this material are located at 1.4 and 1.7 \( \mu \). Additionally, the IR absorption in Si containing high Li concentration was found to be due to intraband absorption by free carriers and is in general agreement with predictions of theory.\(^{29}\)

In samples containing both high Li and high O concentrations (\( \gtrsim 10^{17} \text{ cm}^{-3} \)), we can conclude that radiation-induced vibrational bands in the 700 \( \text{cm}^{-1} \)–1000 \( \text{cm}^{-1} \) frequency range (10–14.3 \( \mu \) wavelength range) must arise from defect complexes that consist of Li plus O atoms in addition to vacancies and/or interstitials.

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Fowler–Nordheim Tunneling into Thermally Grown SiO\(_2\)

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Electronic conduction in thermally grown SiO\(_2\) has been shown to be limited by Fowler–Nordheim emission, i.e., tunneling of electrons from the vicinity of the electrode Fermi level through the forbidden energy gap into the conduction band of the oxide. Fowler–Nordheim characteristics have been observed over more than five decades of current for emission from Si, Al, and Mg. If previously measured values of the barrier heights are used, the slopes of the Fowler–Nordheim characteristics (\( \log J/E^2 \) vs \( 1/E \)) imply values of the relative effective mass in the forbidden band of about 0.4. These values take into account corrections for image-force barrier lowering and for temperature effects. The absolute values of the currents are lower by a factor of five to ten than the theoretically expected values, probably due to trapping effects. The temperature dependence of the current was found to follow the theoretical curve from 80° to 420° K. However, an inconsistent relative effective mass of about 0.95 had to be assumed. These results are believed to provide the most complete examination of the Fowler–Nordheim-emission theory.

INTRODUCTION

Electrical conduction in thin insulating films has been the subject of numerous experimental investigations.\(^{1}\) The currents in such films can generally be classified as being either bulk limited or electrode limited. In most cases where a detailed study has been made, the conduction has been found to be bulk limited by one of several mechanisms. In organic films,\(^{2}\) space-charge-limited currents are commonly observed. In tantalum oxide\(^{3}\) and silicon nitride\(^{4}\) the currents are limited above room temperature by Schottky emission from traps (Poole–Frenkel effect) and at lower temperatures by field ionization of the same traps.

Because it has an extremely wide bandgap and consequently high-energy barriers at its electrodes, thermally grown silicon dioxide is more likely to show electrode-limited conduction than other insulators. In addition, bulk-limited mechanisms are less likely to play a role because of a low density of traps in the forbidden band\(^{5}\) and a relatively high electronic mobility in the conduction band.\(^{6}\) The energy-band diagram of a metal–silicon dioxide–silicon (MOS) structure, which can be inferred from photoemission\(^{7,8}\) and capacitance–voltage\(^{9}\) measurements, is illustrated in Fig. 1(a). (For the sake of simplicity the effects of image-force barrier lowering are not shown.) The barrier energy \( \Phi_0 \) from the silicon conduction band edge to the oxide conduction band has been determined to be 3.25 eV. The barrier for holes \( \Phi_M \) from the silicon valence-band edge to the oxide valence band is 3.8 eV. The barrier energy \( \Phi_M \) from the metal Fermi level to the oxide conduction band depends on the metal, and can be varied between 2.3 eV for magnesium and 4.2 eV for gold.

The energy-band diagram for the MOS structure with negative bias applied to the metal electrode is shown in Fig. 1(b). In the dark, and in the absence of a bulk limitation, the current in this case will be due either to Schottky emission of electrons over the barrier \( \Phi_M \), or to Fowler–Nordheim tunneling of electrons through the triangular barrier into the oxide conduction band. It can be argued\(^{10}\) that the latter mechanism

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\(^{10}\) E. L. Murphy and R. H. Good, Jr., Phys. Rev. 102, 1464 (1956).
should dominate at room temperature. (Emission of holes from the valence band of the silicon into the valence band of the oxide is also possible. However, because of the high barrier, \( \Phi_{\text{si}} = 3.8 \text{ eV} \), hole emission is not expected to occur, except with Au electrodes.)

Figure 1(c) shows the energy-band diagram corresponding to positive bias on the metal. Note that in this case the polarity is such that for a large applied bias, the silicon surface will be degenerate \( n \)-type regardless of the bulk doping. Hence the silicon can be treated at least qualitatively like a metal, and the current should be limited by Fowler–Nordheim tunneling from the vicinity of the silicon conduction band edge through the triangular barrier into the oxide conduction band. Note also that the voltage drop in the silicon is always less than the silicon bandgap, and hence for large applied voltages the oxide field is approximately the applied voltage divided by the oxide thickness.

