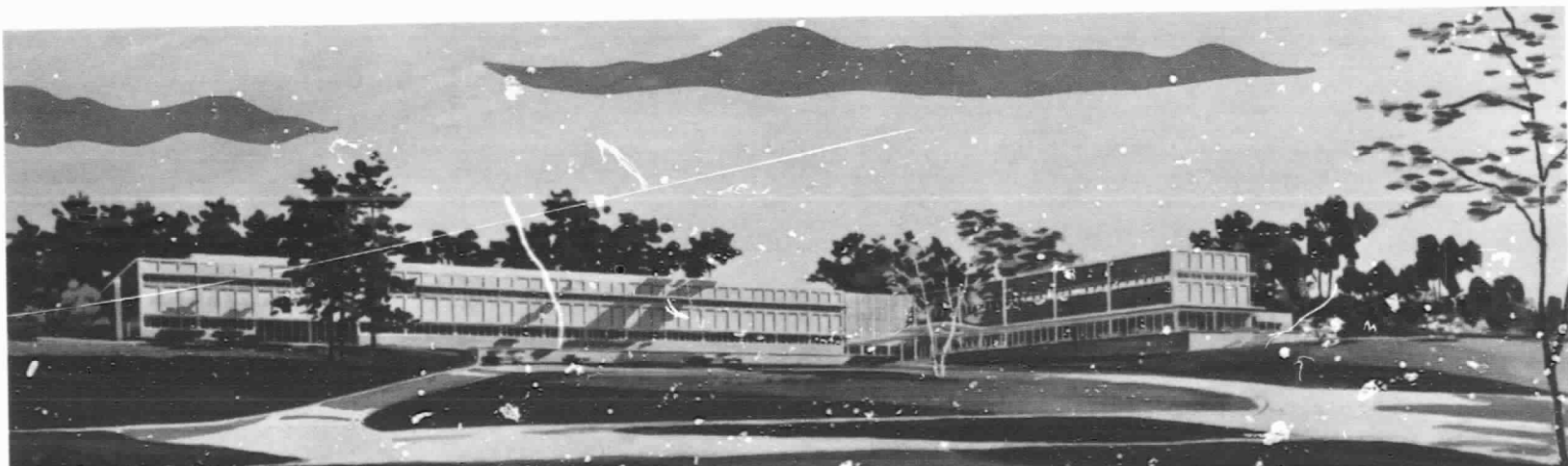


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I. INTRODUCTION

This report discusses the conduction mechanisms in the insulator structure of the MI_2I_1S memory device and develops the equations necessary to describe the transient behavior of the device, including the effect of the semiconductor space charge layer. The existence of a space charge in the silicon has been clearly evidenced in earlier reports and, as such, requires a quantitative account. Since the silicon space charge is sensitive to radiation in both the infrared and visible spectra, the memory device can then be utilized as a light sensor.

From the analysis of the conduction mechanisms in the insulator structure, a model is proposed that accounts for the storage of both positive and negative charge. This is accomplished by considering the effects of electronic traps quantitatively. Both the density of traps and their depth have a distinct influence on the charging characteristics.

II. ANALYSIS OF CONDUCTION MECHANISMS IN THE MI_2I_1S MEMORY DEVICE

A. Introductory Remarks

The analysis to be presented will consider insulator structures that consist of a layer of silicon nitride, approximately 1000 Å thick, which have been pyrolytically deposited on either a thin insitu silicon oxide layer or directly on an "oxide-free" silicon surface. The "oxide-free" surface was achieved by exposing the silicon surface to either hydrogen or ammonia at 1250°C prior to the deposition of silicon nitride. This device structure has already been studied in some detail and the results have been reported in earlier correspondence.

It has been shown that these memory device structures store charge as a result of the presence of two different conduction mechanisms. One of these mechanisms is inherent to the silicon nitride, i.e., Poole-Frenkel, and the other is a silicon-silicon nitride interface controlled mechanism. In order to determine the nature of the interface conduction a method was developed that allowed for its calculation. The conduction characteristic so derived was found to correspond to a Fowler-Nordheim tunneling equation. During a charging pulse this conduction mechanism transfers charge at a greater rate than that of the bulk silicon nitride. This results in a charge accumulation in the region that is defined by the boundary between the two conduction mechanisms. In the course of this investigation it was anticipated that if a tunneling mechanism was to describe the process of transferring electrons into and out of the silicon nitride, then the corresponding energy barriers should be different. This was found to be the case. When electrons are being transferred into the nitride the energy barrier is that created from the difference between the conduction band of silicon and that of the adjacent insulator. Whereas, when electrons are being transferred from electronic traps in the nitride into the silicon, the energy barrier is essentially that of the electronic trap depth.

All of the above has essentially been confirmed experimentally. However, there have been several experimental observations that do not fit into a simple interpretation of these basic conduction mechanisms. These observations include a polarity dependence on both the static current vs field characteristics and the location of the charge center in the silicon nitride. Activation energy data derived from current vs temperature measurements indicate the presence of either two or three dominant electronic trap levels. Most of the devices measured indicate the presence of two trap levels. When this result is then combined with a tunneling conduction law, a single

energy barrier interpretation is not possible. If both levels are appreciably filled prior to the transfer of electrons from these traps into the conduction band of the silicon, then the energy barrier, derived from the conduction characteristic will be only an effective barrier since tunneling from both levels is possible. The density of such levels and their occupancy when neutral do play an important role in governing some of the characteristics of the stored charge as to its rate of transfer, magnitude, and persistence.

In the following sections an attempt will be made to relate these experimental observations to some of the microscopic properties of the insulator structure.

B. Experimental Observations

1. Polarity Dependence of Static I-V Curves

As mentioned above, a polarity dependence was observed in the static current-voltage characteristics for most of the device structures measured. A typical characteristic is shown in Fig. 1. However, in other device structures either very little or no such polarity dependence was found to exist. This was especially the case when the silicon nitride was silicon rich. If such an observation was the result of rectifying contacts, then there would be no significant difference between the measured characteristics of silicon nitride and silicon-rich silicon nitride. Since charge is being stored during such static measurements, then it is possible for differences to exist in the distributions of such charges that could account for a polarity dependence in these static I-V curves. Of course, this would also have to be related to variations in the density of electronic traps as manifested by changes in the stoichiometry of the silicon nitride.

