq. (6.11):
\[ \varepsilon_r \frac{Q_m}{Q_m^{\text{vac}}} = \frac{\varepsilon_0 F^{\text{vac}} + \varepsilon_0 \chi F^{\text{vac}}}{\varepsilon_0 F^{\text{vac}}} = 1 + \chi \]  

(6.13)

The law of superposition can be used to show that the effect of the dielectric on the electric field can be calculated by replacing the polarized dielectric with the bound surface and bulk charge densities \( \sigma_b \) and \( \rho_b \) given by

\[ \sigma_b = - \mathbf{P} \cdot \mathbf{n} \quad \text{and} \quad \rho_b = - \frac{d\mathbf{P}}{dx} \]  

(6.14)

It is useful to develop another form of Poisson's equation for dielectric materials. Writing Poisson's equation in terms of the \( \rho_b \)

\[ \frac{dF}{dx} = \frac{\varepsilon_r \varepsilon_0}{\varepsilon_0} = \frac{\rho_f + \rho_b}{\varepsilon_0} \]  

(6.15)

where \( \rho_t \) denotes the total charge density and \( \rho_f \) the free charge density. Substituting for \( \rho_b \) from Eq. 6.14, and solving for \( \rho_f \)

\[ \rho_f = \frac{d}{dx} \left( \varepsilon_0 F + P \right) \]  

(6.16)

The electric displacement, \( D \), is defined as

\[ D = \varepsilon_0 F + P \]  

(6.17)

so that

\[ \frac{d}{dx} D = \rho_f \]  

(6.18)

From \( P = \varepsilon_0 \chi F \)

\[ D = \varepsilon_r \varepsilon_0 F = \varepsilon F \]  

(6.19)

since \( \varepsilon_r = 1 + \chi \), and for convenience we use \( \varepsilon_r \varepsilon_0 = \varepsilon \). Using \( D = \varepsilon F \) in Eq. 6.18,

\[ \frac{d}{dx} F = \frac{\rho_f}{\varepsilon} \]  

(6.20)

which is simply a restatement of Poisson's equation, with
\[ \rho_i \rightarrow \rho_f \text{ and } \varepsilon_0 \rightarrow \varepsilon \]  \hspace{1cm} (6.21)

To calculate \( F(x) \) inside the dielectric, Eq. 6.20 is integrated:

\[ F(x) = F(x=0) + \frac{1}{\varepsilon} \int_0^x \rho_f \, dx \]  \hspace{1cm} (6.22)

Since the dielectric constant, \( \varepsilon \), contains the dielectric response (\( \rho_b \) and \( \sigma_b \)), only the free charge density \( \rho_f \) is integrated. \( F(x=0) \) is evaluated in the next section.

Finally, the electrode charge \( Q_m \) is expressed in terms of the dielectric constant:

\[ Q_m = Q_m^{\text{vac}} + \mathbf{P} \cdot \mathbf{n} = (1+\chi)\varepsilon_0 \mathbf{F} \cdot \mathbf{n} = \varepsilon \mathbf{F} \cdot \mathbf{n} \]  \hspace{1cm} (6.23)

6.2.3. Space Charge in an Insulator

Uniform dielectric polarization gives rise to bound charge densities only at the insulator surface. In general, however, a space charge, \( \rho_f(x,t) \), appears within the insulator. See Fig. 6.1. What effect does \( \rho_f(x,t) \) have on electrode charge?

As in Eq. 6.8, we use Poisson's equation for the electrode charge.

\[ Q_m = \varepsilon \mathbf{F}_{\text{electrode}} \cdot \mathbf{n} \]  \hspace{1cm} (6.24)

As shown in Fig. 6.4 \( F(x) \) is no longer constant because of \( \rho_f(x) \), and, in general, \( F(x=0) \neq F(x=d) \). In contrast to the vacuum and uniformly polarized dielectric, the electrodes no longer hold equal and opposite charge.

To calculate \( F_0 \) and \( F_a \), consider the fields \( F_1 \) and \( F_2 \) due only to the applied bias and the differential element at \( x \) of width \( dx \) shown in Fig. 6.5. The element is a sheet of charge \( \sigma(x) = \rho_f(x) \, dx \). Since \( F_1 \) and \( F_2 \) are constant in \( x \), Eq. 6.4 becomes

\[ V_a = \int_0^d F(x) \, dx = F_2 (d-x) - F_1 x \]  \hspace{1cm} (6.25)
Figure 6.4: Electric potential, electric field, and space-charge within metal-insulator-metal system which contains space-charge when $V_a$ is the applied bias.
Applying Poisson's equation

\[ \varepsilon ( F_1 + F_2 ) = \sigma = \rho_f \, dx \]  

(6.26)

We now have two equations for two unknowns. Solving for \( F_1 \) and \( F_2 \), and using Eq. 6.24, the charge on the electrode at \( x = d \) due to the differential element is

\[- \, \delta Q_d = \varepsilon F_2 = \frac{x \sigma + \varepsilon V_a}{d} \]  

(6.27)

By superposition, the total electrode charge due to all space charge \( \rho_f(x) \)

\[ Q_d = - \int \frac{x \rho_f(x) \, dx + \varepsilon V_a}{d} \]  

(6.28)

and

\[ Q_0 = - \int \frac{(d-x) \rho_f(x) \, dx - \varepsilon V_a}{d} \]  

(6.29)
\[ Q_0 + Q_d = - \int_0^d \rho_f \, dx = - Q(t) \]  \hspace{1cm} (6.30)

where \( Q(t) \) is the total insulator charge at time \( t \). These expressions for electrode charge are used in Section 6.2.4 when calculating external currents. Note that for the vacuum case, where \( Q(t) = 0 \), \( Q_{0}^{\text{vac}} = - Q_{0}^{\text{vac}} \) as expected.

To calculate \( F(x) \) for \( 0 < x < d \), using Eqs. 6.4 and 6.22,

\[ \int_{x=0}^{x=d} F(x) \, dx = - [ \psi(d) - \psi(0) ] = V_a \] \hspace{1cm} (6.4)

\[ F(x) = F_0 + \frac{1}{\varepsilon} \int_0^x \rho_f \, dx \] \hspace{1cm} (6.22)

Putting Eq. 6.22 into Eq. 6.4 and solving for \( F_0 \):

\[ F_0 = - \frac{1}{d} \left( V_a + d \int_x^d \frac{\rho_f}{\varepsilon} \, dx - \int_0^d \frac{\rho_f}{\varepsilon} \, x \, dx \right) \] \hspace{1cm} (6.31)

Evaluating Eq. 6.22 at \( x = d \) gives.

\[ F_d - F_0 = \int_0^d \frac{\rho_f}{\varepsilon} \, dx = \frac{Q(t)}{\varepsilon} \] \hspace{1cm} (6.32)

Unless the total insulator charge \( Q(t) = 0 \), the electrode fields (and charges) are not equal.

6.2.4. External current

We have asserted that three charge transport mechanisms operate in PI films: dielectric polarization, ion redistribution of polarization, and electronic conduction. Of these, only electronic conduction directly contributes to the experimentally measurable current in the external circuit. Electronic current is called normal current because electrons move from the external circuit to one electrode, cross the insulator, and return to the external circuit at the other electrode. However, internal polarizations (dielectric and ionic) contribute indirectly to the external current. The connection between internal charge migration
and the current in the external circuit is now considered. It is shown that the total external current is always constant in the entire external circuit.

**Internal polarization.** The external current due to internal insulator polarization, \( J_{\text{pol}} \), delivers charge to the electrodes

\[
J_{\text{pol}} = \frac{d}{dt} P(t) = \frac{d}{dt} Q_m = \varepsilon \frac{d}{dt} F_{\text{electrode}}
\]  

(6.33)

In general, the two electrode fields \( F_0 \) and \( F_d \) are not equal. The external current due to internal polarization (electrode charging) is not generally equal at both electrodes. It will be shown that only the total external current is electrode independent.

**Normal current.** The external current due to electronic conduction at either electrode is the net electron current across the interface. At either interface the normal current is

\[
J_{\text{norm}} = J_{\text{inj}} - J_{\text{ej}}
\]  

(6.34)

The external current due to normal current also depends on which electrode is considered.

**Total current.** The total external current, \( J_{ex} \), is the sum of polarization and normal currents:

\[
J_{ex} = J_{\text{pol}} + J_{\text{norm}}
\]  

(6.35)

To see that \( J_{ex} \) is the same at both electrodes, assume the contrary. Evaluate \( J_{ex} \) at either electrode: denote the current at \( x=0 \) by \( J_{ex}(0) \) and at \( x=d \) by \( J_{ex}(d) \).

\[
J_{ex}(0) = \frac{d}{dt} Q_0 + J_{\text{norm}}(0) \quad \text{and} \quad J_{ex}(d) = \frac{d}{dt} Q_d + J_{\text{norm}}(d)
\]  

(6.36)

where \( J_{\text{norm}}(0) \) and \( J_{\text{norm}}(d) \) are the normal currents at \( x=0 \) and \( x=d \), respectively.
Now, apply the equation of charge continuity to the entire metal-insulator-metal system. The difference between $J_x(0)$ and $J_x(d)$ must be the time rate of change of total charge in the system, consisting of the electrode charges, $Q_0$ and $Q_d$, and space charge $\rho(x,t)$.

$$J_x(0) - J_x(d) = \frac{d}{dt} \text{[total charge]} = \frac{d}{dt} \left( Q_0 + \int_0^d \rho dx + Q_d \right)$$

Since $Q_0 + Q_d = -Q(t) = -\int_0^d \rho dx$

$$J_x(0) = J_x(d) = \varepsilon \frac{d}{dt} F_0 + J_{\text{norm}}(0) = \varepsilon \frac{d}{dt} F_d + J_{\text{norm}}(d)$$ \hspace{1cm} (6.37)

This proves that the external current is equal at both electrodes.

6.3. Lewis Polarization Theory

6.3.1. Polarization Current

In Sections 3.8.2 and 5.2.4 the low temperature polarization current in PI of the form $I(t) = I_0 t^{-\alpha}$ described. This behavior has been observed in a number of polymers as well as in some inorganic materials as noted in Section 3.8.2. Several models intended to explain this behavior have been reviewed by Wintle [70]. These include electron tunnelling from metal electrodes into empty traps and electrode polarization. The key to these approaches has been that the electric field caused by these injected charges causes the current to decay in time.

Another experimental observation has been made in a wide range of materials which is closely related to this polarization current. The AC conductivity in chalcogenide glasses [71], organic polymers [72], silicon and aluminum oxides [73], crystalline anthracene [74], and doped silicon [67] have been observed to obey this formula:
\[ \sigma(\omega) = \sigma_0 \omega^m(T) \]  

(6.38)

where \( m(T) \) is weakly temperature dependent and has a value in the range of 1.1 to 0.5. At very low frequencies, the AC conductivity deviates from Eq. 6.38 and tends to a true DC conductivity.

A number of models have been proposed to explain Eq. 6.38. One approach is based on the conventional dielectric view in which the conductivity arises from Debye-like processes having a broad range of relaxation times. Another approach is to consider the conductivity as arising from carrier hopping between localized states. The origins of the localized states are crystalline defects. This picture was first developed by Pollak and Geballe [67], and was later modified by Mott and Davis [75] and others. Recently, Jonscher [76] has proposed another hopping model based on many-body interactions.

The AC conductivity \( \sigma(\omega) \) is related to the imaginary part of complex dielectric function, \( \varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega) \), by the relation

\[ \sigma(\omega) = \omega \varepsilon''(\omega) \]  

(6.39)

Cole and Cole [77] have shown that the time domain and frequency domain behaviors represent essentially the same phenomenon. If the current response is linear in the applied field, then the superposition principal holds. The dielectric response of the material to a sinusoidal excitation of frequency \( \omega \) is related to the step response current \( I(t) \) by the Fourier transform:

\[ \varepsilon^*(\omega) = \frac{1}{\pi} \int_0^\infty I(t)e^{-i\omega t} dt \]  

(6.40)

This integral can be evaluated for \( I(t) = I_0 e^{-t/n} \). Evaluating the imaginary part of this integral, using \( I(t) = I_0 e^{-t/n} \),
\[ e''(\omega) = \frac{I_0}{\pi} \int_0^\infty t^{-n} \sin(\omega t) \, dt = \frac{I_0}{\pi} \Gamma(1-n) \cos\left(\frac{1}{2} n \pi\right) \omega^{n-1} \]  \hspace{1cm} (6.41)

which gives

\[ \sigma(\omega) = \frac{I_0}{\pi} \Gamma(1-n) \cos\left(\frac{1}{2} n \pi\right) \omega^n \]  \hspace{1cm} (6.42)

By comparing the form of Eqs. 6.42 and 6.38, and by assigning \( m = n \), we conclude that the same physical process responsible for the time dependent polarization current is also responsible for the AC conductivity behavior of Eq. 6.38.

Caution must be taken in this analysis because, although the limits of integration are zero and infinity, the power-laws are valid for only limited time and frequency ranges.

6.3.2. Lewis Theory: Physics

The traditional approach to the power-law response has been to use a set of Debye-like relaxation processes, characterized by a distribution of relaxation times, \( g(\tau) \). The dielectric response is then given by

\[ \varepsilon(\omega) = \varepsilon_\infty + \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau} \, d\tau \]  \hspace{1cm} (6.43)

Debye originally calculated the response of a collection of dipoles in a viscous medium oriented by an applied field. Random thermal motions tended to disorient the dipoles. In the solid state, the motion of each dipole is considered to be limited by energetics and steric hindrances, and thermal effects tend to disorient the dipoles.

Lewis [36] has noted that this approach has the disadvantage of shifting the difficulty from explaining the time or frequency dependence to explaining the necessary distribution of relaxation times. Often the distributions are purely empirical, and the concept of rigid rotator dipoles can be taken too literally.
In 1961 Pollak and Geballe [67] made a significant contribution when they interpreted their data from n-type single crystal silicon which obeyed Eq. 6.38 with $m$ approximately equal to 0.8 in terms of carrier hopping. Silicon is characterized as an electronic semiconductor with known concentrations of donors and acceptors. In this type of material, the molecular dipole interpretation of the dielectric response would be most unsatisfying. In the theory of Pollack and Geballe, electrons hopped between states located energetically in the band-gap and having the random spatial distribution of the donor atoms. This electron transport gave rise to a current in the external circuit which was indistinguishable from classical dipole orientation.

In amorphous materials, localized states are known to be distributed in the band-gap. Hopping transport is thought to be responsible for steady-state DC conductivity in amorphous solids. A more restricted carrier transport in localized sites within a limited spatial range can give rise to a time dependent polarization current, $I(t)$, under a steady applied field, and, in an alternating field, carriers which hop back and forth between the same sites can give rise to $\sigma(\omega)$.

The electronic states of molecular solids are localized on individual molecules. In the case of a macro-molecule such as a polymer there can be several sites along the chain which are partially or totally localized. Fig. 6.6 shows a model of the density of states in a molecular solid due to Mott and Davis [75]. In this model there are bands of localized states far from the conduction and valence band edges which are due to impurities and defects. These bands contain donor and acceptor states separated into sub-bands which locates the Fermi level, $E_F$. Fig. 6.7 shows schematically the distribution of localized states in space and energy. Donor states, such as $E_D$, are positive holes when empty but are also ionized molecules $M^+$ which are fixed in space. The holes may move, but the ionized molecules may not. Likewise, when occupied by electrons, acceptor states $E_A$ are negative molecular
Figure 6.6: Density of states in molecular solid after Mott and Davis [75].
Figure 6.7: Localized donor and acceptor states of molecular solids. Gaussian distributions have been assumed. g(E) is the tail of the tail of the acceptor states distribution. After Lewis [68].

ions, \( M^- \), which are immobile. The electron can move, leaving behind a neutral molecule. A molecular solid differs from a conventional semiconductor in that \( E_A \) and \( E_D \) cannot both be occupied on the same molecule. The donor and acceptor states have an energy distribution characteristic of the solid. This is often taken to be gaussian in form, as illustrated in Fig. 6.7. Fig. 6.7 also indicates that these states are randomly distributed in space.

Coulombic interactions will tend to form electron-hole pairs on neighboring molecules. The carriers will be able to hop to other equivalent vacant sites, but will remain bound to its counter ion. The simplest element of polarization is shown in Fig. 6.8, where \( i \) and \( j \) are adjacent acceptor states. One electron is shared by these two sites. The sites are an average distance \( r \) apart and require activation energies \( W_{ij} \) and \( W_{ji} \) for transition, where \( W_{ij} = E_0 - E_i \) and \( W_{ji} = E_0 - E_j \). These energies are modified by an applied field, causing the electron to tend to shift to the more favorable site. This charge transfer is
Figure 6.8: The pair element for electron transitions in acceptor states giving rise to an element of polarization [36].

equivalent to dipole orientation and is the basis of the Lewis polarization theory. A similar picture can be made for hole hopping.