![Energy-band diagram](image)

**Fig. 1.** Energy-band diagram of a metal–silicon dioxide–silicon structure (a) at zero bias; (b) with large negative bias on the metal electrode; (c) with large positive bias on the metal electrode.

Fowler–Nordheim emission from a magnesium electrode into thermally grown SiO\(_x\) has been reported previously.\(^{11}\) In the present paper, this phenomenon is studied in much greater detail. The effects of electrode area, oxide thickness, barrier energy (electrode metal), electric field, and temperature are investigated experimentally. All of the functional dependences predicted by the Fowler–Nordheim theory have been observed, but inconsistencies are noted in the required value of the only adjustable parameter, the effective mass in the oxide forbidden band.

**THEORY**

The theory of Fowler–Nordheim emission can be worked out to various degrees of sophistication.\(^{12}\) In the simplest case for emission into vacuum, a triangular barrier and the temperature \( T = 0 \text{K} \) are assumed. Using a free-electron gas model for the metal and the WKB approximation for the tunneling probability expressed as a Taylor series expansion at the Fermi level, one obtains the following expression for the current density:

\[
J = \left( q^2 E^2 / 8 \pi \hbar \Phi \right) \exp \left[ -4 \left( 2m \right)^{1/2} \Phi^{3/2} / 3 \hbar q E \right],
\]

where \( \hbar = \) Planck’s constant, \( q = \) electronic charge, \( E = \) electric field, \( \Phi = \) barrier height, and \( m = \) free-electron mass. In a Fowler–Nordheim plot (\( \log J / E^2 \) vs \( 1 / E \)), this equation is represented by a straight line.

If the effect of the image force on the barrier is taken into account (Fig. 2), two correction factors, \( t(y) \) and \( v(y) \), are introduced into the Fowler–Nordheim equation. Both terms are tabulated elliptic integrals, depending on the normalized image-force barrier lowering

\[
y = \left( 1 / \Phi \right) \left( q^2 E / 4 \pi \epsilon_0 \right)^{1/2},
\]

where \( \epsilon_0 = \) dielectric permittivity of free space. Both \( t(y) \) and \( v(y) \) are slowly varying functions of \( y \). This correction causes an essentially parallel shift of the Fowler–Nordheim plot to higher values of \( J / E^2 \). The change in slope is less than 1% for \( y < 0.23 \), i.e., for all cases considered in this paper.

Tunneling, in itself, is a temperature-independent process, but the number of electrons of a given energy incident on the barrier depends on the temperature. The

nonzero temperature introduces into the Fowler-Nordheim equation a multiplicative term $\frac{\pi c k T}{\sin(\pi c k T)}$, where

$$c = 2(2\phi) \frac{1/2(\gamma)}{3\hbar q E}.$$

For a small temperature-correction factor the resulting Fowler-Nordheim plot is still close to a straight line, but with a slightly smaller slope.

If the image-force-barrier lowering and the temperature effect are included, the following equation is obtained:

$$J = \left(\frac{q^2 E^3}{8\pi \hbar m^*}\right) \left[1/\beta(y)\right] \left[\frac{\pi c k T}{\sin(\pi c k T)}\right]$$

$$\times \exp\left[-\frac{4(2m^*)^{1/2}\beta^{1/2}}{3\hbar q E}\varepsilon(y)\right].$$

The above equation was developed for emission from a metal into a vacuum. For emission into a dielectric, this has to be modified in two ways: First, in the expression for the tunneling probability the free electron mass has to be replaced by the effective mass $m^*$ of the electron in the forbidden gap of the dielectric. Since the effective mass is expected to depend on the energy of the electron within the energy gap, a suitable average over the actually traversed part of the energy gap has to be used (see Appendix I). This effective mass is the only adjustable parameter of the present investigation. The modified equation has the following form:

$$J = \left(\frac{q^2 E^3}{8\pi \hbar m^*}\right) \left[1/\beta(y)\right] \left[\frac{\pi c k T}{\sin(\pi c k T)}\right]$$

$$\times \exp\left[-\frac{4(2m^*)^{1/2}\beta^{1/2}}{3\hbar q E}\varepsilon(y)\right]$$

where

$$c = 2(2\phi) \frac{1/2(\gamma)}{3\hbar q E}.$$

Second, the relative dielectric constant $\varepsilon_r$ has to be taken into account in the expression for the image force lowering, which becomes

$$y = \left(1/\phi\right) \left(\frac{q^2 E}{4\pi \varepsilon_0}\right)^{1/2}.$$

(The low-frequency dielectric constant $\varepsilon_r = 3.9$ was used.)