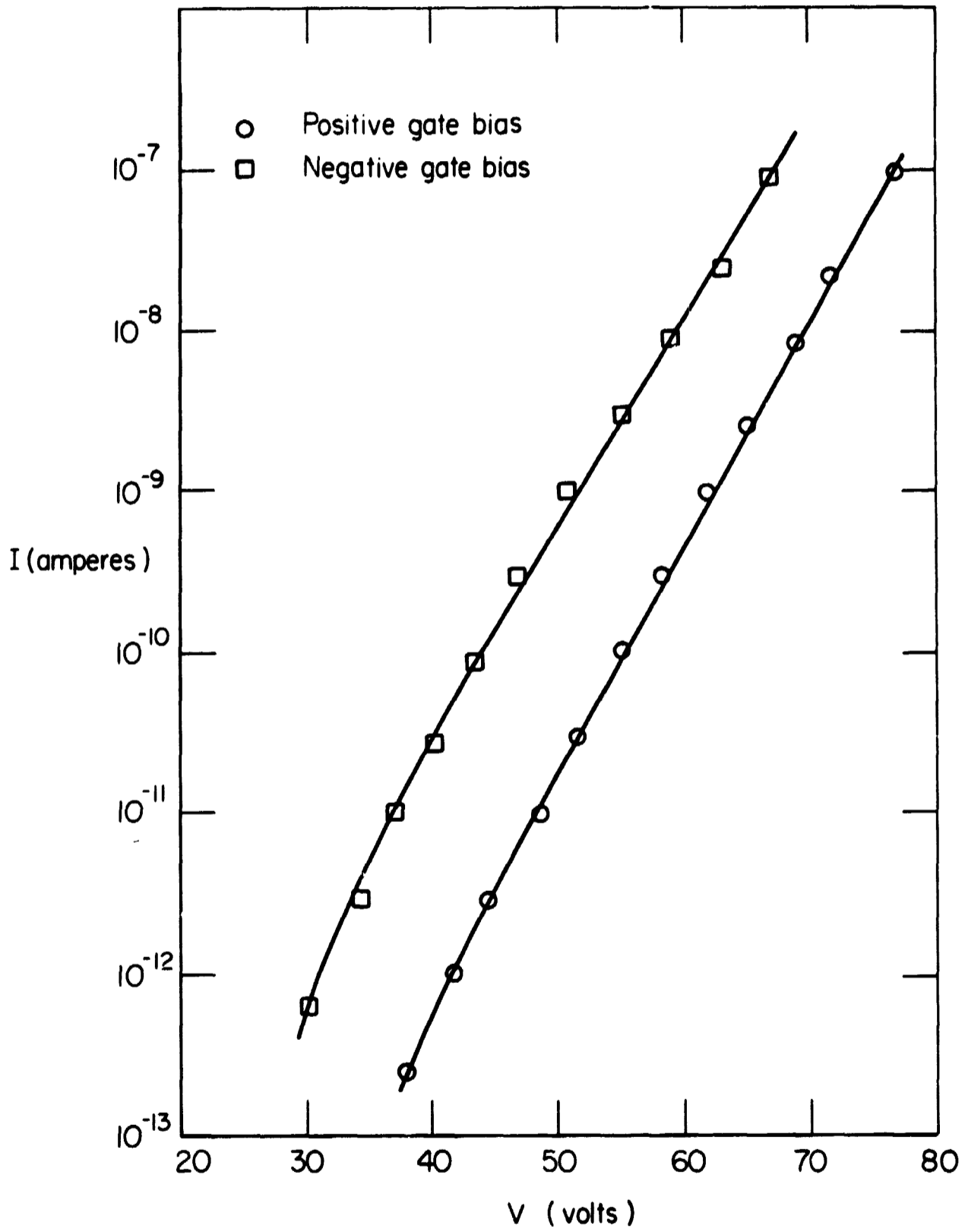


FIG. 1 Polarity dependence of static current-voltage characteristic.

2. Position of Stored Charge

The location of the center of stored charge was determined with the use of the analog computer mentioned in previous reports. Depending on the device being investigated, there were wide variations in these results. Differences were also observed depending on whether the device was storing positive or negative charge. The differences that were the most pronounced were in the storage of positive charge. Assuming an electron conduction model, then the removal of electrons from the nitride occurred over widely varying distances. Centers of positive charge were determined to range from 50 Å to 300 Å depending on the device being measured. For negative charge storage, such centers never exceeded 100 Å. The location of stored negative charge was not always possible to determine. This was the result of a pronounced relaxation. It appears that for the storage of electrons to be effective there must be available unfilled electron traps, in which electrons can be held for an extended period of time. This does not preclude the existence of a two-conductivity model that can sustain a large discontinuity in displacement vectors under the application of an external field. Under the assumption of an interface tunneling model the primary requirements are barrier height, width, and availability of states. Tunneling can therefore take place between the conduction bands of the silicon and the silicon nitride. With the absence of an appreciable number of electron traps, then this charge would have to reside in the conduction band of silicon nitride. When the sustaining field is removed, this charge would then relax via a conduction mechanism not limited by the capture and reemission of electrons from trapping centers.

The fact that a center of stored negative charge was determinable in some devices indicates that a relatively large density of unfilled electron

traps exists either at the interface between an insitu oxide layer and the silicon nitride or in the bulk of the silicon nitride.

3. Activation Energy Measurements

An indication of the various trap levels that exist in the nitride can be obtained from the slope of a current vs reciprocal temperature plot. Shown in Figs. 2 and 3 are the results of such plots for two separate devices. For the device shown in Fig. 2 there was no appreciable polarity dependence on its current-voltage characteristic, whereas for the device shown in Fig. 3 a significant polarity dependence was observed.

The activation energies obtained from these slopes agree relatively well with the equivalent barrier energies involved in the tunneling of electrons from traps in the nitride to the silicon conduction band. For the device shown in Fig. 2 a barrier energy of 0.29 eV was calculated. This corresponds to the 0.24 eV trap level. The probability of tunneling from the 0.84 eV level is relatively low, and is therefore not greatly involved in the interface conduction process. The 0.08 eV level is apparently empty in its neutral state and, therefore, does not contribute carriers for electron transfer.

As mentioned, the device shown in Fig. 3 was polarity dependent in its static I-V characteristic. This device also displayed a positive charge center located approximately 300 Å from the silicon interface. Since the activation energy data do not give a quantitative measure of the trap density, it can only be inferred that it is low. The tunneling barrier energy calculated for this device was 0.5 eV, and thus agrees relatively well with the 0.4 eV level indicated in the figure.

