

## Transition from Electrode-Limited to Bulk-Limited Conduction Processes in Metal-Insulator-Metal Systems

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If a blocking contact exists at a metal-semiconductor interface, the conduction process is electrode-limited and will normally remain so, that is, it will not become bulk-limited with increasing applied voltage unless the semiconductor is inordinately thick. It is shown, however, that in an insulator containing a high density of traps and donors, such as one might expect in evaporated insulating films, the conduction process can change from being electrode-limited to being bulk-limited. This process results at low voltages in a very steep  $I-V$  characteristic which is essentially thickness-independent (electrode-limited), and at high voltages in a law  $I \propto \exp \beta V^{1/2}$  which is thickness-dependent (bulk-limited). The results are shown to be in agreement with existing experimental data.

### 1. INTRODUCTION

STOICHIOMETRIC films of compound insulators are notoriously difficult to prepare by evaporation, because of decomposition and the preferential evaporation of the lower-vapor-pressure constituent atom. For example, using the compound as starting material, elemental Cd tends to evaporate more rapidly from CdS; thus CdS films tend to have donor centers of free cadmium.<sup>1</sup> SiO yields a film containing a mixture of compounds varying from SiO to SiO<sub>2</sub>, as well as free Si.<sup>2-5</sup> A further problem that arises is contamination of the film by deposits arising from the sublimation of the crucible and by residual gases. Thus, it requires dissociation of only 1 molecule per million to yield a possible impurity level of the order 10<sup>17</sup> cm<sup>-3</sup>; similar doping concentrations are possible if the crucible sublimes at one millionth the rate of the evaporant.

Insulating films deposited onto amorphous (glass) substrates are usually at best polycrystalline, and in many cases are amorphous. For crystallite sizes of 100 Å, trapping levels as high as 10<sup>18</sup> cm<sup>-3</sup> are possible due to grain boundary defects alone, and in vacuum-deposited CdS, trapping densities as high as 10<sup>21</sup> cm<sup>-3</sup> have reported.<sup>6</sup> Furthermore, vacuum-deposited films contain large stresses, which induce further trapping centers. It follows, then, that thin-film vacuum-deposited insulators can contain a very high density of both donor and trap centers.

Donor and trap centers in concentrations of the order 10<sup>17</sup> cm<sup>-3</sup> and higher can give rise to interesting conduction phenomena in thin-film insulators; in particular, we wish to show that under such conditions a transition from electrode-limited to bulk-limited conduction can occur in metal-insulator-metal sandwiches. As we shall see, this process is not observable in semiconductors

(unless they are of inordinately large dimensions) or in normal insulators, because it is not possible to form a suitable barrier at the metal-insulator contact. The concepts developed in the subsequent discussion are in good agreement with existing experimental data.

### 2. METAL-SEMICONDUCTOR CONTACT

In order to observe a transition from electrode-limited to bulk-limited conduction in a metal-semiconductor-metal system, the metal is required to form a blocking contact on the semiconductor surface; that is, in the absence of surface states,  $\Psi_m$  must be greater than  $\Psi_s$ , as shown in the energy diagram of Fig. 1. In order to observe this transition the semiconductor must be thick, as shown by comparing the  $I-V$  equations for the contact<sup>7</sup> and bulk:

$$I_c = 120T^2 \exp \left[ -\frac{\phi_0 - 8.26 \times 10^{-6} (N_d V_c / K^3)^{1/4}}{kT} \right] \quad \text{A/cm}^2 \quad (1)$$

and

$$I_b = 1.60 \times 10^{-19} (\mu N_d / L) V_b \text{ A/cm}^2, \quad (2)$$

where  $\phi$  is the metal-semiconductor barrier height in electron volts,  $k$  is Boltzmann's constant in electron

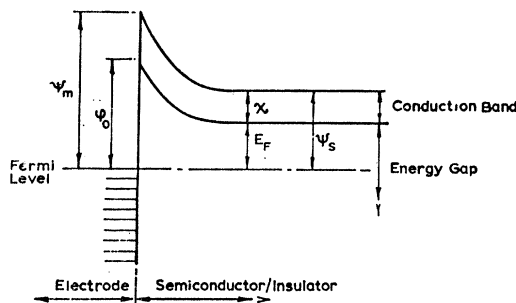


FIG. 1. Energy diagram of metal-(semiconductor or insulator) blocking contact.  $\Psi_m$  is the work function of metal, and  $\chi$  is the electron affinity of the insulator.

<sup>7</sup> H. K. Hensch, *Rectifying Semiconductor Contacts* (Oxford University Press, England, 1957), Chap. VII.

<sup>1</sup> M. Bujatti and R. S. Muller, *J. Electrochem. Soc.* **112**, 702 (1965).

<sup>2</sup> G. Hass, *J. Am. Ceram. Soc.* **33**, 353 (1958).

<sup>3</sup> E. Ritter, *Opt. Acta* **9**, 197 (1962).

<sup>4</sup> G. W. Brady, *J. Phys. Chem.* **63**, 1119 (1959).

<sup>5</sup> Von A. Faessler and H. Kramer, *Ann. Physik* **7**, 263 (1959).

<sup>6</sup> J. Dresner and F. V. Shallcross, *Solid State Electron.* **5**, 205 (1962).

volts,  $T$  is the temperature in  $^{\circ}\text{K}$ ,  $V_c$  and  $V_b$  are, respectively, the voltage drop across contact and bulk,  $\mu$  is the mobility in  $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ ,  $N_d$  is the impurity density (assumed to be fully ionized) per  $\text{cm}^3$ ,  $K$  is the dielectric constant, and  $L$  is the semiconductor thickness in cm.