**EXPERIMENTAL PROCEDURES**

All experiments were performed on silicon dioxide thermally grown at 1200°C in dry $O_2$. The substrates were $n$-type silicon wafers with a resistivity of 1–10 $\Omega \cdot \text{cm}$. The oxide thicknesses ranged from 640 to 5000 Å. Unless otherwise noted, the samples had nominal thicknesses of 1000 Å. The thickness was determined by capacitance measurement. In some cases these measurements were confirmed by Tolanski interferometry. Metal electrodes were evaporated by the electron-beam method. Aluminum electrodes were delineated by standard photoresist techniques. Other metal electrodes were evaporated through a metal mask. Circular dots of 4–30 mil diameter were used as electrodes in most cases.

The currents were measured with either a Keithley 610A ammeter or a Keithley 413A logarithmic pico-

ammeter. With the exception of the temperature-dependence investigation, all measurements were made at room temperature on the wafer. It was established that the ambient did not influence the measurements. The temperature measurements were made on encapsulated devices (TO-5 cans). The temperature was monitored with a thermocouple, which was in metallic contact with the can.

All devices exhibited a decrease in current over the first few hours. Most measurements were taken after the devices had been subjected to a current density of about $10^{-10}$ A/cm² for 2 h. During this time the current decreased by about one order of magnitude. After this standard treatment there was no further drift during the time required to measure the device characteristics. This drift might be due to electron trapping in the oxide. Further investigation of this phenomenon is planned.

**RESULTS AND DISCUSSION**

The currents through the MOS capacitors were observed to be proportional to the area of the metal electrode, as shown in Fig. 3. Also indicated is the area-to-perimeter ratio $A/P$. A 10:1 variation in this ratio did not affect the proportionality; this excludes any edge effect. The current expressed as a function of the field was observed to be independent of the thickness of the oxide. In Fig. 4, the field necessary to obtain a current density of $J = 0.2 \mu A/cm²$ is plotted vs oxide thickness. Both of these plots are for positive bias on the metal electrode (electron emission from the silicon).

The most conclusive proof that the observed currents are electrode limited is realized by investigating

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[Fig. 3. Current for a given field ($E=7.4 \times 10^8$ V/cm) vs area of metal electrode. Also indicated is the area-to-perimeter ratio $A/P$ for each electrode.](#)

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the effects of different electrode materials on the current-voltage characteristics. It was found that for positive bias on the metal the current was independent of the metal counter electrode, and thus could be attributed to electron emission from the silicon. For negative bias on the metal, the current depended on the particular metal used, and could thus be attributed to electron emission from the metal. In Fig. 5, the current density is plotted vs the electric field for emission from Mg, Al, and Si. The Al and Si characteristics are from the same type of device, but using opposite polarity of bias. Devices with Au electrodes did not exhibit any measurable currents (>10^{-10} A/cm²) up to a field of E=8.8X10⁶ V/cm. These findings agree qualitatively with the barrier energies found from photoemission experiments (Mg: 2.4 eV; Al: 3.2 eV; Si: 3.25 eV; Au: 4.2 eV) and show conclusively that the observed current is electrode limited.

![Fig. 4. Electric field at a given current density (J=0.2 μA/cm²) vs oxide thickness.](image)

The same characteristics are plotted in Fig. 6 in the form of a Fowler-Nordheim plot. Over five decades the currents are on straight lines, the slopes of which correspond to relative effective masses of 0.48 (Mg), 0.39 (Al), and 0.42 (Si), respectively, taking into account the effects of temperature and assuming the values of the barrier heights given above. The small differences in relative effective mass can be due to inaccuracies in the barrier-height determination or to the averaging of the effective mass over slightly different portions of the forbidden energy gap (see Appendix 1). The absolute values of the currents are lower by a factor of five to ten than theoretically expected. Since the initial drift reduced the current by a similar factor, it is believed that this discrepancy is due to the same phenomenon as the drift.