C. Analysis

1. Model for Electron Tunneling

A model for the process of tunneling electrons both into and out of

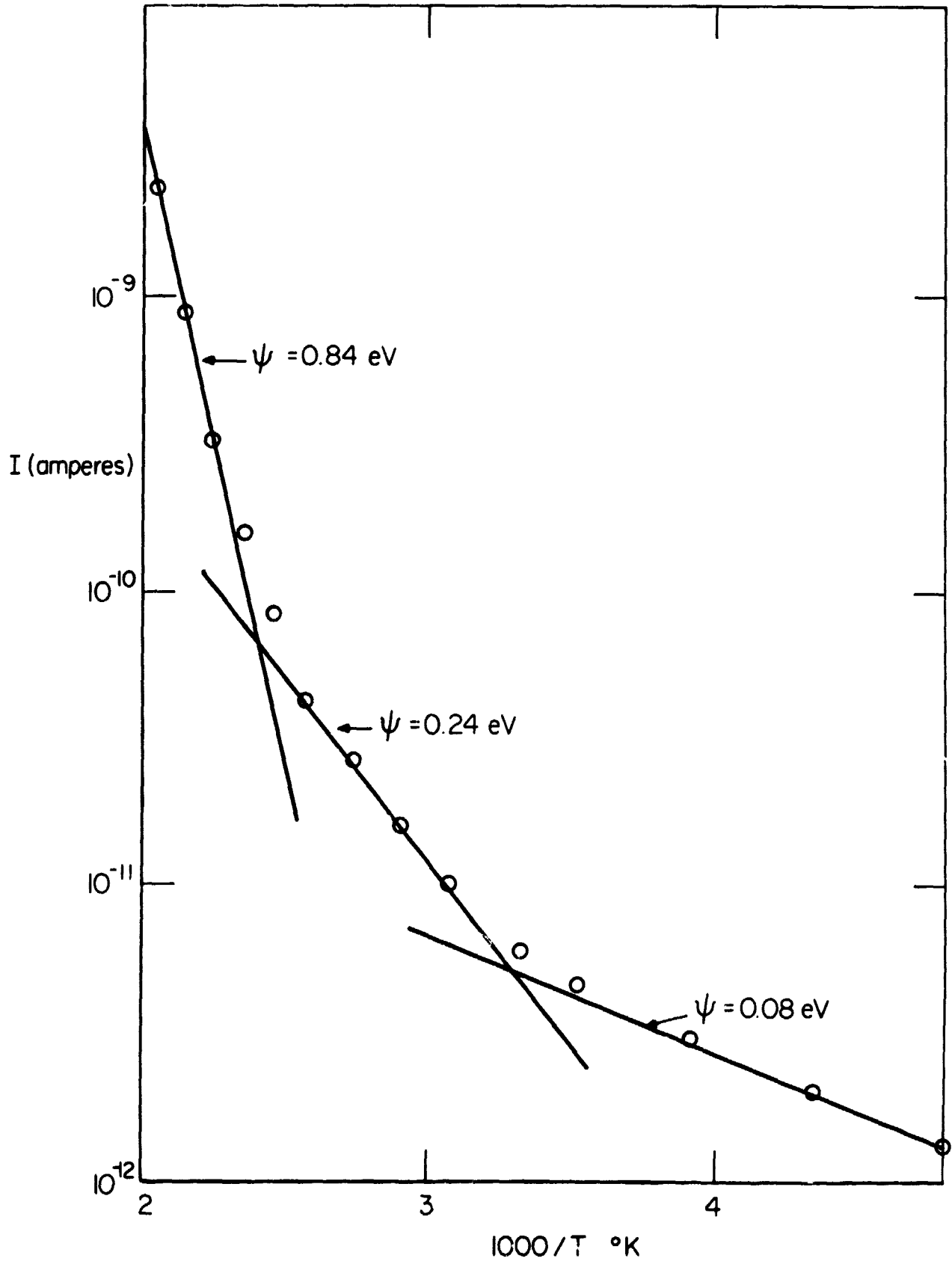


FIG. 2 Measurement of trap activation energy.

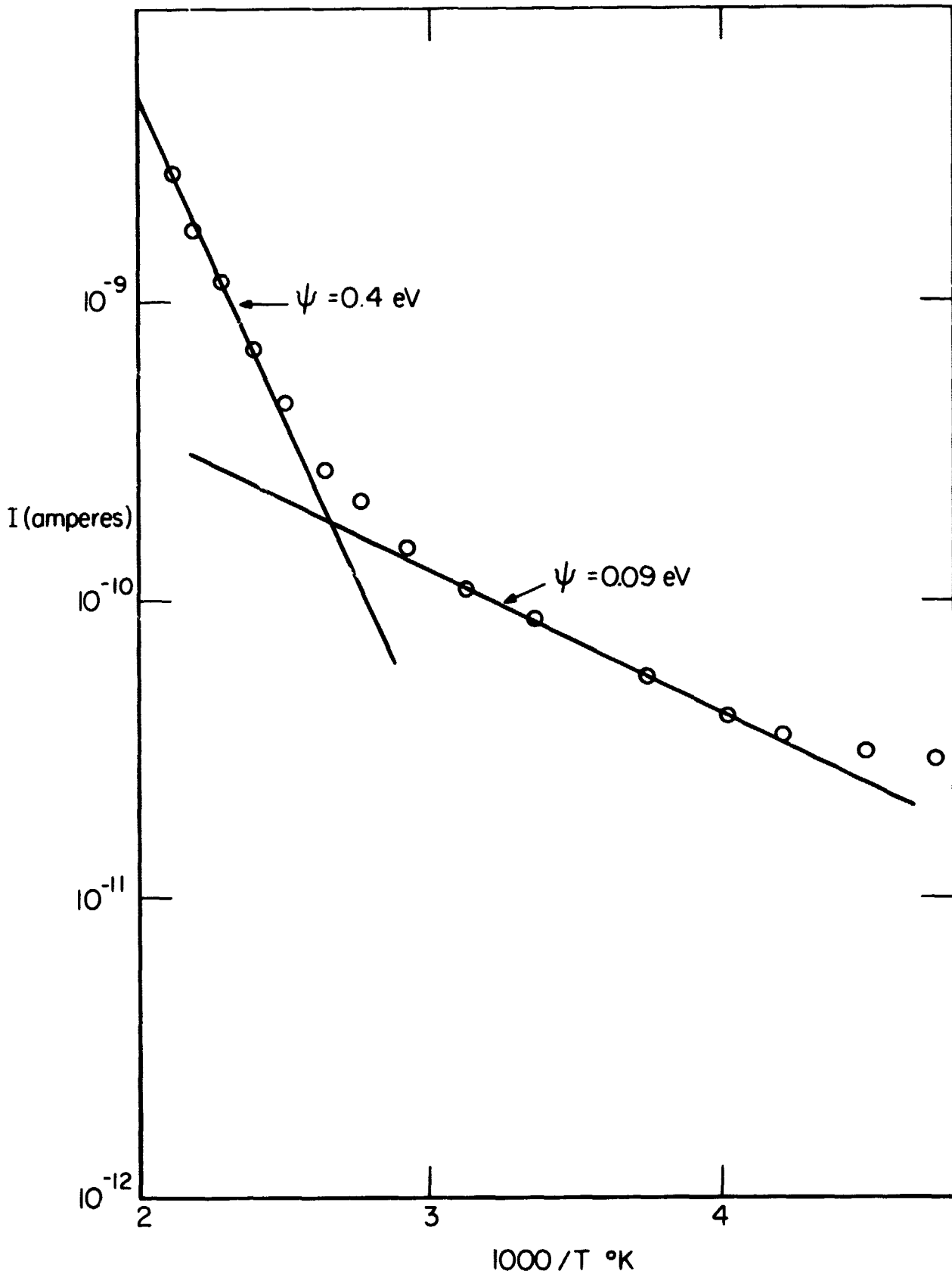
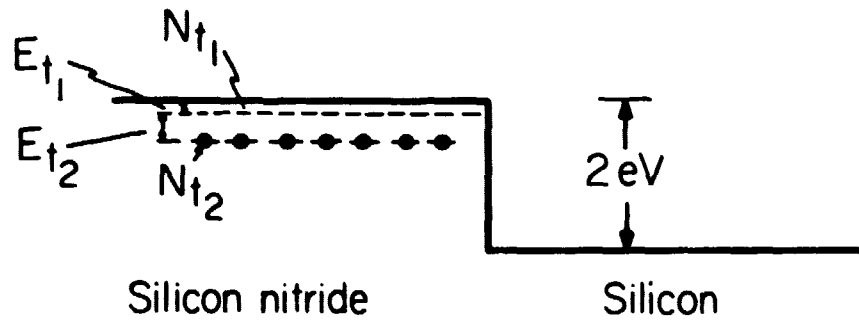


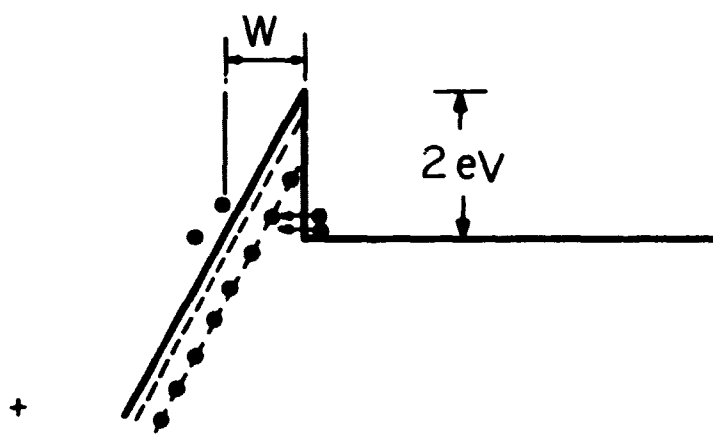
FIG. 3 Measurement of trap activation energy.

