# Electron Transport Mechanisms in Thin Insulating Films*

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Tests have been performed on a number of Ta-$Ta_2O_5$-Au diodes of various thicknesses over a range of temperatures to determine the mechanism of current flow. The mechanism proposed for the current flow is field ionization of trap-type states at low temperatures and thermal ionization of these states at high temperatures and thermal ionization of these states at high temperature. High-temperature voltage-current data and low-temperature comparisons between forward and reverse characteristics agree well with the bulk-limited hypothesis and are in striking disagreement with barrier mechanisms. A discontinuity in the oxide properties is noted at a thickness of approximately 500 Å. High-temperature measurements at applied voltages less than the difference in the metal work functions yield an Ohmic characteristic with an activation energy of approximately 0.1 eV, consistent with an impurity conduction process but not with a barrier process.

## INTRODUCTION

A LARGE number of nearly amorphous insulating materials are known which, when a high electric field is applied to thin films of the substance, exhibit current flow which increases roughly exponentially with applied voltage over many decades. The voltage required for a given current in many of these materials decreases monotonically with absolute temperature and varies by a factor of 2 or more between 77°K and room temperature as shown in Fig. 1. Mechanisms which might explain one or more of the observed characteristics are: ionic flow, space-charge-limited flow with distributed traps, Schottky effect, or tunneling. In order to gain an understanding of the current flow process, tantalum oxide was selected for study, since a great deal of pertinent information was available,[1] and films of the material may be formed easily to a given thickness by anodic oxidation.

## EXPERIMENTAL

All films were formed on electropolished metallurgical grade Ta sheet[2] and test devices were completed by the evaporation of gold dots approximately $10^{-3}$ cm$^2$ in area. All results are reported for the "forward" direction (gold electrode positive) unless otherwise specified. At high current levels (>0.1 mA) data was taken by pulse techniques,[3] while at low levels dc measurements were used. All specimens were prepared in vacuums of $10^{-7}$ torr or better and no instabilities or erratic behavior were observed.[4]

## MECHANISMS ELIMINATED

Since the $Ta_2O_5$ films are formed by the anodic process, it is clear that at high electric fields ions can be induced to flow through the material. Ionic conduction would exhibit an exponential volt-ampere characteristic and a decreasing voltage-temperature characteristic. In order to eliminate this possibility from the case at hand, two properties of the ionic currents should be noted. First, the transit time for ions should be quite large. Second, there should be a transport of material from one electrode to the other. The first effect was investigated by applying periodic rectangular voltage pulses to the unit and looking for a delay in the current response. The capacitance of the unit was nulled out by a bridge arrangement. No effect was observed for units up to 500 Å thick within the time resolution of the experiment which was better than 0.1 μsec. The second effect should be detectable by biasing the unit to a reasonable current level for a long period of time and looking for mechanical changes or plating of one electrode material onto the other electrode. A current of 10 mA was passed through one unit at room temperature for over 200 h and no effect was observed. It is felt that these experiments eliminate ionic current as an explanation in the present case.

Tunneling is eliminated from consideration at the higher temperatures since it would not show the large temperature dependence observed. At low temperatures where the voltage for a given current becomes inde-

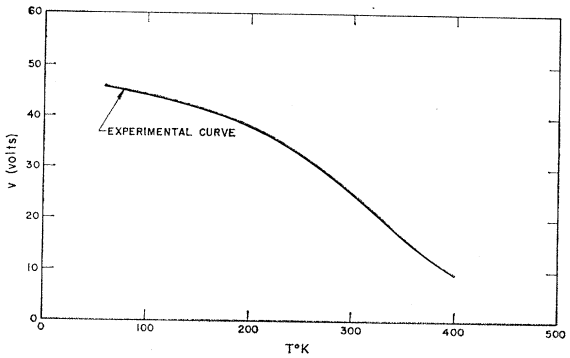


FIG. 1. Experimental curve of voltage required for 1 mA as a function of absolute temperature. (870 Å oxide thickness.)

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[1] See, e.g., V. D. Freschette, *Non-Crystalline Solids* (John Wiley & Sons, Inc., New York, 1960), p. 328; or L. Young, *Anodic Oxide Films* (Academic Press Inc., New York, 1961), and references cited therein.

[2] C. A. Mead, J. Appl. Phys. **32**, 646 (1961).

[3] C. A. Mead, Rev. Sci. Instr. **33**, 376 (1962).

[4] T. W. Hickmott, J. Appl. Phys. **33**, 2669 (1962).

pendent of temperature, it is believed that a tunneling mechanism is responsible, as will be discussed later.

Schottky emission appears at first sight to meet the requirements involved. The current is quite accurately exponential when plotted against $v^{1/2}$ and the temperature dependence exhibits the correct general behavior. However, when detailed correlations are attempted it rapidly becomes clear that the slope of the predicted characteristic is less than that observed by about a factor of 2. In addition, the temperature dependence predicted is much steeper than that observed and the current extrapolated to zero voltage is neither equal to the theoretical value nor is it constant between samples.