These two equations have been plotted in Fig. 2 in terms of the parameters  $N_d/K^3$  and  $N_d\mu/L$ , for  $T = 300^{\circ}\text{K}$  and various values of  $\phi_0$ . The straight lines correspond to the contact characteristic and the curved lines to the bulk characteristic. Consider the case of a metal-silicon contact in which  $\phi_0 = 0.5 \text{ eV}$ . From the upper two curves it will be apparent that for  $N_d\mu/L = 10^{21} (\text{cm}^2 \text{V sec})^{-1}$  and  $N_d/K^3 = 10^{16} \text{ cm}^{-3}$ , the contact characteristic predominates for applied voltages up to approximately 1000 V (500 V each across the contact and the bulk); thereafter, the bulk characteristic predominates. In order to determine the thickness of semiconductor, we first require the magnitude of  $N_d$  to which the curves correspond. Assuming that we know the value of  $K$  for the material under consideration,  $N_d$  is determined from the contact characteristic parameter  $N_d/K^3 = 10^{16} \text{ cm}^{-3}$ , which for  $K = 11.5$  (the value for silicon) yields  $N_d = 1.5 \times 10^{19} \text{ cm}^{-3}$ . Then, from  $N_d\mu/L = 10^{21} (\text{cm}^2 \text{V sec})^{-1}$ , assuming  $\mu = 1350 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$ , we have  $L = 20 \text{ cm}$  as the minimum thickness of silicon in which bulk processes will be observed for  $V = 1000 \text{ V}$ ,  $\phi_0 = 0.5 \text{ eV}$ , and  $N_d = 1.5 \times 10^{19} \text{ cm}^{-3}$ . If a smaller value of  $N_d\mu/L$  than  $10^{21} (\text{cm}^2 \text{V sec})^{-1}$  is chosen, say  $\alpha$ , it will be apparent that the bulk characteristic will intersect the contact characteristic at lower voltages; thus the bulk characteristic will be manifest at a lower voltage than described above. However, since  $L = N_d\mu/\alpha$ , it also follows that the semiconductor would have to be thicker than previously described (20 cm) in order to observe the effect at the lower voltage level.

The value of  $\phi_0 = 0.5 \text{ eV}$  used in the above example is, in fact, on the low side, values closer to 0.8 eV being more practical for a silicon-metal contact. In the case of metal-insulator contacts, barriers higher than 1 eV are usual. Also, the value of  $N_d = 1.5 \times 10^{19} \text{ cm}^{-3}$  used in the above example is extremely high, doping levels closer to  $10^{16} \text{ cm}^{-3}$  being more usual in semiconductors. It will be clear from a consideration of these points in conjunction with the additional curves of Fig. 2 that the transition from electrode- to bulk-limited conduction will not normally be observed in practice, even for mobilities and dielectric constants substantially less than those of silicon.

In the higher voltage ranges shown in Fig. 2, impact ionization or tunneling processes can occur at the contact where the field is highest. Once initiated, these processes cause the contact resistance to decrease far more rapidly with increasing voltage than does the Schottky effect, Eq. (1). It follows, then, that the transition from electrode- to bulk-limited conduction can occur at substantially lower voltages than if the contact impedance were limited only by the Schottky

effect. Under these conditions the possibility thus exists for observing the transition in semiconductors of practical dimensions. In the case of thin-film semiconductors, however, this possibility is completely ruled out, even if impact ionization or tunneling does occur at the contacts, because of power dissipation in the sample. For example, consider a film of thickness  $10 \mu$  with a depletion region small compared to its thickness, which means a donor concentration in the region of the order  $10^{17} \text{ cm}^{-3}$ . Even with an applied voltage of only 10 V across the bulk, there is a power dissipation of  $2 \times 10^6 \text{ W cm}^{-2}$  or  $2 \times 10^9 \text{ W cm}^{-3}$  in the silicon film, which is clearly impracticable.

### 3. IMPERFECT INSULATOR FILM

It follows from the above discussion that in order to observe the transition to the bulk-limited process in a trap-free, thin-film metal-(semiconductor or insulator)-metal system, a low bulk conductivity (to minimize power dissipation) and a narrow depletion region (to minimize the contact impedance) are required. These two requirements would appear to be incompatible, since the former requires a low donor density and the latter a high donor density. In the above discussion, however, we tacitly assumed a perfect solid—in the sense, that is, of one not containing imperfections, or more specifically, electron traps. We will now proceed to show that if an insulator contains a high density of

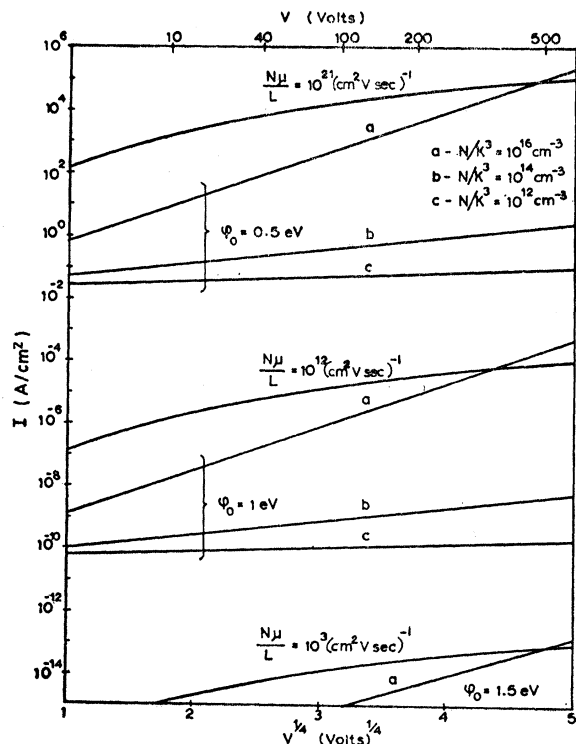


Fig. 2. Contact (straight lines) and bulk (curved lines)  $I$ - $V$  characteristics for metal-semiconductor-metal system.

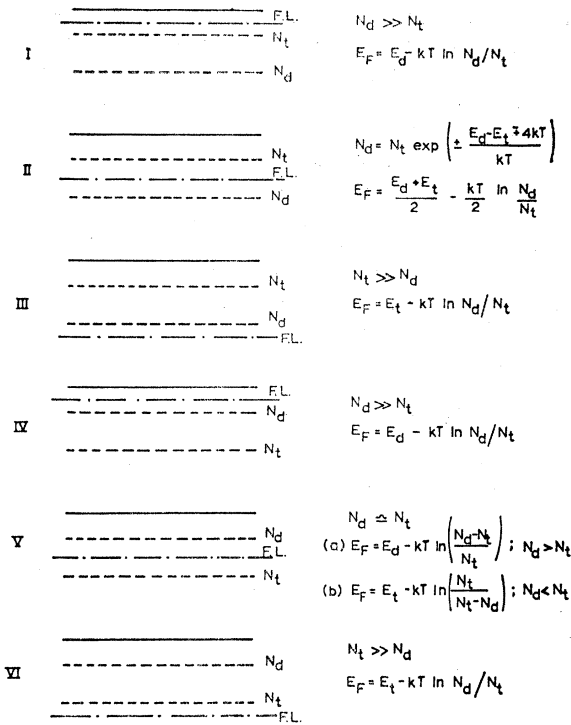


FIG. 3. Insulator band models. The relationships between  $N_d$ ,  $N_t$ , and  $E_F$  given alongside each diagram are the conditions required for that particular energy configuration, assuming non-degenerate positioning of  $E_F$  with respect to any of the levels, and that  $N_i \gg n$ .

donors and traps, a low bulk conductivity and a narrow depletion layer are quite compatible.