The temperature dependence of the current has been observed to conform to the predicted $\pi c k T / \sin(\pi c k T)$ relation. This is shown in Figs. 7 and 8 for emission from Si and from Al, respectively. However, the values of $c$ required to fit the experimental results correspond to values of the effective mass of $m^*/m=0.96$ (Si) and $m^*/m=0.94$ (Al), which are incompatible with the respective slopes of the Fowler-Nordheim plots. That the discrepancy is significant is illustrated in Figs. 6 and 7, where the theoretical curves for both values of the relative effective mass are indicated.

![Fig. 5. Current density vs electric field for emission from Mg and Al electrodes (metal biased negatively) and from Si substrate (metal biased positively). Also indicated is an upper limit for the emission from an Au electrode.](image)

![Fig. 6. Characteristics of Fig. 5 replotted as a Fowler-Nordheim characteristic (log J/E vs 1/E). The values of the relative effective mass $m^*/m$ corresponding to the respective slopes are indicated. Also indicated as a dotted line is the slope corresponding to a relative effective mass $m^*/m=0.96$, as obtained from current vs temperature measurements.](image)
inaccuracies in the barrier-height determination cannot account for it. (It should be noted that similar differences have been found by Hartman\textsuperscript{14} for tunneling in Al–Al₂O₃–Al systems and by Lewicki and Mead\textsuperscript{16} in Al–AlN–Mg structures.) Also, since the same difference exists for emission from Si and from Al, the distribution of states in the respective conduction bands cannot be the reason for this inconsistency.

In the derivation of the Fowler–Nordheim equation, a constant effective mass in the forbidden band of the oxide and consequently a parabolic $W(k)$ relation (energy $W$ vs wavenumber $k$) was assumed. This violates the requirement for zero momentum at the valence band edge. As shown in Appendix I, a $W(k)$ relation which satisfies this requirement results in two apparent effective masses; the one describing the temperature dependence always being smaller than the one describing the slope of the Fowler–Nordheim characteristic. This is opposite to what has been observed, and therefore the experimental discrepancy cannot be explained by a simple $W(k)$ relation. One possible explanation, in the absence of contrary experimental evidence, is that the barrier height itself is temperature dependent. Calculated in Appendix II is the temperature dependence of the barrier height $\Phi$ necessary to explain the strong temperature dependence of the current. The result of such a calculation for the barrier

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig7.png}
\caption{Current vs temperature for emission from Si at $E = 6.9 \times 10^5$ V/cm. (\texttimes Experiment; --- Theory $m^*/m = 0.96$; --- Theory $m^*/m = 0.42$.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig8.png}
\caption{Current vs temperature for emission from Al at $E = 6.1 \times 10^6$ V/cm. (\texttimes Experiment; --- Theory $m^*/m = 0.94$.)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9.png}
\caption{Temperature dependence of the barrier height $\Phi$ necessary to explain the observed temperature dependence of the Fowler–Nordheim current for emission from Al.}
\end{figure}

height $\Phi$ of the Al–SiO₂ interface is shown in Fig. 9. Similar results are obtained for the barrier height $\Phi$ of the Si–SiO₂ interface. These are open to experimental verification by photoemission measurements as a function of temperature.

\section*{Conclusion}

It has been shown that the current through thermally grown silicon dioxide is electrode limited. All essential functional dependencies of the Fowler–Nordheim emission theory have been observed. Two discrepancies remain: The absolute value of the currents is low by up to one order of magnitude; this is probably related to the initial current drift. Second, the value of the effective mass $m^*$ necessary to fit the temperature dependence is incompatible with the slope of the Fowler–Nordheim plot; this has not been satisfactorily explained. These results are believed to provide the most complete experimental examination of the Fowler–Nordheim emission theory reported to date.

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APPENDIX I

In the derivation of the Fowler–Nordheim characteristics, a constant effective mass \( m^* \) in the forbidden band of the oxide was assumed. This implies a parabolic \( W(k) \) relationship

\[ k^2 = \left( \frac{2a}{\hbar^2} \right) (W - E_c), \]

with

\[ m^* = \frac{\hbar^2}{(\partial W/\partial k^2)} = a, \]

where \( E_c \) is the energy at the conduction band edge. However, this violates the requirement that \( k^2 = 0 \) at the edge of the valence band. A simple empirical equation, which satisfies this requirement was given by Franz\(^{16}\):

\[ k^2 = \frac{(2a/E_c)[1 + (W - E_c)/E_o]}{(W - E_c)}, \]

where \( E_c \) is the width of the forbidden energy band. The effective mass \( m^* \) is now a function of \( W \):

\[ m^* = \frac{\hbar^2}{(\partial^2 W/\partial k^2)} = a [1 + (2W - E_c)/E_o]^{1/2}. \]