An important simplification of the hopping theory is the independent-pair approximation. The idea is that coulombic repulsion between similar electron-hole pairs tends to decouple the polarization into a set independent transfer processes where the occupancy of a donor (or acceptor) is correlated only with the non-occupancy of a neighboring donor (or acceptor).
6.3.3. Lewis Theory: Mathematical Formalism

Elementary Polarization Process. This development follows that of Lewis [36, 67]. Consider a set of states as shown in Fig. 6.7. The total polarization $P(t)$ is given by

$$P(t) = \frac{1}{V} \sum_D e (1-f_i) r_i \cos \phi_i - \frac{1}{V} \sum_A e(f_i) r_i \cos \phi_i$$  \hspace{1cm} (6.44)

where $e$ is the electronic charge, $f_i$ is the probability that state $i$ is occupied by an electron, $r_i$ is the distance of this state to the origin, and $\phi_i$ is the angle between $r_i$ and $F$. The sums run over all donor and acceptor states in the solid of volume $V$. The polarization current is

$$J(t) = \dot{P}(t) = -\frac{e}{V} \sum_{D,A} \dot{f}_i r_i \cos \phi_i$$ \hspace{1cm} (6.45)

If it is assumed that the occupancy of a state $i$ implies the non-occupancy of neighboring states, then Boltzmann statistics apply within this set of states, and $\dot{f}_i$ is given by

$$\dot{f}_i = \sum_{j \neq i} (p_{ji} f_j - p_{ij} f_i)$$ \hspace{1cm} (6.46)

where $p_{ji}$ is the transition rate from state $j$ to $i$. Here the exclusion factors $(1-f_i)$ and $(1-f_j)$ have been omitted as per the above assumption of Boltzmann statistics. The formal solution to this equation is too complex to be of practical value, however, under the pair approximation described in the previous section an approximate solution can be found. The approximation is that the carrier hops only between a pair of states which are spatially aligned. With this approximation Eq. 6.46 becomes

$$\dot{f}_i = p_{ji} f_j - p_{ij} f_i$$ \hspace{1cm} (6.47)

and

$$f_i + f_j = 1$$ \hspace{1cm} (6.48)

The solution to Eqs. 6.47 and 6.48 is

$$f_i = f_i(\infty) - [f_i(\infty) - f_i(0)] e^{-\omega_{ij} t}$$ \hspace{1cm} (6.49)

where $f_i(\infty) = p_{ji}/\omega_{ij}$, $f_i(0)$ is the initial probability of state $i$ being occupied at $t=0$, and
\( \omega_{ij} = p_{ij} + p_{ji} \) is the characteristic relaxation frequency for the pair element. \( f_i(0) \) depends on the initial state of the system and, therefore, on its previous history. The element of current \( \delta J \) contributed by the pair element is given by

\[
\delta J = -e [f_i(\infty) - f_i(0)] r \cos \phi \omega_{ij} e^{-\omega_{ij}t}
\]

(6.50)

where \( r \) is separation between states \( i \) and \( j \), and \( \phi \) is the angle between the applied field and the line joining the two states.

If the field \( F \) is applied at time \( t=0 \), and the transition rates are changed by the effect of the field in the state energies from \( p_{ji} \) to \( p'_{ji} \), then \( f_i(0) \) and \( f_i(\infty) \) may be evaluated. After some algebra, Eq. (6.50) becomes

\[
\delta J = -er \cos \phi \frac{p'_{ji} \omega_{ij} - p_{ji} \omega'_{ij}}{\omega'_{ij}} e^{-\omega'_{ij}t}
\]

(6.51)

If a thermally activated transition process is assumed, then the transition rate may be written as

\[
p_{ij} = \gamma e^{-\frac{W_{ij}}{kT}}
\]

(6.52)

where \( \gamma \) is a frequency, and \( W_{ij} \) has been defined in Fig. 6.8 and in the previous section as the transition activation energy for hopping from state \( i \) to \( j \). Under the applied field \( F \), the modified transition rates may be written as

\[
p'_{ij} = p_{ij} e^{\frac{erF \cos \phi}{kT}}
\]

\[
p'_{ji} = p_{ji} e^{-\frac{erF \cos \phi}{kT}}
\]

\[
\omega'_{ij} = p'_{ij} + p'_{ji}
\]

(6.53)

If \( erF \ll kT \), then the exponentials may be replaced by the first-order approximations, so that Eq. (6.51) becomes
\[ \delta J = e^{2r^2 \cos^2 \phi} \frac{P_{ij}P_{ji}}{kT} \frac{1}{\omega_{ij}} e^{-\omega_{ij}t} \]  

(6.54)

This shows that the polarization of the pair element relaxes with a characteristic time \( \omega^{-1}_{ij} \), and that the strength of the relaxation is linear in the applied field.

**The Total Response.** The total current density \( J(t) \) is given by the sum of the elemental response over all the elements on the solid. Writing the compound probability distribution that a pair element has parameters \( W_{ij}, W_{ji} \) and is singly occupied, at temperature \( T \), as \( P(W_{ij}, W_{ji}, T) \), then

\[ J(t) = \frac{e^{2FN^2}}{3kT} \int r^2 P(W_{ij}, W_{ji}, T) \frac{P_{ij}P_{ji}}{\omega_{ij}} e^{-\omega_{ij}t} dW_{ij} dW_{ji} \]  

(6.55)

where \( N \) is the density of localized states, \( \cos^2 \phi \) has been replaced by its average \( \frac{1}{3} \), and the integral runs the \( W_{ij} \) and \( W_{ji} \) of all pair elements. In Eq. 6.55 the term \( \frac{P_{ij}P_{ji}}{\omega_{ij}} e^{-\omega_{ij}t} \) has a sharply peaked maximum at \( \frac{W_{ij}}{kT} = \frac{W_{ji}}{kT} = \ln(2r_t) \). Thus the polarization current at a time \( t \) comes almost entirely from pair elements that satisfy this condition. Then the integral may be approximated as

\[ J(t) = \frac{e^{2FN^2}}{3kT} t^{-1} [r^2 P(W, W, T)] \]  

(6.56)

which must be evaluated at

\[ \frac{W}{kT} = \ln(2r_t) \]  

(6.57)

where \( r \) is a frequency consistent with the hopping process.

**Required Form of \( P \).** The requirement that the total current have the \( t^{-a} \) form sets a requirement on the form of the probability distribution \( P(W_{ij}, W_{ji}, T) \). From Eq. 6.56

\[ \frac{d \ln J(t)}{d \ln t} = -1 + \frac{kT}{P} \frac{dP}{dW} \]  

(6.58)
since \( W = kT \ln(2\gamma t) \). Also, we have experimentally

\[
\frac{d \ln J(t)}{d \ln t} = -n(T)
\]  

(6.59)

Thus, in the range where \( J(t) \) varies as \( t^{-\kappa(T)} \)

\[-1 + \frac{kT}{P} \frac{dP}{dW} = -n(T)\]

(6.60)

or

\[P = Ae^{\frac{(1-\kappa(T))W}{kT}}\]

(6.61)

where \( A \) is a normalizing constant. Using Eqs. 6.56, 6.57 and 6.61 together we get the desired current formula

\[J(t) = \frac{e^{2\kappa^2FAN^2}}{3kT} (2\gamma)^{1-\kappa(T)} t^{-\kappa(T)}\]

(6.62)

**Density of Localized States.** This result can be used to describe the density of localized states illustrated in Fig. 6.7. The tail of the acceptor state distribution, \( g(E) \), can be expressed as

\[g(E) = Ge^{-\delta}\]

(6.63)

where \( \delta \) will be function of the energy \( E \) or of \( (E_0 - E) = W \) and of \( T \). By definition

\[P = g^2(E)e^{-\frac{E-E_F}{kT}}\]

(6.64)

where \( E_F \) is the Fermi energy of the electron system. Substitution of Eq. 6.63 into Eq. 6.64 gives

\[P = G^2 e^{-\frac{E_0-E_F}{kT}} \frac{W}{e^{\frac{W}{kT}}} \]

(6.65)

or, assuming that \( E_0 - E_F \) is only weakly temperature dependent
\[ P = G' \cdot \frac{e^{\frac{W}{kT}}}{W} \left( 1 - \frac{2kT \delta}{W} \right) \] (6.66)

By comparison with Eq. 6.61 we have

\[ 1 - n = 1 - \frac{2kT \delta}{W} \] (6.67)

or

\[ \delta = \frac{nW}{2kT} \] (6.68)

Therefore

\[ g(E) = Ge^{-\frac{nW}{2kT}} = Ge^{-\frac{nE_0}{2kT}} \cdot e^{-\frac{E}{2kT}} \] (6.69)

For \( n \) near unity, this model predicts the density of localized states in the range contributing to \( J(t) = J_0 t^{-n} \) where \( \frac{W}{kT} = \ln(2\gamma t) \) is proportional to \( e^{-\frac{E}{2kT}} \). Lewis notes that this behavior is reminiscent of the Urbach absorption edge phenomena.

**Effect of Temperature.** Experimentally, it is observed that the power-law index \( n \) varies with temperature roughly as \( a - bT \). The temperature dependence of charge transport is often investigated with an Arrhenius plot (\( \ln J \) versus \( 1/T \)). The current given in Eq. 6.62 does not have a constant slope on such a plot and therefore has no well defined activation energy. To see this, consider the following derivative of Eq. 6.62:

\[
\frac{d \ln J(t)}{d(1/T)} = T + \ln(2\gamma t) \frac{dn(T)}{dT} T^2
\]

\[ = -T^2 \left[ -\ln(2\gamma t) \frac{dn(T)}{dT} - \frac{1}{T} \right] \]

\[ = -T^2 \left[ b \ln(2\gamma t) - \frac{1}{T} \right] \] (6.70)
Thus, even though the fundamental process shown in Fig. 6.8 is one of thermal activation, the Arrhenius plot does not have constant slope. The slope tends to zero as \( \frac{1}{T} \) tends to \( b \ln(2\gamma t) \). This condition will be reached at increasingly lower \( T \) as \( t \) grows.

6.3.4. Comparison of Lewis Theory with PI Data

Smith [15] has made a complete comparison of the Lewis theory with PMDA-ODA PI data, and his findings are reviewed here. Smith reported that the PI data closely followed the Lewis theory: the current was of the form \( t^{-n(T)} \); the charging and discharging currents were symmetric; the polarization current was linear in the applied field; and an Arrhenius plot of the data did not have a constant slope.

Smith also fitted power-law index of the polarization current at various temperatures to the formula \( n(T) = a - bT \). The best fit values were \( a = 1.4 \) and \( b = 0.002 \degree \text{K}^{-1} \). The value of \( b \) can be used to estimate the hopping transition rate prefactor \( \gamma \) from the expression

\[
b = \frac{\ln(2\gamma t)}{T}
\]

(6.71)

This formula is derived from Eq. 6.70 under the condition that the Arrhenius plot has approximately zero slope. (Smith's data in the temperature range 25-120\degree \text{C met this condition.}) This gave an estimate of \( \gamma = 0.016 \text{ sec}^{-1} \).

This value was unexpectedly low, since Lewis assigned \( \gamma \) a phonon frequency on the order of \( 10^{12} \text{ to } 10^{13} \text{ sec}^{-1} \). If a phonon frequency is substituted into Eq. 6.71, the derived value of \( b \) at room temperature is \( 3 \times 10^{-3} \degree \text{K}^{-1} \). Such a small temperature dependence would not be observable in the temperature range examined, in contradiction with Fig. 5.9b.

This discrepancy has not been fully explained, but it is clear from the experimental data that the frequency \( \gamma \) cannot be a phonon frequency. Smith speculated that the low
value of $\gamma$ might arise if the rate limiting step in the relaxation process were a slow moving species or defect. For example, the diffusion of a micro-void into the region of the charge carrier may be necessary in order for hopping to occur.

Aside from the interpretation of parameter $\gamma$, the Lewis theory of polarization by carrier hopping has been shown to be in good agreement with the experimental PI data.

6.4. Metal-Polyimide Contacts

When two materials with different Fermi levels are brought into contact, charge will flow from one material to the other until an equilibrium is reached, that is when a single system Fermi level is established. The transfer of charge creates space-charge regions in the two materials, and it is the electrostatic energy associated with these space-charge regions that aligns the Fermi levels.

In this section, metal-insulator contacts are discussed. The simplest metal-insulator contact occurs between a metal and a vacuum. There is a barrier to current flow across this contact because the highest occupied electronic state in the metal (at the Fermi level) is at a lower energy than the lowest energy level in the vacuum. The energy difference between the Fermi level of the metal and the lowest energy level in the vacuum is called the work function of the metal, $\phi_m$.

The work function concept can be generalized to an insulator, even if there are no electron states at the insulator Fermi level. Using the fictitious lowest vacuum state as a reference level, sometimes called the vacuum level, the work function of a material, $\phi$ is defined as the energy difference between the vacuum level and the Fermi level.

There are, in general, three kinds of metal-insulator contacts: neutral, ohmic, and blocking. A neutral contact occurs when the metal and insulator work function are equal.
As the name suggests, no space-charge is found at such a contact because no charge transfer takes place, and this case will not be considered here. An ohmic contact is formed when the metal work function is less than that of the insulator, while a blocking contact is formed when the metal work function is greater than that of the insulator. Before these two cases are discussed, the physics of insulator band bending is reviewed.

6.4.1. Insulator Band Bending

In this section, a simplified insulator model is considered, shown in Fig. 6.9a. Here a wide-gap insulator is shown with two levels of localized states in the gap. The upper set of localized states are acceptors which are negatively charged when occupied by an electron and neutral when empty, and the lower set are donors which are positively charged when occupied by a hole and neutral when filled by an electron. There are an equal concentration of acceptor and donor states, given by $N_t$. The location of the intrinsic Fermi level, $E_{Fi}$, in the isolated insulator is determined by these states and is centered between the two energy levels. The work function of the insulator is $\phi_i$.

When contact to a metal is made, the resultant space-charge shifts the energy of the electron states in the insulator. The energy of a given set of states is then a function of position. This process is called band bending and is shown schematically in Fig 6.9b. The same process takes place in the metal, but, due to the high density of states at the metal Fermi level, the bending is restricted to a thin region near the contact, and the metal space-charge may be treated as a sheet-charge. The total charge in the metal is equal and opposite the insulator charge to maintain overall neutrality.

The band bending in the insulator can be described by the band bending potential, $\psi(x)$, which is given as the difference in electrostatic potential between the Fermi level and an arbitrary level. In Fig. 6.9b, the acceptor level has been chosen so that $-q\psi(x) = E_a(x) - E_F$. (The $-q$ factor converts the electrostatic potential to an energy
Figure 6.9: Wide-gap insulator with two levels of localized states in the gap before (a) and after (b) contact with low work function metal.

The value of $\psi$ in the bulk of the insulator far from the contact is denoted by $\psi_B$ and by $\psi_S$ at the contact (surface). By the choice of reference levels $\psi_B < 0$.

The curvature of the band bending potential is determined by Poisson's equation

$$\frac{d^2 \psi}{dx^2} = \frac{\rho}{\varepsilon}$$

(6.71)

The boundary conditions to be applied to this equation are:
\[ \psi_B = -\frac{1}{q}[E_A - E_{F1}] \] (6.72)

and, using the continuity of the vacuum level,

\[ \psi_S = \frac{1}{q} \Delta \phi + \psi_B \] (6.73)

where

\[ \Delta \phi = \phi_i - \phi_m \] (6.74)

The total band bending \( \psi_S - \psi_B \) is equivalent to the work function difference, so that

\[ \psi_S - \psi_B = \frac{1}{q} \Delta \phi. \]

### 6.4.2. Ohmic Contact

If the metal work function is less than the insulator work function, so that \( \Delta \phi > 0 \), then the insulator bands bend downward, acceptor states near the contact are filled, and the insulator develops an excess of electrons at the contact. This is the definition of an ohmic contact. The mathematics of ohmic contacts have been reviewed by Simmons [78].

The donor states are filled before the contact is formed. Since the bands bend downward, the donor occupancy is not affected, and the donors may be neglected in an ohmic contact. The insulator space-charge resides in the acceptor states, and is may be written in terms of the band bending potential, \( \psi(x) \)

\[
\rho(x) = -qN_i \frac{1}{1 + e^{\frac{E_A(x) - E_F}{kT}}} = -qN_i \frac{1}{1 + e^{\frac{-q\psi(x)}{kT}}} \]

(6.75)

If it is assumed that the acceptor level is initially shallow, that is well above \( E_{F1} \), then three possible cases are possible: (1) all acceptor states remain shallow, (2) some acceptor states near the contact are pulled below \( E_F \) while others remain shallow, and (3) all the acceptor states throughout the insulator are pulled below \( E_F \). Each of these cases will now be considered.
Case 1: All Shallow. By assumption $E_A(x) > E_F$ for all $x$, so $\psi(x) < 0$. Thus implies that $\Delta \phi < -q \psi_B$ by Eq. 6.73. Eqs. 6.71 and 6.75 can be written as

$$\frac{d^2 \psi}{dx^2} = \frac{4}{\varepsilon N_t} e^{q\psi(x)/kT}$$

(6.76)

When Eq. 6.76 is viewed as a differential equation in $\frac{d\psi}{dx}$, the boundary condition at $x=0$ can be written $\frac{d\psi}{dx} = -F_0$. The second boundary condition is $\frac{d\psi}{dx} = 0$ for some $\psi$ and $x$. This condition may be met at $\psi$ such that (i) $\psi = \psi_B$ or (ii) $\psi = \psi_{max} < \psi_B$. Case (i) corresponds to an insulator thick enough that the bulk is screened from contact effects, and a neutral region is found between two accumulation regions. In case (ii) there is no neutral region in the insulator. Fig. 6.10 illustrates these two cases, where, for generality, the work functions of the two electrodes are assumed to be different.