**A. Band Models**

Consider a simple system containing  $N_d$  traps  $\text{cm}^{-3}$  and  $N_a$  donors  $\text{cm}^{-3}$  positioned, respectively, at energies  $E_t$  and  $E_d$  below the bottom of the conduction band. The Fermi level is at an energy  $E_F$  below the conduction band. The possible relative positions of  $E_d$ ,  $E_t$ , and  $E_F$  are shown in Fig. 3. Alongside each diagram is given the relationship between  $N_d$ ,  $N_t$ ,  $E_d$ ,  $E_t$ , and  $E_F$  for that particular energy configuration, assuming non-degenerate positioning of the Fermi level with respect to the donor or trapping levels. The salient features of these systems have been treated in detail elsewhere.<sup>8</sup> It is noted here, however, that it is system II only that permits a wide degree of flexibility between the relative values of  $N_d$  and  $N_t$ ; the extremities of the range of variation between  $N_d$  and  $N_t$  are given by

$$N_d = N_t \exp \pm (E_d - E_t \mp 4kT)/kT.$$

Model II has an additional important property, as we shall see later when we consider the Poole-Frenkel effect. Let us now use model II of Fig. 3, then, to illustrate the effect of traps on the conductivity.

<sup>8</sup> J. G. Simmons, Phys. Rev. **155**, 657 (1967).

**B. Effect of Traps on Bulk Conductivity**

The number of free carriers  $n$  in the trap-free insulator is given by

$$n = N_c \exp(-E_F/kT), \tag{3}$$

where  $N_c$  is the effective density of states in the insulator. The position of the Fermi level in terms of  $E_d$ ,  $N_c$ , and  $N_d$  is determined by equating the number of free carriers in the conduction band to the number of ionized donors:

$$N_c \exp(-E_F/kT) = N_d \exp[-(E_d - E_F)/kT].$$

This may be written in the form

$$E_F = \frac{1}{2} E_d - \frac{1}{2} (kT) \ln N_d/N_c,$$

which on substitution in (3) yields

$$n = (N_c N_d)^{1/2} \exp(-E_d/2kT).$$

The conductivity of the insulator,  $\sigma_0 = en\mu$ , is thus given by

$$\sigma_0 = e\mu (N_c N_d)^{1/2} \exp(-E_d/2kT). \tag{4}$$

The number of free carriers in the defect insulator in hand is obtained by substituting  $E_F = \frac{1}{2}(E_d + E_t) - \frac{1}{2}kT \times \ln N_d/N_t$  (see II in Fig. 3) into (3). This yields (assuming  $N_t = N_c$ , which is not unreasonable)

$$n = (N_c N_d)^{1/2} \exp[-(E_d + E_t)/2kT], \tag{5}$$

from which the conductivity is calculated to be

$$\sigma_0 = e\mu (N_c N_d)^{1/2} \exp[-(E_d + E_t)/2kT]. \tag{6}$$

Thus, comparing (4) and (6), it is seen that the traps have reduced the conductivity by an amount  $\exp(-E_t/2kT)$ , which for  $E_t = 0.75$  eV amounts to  $10^{-7}$ .

Similar conclusions are reached for the other five configurations shown in Fig. 3.

**C. Depletion Region**

The role of traps in the formation of the depletion region can be readily appreciated if it is recognized that a trap and donor are thermodynamically equivalent regarding their occupancy by electrons. For example, if there exists an equal number of donors and traps in the insulator ( $N_d = N_t$ ), and they are positioned exactly the same energy below the conduction band ( $E_d = E_t$ ), there will be the same number ( $= \frac{1}{2} N_d$ ) of electrons in traps as there are in donor centers at all temperatures, provided that the insulator is in thermodynamic equilibrium.

Consider now the metal-insulator interface<sup>9</sup> resulting from attaching metal electrodes to the insulators I-III shown in Fig. 3. Assuming  $\Psi_m > \Psi_i$ , where  $\Psi_i$  is the insulator work function, a blocking contact results (see Fig. 1). Providing  $\phi_0 > E_d$  and  $N_d \gtrsim 10^{17} \text{ cm}^{-3}$ ,

<sup>9</sup> For simplicity we have ignored the effect of surface states; their inclusion is fairly straightforward.

there will exist a thin depletion region of width  $\lambda$ . In this depletion region *both* donors and traps can be assumed empty, since they lie *above* the Fermi level, which means a positive charge density ( $=N_d$ ) exists there. Figure 4 illustrates the conditions at the interface for blocking contacts on the insulators I-III of Fig. 3 when a voltage  $V$  is applied. These cases are directly analogous to conditions existing at a metal-semiconductor contact in which there is a single donor level; this problem has been treated elsewhere,<sup>7</sup> and we quote the desired results. At zero bias (in the mks system)

$$\lambda = [2\epsilon_0 K (\Psi_m - \Psi_s) / e^2 N_d]^{1/2} \text{ m}, \quad (7)$$

where  $N_d$  is the donor density in the bulk of the insulator,  $K$  is the dielectric constant of the insulator, and  $\epsilon_0$  is the permittivity of free space. The rate of change of the potential  $V(x)$  of the bottom of the conduction band as a function of distance  $x$  from the interface and voltage bias  $V$  is given by

$$\frac{dV(x)}{dx} = \frac{N_d e}{K \epsilon_0} \left\{ \left[ \frac{2K \epsilon_0 (eV + \Psi_m - \Psi_s)}{N_d e^2} \right]^{1/2} - x \right\} \text{ V m}^{-1} \quad (8)$$

For  $N_d = 10^{18} \text{ cm}^{-3}$  and  $K = 6$ , it is seen from (7) that  $\lambda$  is approximately  $250 \text{ \AA}$ , and from (8), even for low applied voltages, that fields in excess of  $10^6 \text{ V cm}^{-1}$  are possible.