the nitride through an interface barrier must be capable of accounting for the directional difference in calculated energy barriers, charge distributions, and variations in both the trap depth and density. For this, consider the simplified energy band representation shown in Fig. 4a. Between the conduction band of silicon and that of silicon nitride there is an energy difference of approximately 2 eV. Two trap levels have been shown in the silicon nitride. The level at energy E_{t2} has been assumed to be essentially filled. This would correspond to the 0.24 eV activation energy in Fig. 2 or to the 0.4 eV level in Fig. 3. The existence of a set of relatively filled, neutral electron traps is a requirement for the Poole-Frenkel conduction mechanism. This model is therefore reinforced by both the observed conduction law and the activation energy plots of Figs. 2 and 3. The shallow trap, E_{t1} , shown in Fig. 4a corresponds to the activation energies 0.08 eV and 0.09 eV shown in Figs. 2 and 3, respectively. From reports in the literature this low activation energy has often been attributed to the result of a hopping mechanism where this energy is associated with a mobility dependence. However, a hopping mechanism should display an ohmic conduction characteristic. This is not substantiated by the measurements of Fig. 5. In this figure the current-voltage characteristics were recorded at temperatures ranging from 150°C to -50°C. If hopping were to exist at -50°C, then one should not observe the recorded Poole-Frenkel conduction, i.e. $I \propto \epsilon^{a\sqrt{V}}$. It is thus inferred that field-aided emission is occurring from these shallow traps at this temperature to account for the observed conduction law.

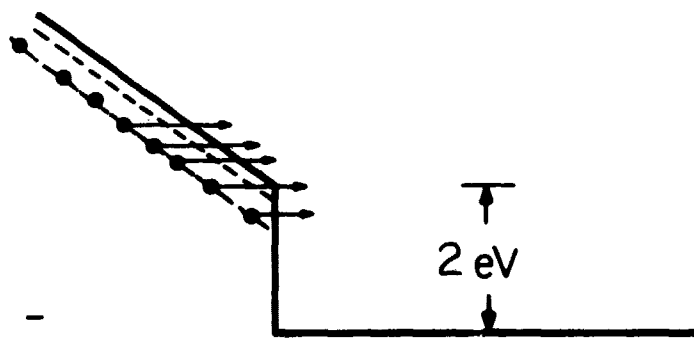
Now consider the application of a positive gate potential. This produces the effect shown in Fig. 4b. In this figure space charge effects have been neglected. As can be seen in the figure, when the barrier width, w , has been reduced significantly ($\approx 50 \text{ \AA}$), then an appreciable tunnel current can be



(a)



(b)



(c)

FIG. 4 Simplified energy band diagram between silicon and silicon nitride with various bias conditions.

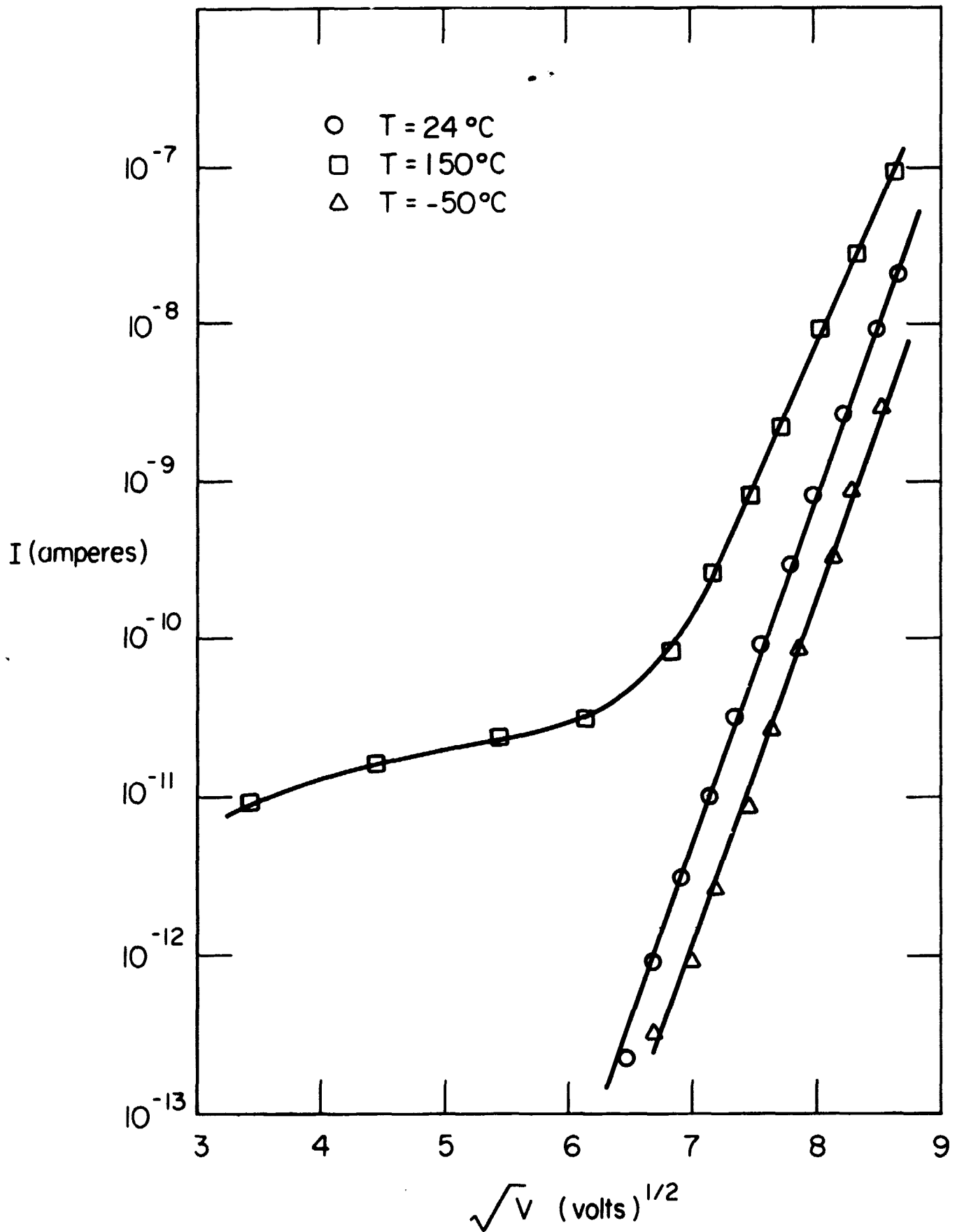


FIG. 5 I vs \sqrt{V} at various temperatures.

sustained. The tunneling can occur directly into the silicon nitride conduction band or into the shallow traps that are empty. An appreciable charge can be held in the conduction band, provided the conductivity of the nitride is lower than that of the tunneling interface. When the sustaining voltage is removed, then the persistence of this stored charge will be quite dependent on the density of these shallow traps. If the trap density is high, then the charge will be accommodated by the traps and decay via a trap limited conduction process. Whereas, if the trap density is low, then decay will occur primarily via an ohmic trap-filled-limit law. This is essentially a "free" carrier process. These two conditions are exemplified by the capacitance vs voltage traces of Fig. 6. Note that in Fig. 6a the negative stored charge has completely dissipated with a few seconds after removal of the sustaining voltage. This is not the case for the device shown in Fig. 6b.