Considering case (i) first, Eq. 6.76 may be integrated twice to yield, in a region not near the contact,

$$x = \left[ \frac{2kT \varepsilon}{q^2 N_t} \right] \frac{1}{2} e^{\frac{-q \psi_B}{2kT}} \sin^{-1} \left[ e^{\frac{-q(\psi - \psi_B)}{2kT}} \right]$$

(6.77)

for $\Delta \phi > 4kT$. Away from the edge of the accumulation region, this may be approximated as

$$x = \left[ \frac{2kT \varepsilon}{q^2 N_t} \right] \frac{1}{2} e^{\frac{-q \psi}{2kT}}$$

(6.78)

At the edge of the accumulation region, $\psi = \psi_B$ and $x = W_A$. Then Eq. 6.77 gives the width of the accumulation region as

$$W_A = \frac{\pi}{2} \left[ \frac{2kT \varepsilon}{q^2 N_t} \right] \frac{1}{2} e^{\frac{-q \psi_B}{2kT}}$$

(6.79)

Thus, $\psi - x$ and the width of the accumulation regions are independent of $\phi_m$. (Both
Figure 6.10: Ohmic contacts with shallow acceptor states. (a) Insulator is thick enough that bulk is screened from contact effects. (b) No neutral region in insulator. For generality, the work functions of the two electrodes are assumed to be different.
accumulation regions have the same width). The boundary condition of case (i) implies the
d \geq 2W_A. For a given \psi_B and N_I, this limits the minimum thickness insulator which can
fall into case (i). If d < 2W_A, then case (ii) applies.

The total charge in the accumulation region in case (i) is given by

$$Q = (2kTeN_I)^{1/4} \left[ e^{\frac{\psi_F}{kT}} - e^{\frac{\psi_B}{kT}} \right]^{1/2}$$  \hspace{1cm} (6.80)

In case (ii), where the maximum \psi is less than \psi_B, integration of Eq. 6.76 yields the
same expressions as case (i) except that \psi_B \rightarrow \psi_{\text{max}}. Making this substitution into Eq. 6.77, we get

$$x = \left[ \frac{2kTe}{q^2N_I} \right]^{1/2} e^{-\frac{q\psi_{\text{max}}}{2kT}} \sin^{-1} \left[ e^{-\frac{q(\psi - \psi_{\text{max}})}{2kT}} \right]$$  \hspace{1cm} (6.81)

Again, \psi - x is independent of the metal work function, \phi_m. \psi = \psi_{\text{max}} occurs at \hspace{1cm} x = \frac{d}{2}.

Then

$$\frac{d}{2} = \frac{\pi}{2} \left[ \frac{2kTe}{q^2N_I} \right]^{1/2} e^{-\frac{q\psi_{\text{max}}}{2kT}}$$  \hspace{1cm} (6.82)

Rearranging, the maximum energy of the acceptor level is

$$-q\psi_{\text{max}} = kT \ln \left[ \frac{d}{\pi} \left( \frac{N_I}{2kTe} \right)^{1/2} \right]$$  \hspace{1cm} (6.83)

The total charge in the insulator is given by

$$Q = (8kTeN_I)^{1/4} \left[ e^{\frac{\psi_F}{kT}} - e^{\frac{\psi_{\text{max}}}{kT}} \right]^{1/2}$$  \hspace{1cm} (6.84)
Case 2: Mixed Shallow and Deep. If $\Delta \phi \geq -q\psi_B$, then $\psi_s \geq 0$, acceptor states are pulled below the Fermi level and become deep states. If the maximum band bending potential $\psi_{\text{max}} < 0$ then a portion of the acceptor states remain shallow, but if $\psi_{\text{max}} > 0$ then all the acceptor states are made deep and case 3 applies. Here, we consider the mixed shallow and deep case.

Fig 6.11 shows that $\psi(x)$ crosses zero at $x = x_0$. Between $x = 0$ and $x = x_0$ the states are deep and the space-charge may be approximated by assuming that all the states in this region are filled. Beyond $x = x_0$ the states are shallow and Boltzmann statistics may be used. Then

---

Figure 6.11: Ohmic contact with mixed shallow and deep acceptor levels. $\psi(x)$ crosses zero at $x = x_0$. 
\[ \rho = -qN_t \text{ for } x < x_0 \]

\[ = -qN_t e^{\frac{\psi}{kT}} \text{ for } x > x_0 \] (6.85)

Then integration of Poisson's equation in the range \(0 < x < x_0\) gives

\[ \psi - \psi_s = \frac{qN_t}{2\epsilon} x^2 - F_0 x \] (6.86)

where \(F_0 = -\frac{d\psi}{dx}\) at \(x = 0\). For the region \(x > x_0\), there are two possibilities as in case 1:

(i) \(\frac{d\psi}{dx} = 0\) at \(\psi = \psi_B\), and (ii) \(\frac{d\psi}{dx} = 0\) at \(\psi = \psi_{\text{max}} < \psi_B\). Again, case (i) corresponds to an insulator thick enough that the bulk is screened from contact effects, while (ii) corresponds to a thinner insulator which contains space-charge throughout the bulk.

Considering case (i), integration of Poisson's equation from \(x_0\) to \(x\) yields

\[ x = x_0 + \left[ \frac{2kT}{qN_t} \right]^{\frac{1}{2}} e^{-\frac{\psi_B}{2kT}} \left[ \sin^{-1} \left( \frac{-q(\psi - \psi_B)}{e^{\frac{\psi_B}{2kT}}} \right) - \sin^{-1} \left( \frac{-q(\psi)}{e^{\frac{\psi_B}{2kT}}} \right) \right] \] (6.87)

Now, an expression of \(x_0\) must be found. From the continuity of \(\psi\) and \(\frac{d\psi}{dx}\) at \(x = x_0\) one can show that

\[ x_0 = \left[ \frac{2\epsilon}{qN_t} \right]^{\frac{1}{2}} \left( \psi_s + \frac{kT}{q} \right) ^{\frac{1}{2}} - \left( \frac{kT}{q} \right) ^{\frac{1}{2}} \] (6.88)

The total charge in the accumulation region is given by

\[ Q = \left[ \frac{2qN_t}{\epsilon} \right]^{\frac{1}{2}} \left[ \psi_s + \frac{kT}{q} \right]^{\frac{1}{2}} \] (6.89)

In case (ii), we may again replace \(\psi_B\) with \(\psi_{\text{max}}\) to get

\[ \frac{d}{2} - x_0 = \frac{\pi}{2} \left[ \frac{2kT}{q^2N_t} \right]^{\frac{1}{2}} e^{-\frac{q\psi_{\text{max}}}{2kT}} \] (6.90)
Rearranging this expression, and using Eq. 6.88 for \( x_0 \) yields the following expression for \( \Psi_{\text{max}} \):

\[
e^{-\frac{\psi_{\text{max}}}{kT}} = \frac{d}{\pi} \left[ \frac{q^2 N_i}{2kTe} \right]^{1/2} - \frac{2}{\pi} \left[ \left( \frac{q \psi_S}{kT} + 1 \right)^{1/2} - 1 \right]
\] (6.91)

The criterion for selecting case (i) or (ii) is derived from setting \( \psi_{\text{max}} = \psi_B \) in Eq. 6.91 and solving for \( d \):

\[
d \geq 2x_0 + \pi \left[ \frac{2kTe}{q^2 N_i} \right]^{1/2} e^{-\frac{-q \psi_B}{2kT}}
\] (6.92)

If Eq. 6.92 is satisfied, then there is a neutral region which is screened from the contact effects and case (i) applies. Otherwise, case (ii) must be used.

Case 3: All Deep. Now we consider the case in which all the acceptor states are pulled below the Fermi level. This implies that all the localized states are filled and \( \rho = qN_i \). The statistics of deep trapping generally makes stronger band bending. Then integration of Poisson’s equation yields

\[
\psi(x) = \psi_S - \frac{qN_i}{2\varepsilon} (d - x)x
\] (6.93)

This means the bands bend quadratically. In order for all the states to be deep, \( \psi_{\text{max}} \) must be greater than zero. This implies that

\[
\psi_S > \frac{qN_i}{8\varepsilon} d^2
\] (6.94)

The total charge in the insulator is simply

\[
Q = qN_id
\] (6.95)
6.4.3. Blocking Contact

A metal-insulator contact is electron blocking if $\phi_m > \phi_i$. Under this condition, electrons will flow from the insulator to the metal, leaving behind a positive space-charge or depletion region. The bands bend upward as shown in Fig. 6.12. This is called a blocking contact (for electrons).

The analysis of blocking contacts closely follows that for ohmic contacts, in which Poisson's equation is solved under appropriate boundary conditions. The acceptor levels cannot become deep since the bands bend upward, but it is possible for the donors to become shallow (move above the Fermi level) if the bands bend enough. This possibility will not be considered here. The donor states are assumed to be fully occupied.

---

Figure 6.12: Blocking metal-insulator contact.
Since the acceptors become more shallow, the depletion approximation is often used to describe blocking contacts. In the depletion approximation, it is assumed that the electrons are completely depleted from the acceptor states up to a distance $W_d$ from the contact. $W_d$ is called the depletion width. Beyond $x = W_d$, the insulator is assumed to be neutral. Then, the space-charge density is given by

$$\rho = qN_t$$

$$= 0 \text{ for } x > W_d$$ \hfill (6.96)

Integration of Poisson's equation yields

$$\psi(x) = \psi_s + \frac{qN_tW_d}{\epsilon}\left[ x - \frac{x^2}{2W_d} \right]$$ \hfill (6.97)

where the depletion width is given by

$$W_d = \left( \frac{2\epsilon}{q^2N_t}\Delta \psi \right)^{\frac{1}{2}}$$ \hfill (6.98)

The total charge in the depletion region is given by

$$Q = qN_tW_d = (2N_t\epsilon\Delta \psi)^{\frac{1}{2}}$$ \hfill (6.99)

### 6.5. Space-Charge Limited Conduction

In contrast to the low-temperature polarization transients, the high temperature transients in MPM structures having Al-cathodes are clearly non-monotonic. These transients exhibit a peak which is characteristic of a space-charge limited transient as described by Many and Rakavy [30]. Since the charge transported is much greater than can be accounted for by any purely ionic mechanism, and since the transient peak is present when a low work function cathode (Al) is used but not when a high work function cathode (Au) is used, it is plausible that electron injection from the Al electrode is the source of the space-charge.
In the following sections, the theory of space-charge limited conduction is reviewed. First, a phenomenological description of space-charge-limited conduction is given, followed by a more formal analysis of the steady state and transient cases. Rose [79] and Lampert and Mark [2] have given complete reviews of space-charge-limited conduction phenomena.

6.5.1. Phenomenological Description

The simplest space-charge-limited (SCL) current occurs in a vacuum diode. Electrons can be emitted from a hot cathode into a vacuum as shown in Fig. 6.13. The cathode supplies a reservoir of free electrons into the space near the cathode. The amount of charge in this reservoir must be approximately equal to the applied voltage times the capacitance of

---

**Figure 6.13:** Space-charge-limited (SCL) current in a vacuum diode.
the diode, \( Q = CV_a \). An applied electric field draws these electrons toward the anode. The current can be estimated from the ratio of the amount of charge to the time for an electron to cross from the cathode to the anode:

\[
I = \frac{Q}{t_e} = \frac{\varepsilon_0 V_a \bar{v}}{d^2}
\]  

(6.100)

where \( t_e = \frac{d}{\bar{v}} \) is the electron transit time, \( C = \frac{\varepsilon}{d} \) is the diode capacitance, \( d \) is the electrode spacing, and \( \bar{v} \) is the average electron velocity in the vacuum under the applied field. If the amount of charge in the vacuum is not too great, then the electric field and resultant electron acceleration are approximately constant. Then the average electron velocity \( \bar{v} \) can be estimated as one half of the final velocity, or

\[
\bar{v} = \left(\frac{eV_a}{2m}\right)^{\frac{1}{2}}
\]  

(6.101)

where \( m \) is the electron mass, and \( e \) is the electron charge. Inserting Eq. 6.101 into Eq. 6.100 yields the well known Child-Langmuir law for SCL current in a vacuum:

\[
I = \frac{\varepsilon_0}{d^2} \left(\frac{e}{2m}\right)^{\frac{1}{2}} V_a^{\frac{3}{2}}
\]  

(6.102)

Mott and Gurney [80] predicted a solid-state analog to Eq. 6.102. In a solid electrons emitted from the cathode suffer collisions which limit their velocity. Now, the transit time, \( t_e \), is given by

\[
t_e = \frac{d^2}{\mu V_a}
\]  

(6.103)

where \( \mu \) is the electron drift mobility in the solid. The SCL current is approximately given by

\[
I = \frac{Q}{t_e} = \varepsilon \mu \frac{V_a^2}{d^3}
\]  

(6.104)
In the solid, the SCL current is much smaller than in the vacuum for the same $d$ and $v_o$ because collisions in the solid reduce the electron velocity.

### 6.5.2. Steady-state Space-charge Limited Conduction

The analysis given above is only approximate because the effect of the space-charge on the electric field has been neglected. In this section, a better approximation will be given where the space-charge distribution and resultant electric field are calculated. As before, carrier diffusion will be neglected, and the band model is assumed to be appropriate to solid state charge transport. In Section 6.6, the hopping model used in the Lewis Theory is extended to the analysis of SCL currents. An ideal ohmic metal-insulator contact has been assumed. In other words, there is no electrode limitation on the current.

The effect of the space-charge in the electric field is given by Poisson's equation

$$\frac{dF(x)}{dx} = \frac{\rho(x)}{\varepsilon}$$  \hspace{1cm} (6.20)

In Section 6.2.2 the symbol $\rho_f$ was used to distinguish between free and bound charges. The subscript $f$ will be omitted in the following, and it is understood that the dielectric constant includes the bound charge. If holes can be neglected then the charge density is the sum of mobile and trapped electron densities

$$\rho(x) = e[n(x) + n_t(x)]$$  \hspace{1cm} (6.105)

where $n$ is the mobile electron density, and $n_t$ is the trapped electron density. Since carrier diffusion is neglected, the current can be written

$$J = e\mu n(x)F(x)$$  \hspace{1cm} (6.106)
Trap-free Case. In a perfect crystal, $n_e(x) = 0$. Then, by multiplying both sides of Eq. 6.20 by $F(x)$ and substituting in Eq. 6.106, the following differential equation for $F(x)$ is obtained

$$F(x) \frac{dF(x)}{dx} = \frac{J}{\varepsilon \mu}$$

(6.107)

where $J$ is constant. This is easily integrated to yield

$$F(x) = \left[ \frac{2Jx}{\varepsilon \mu} \right]^{1/2}$$

(6.108)

The boundary condition Eq. 6.4 due to the applied bias gives

$$V_a = \int_0^d F(x) dx = \left[ \frac{8Jd^3}{9\varepsilon \mu} \right]^{1/2}$$

(6.109)

Solving for the constant $J$ gives the Mott and Gurney expression for trap-free SCL conduction

$$J = \frac{9}{8} \varepsilon \mu \frac{V_a^2}{d^3}$$

(6.110)

The more rigorous analysis of the effect of the space-charge on the electric field has introduced the constant $9/8$, but the expression is otherwise the same as Eq. 6.104.

At low fields, thermally generated (as opposed to injected) electrons dominate the current. If the bulk concentration of electrons at temperature $T$ is $n_0(T)$, then an Ohmic current $J_\Omega = en_0(T)\mu \frac{V_a}{d}$ will also flow. The crossover voltage $V_x$ is defined as the voltage at which the Ohmic and SCL currents are equal:

$$V_x = \frac{8}{9} \frac{en_0(T)d^2}{\varepsilon}$$

(6.111)

Fig. 6.14 illustrates the current-voltage relation, which is linear in $V_a$ below $V_x$ and above $V_x$ the current is quadratic in $V_a$. 
Figure 6.14: SCL current-voltage relation: linear in $V_s$ below $V_s$, and above $V_s$ the current is quadratic in $V_s$.

Eq. 6.108 gives the electric field as a function of $x$. The steady-state electron distribution is given by the derivative of this expression (Poisson's equation)

$$n(x) = \frac{e}{e} \frac{dF}{dx} = \frac{1}{2} \left( \frac{2J}{e\mu} \right) \frac{1}{2} x^{-\nu_h}$$

(6.112)

Shallow-trap Case. The presence of traps in the solid reduces the SCL current by immobilizing charge carriers, but the total amount of charge is unchanged. The relation between $n$ and $n_t$ is determined by the equilibrium between electron capture from and emission to the conduction band. Elementary semiconductor statistics gives
\[ n(x) = N_e e^{-\frac{E_c(x) - E_F}{kT}} \]  

(6.113)

where \( N_e \) is the effective density of states in the conduction band, and \( E_c(x) - E_F \) is the energy difference between the bottom of the conduction band and the system Fermi level. If \( N_t \) is the concentration of traps at energy \( E_t \) below \( E_c \) then the trapped electron density is

\[ n_t(x) = \frac{N_t e^{-\frac{E_t(x) - E_F}{kT}}}{1 + e^{-\frac{E_c(x) - E_F}{kT}}} \]  

(6.114)

where the trap degeneracy has been assumed to be one.