#### 4. CONDUCTION PROCESSES AND $I$ - $V$ CHARACTERISTICS OF AN IMPERFECT INSULATOR

We are concerned with several distinct conduction processes depending on the voltage range under consideration, so it is worth while at this stage to present a brief qualitative step-by-step review of what is to be expected. At very low voltages the conduction is by the thermal excitation over the interfacial barrier of electrons from the electrode [Eq. (1)]. The current is only a slow function of the applied voltage for this process, and for barriers in excess of about  $0.5 \text{ eV}$  it will not be normally observable.

At higher voltages, one of two processes can occur. If the barrier at the Fermi level becomes thin enough, field emission from the electrode into the conduction band of the insulator can occur; or when the voltage bias exceeds  $\frac{3}{2}E_g$ , impact ionization can occur in the depletion region of the insulator. Both of these processes are characterized by a rapid increase of current with applied voltage, i.e., the contact resistance decreases extremely rapidly with increasing voltage bias. It will be shown that at relatively low voltages the contact resistance under these conditions is much higher than that of the bulk. It follows, then, that while either or both of these processes predominate, the  $I$ - $V$  characteristic will be virtually thickness-independent (because essentially all of the applied voltage appears across the contact and very little across the bulk) and very steep.

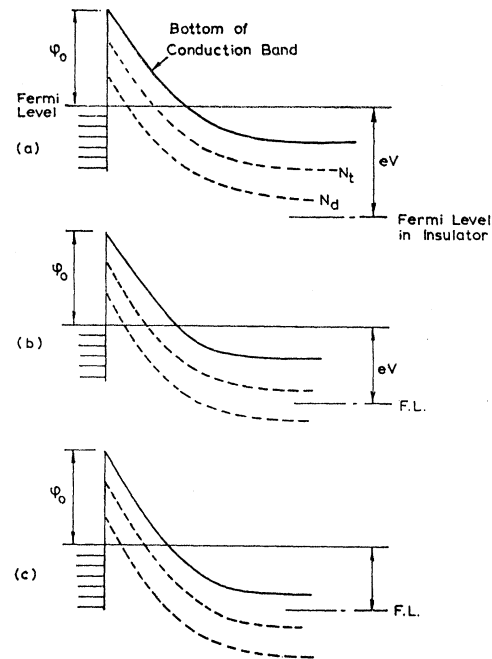


FIG. 4. Energy diagram of blocking contact on insulator models I, II, and III of Fig. 3.

The electrode-limited process cannot continue indefinitely, however, because the bulk resistance decreases much slower with increasing voltage than does the contact. Thus, at some voltage  $V_T$ , the transition voltage, the contact resistance falls to a value equal to that of the bulk. When this occurs, the applied voltage  $V_T$  is shared equally between the contact and the bulk. Thereafter, practically all of the voltage in excess of  $V_T$  will fall across the bulk and the remaining fraction across the barrier, just sufficient to ensure current continuity throughout the system. Hence, for voltages in excess of  $V_T$ , the current will cease to rise as rapidly as for  $V < V_T$ , since it is controlled by bulk processes; it will now be thickness-dependent.

From the above discussion it will be apparent that there are three distinct voltage ranges to consider: (i) low voltages where the characteristic is determined purely by thermal processes, i.e., the Richardson-Schottky effect; (ii) intermediate voltages where the conduction process is electrode limited and in which (a) contact tunneling and/or (b) impact ionization occurs; and (iii) high voltages where the characteristic is determined by the bulk.

##### A. Richardson-Schottky Effect

In this process the electrons require sufficient energy to surmount the barrier at the metal-insulator interface, and the relevant  $I$ - $V$  relationship is given by (1). The effect of increasing voltage is to increase the field at the metal-insulator interface, which in turn interacts with the electrode image force. This interaction causes

the attenuation of the barrier height from its zero-bias height  $\phi_0$ , permitting more current to flow over the barrier with increasing applied voltage. The term containing the voltage  $V$  in the exponential reflects the lowering of the barrier.

### B. Contact Tunneling

This process becomes observable when the thickness of the depletion region at the Fermi level is less than about 50 Å. The  $I$ - $V$  characteristic for this case can be derived approximately in the following elementary manner. For voltage biases such that  $V \gtrsim \phi_0$ , the barrier above the Fermi level is approximately triangular. We can thus use the Fowler-Nordheim tunnel equation to describe the current tunneling from the metal electrode into the semiconductor:

$$I = \left( \frac{3.38 \times 10^{-6} F_0^2}{\phi_0} \right) \exp \left( - \frac{6.9 \times 10^7 (m^* \phi^3)^{1/2}}{F_0} \right) \quad \text{A cm}^{-2}, \quad (9)$$

where  $F_0$  is the field at the interface in  $\text{V cm}^{-1}$ ,  $\phi_0$  is the barrier height in eV, and  $m^*$  is the ratio of the insulator effective mass to the free-electron mass. From (8) the field at the interface ( $x=0$ ) can be written

$$F_0 = 1.9 \times 10^{-3} (N_d V^* / K)^{1/2} \text{ V cm}^{-1}, \quad (10)$$

where  $N_d$  is expressed in donors  $\text{cm}^{-3}$  and  $V^* = V + \Psi_m - \Psi_i$ . Substituting (10) into (9) yields

$$I = (1.22 \times 10^{-11} N_d V^* / \phi_0 K) \exp[-3.65 \times 10^{10} \times (m^* K \phi^3 / N_d V^*)^{1/2}] \text{ A cm}^{-2}. \quad (11)$$

It will be noted that (11) differs from the Fowler-Nordheim equation which one associates with metal-vacuum tunneling in that the dependence of current on voltage is different,  $\log I / V^*$  being proportional to  $(V^*)^{-1/2}$  rather than  $\log I / V^2$  proportional to  $V^{-1}$ .

### C. Carrier Multiplication

At the high fields possible in the depletion region it may be possible for the electron to gain sufficient energy ( $> \frac{3}{2} E_g$ ) to cause impact ionization, providing the mean free path of the electron in the insulator is sufficiently long. If we assume an impact ionization energy of 5 eV, then for fields of approximately  $10^6 \text{ V cm}^{-1}$  a mean free path of the order of 500 Å is required for carrier multiplication.