When a negative gate bias is applied the band diagram of Fig. 4c applies. Electrons can then tunnel directly into the conduction band of the silicon nitride and then enter the conduction band of the silicon. The tunnel barrier for this case is the trap depth. The extent to which charge is uncovered in the silicon is determined by the constraints of the system. Such constraints consist of the density of filled electron traps that are available for tunneling, the depth of such traps, and the conductivity of the silicon nitride. Some of these constraints are interrelated, such as trap density and nitride conductivity. In general, a greater trap density implies a more conductive nitride. The extent of the uncovered charge can have a profound effect on the measured static current-voltage characteristic. This can be illustrated by the following analysis and the sketch shown in Fig. 7. This figure depicts the result of removing electrons from traps in the silicon nitride. A uniform density of traps, N_t , of which

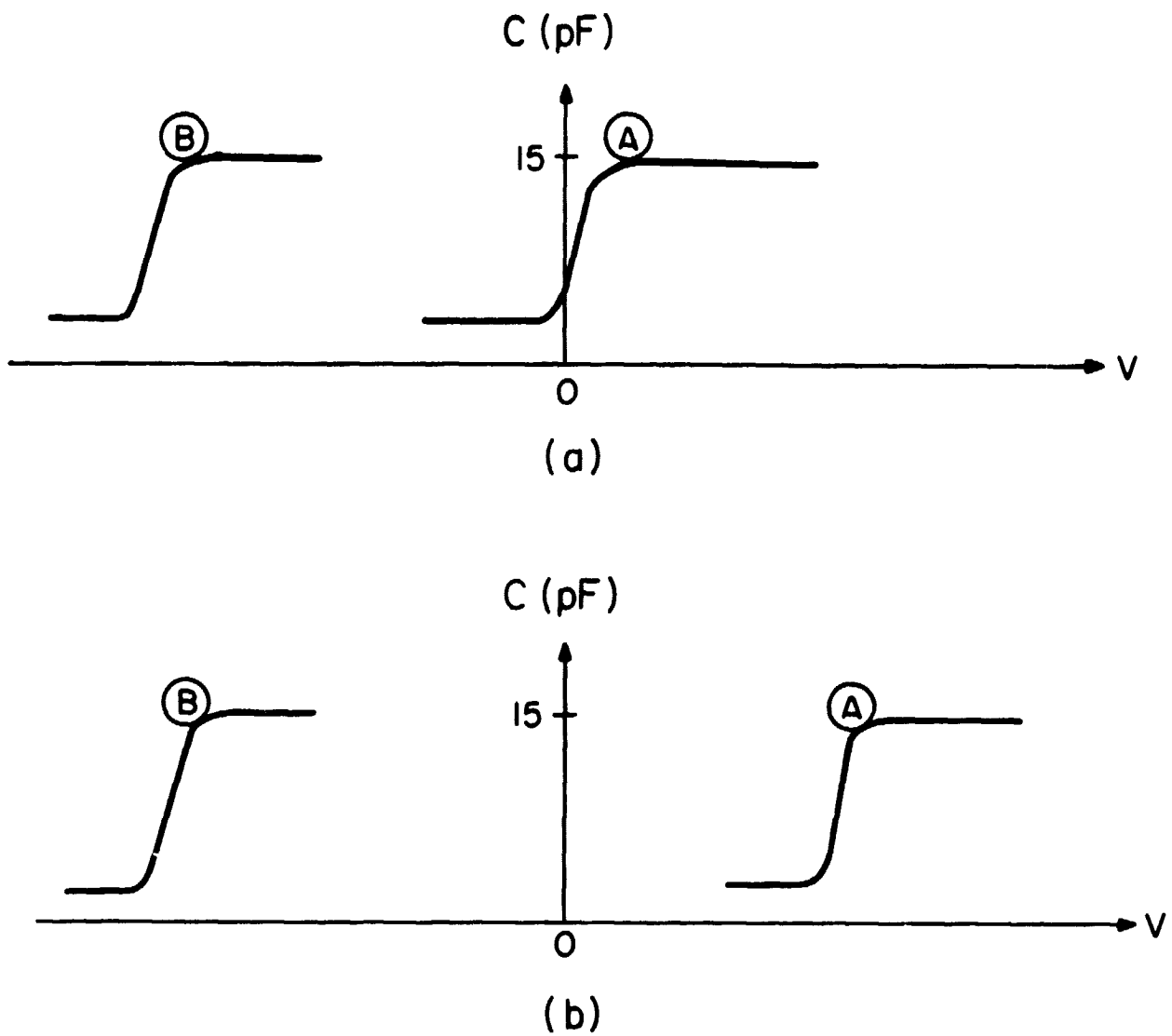


FIG. 6 (a) Device with rapid decay of stored electrons.
 (b) Device without rapid decay of stored electrons.
 Curve A: gate bias held at +60 V for 10 minutes
 and then removed for several seconds
 prior to obtaining trace.
 Curve B: gate bias held at -60 V for 10 minutes
 and then removed for several seconds
 prior to obtaining trace.

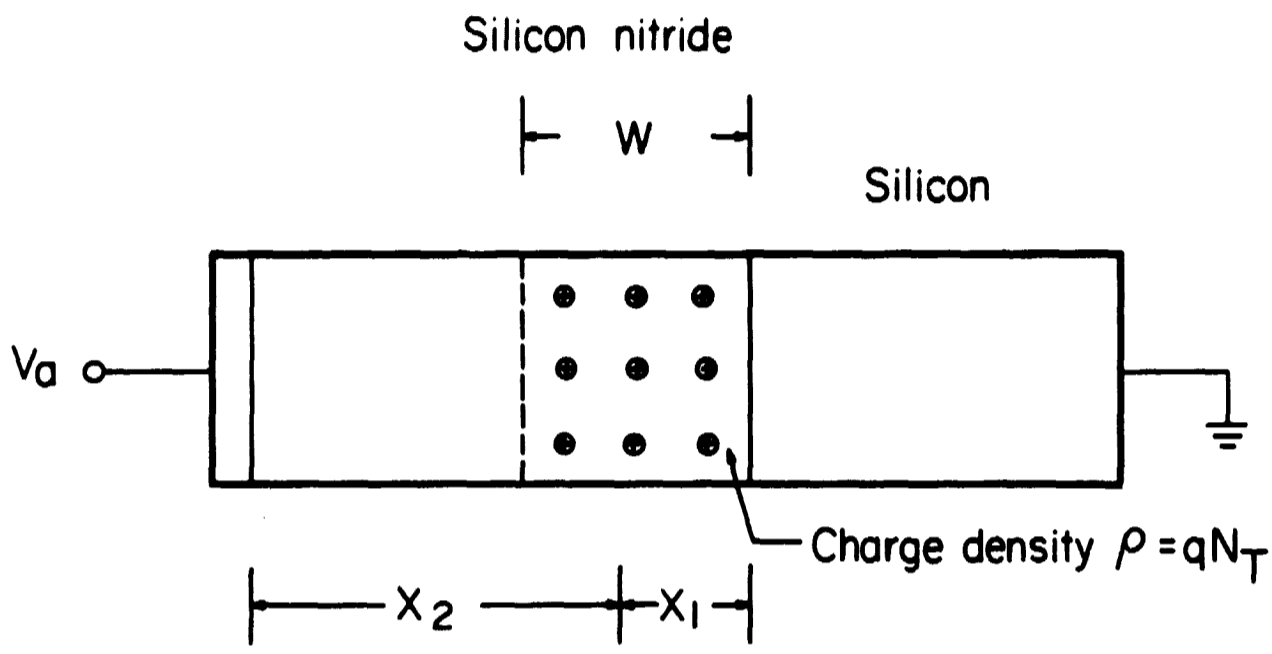


FIG. 7 Uncovered charge produced by the tunneling of electrons from electron traps in the silicon nitride.