A trap is shallow if it lies above the Fermi level, \( E_t > E_F \). In this case, Eq. 6.114 can be approximated by

\[ n_t(x) = N_t e^{-\frac{E_t(x) - E_F}{kT}} \]  

(6.115)

The ratio of free to trapped charge is then given by

\[ \theta = \frac{n(x)}{n_t(x)} = \frac{N_e e^{-\frac{E_t - E_c}{kT}}}{N_t} \]  

(6.116)

where \( \theta \) is a constant. Then Poisson’s equation becomes

\[ \frac{\varepsilon}{e} \frac{d\phi}{dx} = n(x) + n_t(x) = (1 + \theta^{-1}) = \theta^{-1} n(x) \]  

(6.117)

This modification can be interpreted as \( \varepsilon \rightarrow \theta \varepsilon \). Thus, in the presence of shallow traps, the SCL current is given by

\[ J = \frac{9}{8} \theta \varepsilon \mu \frac{V_a^2}{d^3} \]  

(6.118)
6.5.3. Space-charge Limited Transients

In this section the time dependence of the SCL current is analyzed in the trap-free case. Now, the current, electric field, and electron concentrations depend on time. The constant bias is applied at \( t = 0 \) to a neutral insulator. As before, carrier diffusion will be neglected. The time dependent current \( J(x,t) \) is given by the sum of conduction and displacement currents:

\[
J(x,t) = J_e(x,t) + e \frac{\partial F(x,t)}{\partial t} = e \mu n(x,t) F(x,t) + e \frac{\partial F(x,t)}{\partial t} \quad (6.119)
\]

In fact, the current is a function of time alone, \( J(x,t) = J(t) \). To see that this is so, consider the equation of charge continuity:

\[
\frac{\partial J_e(x,t)}{\partial x} + e \frac{\partial n(x,t)}{\partial t} = 0 \quad (6.120)
\]

Using Poisson's equation to replace \( n(x,t) \) in Eq. 6.119 gives

\[
\frac{\partial J_e(x,t)}{\partial x} + e \frac{\partial}{\partial t} \left[ \frac{\varepsilon}{e} \frac{\partial F(x,t)}{\partial x} \right] = 0 \quad (6.121)
\]

Changing the order of differentiation

\[
\frac{\partial}{\partial x} \left[ J_e(x,t) + e \frac{\partial F(x,t)}{\partial t} \right] = \frac{\partial}{\partial x} J(x,t) = 0 \quad (6.122)
\]

which proves that the total current is a function of time only.

Integration of Eq. 6.119 over \( x \) from 0 to \( d \) using \( J = J(t) \) and \( \frac{\partial}{\partial t} \int_0^d F(x,t) \, dx = 0 \) yields

\[
J(t) = \frac{e \mu}{2d} \left[ F^2(d,t) - F^2(0,t) \right] \quad (6.123)
\]

The relation between \( F(0,t) \) and \( F(d,t) \) has been given in Eq. 6.32:

\[
F(d,t) = F(0,t) = \frac{Q(t)}{\varepsilon} \quad (6.32)
\]
If an ohmic contact is formed at the cathode (at \(x=0\)), then electrons are injected into the insulator, and a reservoir of charge is formed which tends to force the electric field at \(x=0\) to zero, \(F(0,t) = 0\). In this case Eq. 6.123 becomes

\[
J(t) = \frac{\mu}{2d} F^2(d,t)
\]  

(6.124)

From the time the bias is applied at \(t=0\), until some later time \(t_1\), the total current is simply the displacement current at the anode \((x=d)\)

\[
J(t) = \varepsilon \frac{\partial F(d,t)}{\partial t}
\]  

(6.125)

where \(t_1\) is the time required for a injected electron to cross the insulator. In other words, before \(t_1\) the conduction current at the anode, \(J_\varepsilon(d,t< t_1)\), is zero because no injected charge is collected at the anode. Combining Eqs. 6.124 and 6.125

\[
\frac{dF(d,t)}{dt} = \frac{\mu}{2d} F^2(d,t)
\]  

(6.126)

The solution to this differential equation, using the boundary condition that \(F(x,0) = \frac{V_a}{d}\), is

\[
F(d,t) = \left( \frac{V_a/d}{1 - \frac{\mu V_a}{2d^2} t} \right)
\]  

(6.127)

Thus the current between \(t=0\) and \(t=t_1\) is given by

\[
J(t) = J(0) \left[ 1 - \frac{\mu V_a t}{2d^2} \right]^{-2}
\]  

(6.128)

where \(J(0) = \frac{\varepsilon \mu V_a^2}{2d^3}\). \(t_1\) is the time that the leading front of the injected charge reaches the anode, and is given by the relation

\[
d = \int_0^{t_1} \mu F(d,t) dt
\]  

(6.129)
since the field at the leading edge of the injected charge equals the anode field in this time range. Eq. 6.129 may be evaluated to give
\[ t_1 = 0.8 \frac{d^2}{\mu V_a} \]
This relation should be compared with the phenomenological result given in Eq. 6.103. The true transit time is 20% shorter than the estimated time because the charge is accelerated by the enhanced space-charge field.

At time \( t = t_1 \) the injected charge reaches the anode, the insulator contains the maximum space-charge, and \( J(t) \) reaches a peak value. For later times, the current decays toward the steady-state SCL current given by Eq. 6.110, and the space-charge relaxes to its steady state distribution given by Eq. 6.112. Many and Rakavy note that since at \( t = t_1 \) the insulator holds more charge than it can in steady-state, the current undershoots the steady-state value [30]. Fig. 6.15, from Many and Rakavy [30], shows the theoretical SCL transient current versus time for no trapping and a range of shallow trapping configurations.

The diffusion of charge carriers has been neglected in these calculations. Rosental [81] has shown that carrier diffusion introduces several features in the SCL transient not predicted by the simple theory of Many and Rakavy [30]. In particular, a minimum occurs before the characteristic peak. Also, the peak is rounded by the effect of diffusion. Rosental interprets the minimum as evidence that the transient is diffusion dominated at short times. The current decreases initially because the gradient of the carrier density decreases as injected charge spreads into the insulator. At the same time, the drift component increases, and by the time the minimum is reached the transient is drift dominated. The main effect of diffusion, then, is to influence the dispersion of the leading edge of the injected space-charge front. The model results presented in Section 7.4 for SCL transient current including diffusion effects confirm the findings of Rosental.
Figure 6.15: Theoretical SCL transient current for no trapping and a range of shallow trapping configurations [30].

6.6. Hopping Model

In this section the idea of carrier hopping between localized states is applied to DC conductivity. The hopping model is due to Mott and Gurney [80]. In contrast to the Lewis theory for polarization where net carrier transport was limited to only a few nearby sites, we will now consider carrier hopping through many localized sites, resulting in macroscopic charge transport.

Until now, only electron hopping has been considered, but ions are also mobile in PI and other polymer films. It is reasonable to extend the hopping model to ion transport, since ions rapidly move between relatively stable sites in the polymer matrix. Therefore,
the hopping formalism developed will be applied to both electron and ion transport, but with different activation energies and hopping distances.

It has been argued that the hopping model for electron transport is physically more reasonable than band-type transport in disordered materials because of the narrowness of the bands, and for ion transport because of the limited number of sites able to contain an ion. The hopping model also has a computational advantage over band-type transport. The combination of the drift contribution to the current, \( q \mu n(x,t)F(x,t) \), with Poisson's equation, \( n(x,t) = \frac{\varepsilon}{q} \frac{\partial F(x,t)}{\partial x} \), results in an expression which is non-linear in the electric field. A self-consistent solution to the charge-field problem is difficult to find analytically except in the simplest of approximations, and numerical approaches tend to be unstable. A formalism due to Iwamoto and Hino [69] reduces the problem in one-dimension to a set of \( N \) linear algebraic equations, where \( N \) is the number of hopping sites in the solid. This formalism is used in Chapter 7 to model space-charge effects in PI films.

6.6.1. Mathematical Formalism

The basis of the hopping model is the assumption that the unit of electron or ion motion is a jump to a neighboring site with the same energy. These sites are sometimes called wells. The distance between wells, the hopping length, is \( r \). Without an applied field, there is a barrier of height \( W \) between these wells. Fig. 6.16a depicts the zero bias situation. The probability of an ion overcoming the barrier, \( p \), is

\[
p = \gamma e^{-\frac{W}{kT}}
\]  

(6.130)

where \( \gamma \) is a frequency. There is no net current since the probability of travel in one direction is the same as in the reverse.

When a field is applied, the barrier is changed by an energy \( \pm qrF/2 \), depending whether hopping along the field direction (minus) or against it (plus) is considered, and \( q \)
Figure 6.16: Hopping model: (a) no applied field, and (b) with applied field.

is the carrier charge. The barrier raising and lowering are shown in Fig. 6.16b. With the field applied the hopping probabilities are

\[ p_f = \gamma e^{-\frac{w}{kT}} e^{-\frac{q_f}{kT} \left( \frac{eF}{2} \right)} \]  

(6.131)
\[ p_b = \gamma e^{\frac{-w}{kT} e^{-\frac{q_j r_F}{2}}} \]  \hspace{1cm} (6.132)

where subscripts \( f \) and \( b \) refer to 'forward' and 'backward,' respectively. For \( V_a > 0 \) and \( F > 0 \), positive ions will have a greater probability of moving to the right, i.e. \( p_f > p_b \).

The net current between wells \( j \) and \( j+1 \) is

\[ J_{j,j+1} = q \left[ p_{f,j} N_j - p_{b,j+1} N_{j+1} \right] \]  \hspace{1cm} (6.133)

where \( N_j \) is the number of carriers per unit area in the \( j \)th well.

### 6.6.2. Equivalence of Hopping Model with Drift and Diffusion Model

The expression for the current given in Eq. 6.133 is closely related to the usual expression for current due to drift and diffusion:

\[ J(t) = \mu \rho(x,t) F(x,t) + D \frac{\partial \rho(x,t)}{\partial x} \]  \hspace{1cm} (6.134)

To establish the relationship, consider the limit where the hopping length tends to zero, such that \( d = N r \) is constant, where \( N \) is the number of wells. The key step is to replace the exponentials in Eqs. 6.131 and 6.132 with the first order approximations:

\[ \lim_{x \to 0} e^x = 1 - x \]  \hspace{1cm} (6.135)

Substituting Eqs. 6.131 and 6.132 into Eq. 1.133 with the exponentials replaced gives

\[ J = q \gamma e^{\frac{-w}{kT}} \left\{ \left[ 1 - \frac{q}{kT} \frac{r F}{2} \right] N_j - \left[ 1 + \frac{q}{kT} \frac{r F}{2} \right] N_{j+1} \right\} \]

\[ = \frac{q}{kT} r^2 \gamma e^{\frac{-w}{kT}} \frac{q N F}{r} - r^2 \gamma e^{\frac{-w}{kT}} \frac{q N_{j+1} - N_j}{r^2} \]

\[ = \frac{q}{kT} D \rho F - D \frac{d \rho}{dx} \]  \hspace{1cm} (6.136)

where the following substitutions have been made
\[ D = r^2 \gamma e^{-\frac{W}{kT}} \]  
(6.137)

\[ \rho = \frac{q\bar{N}}{r} \]  
(6.138)

\[ \bar{N} = \frac{N_i + N_{i+1}}{2} \]  
(6.139)

\[ \frac{dp}{dx} = \frac{q}{r} \frac{N_{i+1} - N_i}{r} \]  
(6.140)

The Einstein relation gives the mobility from \( D \):

\[ \mu = \frac{q}{kT} D \]  
(6.141)

Thus, Eq. 6.136 demonstrates that the drift and diffusion view of transport is a special case of the hopping model, i.e. in the limit \( a \to 0 \). Expressions for the mobility and diffusivity in terms of the hopping model parameters \( a, \gamma \) and \( W \) are given.

6.6.3. Contacts in the Hopping Model

A schematic diagram of the entire insulator is shown in Fig. 6.17a for ions and in Fig. 6.17b for electrons. There are \( N \) wells between potential barriers at the electrodes. These barriers confine ions to the insulator, but electron transfer across these barriers is permitted.

The condition that the electrodes block ion transport is represented mathematically by the following:

\[ J^{i}_{0,1} = J^{i}_{N,N+1} = 0 \]  
(6.142)

where \( J^{i}_{0,1} \) is the net ion current between the 0th well (the electrode at \( x = 0 \)) and the 1st ion well, and \( J^{i}_{N,N+1} \) is the net ion current between the Nth (last) well and the (N+1)th well (the electrode at \( x = d \)). The net electron current from the external circuit (0th well)
to the 1st electron well, in analogy to Eq. 6.133, is given by

\[ J_{0,1}^* = q \left[ \rho_{b,1} N_1 - p_{f,0} (N_f - N_i) e^{-\frac{q \Psi_s}{kT}} \right] \]  

(6.143)

where \((N_f - N_i)\) is the number of vacant states per unit area in the first well, \(p_{f,0}\) is the
transition rate from the electrode into the first well, and the Boltzmann factor, $e^{-\frac{\psi_s}{kT}}$, is
needed to account for the applied bias in the external circuit. Similarly, the current from
the Nth well to the external circuit is given by

$$J_{e,N,N+1} = -q \left[ p_{f,N} N_N e^{-\frac{\psi_s}{kT}} - p_{b,N+1} (N_i - N_N) \right]$$

(6.144)

where $N_i - N_N$ is the number of vacant states per unit area in the Nth well, $p_{b,N+1}$ is the
transition rate from the electrode into the Nth well.

Since an electron leaving the insulator must overcome an energy barrier $-q\psi_s$ to
enter the metal, the transition rate for an electron leaving either the first or Nth well into
the external circuit is given by

$$p_{b,1} = p_{f,N} = \gamma e^{\frac{-\psi_s}{kT}}$$

(6.145)

where $-q\psi_s$ is the energy barrier between the first (or Nth) well and the Fermi level of the
electrode.

The two remaining transition rates, $p_{f,0}$ and $p_{b,N+1}$ can be found from the equilibrium
condition that $J = 0$ when $V_a = 0$.

$$p_{f,0} = p_{b,N+1} = \frac{N_0}{N_i - N_0} p_{f,1} = \frac{N_0}{N_i - N_0} \gamma e^{\frac{-\psi_s}{kT}}$$

(6.146)

where $N_0$ is the equilibrium value of $N_1 = N_N$ at $V_a = 0$. Fermi-Dirac statistics require
that

$$\frac{N_0}{N_i} = \frac{1}{1 + e^{\frac{-\psi_s}{kT}}}$$

(6.147)

or
\[
\frac{q\Psi_s}{e^{kT}} = \frac{N_t}{N^0} - 1
\]  

(6.148)

Inserting these expressions for the transition probabilities into Eq. 6.143

\[
J^*_{0,1} = q\gamma e^{kT} \left[ N_1 - (N_t - N_1) \frac{N^0}{N_t - N^0} e^{-\frac{\phi}{kT}} \right]
\]

\[
= q\gamma e^{kT} \left[ N_1 N^0 \left( e^{-\frac{\phi}{kT}} - 1 \right) - N_t \left( N^0 e^{-\frac{\phi}{kT}} - N_1 \right) \right]
\]

(6.149)

Similarly, for \( J^*_{N,N+1} \)

\[
J^*_{N,N+1} = q\gamma e^{kT} \left[ N_N N^0 \left( e^{-\frac{\phi}{kT}} - 1 \right) - N_t \left( N^N e^{-\frac{\phi}{kT}} - N^0 \right) \right]
\]

(6.150)

These expressions are used in Chapter 7 to calculate electronic transient currents.
CHAPTER 7

Model for Space-charge Effects

7.1. Introduction

Numerical modeling of conduction transients in PI films is described in this Chapter. Simulated transients for ionic polarization and SCL electron injection transients from ohmic contacts are presented. Also presented are simulated transients for the model system which consists of injected electrons and positive mobile ions. The hopping model described in Section Section 6.6 is used to compute charge transport in PI under a constant applied bias.

The method of calculation is described in Section 7.2. Ionic and electronic transient results are given in Sections 7.3 and 7.4, respectively. Transients due to the transport of electrons and ions together is considered in Section 7.5.

This model reproduces many of the gross trends in the experimental observations in MPM structures which have been described in Chapters 3 and 5. However, quantitative agreement with the experimental data has not been achieved. This model shows that the transients in Al-PI-Al structures at elevated temperatures are consistent with an SCL electron transient modified by the presence of mobile ionic impurities. Although constructed of older, conventional charge transport models, the model presented here provides new insights into conduction in insulators such as polymers which contain mobile ionic impurities in addition to other intrinsic conduction mechanisms.
7.2. Method of Calculation

7.2.1. Assumptions

A homogeneous, one-dimensional insulator of thickness $d$ and static dielectric constant $\varepsilon$ is considered. It is assumed that two identical metal electrodes are applied to the film. Except for contact effects, the insulator is assumed to be overall neutral. At most, two carrier species of opposite charge are considered. They may be positive and negative ions or positive ions and electrons. If only one mobile charge carrier is considered, neutrality is preserved by a fixed background of the opposite sign charge. Hole are not considered, nor is the possibility of the thermal generation of electron-hole pairs.

The distribution of electronic states is assumed to be as shown in Fig. 6.9. Electron transport is assumed to be via hopping between the localized states. Ion transport is also modeled as a hopping mechanism, although electrons and ions hop through distinct sets of sites with different hopping lengths and barrier heights.

Interactions between the charge carriers are limited to the space-charge field and, in the case of electrons, the Pauli exclusion principle. Other modes of interaction are discussed in Chapter 8.

The metal-insulator contacts are assumed to be completely blocking to ions but electron transport across the electrode barriers is permitted. Ideal ohmic metal-PI contacts are assumed for electron injection and emission.