There is very little information in the literature on mean free paths in insulators, and the available data are often conflicting. For example, recent photoemission measurements by Braunstein *et al.*<sup>10</sup> in Al-Al<sub>2</sub>O<sub>3</sub>-Al tunnel junctions imply a mean free path in the amor-

phous Al<sub>2</sub>O<sub>3</sub> of only a few angstroms, while similar measurements by Schuermeyer<sup>11</sup> indicate a value of several-tens of angstroms in the same material. It would seem, anyway, that at fields less than  $10^6 \text{ V cm}^{-1}$  impact ionization in amorphous insulators is not very probable. In the numerical example we consider later we will not include the effect of electron multiplication in the calculations. Rather, we will consider only the effect of the Schottky and tunnel processes, but remain aware that these calculations represent only the minimum conductivity of the contact.

### D. Bulk Conduction

#### 1. Low Fields

At low fields in an imperfect insulator we can no longer use (2) to describe the  $I$ - $V$  characteristic, but must rather use

$$I_0 = e \mu n V_b / L \\ = e \mu N_c (V_b / L) \exp(-E_F / kT), \quad (12)$$

where  $E_F$  for the particular arrangement of donor, trap, and Fermi level is given in Fig. 3;  $V_b$  is the voltage drop across the bulk, and  $L$  is the insulator thickness.

#### 2. High Fields

At high fields, the field interacts with a Coulombic barrier and lowers it by an amount  $\Delta E$  given by<sup>12</sup>

$$\Delta E = (e^3 V_b / \pi \epsilon_0 K L)^{1/2} = \beta F_b^{1/2},$$

where  $\beta = (e^3 / \pi \epsilon_0 K)^{1/2}$  and  $F_b = V_b / L$ . Such a Coulombic barrier exists between a donor center and its electron; it also exists between a charged trap (i.e., a trap which is charged when empty and neutral when full) and an electron. (There is no interaction between the field and the barrier of an uncharged trap.) This field lowering of the barrier is known as the Poole-Frenkel effect and results in the conductivity being field-dependent.

The high-field, bulk conductivities of the models shown in Fig. 3 have been discussed in detail elsewhere,<sup>8</sup> and it will suffice here to quote the results obtained. Assuming charged traps, all of the models in Fig. 3 exhibit a field-dependent conductivity  $\sigma$  given by

$$\sigma = \sigma_0 \exp \beta F_b^{1/2} / kT \quad (13)$$

or

$$I = I_0 \exp \beta F_b^{1/2} / kT, \quad (14)$$

where  $\sigma_0 (= I_0 L / V_b)$  is the low-field conductivity, and  $I_0$  is given by (12). If the traps are neutral, however, the conductivities of the insulators III, Va, and VI are field-independent. If, in the case of model II, the traps are assumed neutral, the conductivity of the

<sup>11</sup> F. L. Schuermeyer, J. Appl. Phys. **37**, 1998 (1966).

<sup>10</sup> A. Braunstein, M. Braunstein, G. S. Picus, and C. A. Mead, Phys. Rev. Letters **14**, 519 (1965).

<sup>12</sup> J. Frenkel, Tech. Phys. USSR **5**, 685 (1938); Phys. Rev. **54**, 647 (1938).

system is given by

$$\sigma = \sigma_0 \exp \beta F_b^{1/2} / 2kT \quad (15)$$

or

$$I = I_0 \exp \beta F_b^{1/2} / 2kT. \quad (16)$$

It will be apparent from (13) that a plot of  $\ln \sigma$  versus  $F_b^{1/2}$  results in a straight line of slope  $\beta/kT$ . This type of behavior appears to have been first incontrovertibly observed by Mead,<sup>13</sup> who suggested that it could be explained if the insulator contained shallow traps whose depth are attenuated by the Poole-Frenkel effect.<sup>12</sup> (In actual fact, the inclusion of impurities in the insulator is required to account for the observed conductivity.<sup>8</sup>) Thus *defect* thin-film insulators which obey a linear  $\ln \sigma$ -versus- $\beta F_b^{1/2}/kT$  relationship are said to obey a *normal* Poole-Frenkel effect.

The conductivity and  $I$ - $V$  characteristic given by (15) and (16) have been described as the anomalous Poole-Frenkel effect,<sup>8</sup> because the coefficient of  $F_b^{1/2}$  is  $\beta/2kT$  as compared to  $\beta/kT$  for the normal Poole-Frenkel effect [see (13) and (14)]. The functional form of (16) is, in fact, identical to the Richardson-Schottky effect at a neutral contact, as distinct from a blocking contact [see Eq. (1)]. It follows, then, that experimental data arising from the anomalous Poole-Frenkel effect can, without close scrutiny, be mistakenly attributed to the Richardson-Schottky effect.

We might point out that the original work of Frenkel<sup>12</sup> on field-assisted thermionic ionization of the constituent atoms of semiconductors and insulators results in an expression of the same form as (16); that is,

$$\sigma = \sigma_0 \exp \beta F_b / 2kT.$$

In this equation  $\sigma_0$  is the low-field (Ohmic) conductivity due to thermal electron-hole pair generation. Assuming that the contribution of holes to the conductivity is negligible compared to that of the electrons, we have from simple insulator statistics

$$I_0 = F \sigma_0 \approx 8 \times 10^{-4} T^{3/2} \mu F \exp(-E_g/2kT) \text{ A cm}^{-2},$$

where  $E_g$  is the energy gap of the material. (In evaluating, from the various fundamental constants, the numerical pre-exponential factor, the effective electron and hole masses were assumed to be equal to the free-electron mass.) It can be shown, however, that this type of field-dependent conductivity is not relevant to the present discussion, since it is negligibly small for insulators. For example, assuming  $E_g = 3$  eV,  $\mu = 100$  cm<sup>2</sup> V<sup>-1</sup> sec<sup>-1</sup> (which is probably on the high side for amorphous insulators), and  $T = 300^\circ\text{K}$ , we have  $I_0 = 4 \times 10^{-18}$  A cm<sup>-2</sup> for  $F = 10^6$  V cm<sup>-1</sup>, which is much lower than observed for materials with  $E_g > 3$  eV.<sup>13-16</sup>

<sup>13</sup> C. A. Mead, Phys. Rev. **128**, 2088 (1962).

<sup>14</sup> H. Hirose and Y. Wada, Japan J. Appl. Phys. **3**, 179 (1964).

<sup>15</sup> T. E. Hartman, J. C. Blair, and R. Bauer, J. Appl. Phys. **37**, 2464 (1966).

<sup>16</sup> M. Stuart, Phys. Status Solidi **23**, 595 (1967).