N_T are uncovered to a distance w in the silicon nitride, has been assumed. The charge density, ρ , is assumed to be related to the charged trap density through the electronic charge q , i.e.

$$\rho = qN_T \quad (1)$$

The effect this uniform charge density has on the silicon can be made equivalent to that of a sheet of charge, σ , acting a distance x_1 from the surface of the silicon, where

$$x_1 = \frac{w}{2}$$

and

$$\sigma = qN_T w$$

Now the nitride can be described as an MI_2I_1S structure where x_2 is the length of I_2 and x_1 is the length of I_1 . By using the vector form of Ohm's law and Gauss's law, the fields E_1 and E_2 in layers I_1 and I_2 , respectively, may be expressed in terms of the constants of the system, V_a and σ . These are

$$E_1 = \frac{\epsilon_2 V_a + \sigma x_2}{\epsilon_2 x_1 + \epsilon_1 x_2} \quad (3)$$

and

$$E_2 = \frac{\epsilon_1 V_a - \sigma x_1}{\epsilon_2 x_1 + \epsilon_1 x_2} \quad (4)$$

If w is much greater than any insitu oxide layer on the surface of the silicon, then $\epsilon_1 = \epsilon_2 = \epsilon$. Thus, after substituting $\sigma = qN_T w$ and setting the permittivities equal, we have

$$E_1 = \frac{\epsilon V_a + qN_T w x_2}{\epsilon (x_1 + x_2)} \quad (5)$$

$$E_2 = \frac{\epsilon V_a - qN_T w x_1}{\epsilon (x_1 + x_2)} \quad (6)$$

The stored charge in the silicon nitride may be expressed in terms of the flatband voltage. This is the voltage that must be applied to the gate to force the field at the surface of the silicon, E_1 , to zero. This is given by

$$V_{FB} = -\frac{\sigma x_2}{\epsilon} = -\frac{qN_T w x_2}{\epsilon} \quad (7)$$

Therefore, Eqs. (5) and (6) become

$$E_1 = \frac{V_a - V_{FB}}{x_1 + x_2} \quad (8)$$

$$E_2 = \frac{V_a + \frac{x_1}{x_2} V_{FB}}{x_1 + x_2} \quad (9)$$

As can be seen by Eqs. (8) and (9), E_1 is not affected by the depth of penetration of the uncovered charge, but E_2 is enhanced as x_1 increases.

From measurements using the analog computer, the center of stored positive charge does not increase significantly with the quantity of charge. The primary change that does occur is in the number of electrons that can tunnel from the total of N_t filled levels over a relatively fixed depth, w , in the nitride. The distance w is probably dependent on the density of such traps and the lifetime of the electrons in the conduction band of the nitride. These two quantities are obviously interrelated. A higher trap density will result in a small w , but also a reduced carrier lifetime.

As an example, consider the device shown in Fig. 1. For various static negative gate voltages the corresponding changes in the flatband voltage were recorded along with the corresponding current. These are shown in the first three columns of Table I. The results from the analog computer indicate that the center of this stored charge is stored approximately 300 Å away from the silicon

surface. The overall thickness of the nitride layer is 1000 Å. Therefore, we have $x_1 = 300$ Å and $x_2 = 700$ Å. With this information, Eq. 9 becomes

$$E_2 = \frac{V_a + 0.43 V_{FB}}{10^{-7}} \text{ volts/meter} \quad (10)$$

Using this equation the actual field in the I_2 layer can be calculated. This is shown in the fourth column of Table I. The resulting I vs E_2 characteristic is plotted in Fig. 8.

In order to have something to compare this with one must have the true I- E_2 characteristic. This is not possible because of the influence of stored charge. However, one may take the I-V characteristic obtained with a positive gate bias and construct an I- E_2 characteristic equivalent to that obtained with the negative gate bias. For this calculation the center of the charge was determined from the analog computer to be approximately 100 Å. Therefore, using Eq. (9), the expression of E_2 becomes

$$E_2 = \frac{V_a + 0.11 V_{FB}}{10^{-7}} \text{ volts/meter} \quad (11)$$

Using the corresponding measured values of ΔV_{FB} the results shown in Table II can be obtained. The I vs E_2 curve so derived is sketched in Fig. 8. Considering the simplifications, the agreement is relatively good.

C. Conclusions

A model has been presented that accounts for the accumulation of charge of either polarity in the gate dielectric of the memory device. The only requirement for this charge storage to occur is that two distinct conduction mechanisms exist that have an appreciable difference in their charge transfer rates. The effect that an insitu oxide layer has on the interface