7.2.2. Bulk Carrier Transport of a Single Species

For simplicity, only one species of charge carrier is considered in this section. In Section 7.2.4 the case of more than one mobile species is considered. The net current between wells $j$ and $j+1$ has been given by Eq. 6.133,
\[ J_{j,j+1} = q \left[ p_{f,j} N_j - p_{b,j+1} N_{j+1} \right] \]  \hspace{1cm} (6.133)

where \( N_j \) is the number of carriers per unit area in the \( j \)th well, and the transition rates are given by

\[ p_f = \gamma e^{-\frac{W}{kT}} - \frac{q}{kT} \left( \frac{e^{\frac{W}{kT}} - 1}{2} \right) \]  \hspace{1cm} (6.131)

\[ p_b = \gamma e^{-\frac{W}{kT}} - \frac{q}{kT} \left( \frac{e^{\frac{W}{kT}} - 1}{2} \right) \]  \hspace{1cm} (6.132)

The current density \( J \) is related to the change in carrier charge density \( \rho \) by the equation of charge continuity

\[ \frac{d\rho}{dt} + \frac{dJ}{dx} = 0 \]  \hspace{1cm} (7.1)

Formally integrating the gradient of the current density in time relates the charge density at time \( t' \) to the density at an earlier time \( t \).

\[ \rho(x,t') = \rho(x,t) + \int_t^{t'} \frac{dJ(x,t)}{dx} dt \]  \hspace{1cm} (7.2)

This integration can be performed numerically with a Runge-Kutta type integration to give the change in charge distribution during a time interval \( \Delta t \) [82].

\[ \Delta \rho(t) = \rho(t + \Delta t) - \rho(t) = \frac{\Delta t}{6} \left( k_1 + 2k_2 + 2k_3 + 2k_4 \right) \]  \hspace{1cm} (7.3)

with

\[ k_1 = - \frac{d}{dx} J(t) \]

\[ k_2 = - \frac{d}{dx} J(t + \frac{1}{2}k_1 \Delta t) \]

\[ k_3 = - \frac{d}{dx} J(t + \frac{1}{2}k_2 \Delta t) \]
\[ k_4 = -\frac{d}{dx}J(t + k_3 \Delta t) \quad (7.4) \]

The current gradient \( \frac{d}{dx}J \) can be written in terms of the transition rates for hopping via the equation of charge continuity with the identification \( qN_j = \rho(x_j)r \):

\[ \frac{d}{dt}N_j = -\frac{r}{q} \frac{d}{dx}J = p_{f,j-1}N_{j-1} - (p_{b,j} + p_{f,j})N_j + p_{b,j+1}N_{j+1} \quad (7.5) \]

where \( r \) is the hopping length, \( x_j = (j - \frac{1}{2})r \), and \( q \) is the charge of the carrier. For \( n \) wells in one-dimension, the problem is reduced to a set of \( n \)-coupled linear, algebraic equations. The population of the \( j \)th well is governed by Eq. 7.5. When \( 2 \leq j \leq n - 1 \), the transition rates \( p_f \) and \( p_b \) are given by Eqs. 6.131 and 6.132. When \( j = 1 \) or \( j = n \), the transitions rates must be modified to take into account the boundary conditions at the electrodes. If an ionic species is under consideration, \( p_{f,0}, p_{b,1}, p_{f,n}, \) and \( p_{f,n+1} \) are set equal to zero. For electrons, these transition rates are not identically zero, but have been given by Eqs. 6.145 and 6.146.

For each time step, the electric field is calculated from

\[ F(x_j, t) = F(0, t) + \frac{1}{\varepsilon} \int_0^{x_j} \rho(x, t) \, dx \quad (6.22) \]

and

\[ F(0, t) = -\frac{1}{d} (V_a + \frac{d}{\varepsilon} \int_0^d \rho(x, t) \, dx - \frac{1}{\varepsilon} \int_0^d \rho(x, t) \, dx) \quad (6.31) \]

In the hopping model, the charge density is no longer a continuum. Converting the integrals to discrete sums:

\[ F(x_j, t) = -\frac{V_a}{d} - \frac{q}{\varepsilon} \sum_{k=1}^s N_k + \frac{qF}{d\varepsilon} \sum_{k=1}^s (k - \frac{1}{2})N_k + \frac{q}{\varepsilon} \sum_{k=1}^s N_k \quad (7.6) \]

since \( dx \rightarrow r \) when converting from the continuum to the discrete case. Note the total.
space-charge density including the fixed background charge, if any, must be used to calculate the electric field in the above expressions. If there is a background charge of density \( \rho_b \), then \( \frac{\rho_b}{e} x_f + d \frac{\rho_b}{2e} \) must be added to Eq. 7.8 for \( F(x_f,t) \).

The transition rates \( \rho_f \) and \( \rho_b \) are given as functions of \( F(x) \) in Eqs. 6.131 and 6.132. Eqs. 7.3, 7.4, and 7.5 can then be used to evaluate \( \frac{d}{dt} N_f \) for each well. In this way the time evolution of \( \rho(x) \) and \( F(x) \) can be calculated.

7.2.3. External Current

In Section 6.2.4 the external current due to ionic and electronic transport and dielectric polarization was given as the sum of displacement and normal currents:

\[
J_{\text{ext}}(0) = J_{\text{ext}}(d) = \varepsilon \frac{d}{dt} F_0 + J_{\text{norm}}(0) = \varepsilon \frac{d}{dt} F_d + J_{\text{norm}}(d)
\]  (6.37)

where the normal current is the net electron flux at the electrode. Since the total external current is equal at both electrodes, it does not which electrode is considered.

Consider the electrode at \( x = 0 \). The displacement current is given by the time derivative of Eq. 7.6 evaluated at \( x = 0 \):

\[
\varepsilon \frac{d}{dt} F_0 = \frac{q r}{d \varepsilon} \sum_{k=1}^{n} (k - \frac{1}{2}) \frac{\Delta N_k}{\Delta t} - \frac{q}{\varepsilon} \sum_{k=1}^{n} \frac{\Delta N_k}{\Delta t}
\]  (7.7)

with \( \frac{\Delta N_k}{\Delta t} = \frac{L}{q} \Delta \rho/\Delta t \).

The normal current at \( x = 0 \) is given by Eq. 6.149:

\[
J^e_{0,1} = q \gamma e \frac{q \psi_{f}}{kT} \left[ N_1 N^0 \left[ e^{-\frac{\psi_{f}}{kT}} - 1 \right] - N_t \left[ N^0 e^{-\frac{\psi_{f}}{kT}} - N_1 \right] \right] \quad (6.149)
\]

For each time step \( \Delta t \), the external current can be evaluated from Eqs. 7.7 and 6.149.
7.2.4. Multiple Carrier Transport

If more than one mobile species are present in the insulator, then the Runge-Kutta integration must be done separately for each species. Each species has a unique hopping length, \( r \), hopping barrier height, \( W \), and charge, \( q \). For a given film thickness \( d \), the number of wells, \( n \), and hopping length must satisfy \( d = nr \) for each species. Thus, in general, each carrier species occupies a different number of wells.

The electric field is determined by the total space-charge density, so for two carrier species identified as A and B, Eq. 7.8 becomes

\[
F(x_j, t) = -\frac{V_x}{d} + \frac{q_A}{\varepsilon} \sum_{k=1}^{n_A} N_{Ak} + \frac{q_B}{\varepsilon} \sum_{k=1}^{n_B} N_{Bk} - \frac{q_A}{\varepsilon} \sum_{k=1}^{n_A} N_{Ak} - \frac{q_B}{\varepsilon} \sum_{k=1}^{n_B} N_{Bk} \\
+ \frac{q_A r_A}{d\varepsilon} \sum_{k=1}^{n_A} (k - \frac{1}{2}) N_{Ak} + \frac{q_B r_B}{d\varepsilon} \sum_{k=1}^{n_B} (k - \frac{1}{2}) N_{Bk}
\]

(7.8)

where \( q_A \) and \( q_B \) are the carrier charges, \( r_A \) and \( r_B \) are the hopping lengths, \( x_j = (j_A - \frac{1}{2})r_A = (j_B - \frac{1}{2})r_B \), \( N_{Ak} \) and \( N_{Bk} \) are the number of per area of charge carriers in the \( k \)th well, and \( d = n_A r_A = n_B r_B \). Then, the displacement current at the electrode at \( x = 0 \) is given by

\[
\varepsilon \frac{d}{dt} F_0 = \frac{q_A r_A}{d} \sum_{k=1}^{n_A} (k - \frac{1}{2}) \frac{\Delta N_{Ak}}{\Delta t} - q_A \sum_{k=1}^{n_A} \frac{\Delta N_{Ak}}{\Delta t} \\
+ \frac{q_B r_B}{d} \sum_{k=1}^{n_B} (k - \frac{1}{2}) \frac{\Delta N_{Bk}}{\Delta t} - q_B \sum_{k=1}^{n_B} \frac{\Delta N_{Bk}}{\Delta t}
\]

(7.9)

When considering two mobile species, the following procedure was followed for each time step \( \Delta t \): (1) the electric field was calculated with Eq. 7.8; (2) \( \Delta \rho_A \) was calculated for species A; (3) \( \Delta \rho_B \) was calculated for species B using the same electric field as used for species A; (4) the external current was computed; (5) the carrier distributions were updated with \( \Delta \rho_A \) and \( \Delta \rho_B \); (6) time was incremented. The procedure was then repeated.
7.3. Simulated Ion Transients

7.3.1. Positive Ions with Fixed Negative Background

Initially, the ions are uniformly distributed through the insulator, and there is a fixed negative background charge. At time $t=0$ a constant bias $V_A$ is applied. Fig 7.1 shows the evolution of space-charge and electric field distributions computed with the hopping model. The charge density is normalized by $qC_0$, where $C_0$ is the total charge per unit area in the film. The applied bias was 10V across 1 $\mu$m of PI. The initial concentration of ions was $10^{17}$ ions/cm$^2$. The times indicated in Fig. 7.1 are in sec. One hundred wells were used, corresponding to an ionic hopping length of 100 Å. The hopping barrier was chosen to be 2.0 eV, the temperature was 300°C, and $\gamma$ was set to $10^{12}$ sec$^{-1}$.

Initially the electric field is constant, but as the ions accumulate at the electrode, the electrode field grows, and the bulk field decreases. This process continues until $F_{\text{bulk}} = 0$. The electrode fields $F_0$ and $F_d$ are equal since the insulator remains overall neutral ($Q(t) = 0$). The steady-state charge distributions is independent of the hopping length.

Computed charge-time data are shown in Fig. 7.2 on log current-log time axes for the same conditions. Transients for several other voltages (1, 3, and 15V) are also shown. The initial current varies linearly with the applied bias. The transient current from a single ion species is characteristically constant until the bulk electric field decreases appreciably due to screening. Then, the current drops rapidly. The time when the current begins to fall is inversely proportional to the applied bias.
Figure 7.1: Evolution of space-charge and electric field distributions computed with the hopping model for a positive mobile ionic species (1 ppm) with fixed negative background. Ten volts were applied across a one micron film.
7.3.2. Positive and Negative Mobile Ions

Here the fixed background charge is replaced with negative mobile ions. In general, the two ionic species have different hopping lengths, $r$, and barrier heights, $W$, and thus different mobilities by Eqs. 6.137 and 6.141:

$$\mu = \frac{q D}{kT} = \frac{q r^2}{kT} e^{-\frac{W}{kT}}$$  \hspace{1cm} (7.10)

Fig. 7.3 shows the evolution of the total space-charge and electric field distributions for -10V applied bias under the special condition of equal mobilities for both species. The charge distribution is more complex than in the single species case of Fig. 7.1. While charge accumulates at the electrodes, localized regions of high charge density form at about
Figure 7.3: Evolution of space-charge and electric field distributions computed with the hopping model for a positive and negative mobile ionic species (1 ppm) with equal mobilities. Ten volts were applied across a one micron film.
0.1-0.2 μm from the electrodes. At longer times, these regions appear to move toward the electrode. The electrode field grows with time while the bulk field is screened.

The total transient current for the case of two ionic species with equal mobility is shown in Fig. 7.4 as curve A. Each species contributes a equal current shown as curve B in Fig. 7.4. The current is roughly constant for 1000 sec, then it decreases as the bulk electric field is screened by the accumulation of space-charge at the electrodes.

Figure 7.4: Computed current transients for positive and negative mobile ionic species. Curve A: Total current when mobilities are equal. Curve B: Contribution from either species mobilities are equal. Curves C-E: Negative species has 25% mobility of positive species. Curve C: Total current. Curve D: Negative species contribution. Curve E: Positive species contribution.
If the ions have different hopping lengths, then the mobilities will also be different. Eq. 7.10 indicates that the mobility is proportional to the square of the hopping length, $r$. The total current under -10V applied bias is shown as curve C in Fig. 7.4 where the hopping length of the negative ions has been halved, but the hopping length of the positive ion and all other parameters are unchanged. Curves D and E are the currents contributed by the negative and positive species, respectively. The evolution of the distribution of positive and negative ions are shown in Figs. 7.5 and 7.6, respectively. The ion density is plotted as number of ions per unit area per well, so the initial densities of positive and negative ions appear to be different. The distribution of charge is complex and non-intuitive. Positive

Figure 7.5: Evolution of of the distribution of positive ions when negative ion mobility is 25% mobility of positive species.
ions are depleted from the right-hand electrode and from a region near the left-hand electrode. Negative ions undergo a similar non-monotonic evolution.

7.3.3. Reverse Polarity Transients

The reverse polarity transient phenomenon has been simulated and is shown in Fig. 7.7 for the case of a positive ionic species and a fixed negative background. For the initial transient, the ions are uniformly distributed. After 1000 sec of polarization, the polarity of the applied bias is suddenly reversed. The reverse transient has a characteristic peak.

The reverse polarity peak occurs only if the ion distribution has been polarized. A system with only an ionic charge carrier which is initially distributed uniformly does not
Figure 7.7: Initial and reverse polarity transients for case of single mobile ionic species and fixed negative background. Ions are initially uniformly distributed, and the bias polarity is switched after 1000 sec.

exhibit a transient peak when a constant bias is applied. This means that the experimental history-free transient in Al-PI-A1 structures cannot be due to ionic transport alone, since the sample is fully depolarized before the bias is applied. On the other hand, when Au-PI-Au structures are subjected to a change in voltage polarity after having been polarized, a transient peak is observed which is consistent with the simulated reverse polarity peak due to ionic transport. It is reasonable to conclude that the reverse polarity peak in Au-PI-Au structures is due to mobile ionic impurities.
7.4. Simulated Electronic Transients

Space-charge limited electron injection transients have been simulated with a fixed positive background charge. The background charge is uniform and its density is equal to the initial bulk electron density. The electron density is not uniform, however, in the contact regions. The contacts are modeled as ohmic contacts. This implies an accumulation of electrons near the contact and a net negative charge in the film.

To establish the zero-bias equilibrium distribution of electrons, the simulator was given a uniform initial distribution of electrons and allowed to run with the applied bias equal to zero until the net electron injection current at each electrode reached zero. The resulting electron distribution was saved and used as the initial distribution of simulations under bias.

The electron hopping length was set to 10 Å, and the barrier height was set to 0.5 eV. The evolution of space-charge in the film under bias is shown in Fig. 7.8. Initially, the film is neutral except for negative space-charge near the contacts. When 10V is applied, electron injection at the cathode creates additional negative space-charge which propagates across the film. Eventually, the space-charge is negative throughout the entire film. The computed steady-state electron distribution varies as $x^{-1/2}$ which is characteristic of the space-charge distribution in the SCL conduction model given in Eq. 6.112:

$$ n(x) = \frac{e}{e} \frac{dF}{dx} = \frac{1}{2} \left[ \frac{2I}{e\mu} \right]^{1/2} x^{-\nu_h} \quad (6.112) $$

The computed current for the SCL electron injection transient is shown in Fig. 7.9. For times less than 20 sec, the current decreases to a minimum. Then, the current increases to a maximum at approximately 1000 sec. Finally, the current decays to a steady value.
Figure 7.8: Evolution of space-charge due to SCL electron injection transient. Applied bias is 10V.
Figure 7.9: Calculated SCL electron injection transient current for 10V applied bias.

This simulated transient should be compared to the theoretical transient predicted by the theory of Many and Rakavy shown in Fig. 6.15 [30]. The simulated current has the characteristic peak predicted by Many and Rakavy, but the initially decreasing current is not in agreement with their theory. Rosental [81] has simulated SCL transient currents and found that, when carrier diffusion was included in the calculation, the initial current decreased. Rosental argues that the current is diffusion limited for short times as the contact charge spreads out into the bulk of the insulator. At longer times the current is drift limited and increase with time.

The model presented here is based on the hopping model, but it was shown in Section 6.6.2 that in the limit of a small hopping length, the hopping model is equivalent to the
standard drift and diffusion model. Therefore, the initial decrease in the current in Fig. 7.9 is attributed to the diffusion of electrons and is in agreement with the results of Rosental.

The SCL transient was simulated at voltages between 0.1 and 20V. The current transients are shown in Fig. 7.10. The peak moves to shorter times for higher applied voltages. For the lowest voltages, 0.1 and 1V, no peak is observed. The steady current varies as the square of the applied bias for the 10 and 20V currents as predicted by the SCL theory.

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Figure 7.10: Simulated SCL transient currents for voltages between 0.1 and 20V.
7.5. **Electronic and Ionic Transients**

Since PI contains mobile sodium ions, and Al appears to form an ohmic contact with PI, the most realistic model for Al-PI-Al structures would have both ion redistribution and SCL electron injection transients. This has been done by releasing the fixed positive background used in the SCL transient simulations. The concentration of ions and electrons are set equal in the bulk of the film. Again, the simulator is run without an applied bias to establish the initial, zero-bias distribution of electrons. During this procedure, the positive ions were held fixed, so that the ion distribution remained uniform throughout the film.

The hopping length of the ion was set to 100 Å and the ion barrier was chosen so that the ion mobility was 10% of the electron mobility. The evolution of the space-charge distribution due to electron injection and ion redistribution is shown in Fig. 7.11. This differs from Fig. 7.8 in that the negative space-charge at the cathode has been neutralized by the accumulation of positive ions, and the net space-charge in the bulk is slightly more negative. The steady-state distribution still has the $x^{-1/2}$ distribution.

Fig. 7.12 compares the simulated transient currents for three different ion mobilities: zero, 10%, and 90% of the electron mobility. As the ion mobility is increased the current increases before the maximum current. The ionic current tends to mask the minimum in the electron current before the peak. Finally, the peak due to the SCL electron injection is preserved when the positive ions are released.
Figure 7.11: Effect of mobile ions on evolution of SCL charge distribution.
Figure 7.12: Simulated transient currents for injected electrons with positive mobile ions. Three ionic mobilities are considered: zero, 10%, and 90% of the electron mobility.
CHAPTER 8

Discussion

8.1. Introduction

In this Chapter, implications of this work for electrical measurements of materials which contain mobile ionic impurities are discussed. Models for interactions between mobile ions and absorbed water and injected electrons are also considered.