### E. Numerical Examples of Isothermal Characteristics

In Fig. 5(a) we have plotted Eqs. (11) and (14) for three thicknesses of dielectric ( $L = 1, 3,$  and  $10 \mu$ ) for model II of Fig. 3 (assuming charged traps), using the parameters  $N_d = 10^{18}$  cm<sup>-3</sup>,  $N_t = 10^{19}$  cm<sup>-3</sup>,  $K = 3$ ,  $\mu = 10$ ,  $\frac{1}{2}(E_t + E_a) = 0.70$  eV,  $\phi_0 = 1.5$  eV. For these parameters, the currents given by (1) are too small to be shown on the graph. The curves in Fig. 5(a) are also consistent with the  $I$ - $V$  characteristics for I, III, IV, and VI using the same parameters, except that  $E_a = 0.75$  eV for I and V, and  $E_t = 0.75$  eV for III and VI.

The dashed and dot-dashed lines in Fig. 5 represent the bulk and contact characteristics given by (14) and (11), respectively. The full lines represent the combined effect of the contact and bulk, that is, the actual characteristic of the junction. Since the contact and bulk impedances act in series, the latter curves are arrived at by adding together the contact and bulk voltages corresponding to a given current on the individual curves. Hence, to obtain the point C on the upper curve of Fig. 5(a) we add the voltages corresponding to the points A and B lying, respectively, on the individual contact and bulk curves. The curves are plotted as  $\log I$  versus  $V^{1/2}$  in order to accentuate the Poole-Frenkel effect in the bulk-controlled region.

The curves clearly delineate contact and bulk effects, the transitional stage occurring at about 12 V. Below 12 V we have the contact-limited portion, which is characterized by the thickness-independent and rapidly increasing current-voltage tunnel curve. Above 12 V we have the bulk-limited region, which manifests the effect of varying dielectric thickness. It will be noted that these curves are displaced to lower current densities and lower slopes than their corresponding individual curves, thus reflecting to a small extent contact effects on the bulk-limited characteristics. It follows, then, that in order to obtain the true bulk characteristic from observed data it is necessary to extrapolate the contact-limited characteristic to higher current densities and subtract its effect from the observed data. This process is, of course, just the reverse of the procedure used to obtain the actual  $I$ - $V$  characteristic from the individual contact and bulk characteristics.

The effect of decreasing  $E_t$ ,  $E_a$ , or  $N_d$  is an increase in the transitional voltage, as shown in Figs. 5(b) and 5(c). In Fig. 5(b),  $\frac{1}{2}(E_a + E_t) = 0.55$  eV, and in Fig. 5(c),  $N_d = 2 \times 10^{18}$ , the other parameters being the same as for Fig. 5(a). Note in Fig. 5(c) how the contact resistance is considerably reduced for only a twofold increase in  $N_d$ . Comparing the curves in this figure with those of Figs. 5(a) and 5(b), it is seen that the lower the contact impedance and the higher the bulk impedance, the closer is the bulk-controlled characteristic to the true bulk characteristic.

The curves in Fig. 6 are for an insulator (II of Fig. 3) having parameters identical to those used for the curves