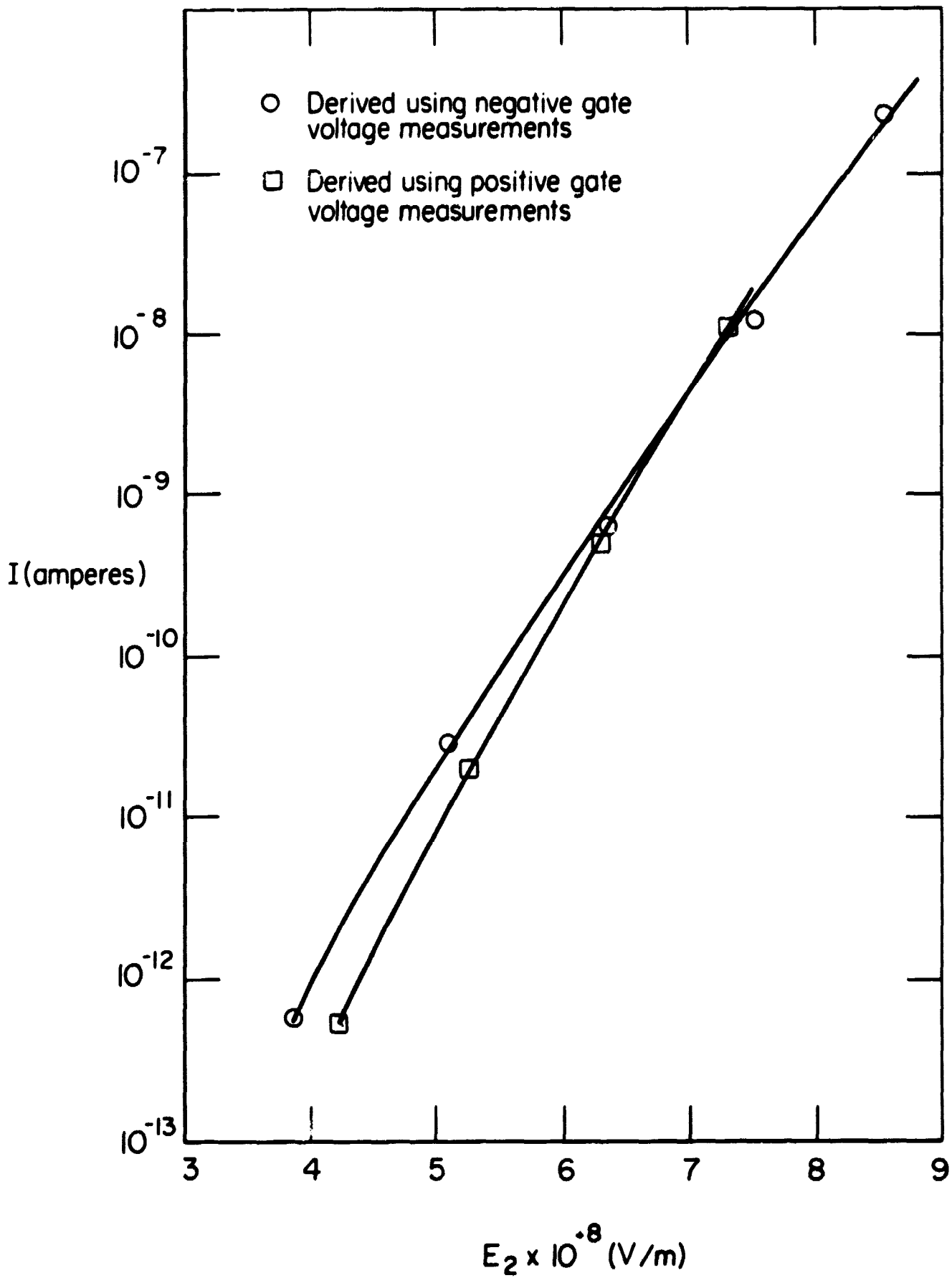


FIG. 9 Derived I- E_2 characteristic which accounts for the influence of stored charge.

Table I

Calculated Field in the Nitride for a Negative Gate Bias

V_a (volts)	ΔV_{FB} (volts)	I (amperes)	E_2 (V/m)
-20	-12.7		
-30	-20.0	6.0×10^{-13}	3.86×10^8
-40	-25.2	2.9×10^{-11}	5.1×10^8
-50	-31.8	6.3×10^{-10}	6.36×10^8
-60	-35.5	1.2×10^{-8}	7.53×10^8
-70	-36.3	2.2×10^{-7}	8.56×10^8

Table II

Calculated Field in the Nitride for a Positive Gate Bias

V_a (volts)	ΔV_{FB} (volts)	I (amperes)	E_2 (V/m)
+30	+15		
+40	+21	5.3×10^{-13}	4.23×10^8
+50	+24	2×10^{-11}	5.26×10^8
+60	+26	5×10^{-10}	6.29×10^8
+70	+27	1.1×10^{-8}	7.3×10^8

conduction characteristic is not well defined. If any effect does exist it would appear that its influence would be on the threshold required to transfer electrons into the nitride. The basic mechanism for electron transfer from the gate dielectric into the silicon appears to be that of tunneling from traps in the nitride. The extent of the uncovered charge is dependent on the trap density and the carrier lifetime. An estimate of the charged trap density can be made using Poisson's equation and the charge width w . This yields a trap density of approximately 10^{18} per cm^3 . For devices showing no polarity dependence and, hence, small charge width w , the approximate trap density is in excess of 10^{19} per cm^3 .

In future work, attempts will be made to construct a controlled interface (e.g., varying oxide thicknesses) and prescribed trap energies and densities.

III. TRANSIENT BEHAVIOR OF $\text{MI}_2\text{I}_1\text{S}$ DEVICE, INCLUDING EFFECT OF SILICON SPACE CHARGE

In this discussion we will derive the formal relationships that describe the transient current flow and charge accumulation in an $\text{MI}_2\text{I}_1\text{S}$ memory system. The influence of the semiconductor space charge region, which can appear when a negative polarity voltage is applied to the metal electrode of an n-type structure and when a positive polarity voltage is applied to the metal electrode of a p-type structure, will be taken into account. A knowledge of the space charge behavior is useful for several reasons. First, it can be influenced by radiation in the infrared and visible regions so that the memory function becomes light sensitive, with obvious application as an optical storage element. Second, in the ordinary electrical memory mode there are circumstances in which the space charge effects cannot be eliminated, and a knowledge of its behavior is necessary to predict the device performance. Finally, the mutual interaction between the semiconductor space charge and

the charge transported into the insulator results in the possibility of new schemes of controlling current flow in a thin film insulator.

Figure 9 shows schematically the MI_2I_1S configuration. A space charge of width w is shown in the semiconductor. We must determine under what conditions this space charge region exists and what effect it has on the charging behavior of the two-layer insulator storage element. When a voltage V_a is applied to the structure, there are instantaneous fields E_1 , E_2 and E_s in the bulk regions and the instantaneous current densities $j_1(E_1)$, $j_2(E_2)$, and $j_s(E_s)$ associated with them. The several charge densities are defined as follows:

- σ_I - the charge per unit area accumulated at the I_2-I_1 interface.
- σ_{ss} the charge per unit area at the I_1 -Si interface due to noncommunicating interface states (no voltage dependence); voltage dependent states are ignored in this treatment;
- σ_s - the total charge per unit area due to unneutralized donors or acceptors in the space charge region
- σ_m - charge per unit area due to accumulated minority carriers at the Si- I_1 interface.