The issue of discharging samples which have been polarized under a DC bias is discussed in Section 8.2. In Section 8.3, the application of Fourier analysis to transient current measurements to extract the frequency-dependent dielectric function is examined. It is shown that ionic or electronic space-charge can lead to significant errors in the apparent dielectric function. The interaction of absorbed water and mobile ions in PI is discussed in Section 8.3, and the interaction between electrons and mobile ions is discussed in Section 8.4.

8.2. Measurement Methodologies When Mobile Ions Are Present

In Sections 3.9.3 and 3.9.4 it was shown that in order to make reproducible, history-free electrical measurements the sample must be fully discharged before each measurement. When mobile ions or space-charge injection are present we cannot expect that equal charging and discharging times at a given temperature will restore the sample to its original state. In Al-PI-Al structures, we saw that the sample must be heated during discharge to remove all history effects from subsequent measurements.

An order of magnitude argument shows why equal charging/discharging times fails to return the sample to its original state. Consider an insulator of thickness $d$ subjected to an
applied bias $V_a$. Assume that there are mobile ions which can respond to the applied field but no other charge carriers. If the initial distribution of ions is uniform, and the ionic mobility is $\mu$, then the characteristic time, $\tau_p$, to polarize the ions in the insulator is approximately

$$\tau_p = \frac{d/2}{\bar{v}} = \frac{d^2}{2\mu V_a}$$

(8.1)

where $\bar{v} = \mu V_a/d$ is the average ion velocity, and $d/2$ is the distance an average ion travels in the insulator.

The depolarization process is dominated by ion diffusion, since the applied bias and the average electric field are zero. Since

$$x = (Dt)^{1/2}$$

(8.2)

and $D = \mu \frac{kT}{q}$, the characteristic time for depolarization, $\tau_D$, is approximately

$$\tau_D = \frac{(d/2)^2}{\mu \frac{kT}{q}}$$

(8.3)

The ratio of characteristic times, at a given temperature (constant $\mu$), is then

$$\frac{\tau_D}{\tau_p} = \frac{V_a}{kT/q} = \frac{V_a}{V_{th}}$$

(8.4)

where $V_{th} = kT/q$ is the thermal voltage. Thus, the characteristic time to depolarize the ionic distribution is on the order of 100-1000 times the characteristic polarizing time. This implies that one must either discharge for a time much longer than the sample was charged, or discharge at a higher temperature.
8.3. Fourier Analysis of Transient Currents

There exists a large literature for the method of extracting the frequency-dependence of the dielectric response from the Fourier transform of DC transients in polymeric materials [83-7]. This analysis is based on two critical assumptions: (1) in order for the principle of superposition to hold, the current response must be linear in the applied electric field, and (2) the electric field in the material must be time- and space-invariant during the transient.

Assumption (1) is questionable at all but the lowest applied fields, and the results of the numerical simulation presented in Chapter 7 shows that assumption (2) is violated when ions or injected electrons are present. Experimentally, we can fix only the integral of the electric field. Thus, the technique of extracting dielectric responses from the Fourier components of the transient response is fundamentally flawed in materials which contain either ionic or electronic space-charge.

The error in the extracted dielectric response due the non-uniform electric field can be calculated using the results of the simulated transients from Chapter 7. Consider a material which contains ions at the 1 ppm level, and the ions have a mobility μ. This model was discussed in Section 7.3.1. The total current response to an applied field may be written as the sum of the ion conduction current and the dielectric displacement current

\[ J(t) = J_c(x,t) + \varepsilon^* \frac{\partial}{\partial t} F(x,t) \]  
(8.5)

where \( \varepsilon^* \) contains the total time dependent (dynamic) dielectric response of the material which may be represented as an integral operator:

\[ \varepsilon^* = \varepsilon_0 \varepsilon_\infty + \varepsilon_0 (\varepsilon_s - \varepsilon_\infty) \int_{-\infty}^{t} ds \psi(t-s) \]  
(8.6)

where \( \varepsilon_s \) is the static dielectric constant, \( \varepsilon_\infty \) is the instantaneous dielectric response, and
\( \psi(t) \) contains the time dependence of the slow dielectric polarization such that \( \psi(0) = 0 \) and \( \psi(\infty) = 1 \). In the Debye model, \( \psi(t) = 1 - e^{-t/\tau} \), where \( \tau \) is a relaxation time.

Since the total current \( J(t) \) is a function of time only, it is equal to its spatial average:

\[
J(t) = \frac{1}{d} \int_0^d J_\varepsilon(x,t) dx + \frac{\varepsilon^*}{d} \frac{\partial}{\partial t} \int_0^d F(x,t) dx
\]

(8.7)

We may write \( J_\varepsilon(x,t) = q\mu p(x,t) F(x,t) - qD \frac{\partial p(x,t)}{\partial x} \), where \( p(x,t) \) is the ion distribution, and \( \int F(x,t) dx = V(t) \), so that Eq. 8.7 becomes

\[
J(t) = \frac{\varepsilon^*}{d} \frac{\partial V(t)}{\partial t} + \frac{q\mu}{d} \int_0^d p(x,t) F(x,t) dx - \frac{qD}{d} [p(d,t) - p(0,t)]
\]

(8.8)

Now, by assumption the applied bias is proportional to the step function, \( V(t) = V_a \theta(t) \), where \( \theta(t) \) is zero for \( t < 0 \), and is one for \( t \geq 0 \). We may write the electric field as the sum of its (constant) average and the non-uniform component:

\[
F(x,t) = \frac{V_a}{d} + \tilde{F}(x,t)
\]

(8.9)

Likewise, for the ion distribution we may write

\[
p(x,t) = p_0 + \tilde{p}(x,t)
\]

(8.10)

where \( p_0 \) is the average (and initial) ion concentration. Note that \( \int_0^d \tilde{p} dx = \int_0^d \tilde{F} dx = 0 \) since the number of ions and average electric field are fixed. Substituting these expressions into Eq. 8.8, we get
\[ J(t) = \frac{\varepsilon^*}{d} \frac{V_a}{d} \delta(t) + \frac{q\mu}{d} \int_0^d (p_0 + \tilde{p}(x,t))(\frac{V_a}{d} + \tilde{F}(x,t))dx \]

\[ - \frac{qD}{d} [\tilde{p}(d,t) - \tilde{p}(0,t)] \] (8.11)

where \( \delta(t) \) is the time derivative of the step function.

The terms of Eq. 8.11 may be separated as follows:

\[ J(t) = J_{ideal}(t) + J_{error}(t) \] (8.12)

where

\[ J_{ideal}(t) = \frac{\varepsilon^*}{d} \frac{V_a}{d} \delta(t) + q\mu p_0 \frac{V_a}{d} \] (8.13)

is the ideal step response current, and

\[ J_{error}(t) = \frac{q\mu}{d} \int_x^d \tilde{p}(x,t) \tilde{F}(x,t)dx - \frac{qD}{d} [\tilde{p}(d,t) - \tilde{p}(0,t)] \] (8.14)

is the error in the total current due to the non-uniform field. (Note that the terms \( \int \tilde{p} \frac{V_a}{d} dx \) and \( \int p_0 \tilde{F} dx \) both vanish.)

The ideal step response current may be evaluated with use of Eq. 8.6:

\[ J_{ideal}(t) = \varepsilon_0 \varepsilon_m \frac{V_a}{d} \delta(t) + \varepsilon_0 (\varepsilon_S - \varepsilon_m) \frac{V_a}{d} \psi(t) + q\mu p_0 \frac{V_a}{d} \] (8.15)

The first term of Eq. 8.15 is the surge current due to the instantaneous dielectric polarization, the second term is the current due to the slow dielectric polarization, and the third term is the steady ohmic current due to the mobile ions.

The true frequency-dependent dielectric function \( \varepsilon^*(\omega) \) is given by the Fourier transform of the ideal step response current, corrected for the steady ohmic current.
\[ \varepsilon^*(\omega) = \frac{d}{V_a} \int_0^\infty (J_{\text{ideal}}(t) - q\mu_0 \frac{V_a}{d}) e^{i\omega t} \, dt \]

\[ = \varepsilon_0 \varepsilon_\infty + \varepsilon_0 (\varepsilon_S - \varepsilon_\infty) \int_0^\infty \psi(t) e^{i\omega t} \, dt \]  

(8.16)

This is the desired insulator dielectric function.

When the Fourier transform of the total current, corrected for the steady current, 
\((J(t) - q\mu_0 \frac{V_a}{d})\), is computed, the error current, \(J_{\text{error}}(t)\), which is due to the non-uniformity of the electric field, gives rise to an error in the dielectric function:

\[ \Delta \varepsilon^*(\omega) = \frac{d}{V_a} \int_0^\infty J_{\text{error}}(t) e^{i\omega t} \, dt \]  

(8.17)

The error in the dielectric function due to the non-uniformity of the electric field has been computed using the simulated ion transient presented in Section 7.3.1. No dielectric relaxation was included in this model. A static dielectric constant of 3.1 was used in the transient simulation. The ionic polarization and subsequent electric field distortions are shown in Fig. 7.1. The transient current is shown in Fig. 7.2 (10V). The computed ion and electric field distributions were used in Eq. 8.14 to find the error current. Then the Fourier transform of this current was found using an algorithm due to Mopsik [88]. The resultant real and imaginary parts of the frequency-dependent dielectric function are shown in Fig. 8.1. Note that the error in the static \((\omega = 0)\) dielectric constant is approximately 0.4, or 12.9\% of the true static dielectric constant and that the form of the error in the dielectric function is indistinguishable from the dielectric response of a dipole relaxation, except that the characteristic frequency is \(10^{-3}\) Hz. (Note that the simulated current is nearly constant until 1000 sec.)
Figure 8.1: Calculated error in real and imaginary parts of apparent frequency-dependent dielectric function. A single mobile ion model without any dielectric relaxation was used.

The error current given in Eq. 8.14 has been derived for the simple case of an insulator with only mobile ions. This result can easily be generalized to include injected electrons. As before, we write the electron density as \( n(x,t) = n_0 + \bar{\eta}(x,t) \) where \( n_0 \) is the initial, uniform electron density and \( \bar{\eta}(x,t) \) is the non-uniform component. Note that, since electron injection is allowed, \( \int_0^d \bar{\eta}(x,t) dx \neq 0 \). The error current in the general case of mobile ions and injected electrons is then
\[ J_{\text{error}}(t) = \frac{q\mu_+}{d} \int_0^d \bar{\rho}(x,t) \bar{F}(x,t) \, dx + \frac{q\mu_-}{d} \int_0^d \bar{\sigma}(x,t) \bar{F}(x,t) \, dx \]

\[ + \frac{q\mu_- V_a}{d^2} \int_0^d \bar{\eta}(x,t) \, dx \]

\[ - \frac{qD_+}{d} [\bar{\rho}(d,t) - \bar{\rho}(0,t)] + \frac{qD_-}{d} [\bar{\eta}(d,t) - \bar{\eta}(0,t)] \quad (8.18) \]

where the subscripts + and − on the mobilities and diffusion coefficients refer to ions and electrons, respectively. The second and fifth terms in Eq. 8.18 are the electronic analogs to the ionic error current given in Eq. 8.14, due to field and electron distribution non-uniformities, respectively. The third term in Eq. 8.18 is new and arises from the space-charge due to the net charge from injected electrons.

Eq. 8.18 shows that the frequency-dependent dielectric function extracted with Fourier analysis of the step response transient current will be in error if mobile ions which are blocked at the electrodes or space-charge due to injected electrons exist in the insulator. These conditions are easily satisfied in polymers, thus the Fourier analysis of transient currents is ill suited for the measurement of polymers.

8.4. Moisture/Ion Interaction

It was reported in Section 5.4 that at low temperatures \((T \leq 40^\circ\text{C})\) the current at a given time and voltage is proportional to the product of the sodium ion concentration and the amount of water absorbed in the PI film. This is interpreted as evidence that the transport current at low temperatures in dry PI films is due to sodium ion transport.

Sodium is known to be present and mobile in dry films, but the role of protons or hydroxyl ions is unknown. Since absorbed water can dissociate into proton and hydroxyl ions, the current in moist films could possibly be due to the transport of these species. However, in that case we would expect the current to be proportional to the sum of sodium
and water concentrations. Since this is not observed, it is reasonable to infer that protons and/or hydroxyl ions do not contribute significantly to the current in moist or dry films.

If the sodium ions were solvated by the absorbed water, their mobility in the polymer matrix would be increased because the effective charge of the solvated sodium ion is decreased. The current is linear in number density of sodium ions and their mobility. If the change in sodium ion mobility were proportional to the amount of absorbed water, then the current would be proportional to the product of the amount of sodium and the amount of absorbed water.

Another possible model is that the change in the PI dielectric constant due to absorbed water increases the amount of ionized or free sodium through increases in dielectric screening. Then the current would again be proportional to the product of sodium and water concentrations since the change in dielectric constant is proportional to the amount of absorbed water. See Section 3.3.1.

8.5. Electron/Ion Interaction

At high temperatures it is observed in Al-FI-Al structures that the transient current is roughly proportional to the sodium ion concentration, but that the total amount of charge transported is too great to be accounted for by ion transport. This is interpreted as evidence for a electron/sodium interaction in PI.

The model presented in Section 7.5 considers only the space-charge interaction between electron and sodium transport through the bulk electric field. Also, the model requires the initial bulk electron and ion concentrations be equal for neutrality. Since the transient current has been shown to be due to injected electrons, this model fails to account for the increase in current with increased doping.
One model which might explain this phenomenon is that the sodium can lower the energy of the acceptor states by decreasing the polarization energy. This would increase the current because injected electrons would have increased mobility. Alternately, the sodium may introduce new extrinsic acceptor states in the PI. In other words, the sodium counterion may be an electron. Then, the number of electron states would be proportional to the number of sodium ions, and the current would be proportional to the sodium concentration.

Both of these pictures are similar to substitutional doping in semiconductors but with an important difference. The sodium ions have a high mobility in the PI and migrate to the electrode under an applied field. This means that their influence on bulk PI electronic conductivity is transient. After a bias has been applied for a sufficiently long time, the ions are no longer present in the bulk of the film, and the intrinsic electronic structure is restored.
References

1 Simmons, JG; DC Conduction in Thin Films, Mills and Boon, London 1971.


13 Sharma, BL, and Pillai, PKC; Electrical Conduction in Kapton Polyimide Films at High Electric Fields, Polymer, 23, 17 (1982).


31 Hershkowitz, GB; Effects of Moisture and Sodium Ions on Polyimide Thin-Film Conduction, Bachelor’s Thesis, Dept. of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA (1987).


34 Neuhaus, HJ, and Senturia, SD; Conduction Transients in Polyimide, ACS Symposium Series Book: Polymeric Materials for Electronic Packaging and Interconnection, manuscript in review.


38 Bogert, MT, and Renshaw, RR; 4-Amino-o-Phthalic Acid and Some of its Derivatives, Journal of the American Chemical Society, 30, 1135 (1908).


45 Mario, JP; Bachelor Degree student, Dept. of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA (1980).


48 Van Turnhout, J; Thermally Stimulated Discharge of Polymer Electrets, Elsevier, Amsterdam 1975.


56 DuPont product literature


59 Feit, Z; private communication


68 Lewis, TJ; private communication.


71 Lakatos, AI, and Abkowitz, M; *Electrical Properties of Amorphous Se, As2Se3, and As2S3*, Physical Review (B), 3, 185 (1971).


73 Argall, P, and Jonscher, AK; *Dielectric Properties of Thin Films of Aluminium Oxide and Silicon Dioxide*, Thin Solid Films, 2, 185 (1968).


77 Cole, KS, and Cole, RJ; *Dispersion and Absorption in Dielectrics II: Direct Current Characteristics*, Journal of Chemical Physics, **10**, 98 (1942).