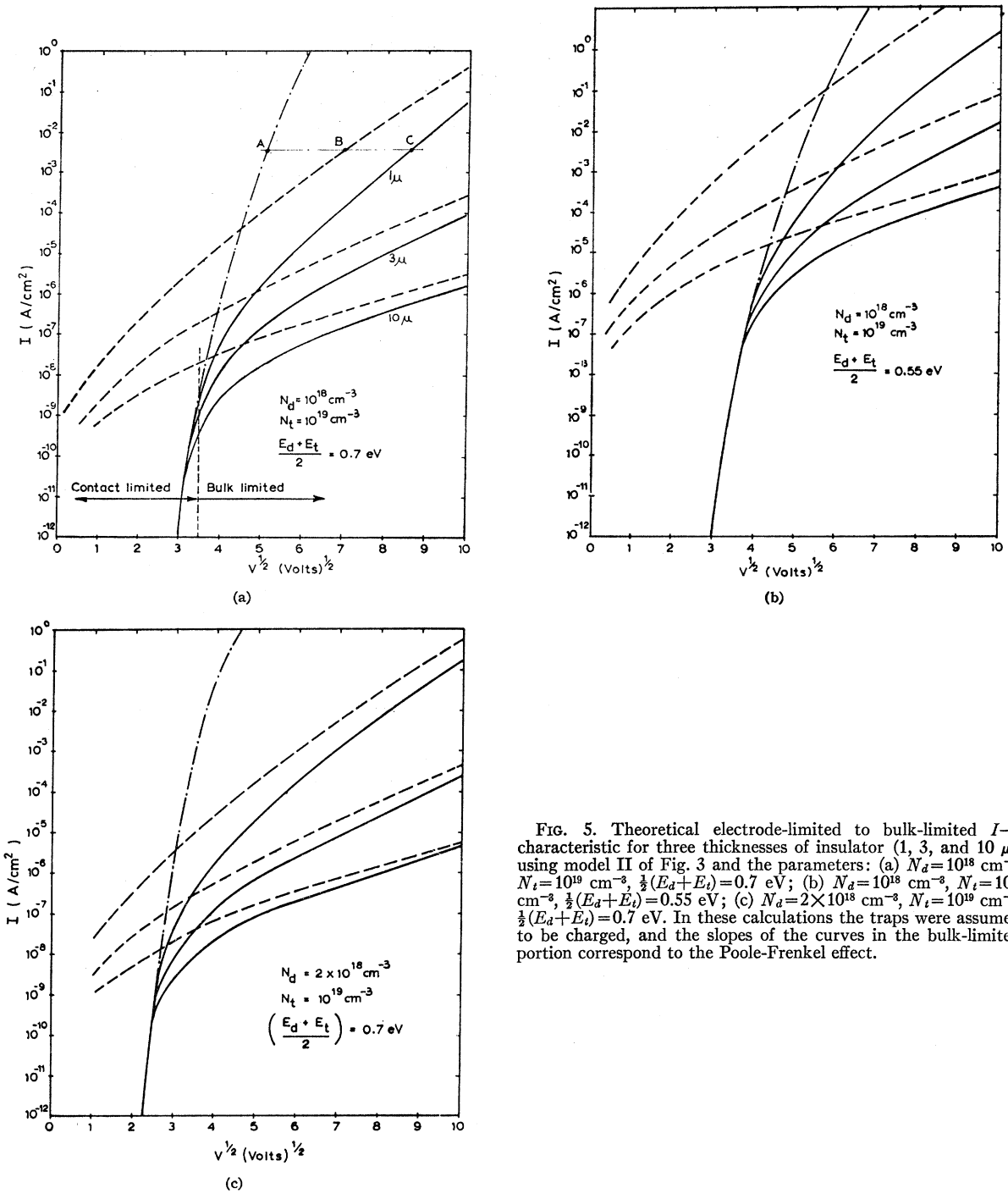


FIG. 5. Theoretical electrode-limited to bulk-limited  $I-V$  characteristic for three thicknesses of insulator (1, 3, and 10  $\mu$ ), using model II of Fig. 3 and the parameters: (a)  $N_d = 10^{18} \text{ cm}^{-3}$ ,  $N_t = 10^{19} \text{ cm}^{-3}$ ,  $\frac{1}{2}(E_d + E_t) = 0.7 \text{ eV}$ ; (b)  $N_d = 10^{18} \text{ cm}^{-3}$ ,  $N_t = 10^{19} \text{ cm}^{-3}$ ,  $\frac{1}{2}(E_d + E_t) = 0.55 \text{ eV}$ ; (c)  $N_d = 2 \times 10^{18} \text{ cm}^{-3}$ ,  $N_t = 10^{19} \text{ cm}^{-3}$ ,  $\frac{1}{2}(E_d + E_t) = 0.7 \text{ eV}$ . In these calculations the traps were assumed to be charged, and the slopes of the curves in the bulk-limited portion correspond to the Poole-Frenkel effect.

in Fig. 5(c), but in this case the traps are chosen to be neutral in order to demonstrate the anomalous Poole-Frenkel effect. The bulk-limited portions of the curves have the same slope as for the Schottky effect in an undoped insulator with *neutral* contact, that is, an electrode-limited process, and without scrutiny can be misattributed to that process.<sup>8</sup>

5. THERMAL CHARACTERISTICS

A. Contact

Equation (11) was derived assuming direct tunneling from the electrode into the insulator conduction band. For the barrier heights we have in mind here ( $\phi_0 > 1 \text{ eV}$ ), such an  $I-V$  characteristic is temperature-independent,

at least to the extent that one is concerned with field emission or tunneling through very thin films.<sup>17,18</sup> However, there are indirect tunnel processes that can occur, such as the tunnel-hopping process *abd*, as shown in Fig. 7(a), or *acd*, or *abcd*. Such processes modify the transparency of the barrier quite markedly from that corresponding to a direct transition. Also, they will normally be associated with the emission or absorption of a phonon (phonon-assisted tunneling), since the *y* and *z* components of momenta of the electron entering the donor or trap center will not generally be compatible with that of the donor or trap. Phonon-assisted tunneling is a temperature-dependent process, since the probability of such an indirect transition depends on temperature through the occupation number of the phonon states.

A second thermal process that can take place is that of indirect tunneling into a trap, followed by a thermal leap over the barrier, as indicated by the path *ace* in Fig. 7(b). This process will have a thermal activation energy that reflects the depth of the trap or donor—that is,  $I = I_T \exp(-\varphi/kT)$ , where  $I_T$  is the tunneling component of current and  $\varphi$  represents the donor or trap depth—depending on the center from which thermal activation takes place. At sufficiently low temperatures, however, the tunnel transition through the total barrier will be preferred.

### B. Bulk

At sufficiently low temperatures there will be competition between the thermal and tunnel process for the ionization of traps and donors. When thermal activation predominates, an activation energy of  $E_d$ ,  $E_t$ , or  $\frac{1}{2}(E_d + E_t)$  will prevail, depending upon which of the models in Fig. 3 is to be associated with the insulator. When tunneling predominates, as it will at low temperatures, the bulk process will be temperature-independent, and the conductivity will become field-dependent in a manner described approximately by

$$\sigma = A \exp(-\beta/V) (\Omega \text{ cm})^{-1}, \quad (17)$$

where  $A$  and  $B$  are constants. In terms of current, (17) becomes

$$I = AF_b \exp(-\beta/V) A \text{ cm}^{-2}. \quad (18)$$

## 6. DISCUSSION

The existing experimental data on thin SiO films due to Hirose and Wada<sup>14</sup> (note in particular their Fig. 6) and Hartman *et al.*<sup>15</sup> (note in particular their Fig. 2) are suspiciously similar to the transition processes described here.

The data from the comprehensive studies by Hartman *et al.*, in particular, are strikingly similar to our results

<sup>17</sup> R. Stratton, J. Phys. Chem. Solids **23**, 1177 (1962).

<sup>18</sup> J. G. Simmons, J. Appl. Phys. **35**, 2655 (1964).

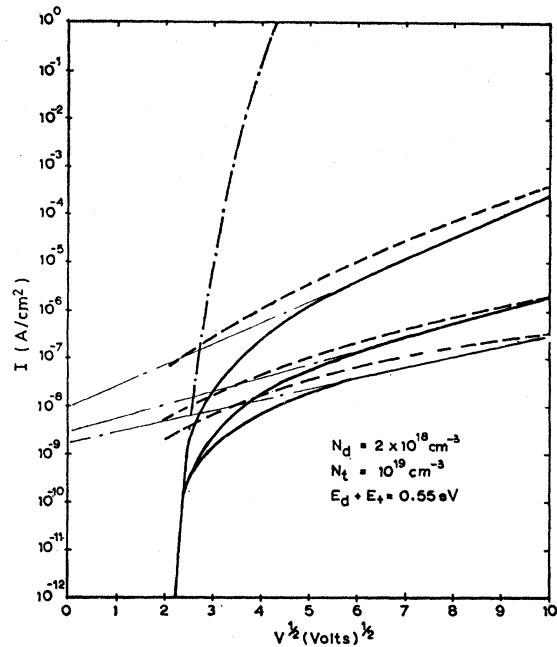


FIG. 6. Theoretical electrode-limited to bulk-limited curve arising from model II of Fig. 3 for the parameters  $N_d = 2 \times 10^{18} \text{ cm}^{-3}$ ,  $N_t = 10^{19} \text{ cm}^{-3}$ ,  $\frac{1}{2}(E_d + E_t) = 0.7 \text{ eV}$ . In these calculations the traps were assumed neutral. This assumption, and the slopes of the curves in the bulk-limited region, corresponds to the anomalous Poole-Frenkel effect. Compare these curves with those of Fig. 5(c); note the difference in the slopes in bulk-limited region.