The problem now is to derive expressions for

$$E_1 = f_1(V_a, \sigma)$$

$$E_2 = f_2(V_a, \sigma)$$

$$E_s = f_3(V_a, \sigma)$$

where $\sigma = \sigma_I + \sigma_{ss} + \sigma_s + \sigma_m$. We note that

$$V_a = V_I + V_s \tag{12}$$

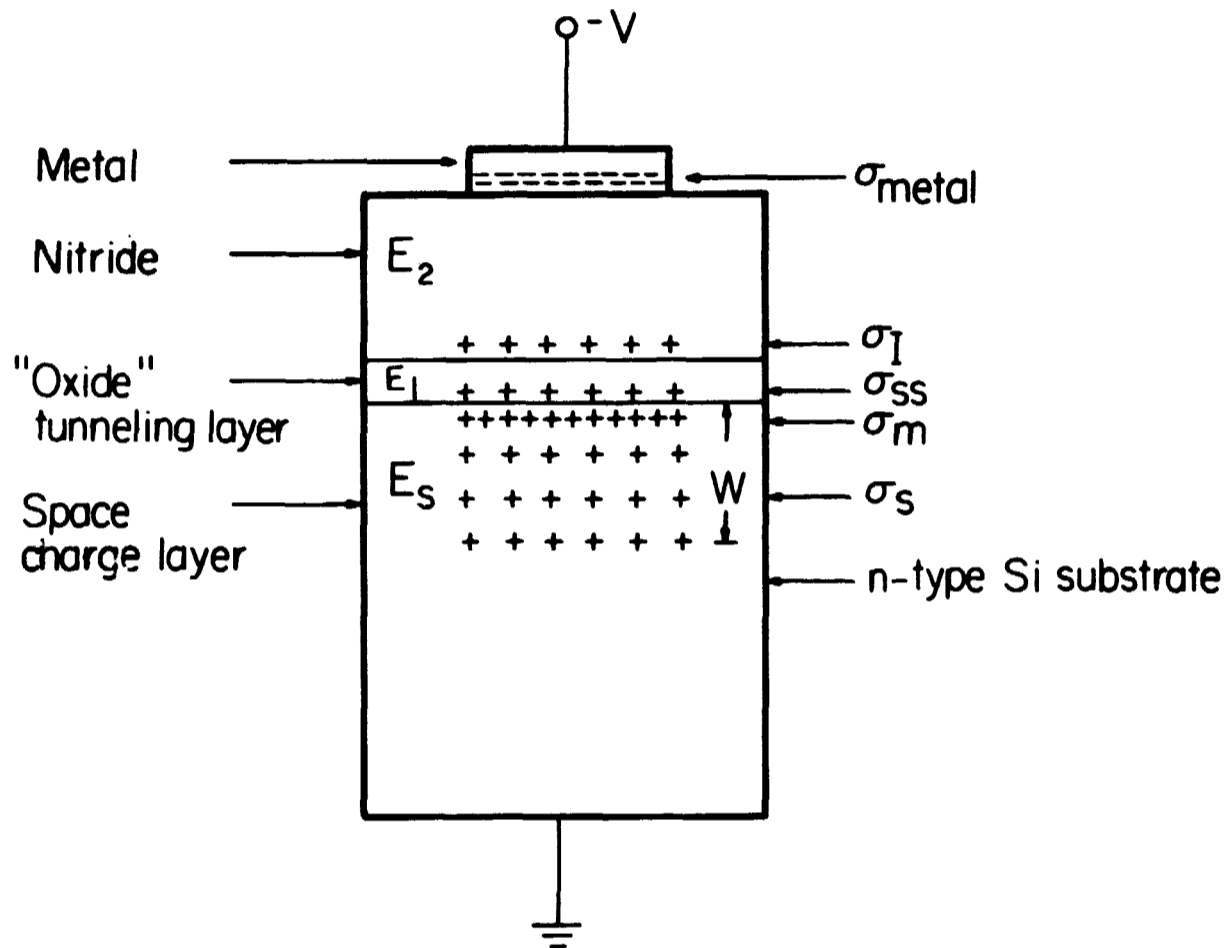


FIG. 9 Schematic representation of MI_2I_1S device.

where V_I is the voltage drop across the total insulator thickness and V_s is the voltage drop across the space charge region. Considering only the double insulator layer, we can write

$$E_1 x + E_2 (d-x) = V_I$$

$$E_1 \epsilon_1 - E_2 \epsilon_2 = \sigma_I$$

Solving for E_1 and E_2 , we obtain

$$E_1 = \frac{\epsilon_2 V_I - \sigma_I (d-x)}{\epsilon_2 x + (d-x)\epsilon_1}$$

$$E_2 = \frac{\epsilon_1 V_I + \sigma_I x}{\epsilon_2 x + (d-x)\epsilon_1}$$

The discussion will be limited to the important practical case where $\frac{x}{d} \ll 1$.

Thus

$$E_1 = \frac{\epsilon_2}{\epsilon_1 d} (V_I - \sigma_I d) \quad (13)$$

$$E_2 = V_I/d \quad (14)$$

We must now express V_I in terms of V_a through the appropriate solution to Poisson's equation. Physically, the transient situation involves initially forming a large space charge region (by the sudden application of V_a) with a virtual absence of majority and minority carriers. Minority carriers, however, are generated in the space charge region and can form an inversion layer which will increase in density with time, eventually reaching equilibrium. The equilibrium density of total charge in the silicon, $\sigma_s + \sigma_m$, and the resulting space charge layer potential, V_s , can only be obtained by solving Poisson's equation for the total semiconductor charge:

$$\frac{d^2 V_s}{dx^2} = -\rho/\epsilon_s = -\frac{q}{\epsilon_s} (p - n - N_A). \quad (15)$$

However, in the transient case, we consider the solution involving only the fixed charge centers in the semiconductor

$$\frac{d^2 V_s}{dx^2} = -\rho/\epsilon_s = \frac{q}{\epsilon_s} (N_A). \quad (16)$$

It follows that $E_s = \left(\frac{qN_A}{\epsilon_s} \right) w$ (17)

$$V_s = \frac{qN_A}{2\epsilon_s} w^2 \quad (18)$$

$$Q_s = -qN_A w = - (2q\epsilon_s N_A)^{1/2} V_s^{1/2} \quad (19)$$

Using these equations, plus the equation for the conservation of charge,

$$\sigma = \sigma_I + \sigma_{ss} + \sigma_s + \sigma_m$$

it is possible to derive expression for the fields E_1 , E_2 , and E_s :

$$E_s = \frac{1}{\epsilon_s} \left[\sqrt{2 G^{1/2} (VaCo - \sigma_{ss} - \sigma_I - \sigma_m + \frac{1}{2} G)^{1/2} - G} \right] \quad (20)$$

$$E_1 = \frac{1}{\epsilon_s} \left[\sqrt{2 G^{1/2} (VaCo - \sigma_{ss} - \sigma_I - \sigma_m + \frac{1}{2} G)^{1/2} + \sigma_m + \sigma_{ss} - G} \right] \quad (21)$$

$$E_2 = \frac{1}{\epsilon_2} \left[\sqrt{2 G^{1/2} (VaCo - \sigma_{ss} - \sigma_I - \sigma_m + \frac{1}{2} G)^{1/2} + \sigma_m + \sigma_{ss} + \sigma_I - G} \right] \quad (22)$$

where $G = \frac{q\epsilon_s N_A}{Co}$.

Now the conditions for current continuity form the basis for the charging equations:

$$\epsilon_1 \frac{\partial E_1}{\partial t} + j_1(E_1) = \epsilon_2 \frac{\partial E_2}{\partial t} + j_2(E_2) \quad (23)$$

$$\epsilon_1 \frac{\partial E_1}{\partial t} + j_1(E_1) = \epsilon_s \frac{\partial E_s}{\partial t} + j_s(E_s) \quad (24)$$

From Eq. (23) we obtain

$$dt = \frac{\epsilon_1 dE_1 - \epsilon_2 dE_2}{j_1(E_1) - j_2(E_2)} = \frac{d\sigma_I}{j_1(E_1) - j_2(E_2)} \quad (25)$$

or

$$t = \int \frac{d\sigma_I}{j_1(E_1) - j_2(E_2)}$$

and from Eq. (24) we obtain

$$dt = \frac{\epsilon_1 dE_1 - \epsilon_s dE_s}{j_s(E_s) - j_1(E_1)} = \frac{d\sigma_m}{j_s(E_s) - j_1(E_1)}$$

or

$$t = \int \frac{d\sigma_m}{j_s(E_s) - j_1(E_1)} \quad (26)$$

Thus Eqs. (25) and (26) must be solved simultaneously to provide the desired result, $\sigma_I = F(t)$. Equations (25) and (26) are coupled through Eqs. (20) - (22). It is interesting to note that Eq. (25) is just the time dependent charging solution when there is no space charge to consider. Equation (26) contains the space charge phenomena in the form of $j_s(E_s)$. This is the current relation for the silicon space charge region. Its magnitude, which depends on the recombination time, τ , determines the charging time in conjunction with Eq. (25).

In a future report the solution to Eqs. (25) and (26) will be presented along with experimental confirmation.

NEW TECHNOLOGY APPENDIX

After a diligent review of the work performed under this contract,
no new innovation, discovery, improvement or invention was made.