This \( W(k) \) relation can also be used to calculate the tunneling probability

\[ D(W) = \exp \left( -2 \int_{x_1}^{x_2} k_d dx \right), \]

where \( x_1, x_2 \) are the classical turning points, and \( k_d^2 = -k_t^2 (k_t) \) is the wavenumber in the \( x \) direction, \( k_t \) is the transverse wavenumber, \( k_t^2 = k_x^2 + k_y^2 \).

Since predominantly electrons which have a small transverse wavenumber \( k_t \) tunnel, \( k_t^2 \) can be neglected. Thus,

\[ D(W) = \exp \left( -2 \int_{x_1}^{x_2} \left[ 1 + (W - E_o)/E_o \right]^{1/2} dx \right). \]

For a triangular barrier (neglecting the image force) \( E_o = -qEx \), and therefore

\[ D(W) = \exp \left( -2 \left[ (2a/W^3)^{1/2}/\hbar qE \right] \int_{0}^{1} \left[ 1 + (W/E_o) z \right]^{1/2} dz \right), \]

where \( z = (W + qEx)/W \).

For \( W/E_o < 1 \),

\[ D(W) \approx \exp \left( -2 \left[ (2a/W^3)^{1/2}/\hbar qE \right] \int_{0}^{1} z^{1/2} \left[ 1 + (W/E_o) z \right] dz \right) \]

\[ \approx \exp \left( -\frac{\pi}{4} \left[ (2a/W^3)^{1/2}/\hbar qE \right] \left[ 1 + \frac{3}{4} (W/E_o) \right] \right). \]

If this expression for the tunneling probability is used in the derivation of the Fowler–Nordheim theory, the following equation is obtained:

\[ J = (q^2 E^2 m/8\pi \hbar \Phi m^*_0) \left[ \text{cosh}(\pi cT)/\sin(\pi cT) \right] \times \exp \left[ -4\left( 2m^*_0 \right)^{1/2} \Phi^{1/2}/3\hbar qE \right], \]

where

\[ c = 2(2m^*_0 \Phi)^{1/2}/\hbar qE, \]

and

\[ m^*_0 = a \left[ 1 - \frac{3}{2} \left( \Phi/E_o \right) \right]^2, \]

\[ m^* = a \left[ 1 - \frac{3}{2} \left( \Phi/E_o \right) \right]^2. \]

Consequently, the apparent effective mass \( m^*_0 \) for the temperature dependence is always smaller than the apparent effective mass \( m^*_0 \) for the slope of the Fowler–Nordheim plot.

APPENDIX II

The strong temperature dependence of the observed Fowler–Nordheim currents can be explained by assuming a temperature-dependent barrier height: \( \Phi = \Phi_0 (1 + \alpha(T)) \). If the temperature dependence of the barrier height in the preexponential term and the image force is neglected, the following equation for the current density is obtained:

\[ J = (q^2 E^2 m/8\pi \hbar \Phi m^*_0) \left[ \text{cosh}(\pi cT)/\sin(\pi cT) \right] \times \exp \left[ -4\left( 2m^*_0 \right)^{1/2} \Phi^{1/2}/3\hbar qE \right] \times \exp \left[ -4\left( 2m^*_0 \right)^{1/2} \Phi^{1/2}/3\hbar qE \right]. \]

Expanding \( (1 + \alpha)^{1/2} \) one obtains

\[ J = J_0 \exp \left[ -4\left( 2m^*_0 \right)^{1/2} \Phi^{1/2}/3\hbar qE \right] \times \exp \left[ -4\left( 2m^*_0 \right)^{1/2} \Phi^{1/2}/3\hbar qE \right]. \]

where \( J_0 \) is the current density for constant \( \Phi = \Phi_0 \). Comparing this equation with the experimental points, one obtains the function \( \alpha(T) \). Accordingly, the temperature dependence of the barrier height \( \Phi(T) \) necessary to explain the observed temperature dependence of the Fowler–Nordheim currents can be calculated.

\(^{16}\) W. Franz, in Ref. 12, Vol. XVIII, p. 155.