80 Mott, NF, and Gurney, RW; *Electronic Processes in Ionic Crystals*, Oxford, New York 1940.


88 Mopsik, FI; *The Transformation of Time-domain Relaxation Data into the Frequency-domain*, IEEE Transactions on Electrical Insulation, **EI-20**, 957 (1985).
Appendix A

Transient Simulator Program Listing

# macro definitions
define MAXN 1000
define MAXN1 1001
define UNIT3 3
define UNIT4 4
define UNIT5 5

define VNAME "gsfermi"
define LASTMOD "7/16/1988"

program gsz

# 2/8/88 convert to rational format
# 3/1/88 extended to allow unequal hopping lengths
# 3/12/88 rework boundary conditions to model ohmic contacts
# 5/24/88 modify output file format/ version control
# 7/16/88 modify hopping routine: fermi factor/ contact:bultz factor
# variable definitions
#
#
# global variables
#
# e(x) = electric field [V/cm]
# w(x) = transition probability [normalized by D/a**2]
# rm(x) = rho (in mobile frame) [normalized by qCo/d]
#
# global constants
#
# va = applied bias [V]
# d = thickness [cm]
# c0 = concentration of ions [ions/cm2]
# temp = temperature [C]
# phis = metal insulator interface barrier. [eV]
# eps = dielectric constant [F/cm]
# step = electron hop length over 2
# nt = trap concentration
# w = hopping barrier height
# freq = attempt to escape frequency
# n0 = equilibrium surface concentration
# dcoef = electron diffusion coefficient

common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm, wb, wf

double precision e(0:MAXN), rm(MAXN), wb(MAXN1), wf(0:MAXN)
real va,d,c0,temp,phis,eps,step  
real nt,w,freq,n0,dc0ef

# local variables
#
# ci(x) = ion concentration [normalized by q*c0/d]  
# ce(x) = electron concentration [normalized by q*c0/d]  
# d[ie](x) = change in concentration in dt
#
# phib = bulk potential
# nb = bulk electron concentration
# a[ie] = hopping length
# sdi = scale factor for ion diff normalization
# dt = time step
# dti = time step ion frame
#
# deltait = interval between i-t reports
# timelp = time last post i-t
# tdec = time to post space charge ( steps in decades )
#
double precision ci(MAXN), ce(MAXN), di(0:MAXN1), de(0:MAXN1)
real phib, nb, ai, ae, dt, dti, sdi
real deltait, timelp, tdec
real runtime, time
integer i,ne,ni

# THEORETICAL
#
# transt = electron transit time
# Jinit = instantaneous current
# Jinfin = steady SCLC
# Jth = total current
# J2 = Many&Ravay current (drift only, no traps)
# J1 = ohmic current
real transt,Jinit,Jinfin,Jth,J2,J1,qinj

#
# f2 = input file for ci and ce
#         -OR-  if = "calc_eqm" then call eqdist routine for
#               initial distribution at va= 0
# f3 = output file for current-time
# f4 = output file for space charge distributions
# f5 = output file for final distribution
#
character*8 f2,f3,f4,f5

# vname = version name
# vdate = version date
# rtime = run time
# rdate = run date
# host = host processor
character*8 vname,vdate,host
integer rdate(3),rtime(3)

# cur0 = normal current at x = 0
# curn = normal current at x = d
# pcure = electronic polarization current
# pcuri = polarization due to ions
# curt = total external current [normalized by qDc0/a**2 (electron)]
#
double precision cur0, curn, pcure0, pcured, q
double precision pcuri0, pcurid, curt0, curtd, qtot, qcap, cap

#
# read in parameters from gs.pfile
#
open(unit = 1,file = "gs.pfile",status = "old")
read(1,*va,c0,d,temp,w,sdi
read(1,*nt,phib,phis,freq
read(1,*ni,ne,runtime,dt,loop
read(1,*f2,f3,f4,f5
#
# setup output files
#
open(unit = 3,file = f3,status = "new")
open(unit = 4,file = f4,status = "new")
open(unit = 5,file = f5,status = "new")
#
# initial values
#
ae = d/float(ne)
ai = ae*float(ne-1)/float(ni-1)
sdi= sdi*(ae/ai)**2
step= ae/2.
time = 0.0
dt = dt*sdi
deltait = .1
timelp = dt/9.
tdec = dt
tempc= temp
temp = ( 273. + temp ) * 8.617e-5
epsr = 3.1
eps = epsr * 8.85e-14
q = 1.6e-19
qinj= 0.0
#
dcoef = freq * ae**2 * exp( -1. * w / temp )
n0 = nt / ( 1. + exp( -1.0 * phis / temp ))
nb = nt / ( 1. + exp( -1.0 * phib / temp ))
ct = d*nt/c0
cap = eps / d
\[ J_{\text{init}} = 0.5 \cdot \varepsilon \cdot \text{Va}^{*2} / (\text{temp} \cdot d \cdot \text{ne}^{*2} \cdot q \cdot c0) \]
\[ J_{\text{fin}} = 9.0 / 4.0 \cdot J_{\text{init}} \]
if (va == 0.0)
  |
  \{ qcap = cap 
  transt = 1.0
  \}
else
  |
  \{ qcap = va \cdot cap 
  transt = abs(temp \cdot ne^{*2} / \text{Va})
  \}

#
\text{i= hostnm(host)}
call idate(rdate)
call itime(rtime)
vname = VNAME
vdate = LASTMOD

write(UNIT3, 10) vname, vdate, rdate(2), rdate(1), rdate(3), rtime(1), rtime(2), host
call(rdate(1), rdate(2), rdate(3), rtime(1), rtime(2), host)
write(UNIT3, 15) va, tempc, d, epsr, cap, c0, ae, ai, w, freq, dcoef, sdi*dcoef, nt,
phis, n0, phib, nb
write(UNIT3, 16) n, ni, dt, runtime, loop, f2, f3, f4, f5

write(UNIT4, 10) vname, vdate, rdate(2), rdate(1), rdate(3), rtime(1), rtime(2), host
call(rdate(1), rdate(2), rdate(3), rtime(1), rtime(2), host)
write(UNIT4, 15) va, tempc, d, epsr, cap, c0, ae, ai, w, freq, dcoef, sdi*dcoef, nt,
phis, n0, phib, nb
write(UNIT4, 16) n, ni, dt, runtime, loop, f2, f3, f4, f5

# get initial distribution
if (f2 == "calc_eqm")
  |
  \{ call eqdist(ni, ai, ci, ne, ae, ce, sdi, dt, loop, nb) \}
else
  |
  \{ open(unit = 2, file = f2, status = "old")
  \{read(2,*) (ci(i), i = 1, ni)
  \}{read(2,*) (ce(i), i = 1, ne)}
  
  \}call rho(ne, xe, ce, -1., ni, xi, ci)
qtot = 0.0
doi = 1, ne
  qtot = qtot + rm(i)
qinit = qtot*c0*qaed/qcap
q0 = q * c0 / qcap
t0 = ae**2 / dcoef
J1 = (nb*d/c0*qtot*qaed)*va/temp/ne**2
write(UNIT3,40) qinit qcap,J1,c0*ce(ne/2)/d,
nb-qtot*c0/ne**2,q*c0/t0,t0,transl
write(UNIT3,20)
write(UNIT4,30)
call pout(ni,ai,ci,ne,ae,ce,0.0,de)

# all ready - start simulation
# stop when runtime expires
#
while ( time < runtime )
{
    call rk(ne,ae,ce,-1.,ni,ai,ci,dt,de)
do i = 1,ne
{
    ce(i) = ce(i)+ dc(i)*dt
    if (ce(i)> ct)
        {write(UNIT3,*)"***",time,i,ce(i),dc(i)}
    }
cur0 = dc(0)
curn = de(ne+ 1)
qinj = qinj + (cur0-curn)*dt
call rk(ni,ai,ci,1.,ne,ae,ce,dti,di)
do i = 1,ni
ci(i) = ci(i)+ di(i)*dti
time = time+ dt

# print current each deltait
if (log10(time/timelp)> = deltait)
{
call polcur(pcur0,pcurd,-1.,ne,ae,de)
call polcur(pcur0,pcurd,+ 1.,ni,ai,di)
call rho(ne,xe,ce,-1.,ni,xi,ci)
qtot = 0.0
do i= 1,ne
    qtot= qtot+ rm(i)
qtot= qtot*q0*ae/d-qinit
pcur0= pcur0*sd1
pcurd= pcurd*sd1
curt0 = pcure0+ pcur0+ cur0
curtl = pcure0+ pcur0+ cur0

J2 = Jinit / ( 1.0 - 0.5 * time / transl )**2
Jth = J2 + J1
if ( time > 0.8 * transl )
    jth = Jfin + j1
write(UNIT3,70)time,cur0,jth,j2,cur0,curn,pcur0,qinj*q0
timelp = time
}

# print space charge once each decade
if ( time >= tdec )
    {
        call pout(ni,ai,ci,ne,ae,ce,time,de)
        tdec= tdec*10.
    }
}

# exit
#
# dump final distributions
write(UNIT5,*)(ci(i),i = 1,ni)
write(UNIT5,*)(ce(i),i = 1,ne)
write(UNIT5,10)vname,vdate,rdate(2),rdate(1),rdate(3),rtime(1),rtime(2),host
write(UNIT5,15)va,tempc,d,epsr,ac2,0,ae,ai,w,freq,dcoef,nd*ndcoef,nt,
    phis,n0,phi,nb
write(UNIT5,16)ne,ni,dt,runtime,loop,f2,f3,f4,f5

stop

#
# format block
#
10 format(".remark + + + DIELECTRIC SIMULATOR: Transient Response + + + HJN"/,
    ".remark VERSION: \".a8\", Last Compiled on: \".a8 /,
    ".remark Run Date: \".i2/\",i2/\",i4/\", Run Time: \".i2/\",i2,
    " Machine: \".a8 //")
15 format(".remark EXPERIMENTAL CONDITIONS"/,
    ".remark Applied Bias= \".f7.2\", Temp= \".f4 //,
    ".remark MATERIAL PARAMETERS"/,
    ".remark Thick= \".e9.3\", Diele Const= \".e9.3, " Diele Cap= \".e9.3 /,
    ".remark Ion Conc= \".e9.3, " Hop Length: elec= \".e9.3, " ion= \".e9.3 /,
    ".remark Barrier= \".f4.2, " Freq= \".e8.2, " D(elec)= \".e8.2,
    " D(ion)= \".e8.2 /,
    ".remark Nt= \".e9.3, " phi-s= \".f4.2, " n0= \".e9.3 /,
    ".remark phi-b= \".f4.2, " nb= \".e9.3 // )
16 format(".remark SIMULATOR CONTROLS"/,
    ".remark Number Wells: elec= \".i3, " ion= \".i3, /,
    ".remark dt= \".e9.3, " Run Time= \".e9.3, " # calc_eqm loops= \".i5 /,
    ".remark Files used:\".x,a8,x,a8,x,a8,x,a8 )
20 format(\\".remark TIME Jsim J12 J2 Jinn Jpol Qinj/Qcap" / )
30 format(\\".remark x rho(x) ions electrons e(x) v(x) / ,"par time \")
40 format(\\".remark total charge at t= 0 = \".e9.3, * Qcap= \".e9.3 /,
    ".remark j1= \".e9.3, " nmin= \".e9.3, " nohm= \".e9.3 /,
    ".remark j0= \".e9.3, " t0= \".e9.3, " trans= \".e9.3 //")

end
#
# main
# ---------------------------------------------
# ndot
# main
# ndot
# subroutine ndot(nm,am,cm,sm,nf,af,cf,x)
# # this routine evaluates dn/dt for runga-kutta method
# # works in mobile frame
# # input:
# # cm, nm, am, sm = mobile
# # cf, nf, af = fixed
# # output:
# # x(i) = dn/dt, i= 1,nm
# # x(0) = normal current at 0
# # x(nm+ 1) = norm curr d
# # global variables
# common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm, wb, wf

double precision e(0:MAXN), rm(MAXN), wf(0:MAXN), wb(MAXN1)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
# double precision x(0:nm+ 1),cm(nm),cf(nf)
real am,af,sm
integer i,nm,nf
#
# call rho(nm,am,cm,sm,nf,af,cf)
call eofx(nm,am)
call omegas(nm,am,sm)
#
# interior points
#
do i = 2,nm-1
x(i) =  wf(i-1)*cm(i-1)*(1.0-cm(i)/nt) - wb(i)*cm(i)*(i.0-cm(i-1)/nt) -
       ( wf(i)*cm(i)*(1.0-cm(i+ 1)/nt) - wb(i+ 1)*cm(i+ 1)*(1.0-cm(i)/nt) )
#
# end points {1 and nm} and {0 and nm+ 1}= normal current
#
x(0)= 0.0
x(nm+ 1)= 0.0

if ( sm == -1. )  # if electrons
    call normcur(x(0),x(nm+ 1),nm,am,cm)
\[ x(1) = -1.0 \times x(0) \times d/am - \]
\[ \left( w(1) \times cm(1) \times (1.0-cm(1+1)/nt) - wb(1+1) \times cm(1+1) \times (1.0-cm(1)/nt) \right) \]

\[ x(nm) = w(nm-1) \times cm(nm-1) \times (1.0-cm(nm)/nt) - wb(nm) \times cm(nm) \times (1.0-cm(nm-1)/nt) + \]
\[ x(nm+1) \times d/am \]

return
end
#
# ndot
# ---------------------------------------------
# normcur
#
# subroutine normcur(cur0,curn,nm,am,cm)
#
# this routine calculates the normal
current at the two electrodes
# works in electron frame (must be called with cm=ce)
#
# input:
# nm = number mobile wells
# xm = mobile hopping length
# cm = mobile distribution
#
# output:
# cur0 = current at x= 0
# curn = current at x= d
#
# global variables
#
common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm, wb, wf

double precision e(0:MAXN), rm(MAXN), w(0:MAXN), wb(MAXN1)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
double precision cm(nm)
double precision cur0, curn
real am,x
integer nm
#
x = exp(-1.0 \times q \times va/temp)

# formula of normal current
cur0 = exp((w-phis)/temp)/(nt-n0) \times am/d *
      ( cm(1)n0 * (x-1.0) - nt * (x*n0*d/c0-cm(1)) )
curn = exp((w-phis)/temp)/(nt-n0) \times am/d *
( cm(nm)*n0 *(x-1.) - nt *(x*cm(nm)-d*n0/c0) )

return
end
#
# normcur       normcur
# ---------------------------------------------------------------
# eqdist        eqdist
#
subroutine eqdist (ni,ai,ci,ne,ae,ce,sdi,dt,lstop,nb)
#
  this routine calculates the equilibrium distribution
  of electrons under zero bias for a given temperature
  and interface barrier. (i.e. the insulator band
  bending.)
#
  # Assumptions 1) ions are uniform. they don't move, (this might
  # be very wrong! really expect ions to relax to maintain
  # neutrality.
#
  # input:
  #       ni = number ion wells
  #       ai = ion hopping length
  #       ci = ion distribution
  #       ne = number electron wells
  #       ae = electron hopping length
  #       ce = electron distribution
  #       dt
  #       nb = nulk electron concentration
  # output:
  #       ce and ci
#
# global variables
#
common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm, wb, wf

double precision e(0:MAXN), rm(MAXN), wf(0:MAXN), wb(MAXN1)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
double precision ci(MAXN),ce(MAXN),de(0:MAXN1),di(0:MAXN1)
double precision cur0,curn
real vkeep,dt,dti,sdi,ae,ai,nb
real time,ld,cs,beta
integer ni,ne,i

# set initial values
nb = nb*d/c0
do i = 1, ni
    ci(i) = nb

ld = sqrt(eps*temp/1.6e-19/nt)
cs = n0*d/c0
beta = ae / ld
do i = 1, ne/2
    { x= float(i-.5)*beta
ce(i) = nb + cs*exp(-x)
    ce(ne+ 1-i)= ce(i)
    }
return

# save va in temp variable and set to zero
vkeep = va
va = 0.
dti = dt*sdi

# iterate until equilibrium
loop= 0
while ( loop < lstop )
    { call rk(ne,ae,ce,-1.,ni,ai,ci,dt,de)
do i = 1,ne
    ce(i) = ce(i)+ de(i)*dt
    { call rk(ni,ai,ci,+ 1.,ne,ae,ce,dti,di)
do i = 1,ni
    ci(i) = ci(i)+ di(i)*dti
    loop= loop+ 1
    }
}
# print equilib distrib
call pout(ni,ai,ci,ne,ae,ce,0.0,de)

# restore va and return
va = vkeep
return
end

# eqdist
# -----------------------------------------------
eqdist
# -----

# rho
#
# subroutine rho(nm,am,cm,sm,nf,af,cf)
#
# this routine interpolates rho(x) from cm and cf
# am can be different from af
# rm(k) is set for k= 1 to nm
# works in mobile frame
#
# input:
#     nm = number mobile wells
#     am = mobile hopping length
#     sm = sigm mobile charge
#     cm = mobile distribution
#     nf = number fixed wells
#     af = fixed hopping length
#     cf = fixed distribution
#
# output:
#     rm [global]
#
# global variables
#
common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm

double precision e(0:MAXN), rm(MAXN)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
#     scalea = ratio af/am
#     a1-a4 = interpolation coefficients
#     x = interpolation distance (x/am)
#     ix = next lower fixed well
#     yx = interpolated cf value
#
double precision cm(nm),cf(nf),yx
double precision x,a1,a2,a3,a4, scalea
real am,af,sm
integer nm,nf,k,ix,i

scalea= float(nf-1)/float(nm-1)

rm(1)= sm*(cm(1)-cf(1))
rm(nm)= sm*(cm(nm)-cf(nf))

# interpolate
do k= 2, nm-1
{
    ix= 1 + int ( float(k-1)*scalea )
    x= float(k-1)*scalea-float(ix-1)
    if ( ix == 1 )
    {
        # first cell  forward form
        i= 1
else if ( ix = = nf-1 )
  
  # # last cell   backward form
  i= ix-2
  x= x+ 2.
  
  }
eelse
  
  # # central cell
  i= ix-1
  x= x+ 1.
  
  a1= -1.*x-1.)*x-2.)*x-3.)/6.
  a2= x)*x-2.)*x-3.)/2.
  a3= -1.*x)*x-1.)*x-3.)/2.
  a4= x)*x-1.)*x-2.)/6.
  yx= a1*cf(i)+ a2*cf(i+ 1)+ a3*cf(i+ 2)+ a4*cf(i+ 3))
  rm(k)= sm*(cm(k)-yx)
  