on several counts, and are worth discussing in some detail. They observed a rapidly rising characteristic at low voltages, which is apparently independent of thickness. This is followed by a less rapidly increasing

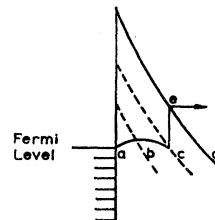
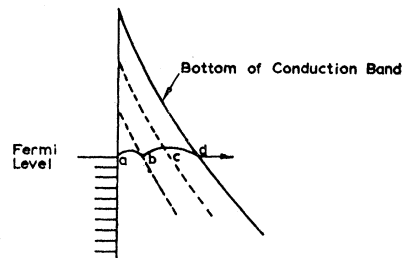


FIG. 7. Energy diagrams illustrating (i) the indirect tunnel process *abd* through the interface barrier, and (ii) the combined indirect tunneling and thermal activation process *ace* through the barrier.



characteristic at higher voltages, which is thickness-dependent and satisfies the relationship  $\log I \propto V^{1/2}$  (Fig. 2, Ref. 15). From the slopes of their measured  $\log I$  vs  $V^{1/2}$  they determined  $K=3$ , assuming the Schottky mechanism, and  $K=12$ , assuming the Poole-Frenkel mechanism. Clearly  $K=12$  is too high for the high-frequency dielectric constant, while  $K=3$  is quite reasonable, thus suggesting Schottky emission at a *neutral* barrier as the mechanism. This conclusion, is, however, incompatible with additional measurements carried out by Hartman *et al.* From photoresponse measurement they determined the metal-insulator barrier height to be  $\phi=1.77$  eV, while thermal measurements where  $\log I \propto V^{1/2}$  indicated an activation energy of only 0.43 eV. The conduction mechanism cannot therefore be due to the Schottky effect; otherwise, these two results would be compatible. An additional complicating observation is that their  $\log I$  versus  $V^{1/2}$  curves, when extrapolated to zero voltage, do not have a common intercept on the  $\log I$  axis as is required for Schottky emission. From this information Hartman *et al.* concluded that their results were inconsistent with both the Schottky and Poole-Frenkel (normal) effects.

The data given by Hartman *et al.* can be explained quite well by our idea of an electrode-limited to bulk-limited transition if it is assumed that the conductivity is electrode-limited in the low voltage, thickness-independent region, and that the apparent Schottky-type field-dependent conductivity at the higher voltages is in fact a bulk effect and attributable to the anomalous Poole-Frenkel effect. These assumptions require the energy diagrams of the contact and the bulk of the insulator to be as shown, respectively, in Figs. 1 and 3 (II), and the traps to be neutral. This band model is in agreement with simple theoretical considerations. Suppose that the SiO does contain free Si atoms which act as donor centers.<sup>19</sup> The ionization potential of the Si can be calculated from Simpson's formula<sup>20</sup> to be 0.51 eV, using values of 4 and 5.8, respectively, for the high-frequency and low-frequency dielectric constant of SiO.<sup>15</sup>  $\phi_0$  is given by  $\phi_0 = \Psi_m - \chi_i$ , and since the work functions of most metals are in the range 3–4.5 eV, and the electron affinities of insulators are thought to be of the order 0.5–1.5 eV,<sup>21</sup> this would put  $\phi_0$  in the range

2–3 eV or so. If the above conclusions are correct, the apparent anomalies observed by Hartman *et al.* are readily resolved. Their threshold photoresponse measurements unambiguously yield the metal-insulator barrier height  $\phi_0$ , while their thermal measurements yield the activation energy of the bulk-limited conductivity, that is,  $\frac{1}{2}(E_d + E_t)$  [see Eq. (6)]. Thus from their data we have  $\phi_0 = 1.77$  eV and  $\frac{1}{2}(E_d + E_t) = 0.43$  eV, which are in reasonable agreement with our computations. The fact that their extrapolated  $\log I$  versus  $V^{1/2}$  curves do not have a common intercept (Fig. 2 of Ref. 15) is also consistent with an electrode-to-bulk-limited conduction process, as shown in Fig. 6, although the order of the intercepts in Fig. 6 differs from the experimental observations. Finally, if we assume  $N_d$  and  $N_t$  to be, respectively, of the order  $10^{17}$  and  $10^{21}$   $\text{cm}^{-3}$ , and  $\mu$  to be  $1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ , it is easy to account for the relatively high bulk-limited currents observed.

It is worth noting that Stuart<sup>16</sup> has very recently shown that his data for highly doped SiO are quite compatible with the conduction process described here.

## 7. CONCLUSIONS

It has been shown that electrode-to-bulk-limited processes can occur in thin insulators which contain a high density of traps and donor centers. We have derived the  $I$ - $V$  characteristics for this process, and it turns out that at low voltages, where the process is determined by the contact, the  $I$ - $V$  characteristic is independent of thickness; at high voltages, where the process is bulk-limited, it is thickness-dependent. In the electrode-limited region the current rises extremely rapidly with voltage. In the bulk-limited region the current rises less rapidly with increasing voltage, and there is a linear relationship between  $\log I$  and  $V^{1/2}$ ; the slope of this curve depends on the nature of the defect structure of the insulator. The theoretical  $I$ - $V$  curves are shown to be compatible with existing and new data on SiO films, from which it has been possible to determine information about the band structure of these films. We note here, however, that a more complicated system of donors and traps can exist in insulators; there is also the possibility of the existence of acceptor, and hence compensating, centers.

## ACKNOWLEDGMENTS

The author is grateful to Dr. S. R. Pollack of the University of Pennsylvania for stimulating discussions, and to R. R. Verderber and M. Stuart of Standard Telecommunication Laboratories for helpful criticism of the manuscript.

<sup>19</sup> We are also of the opinion that the origin of the donor center could be an oxygen vacancy in the SiO; such vacancies most certainly abound in such a film, acting as fairly shallow  $F$  centers.

<sup>20</sup> J. H. Simpson, Proc. Roy. Soc. (London) **197**, 269 (1949).

<sup>21</sup> The electron affinity of SiO<sub>2</sub> has been measured by A. M. Goodman and J. J. O'Neill, Jr. [J. Appl. Phys. **37**, 3580 (1966)], to be 1.0 eV, and while we cannot directly accept this value for SiO, it is probably quite close.