  # do i= 1 , nm
  # if (abs(rm(i)) < 1.e-8 ) rm(i)= 0.0
  return
end

# # rho
# --------------
# # eofx
# # eofx
# subroutine eofx(nm,am)
# 
# # this routine calculates E(x) from rm(x)
# # works in mobile frame
# #
# # input:
# #  rm [global]
# #  nm = number wells
# #  am = hopping length
# #
# # output:
# #  e(x) [global]
# #
# # global variables
# #
# common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm

double precision e(0:MAXN), rm(MAXN)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef
# local variables
#
# suma, sumb = temporary sums
# c3 = qc0/eps
#
double precision suma,sumb,c3
real am
integer nm,i
#
# evaluate e(0)
#
{suma = 0.0;sumb = 0.0}

do i = 1,nm
{
    suma = suma+ rm(i)
    sumb = sumb+ rm(i)*float(i-1)
}
#
# e(0) = v/d + c3 * sum ( x/d rho dx ) - c3 * sum ( rho dx )

c3 = 1.6e-19*c0*am/eps/d  
e(0) = va/d+ c3*(am/d*sumb-suma*(1.-step/d))
#
# now e(x) = e(0) + epsilon * sum ( rho dx )
#
do i = 1,nm
    e(i) = e(i-1)+ c3*rm(i)
return
end
#
# eofx
# EOFX
# ---------------------------------------------------------
# omegas
# OMegas
#
# subroutine omegas(nm,am,sm)
#
# this routine evaluates wf and wb for a given electric field
#
# input:
#    rm(x) = rho [global]
#    nm, am, sm = mobile
#
# output:
#    wf(j) forward transition prob [global]
#    wb(j) backward transition prob [global]
#
# global variables
# common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
common e, rm, wb, wf

double precision e(0:MAXN), rm(MAXN), wf(0:MAXN), wb(MAXN1)
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
# double precision p
real am, sm
integer j, nm

p = sm*0.5*am/temp
#
# regular points - interior
#
# do j = 1, nm - 1
#  
#   (   
#      wf(j) = exp(p*e(j))
#      if (wf(j) = 0.)
#         {wb(j+ 1) = exp(-p*e(j))}
#       else
#         {wb(j+ 1) = 1.0/wf(j)}
#   )
# return
# end
#
# omegas
# -------------------------------
# polcur
# polcur
#
subroutine polcur(f0,fd,sm,nm,am,dc)
#
# this routine calculates the polarization current due to dc
# works in mobile frame
#
# input:
# # dc = change in mobile distribution
# # nm = number wells
# # am = hopping length
#
# output:
# # f = polarization current
#
# global variables
#
common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
#    f1, f2 = temp sums
#
do double precision dc(0:nm+1),f1,f2,f0,fd
real am,sm
integer i,nm
#
#    f1 = 0.0
#    f2 = 0.0
#
do i = 1,nm
#
#    f1 = f1+ float(i-1)*dc(i)
#    f2 = f2+ dc(i)
#
end do
f0 = (f1*am/d-f2*(1.-step/d))*sm*am/d
fd = f0 + f2*sm*am/d

return
end

# polcur                      polcur
# +-----------------------------------------------------------
# rk                      rk
#
# subroutine rk(nm,am,cm,sm,nf,af,cf,dt,dc)
#
# this routine executes the runga kutta method
#
# input: cm(j) = mobile charge at time t
#        nm, am, sm = mobile number, hop length, sign
#        cf(j) = fixed charge
#        nf, af = fixed number, hop length
#        dt = time step (mobile)
# output: dc(j) = d/dt(cm)
#        dc(0) = normal current at 0
#        dc(nm+1) = norm current at d
#
# routine utilizes subroutine ndot with various
# arguments to estimate slope of cm at different points
# in the interval dt
# works in mobile frame
#
# global variables
#
common va,d,c0,temp,phis,eps,step
common nt,w,freq,n0,dcoef
real va,d,c0,temp,phis,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
# dum(j) input to ndot : dummy variable
# a(j) output returned from ndot : rk term
# dt1 = temp constant = dt/6
#
double precision dc(0:nm+1),cm(nm),a(0:MAXN1),cf(nf),dum(MAXN)
real dt1,af,am,sm,dt
integer nm,nf,i

dt1 = dt/6.0
#
# 1st rk term
#
call ndot(nm,am,cm,sm,nf,af,cf,a)
do i = 0,nm+1
   dc(i) = a(i)/6.0
#
# 2nd rk term
#
do i = 1,nm
   dum(i) = cm(i)+ a(i)*dt/2.0
call ndot(nm,am,dum,sm,nf,af,cf,a)
do i = 0,nm+1
   dc(i) = dc(i)+ a(i)/3.0
#
# 3rd rk term
#
do i = 1,nm
   dum(i) = cm(i)+ a(i)*dt/2.0
call ndot(nm,am,dum,sm,nf,af,cf,a)
do i = 0,nm+1
   dc(i) = dc(i)+ a(i)/3.0
#
# final rk term
#
do i = 1,nm
   dum(i) = cm(i)+ a(i)*dt
call ndot(nm,am,dum,sm,nf,af,cf,a)
do i = 0,nm+1
   dc(i) = dc(i)+ a(i)/6.0
return
end
#
# rk
# "----------------------------------------------------------------------"
## pout

```fortran
subroutine pout(ni,xi,ci,ne,x,e,ce,time,de)
#
# this routine prints out the charge distribution,
# along with electric field and potential
# works in electron frame
#
# input:
#   ni = number ion wells
#   xi = ion hopping length
#   ci = ion distribution
#   ne = number electron wells
#   xe = electron hopping length
#   ce = electron distribution
#   time
#
# output:
#   to unit 4 (filename f4)
#   x, rho(x), ci(x), ce(x), E(x), v(x), band bending
#   sum ( ce(x) )
#
# global variables
#
common va,d,c0,temp,ph,eps,step
common nt,w,freq,n0,dcoef
common e, rm

double precision e(0:MAXN), rm(MAXN)
real va,d,c0,temp,ph,eps,step
real nt,w,freq,n0,dcoef

# local variables
#
#   v = workspace for v(x)
#   sumqe = workspace for sum of ce(x)
#
double precision ci(ni), ce(ne),de(0:MAXN)
real xi, xe, time, v, psi, cbar
integer ne, ni, i

# call rho(ne,x,e,ce,-1.,ni,xi,ci)
call cox(n,xe)

write(UNIT4,40)time
write(UNIT4,50)e(0),va
cbar = d*nt/c0
v = va
do i = 1,ne
  
v = v-xe*(e(i)+ e(i-1))/2.
```
if (ce(i) > 0 )
{
    psi= log(cbar/ce(i)-1.0)
}
else
{
    psi= 8888
}
# write(UNIT4,60)xe*(float(i)-.5),rm(i),rm(i)+ ce(i),ce(i),
write(UNIT4,60)xe*(float(i)-.5),rm(i),de(i),ce(i),
e(i),v,psi
}
return

40 format(" */",set time= ",e8.2 /".remark x,r,i,e,E,v,psi")
50 format(" .remark e0= ",e10.3," V= ",e10.3)
60 format(e9.3,x,e10.3,x,e9.3,x,e9.3,x,e10.3,x,e10.3,x,e9.3)
end
#
# pout
# -----------------------------------------------
define ASIZE 100
# time to frequency conversion
#
# 6/11/88 H Neuhaus
#
# plan: a) read in current-time data
# b) make up w array - min,max from time range
# c) cubic poly interp for time data
# d) do loop = for each freq
#   d1) e1 <= cos integ
#   d2) sin = > e2
# e) report e(w)
#
# NOTES
#
# reads data file name from command line
# data runs from tmin to tmax
# integration from 0 to tmax done using cubic spline to the data
# data points added: i= 0, -1.0*tmin
# using cubic polynomial extrapolation
#
# Integration from tmax to infinity is done by extrapolation
# Bexp(-at) is used. B and a are fit to data at tmax
#
# VARIABLES
#
# y(i) current data i= 1,n input data,
# i= -1,0 extra points
# t(i) time data
# y1,y2,y3 polynomial slopes
# e1,2(j) dielectric consts
# w(j) frequencies
#
# n number input data points
# err integration error limit
# tmin,tmax,wmin,wmax
#
# integer n,i,j
REAL y(-1:100),t(-1:100),y1(-1:100),y2(-1:100),y3(-1:100)
real e1h(100),e2h(100),w(100),e3(100),e4(100)
real e1l(100),e2l(100),ys(100),yc(100),targ(100)
real err,tmin,tmax,wmin,wmax,lambda
real upper,lower,a,b,w1,w2
character*10 f1
# read in data
call getarg(1,f1)
open (unit=2,file=f1)
read(2,*)err
read(2,*)n
do i = 1,n
   
      read(2,*)y(i),t(i)

end

# extrapolate to t = 0
t(0) = 0.
y(0) = cubdet(y(1),t(1),y(2),t(2),y(3),t(3))

# extrapolate to t = -tmin
t(-1) = -1.*t(1)
y(-1) = cubext(t(-1),y(0),t(0),y(1),t(1),y(3),t(3),y(5),t(5))

# evaluate a and b for extension to inf
# bexp(-at), need continuous slope and value
a = -1.*((log(y(n))/y(n-1))/(t(n)-t(n-1))
b = y(n)*exp(a*t(n))

# extrapolate extra point n+1 for spline routine
t(n+1) = 1.26*t(n)
y(n+1) = b*exp(-1.*a*t(n+1))

# set up freq array
tmin = t(1)
tmax = t(n)

wmin = 1./tmax
wmax = 1./tmin
lambda = alog10(wmax/wmin)/(n-1)

do i = 1,n
   w(i) = wmin * 10**((i-1)*lambda)

# cubic polynomial interpolation
call cubint(n+3,y,t,y1,y2,y3,er)

# write("i,t,y,y1,y2,y3 returned to main")
# do i = -1,n+1
#    write("i,t,y,y1,y2,y3")i,t,y,y1,y2,y3

# for each w ...
do i = 1, n
  
  w1 = w(i)
  w2 = w(i)**2
  e3(i) = e1cor(B,a,tmx, w(i))
  e4(i) = e2cor(B,a,tmx, w(i))
  e1h(i) = 0.0
  e2h(i) = 0.0
  do j= 0,n-1  # ... cos wt ...
    
    upper = \cos(w1*t(j+ 1))/w2*(y1(j+ 1)+ y3(j+ 1)/w2) +
    \sin(w1*t(j+ 1))/w1*(y(j+ 1)-y2(j+ 1)/w2)
    lower = \cos(w1*t(j))/w2*(y1(j)+ y3(j)/w2) +
    \sin(w1*t(j))/w1*(y(j)-y2(j)/w2)
    e1h(i) = e1h(i) + upper - lower
  
  do j= 0,n-1  # ... sin wt ...
    
    upper = \sin(w1*t(j+ 1))/w2*(y1(j+ 1)+ y3(j+ 1)/w2) -
    \cos(w1*t(j+ 1))/w1*(y(j+ 1)-y2(j+ 1)/w2)
    lower = \sin(w1*t(j))/w2*(y1(j)+ y3(j)/w2) -
    \cos(w1*t(j))/w1*(y(j)-y2(j)/w2)
    e2h(i) = e2h(i) + upper - lower
  
  
  
  
  # for each w ...
  do i = 1, n
    
    do j= 0, n
      
      yc(j+ 1)= y(j)*\cos(w(i)*t(j))
      ys(j+ 1)= y(j)*\sin(w(i)*t(j))
      tar(j+ 1) = t(j)
    
    e1l(i) = cintg(n+ 1,yc,targ,err)
    e2l(i) = cintg(n+ 1,ys,targ,err)
  
  
  
  
  
  # all done except final report
  # write("*"*," results"
  do i = 1, n
    write(*,*),w(i),e1h(i)+ e3(i),e2h(i)+ e4(i),e1l(i)+ e3(i),e2l(i)+ e4(i)
  write(*,*) "remark i W e1(w) e2(w)"
  write(*,*) "remark extrapolated t= 0",y(0)
  write(*,*) "remark extrapolated t= -tmn",y(-1),"err= ",err
  write(*,*) "remark extrapolated to inf y(t)= ",b,"* exp (-",a,"*t)"
  
  stop
  end
# CUBEXT cubic polynomial extrapolation
#
# extend data from (x1-x4) = > x
# return cubic polynomial p(x)
# given 4 (y,x) pairs
#
Function cubext ( x , y1, x1, y2, x2, y3, x3, y4, x4 )

cubext = y1*(x-x2)*(x-x3)*(x-x4)/(x1-x2)/(x1-x3)/(x1-x4) +
         y2*(x-x1)*(x-x3)*(x-x4)/(x2-x1)/(x2-x3)/(x2-x4) +
         y3*(x-x1)*(x-x2)*(x-x4)/(x3-x1)/(x3-x2)/(x3-x4) +
         y4*(x-x1)*(x-x2)*(x-x3)/(x4-x1)/(x4-x2)/(x4-x3)
end

# E1COR correct fourier transform from tm to infinity
Function E1COR ( b , a , tm , w )

Function E2COR ( b , a , tm , w )

# CUBINT cubic spline interpolation routine
#
# 5/23/88 new - algorithm due to TNE Greville, in Mathematical
# methods for digital computers, Vol II, ed Ralston
# and Wilf (1967), p. 156.
# cubic spline interpolation is used
#
# arguments:
# n number points integer
# y(i) data points REAL
# x(i) grid points REAL
# err iteration limit real
# values returned:
#   y1, y2, y3 slopes
#
subroutine cubint ( n, y, x, s1, s2, s3, err )

integer n,i
REAL y(n), x(n)
REAL s1(n), s2(n), s3(n)
real err

# local variables
#   h(i)  x(i+ )-x(i)    REAL
#   h2(i) h(i-1)+ h(i)   REAL
#   b(i)  h(i-1)/h2(i)/2 REAL
#   g(i)  3x2nd diff     REAL
#   omega convergence   real
#   eta  greatest adjust real
#   del  ith adjustment  real
#   l    loop counter    int

REAL h(ASIZE), h2(ASIZE), b(ASIZE), g(ASIZE)
real omega, eta, del
integer l

# initial values
do i= 1,n-1
   h(i) = x(i+1) - x(i)
enddo

do i= 2,n-1
   h2(i) = h(i-1) + h(i)
   b(i)  = .5*h(i-1)/h2(i)
   g(i)  = 3./h2(i)**((y(i+1)-y(i))/h(i)-(y(i)-y(i-1))/h(i-1))
   s2(i) = 2./3.*g(i)
enddo
s2(1) = 0.
s2(n) = 0.

# do i= 1,n
#   write(*,*)"init",i,s2(i)

omega = 1.0717968
teta = err
l= 0

# iterate for s2(i)
#   eta = largest correction in an iteration
while ( abs(eta) > = err )
   l= l+ 1
   eta= 0.
   do i= 2,n-1


```fortran
{ 
  dcl = (g(i)-s2(i)-b(i)*s2(i-1)- (.5-b(i))*s2(i+1))*omega
  if ( abs(dcl/s2(i)) > eta ) [eta= abs(dcl/s2(i))] 
  s2(i) = s2(i)+ dcl 
}

# write(*,*)'l= ",1

do i= 1,n-1
  s3(i) = ( s2(i+ 1) - s2(i) )/h(i)

do i= 1,n-1
  s1(i) = (y(i+ 1)-y(i))/h(i) - h(i)/6.*(2.*s2(i)+ s2(i+ 1))
  s1(n) = (y(n)-y(n-1))/h(n-1)

return
end
#
#
# INTEG cubic spline integration function
#
# 5/23/88 new - algorithm due to TNE Greville, in Mathematical
#      methods for digital computers, Vol II, ed Ralston
#      and Wilf (1967), p. 156.
#
# cubic spline interpolation is used
#
# arguments:
#  n       number points  integer
#  y(i)    data points    real
#  x(i)    grid points    real
#  err     iteration limit real
#
# value returned:
#  integral y dx  real
#
real function cintg ( n, y, x, err )

integer n
real y(n), x(n), err
#
local variables
#  h(i)    x(i+ )-x(i)    real
#  h2(i)   h(i-1)+ h(i)   real
#  b(i)    h(i-1)/h2(i)/2. real
#  s2(i)   second deriv   real
#  g(i)    3x2nd diff     real
#  omega   convergence    real
#  eta     greatest adjust real
#  dcl     ith adjustment real
```
real h(ASIZE), h2(ASIZE), b(ASIZE), s2(ASIZE), g(ASIZE)
real omega, eta, del

# initial values
do i= 1,n-1
   h(i)= x(i+ 1)-x(i)

do i= 2,n-1
   
   h2(i)= h(i-1)+ h(i)
   b(i)= .5*h(i-1)/h2(i)
   g(i)= 3./h2(i)*((y(i+ 1)-y(i))/h(i)-(y(i)-y(i-1))/h(i-1))
   s2(i)= 2./3.*g(i)

   s2(1)= 0.
   s2(n)= 0.

omega= 1.0717968
eta = err
l= 0
# iterate for s2(i)
# eta = largest correction in an iteration
while ( abs(eta) > = err )
   
   l= l+ 1
   eta= 0.
do i= 2,n-1
   
   del= (g(i)-s2(i)-b(i)*s2(i-1)-(5-b(i))*s2(i+ 1))*omega
   if ( abs(del) > eta ) {eta= abs(del)/s2(i)
      i= i}
   s2(i)= s2(i)+ del

# evaluate integral
cintg= 0.0
do i= 1,n-1
   
   cintg= cintg+ .5*h(i)*y(i)+ y(i+ 1)-h(i)*h(i)*h(i)*
   (s2(i)+ s2(i+ 1))/24.

return
end
#
#
# CUBDET cubic polynomial extrapolation to zero
#
# extend data from (x1-x3) = > x= 0
# return y(0) from kramers rule for quadratic poly fit
# given 3 (y,x) pairs
Function cubdet (y1, x1, y2, x2, y3, x3)
real det, num

num = y1*x2*x3**2 - y3*x2*x1**2 +
     y2*x3*x1**2 - y2*x1*x3**2 +
     y3*x1*x2**2 - y1*x3*x2**2

det = x2*x3**2 - x2*x1**2 +
      x3*x1**2 - x1*x3**2 +
      x1*x2**2 - x3*x2**2

cubdet = num / det
return
end

#-----------------------------------------------