When a device of this type is biased to an electric field of nearly $10^7$ V/cm, with several mA of current flowing, if the electron mean free path were about 10 Å or larger, a large number of "hot" electrons would be

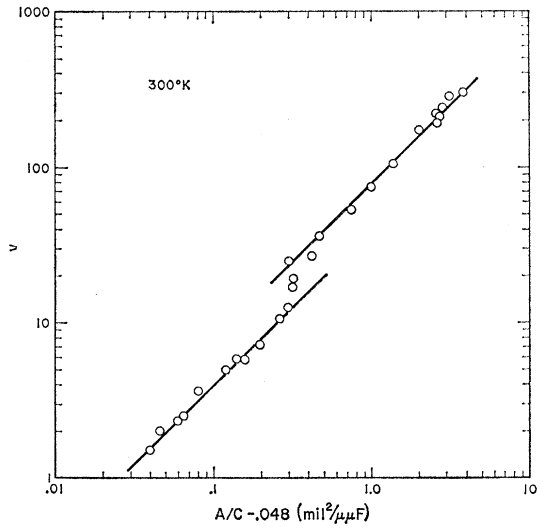


FIG. 2. Voltage required for 1 mA current at room temperature as a function of thickness (measured by capacitance).

expected. These would manifest themselves by the emission of light as they lost energy in the gold layer and as emitted current in tunnel emission experiments. However, neither of these effects are observed.[2] This leads to the conclusion that the mean free path is in fact very short. A possible mechanism for this loss of energy to the lattice is the polaron[5,6] which almost certainly exists in $Ta_2O_5$ and can constitute a very strong coupling between the moving charged particle and the lattice.[7] A short mean free path as implied by these experiments would indicate a low mobility which would in turn give rise to large space-charge effects in thicker samples. The

[5] G. R. Allcock, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 412.
[6] Yu. I. Gorkun and K. B. Tolpygo, Bul. Acad. Sci. USSR Phys. Ser. **24**, 91 (1960); K. B. Tolpygo, *ibid.* **22**, 377 (1958); **24**, 167 (1960).
[7] Y. Toyotawa, Suppl. J. Appl. Phys. **33**, 340 (1962).

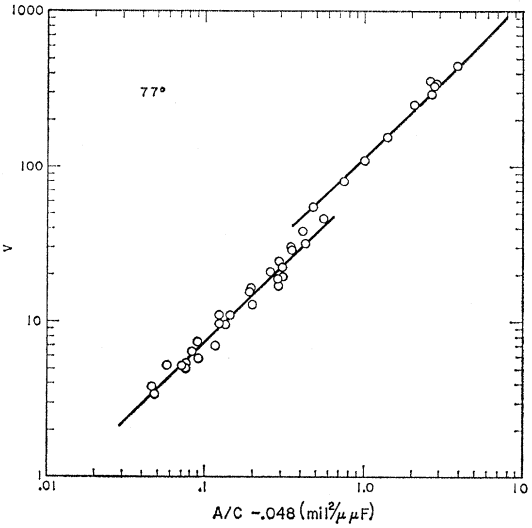


FIG. 3. Voltage required for 1 mA current at 77°K as a function of thickness (note discontinuity in film properties).

presence of space charge would manifest itself in a deviation from linearity in the dependence of voltage for a given current upon thickness in the range where the volt-ampere characteristic is approximately logarithmic. Figure 2 is a plot of voltage required for a current of 1 mA vs inverse capacitance (corrected for anomalous capacitance effect).[8] The solid lines have unity slope. The offset in the curve at approximately 20 V is taken to be a change in the properties of the oxide, the lower points corresponding to a dielectric constant of 21 and the upper to a value of 27. The linearity of the experimental data over this range is a strong indication that the observed currents are not due to space charge limited currents with distributed traps.[9] Figure 3 shows the linearity of voltage with thickness at 77° where the characteristic is nearly temperature independent. Again the discontinuity in oxide properties is in evidence.

## MECHANISM PROPOSED

The significance of this result should be emphasized. Any model in which the electrodes were the rate limiting step in the transport process would predict a deviation from linearity due to the low mobility. However, in this case, no deviation is found and the process involved must be limited by the bulk of the material and not by the potential barriers at the electrodes. Also, since the structure of these films is undoubtedly very poor, one would expect a large density of isolated states randomly distributed throughout the forbidden band. If the effects of such states did not appear somewhere in the electrical characteristic of these devices, one would be very surprised.

[8] C. A. Mead, Phys. Rev. Letters **6**, 545 (1961).
[9] A. Rose, Phys. Rev. **97**, 1538 (1955).

The foregoing considerations have led the author to propose the following mechanism as the rate-limiting step in the current flow through tantalum oxide and other similar films.

(a) At low applied voltage and high temperatures, current is carried by thermally excited electrons hopping from one isolated state to the next. This mechanism yields an Ohmic characteristic, exponentially dependent on temperature.[10]

(b) At high fields and low temperatures, the rate limiting step in the current flow is field ionization of trapped electrons into the conduction band. This process yields a current voltage characteristic (independent of temperature) of the form.[11]

$$J=J_0(E/E_0)e^{-E_0/E}, \tag{1}$$

where

$$E_0=[4(2m^*)/3\hbar q]^{1/2}V^{3/2}. \tag{2a}$$

$J$ is the current density, $E$ is the electric field, $V$ is the depth of the trap potential well, $m^*$ and $q$ are the electron effective mass and charge, respectively. Or one may use the possibly more applicable Piper-Williams expression[12] which leads to

$$E_0=10^7V_g^{1/2}V^{3/2}, \tag{2b}$$

where the field is in V/cm and the energy gap $V_g$ as well as $V$ is expressed in electron volts.

(c) At high fields and high temperatures, the rate-limiting step in the current flow is field-enhanced thermal excitation of trapped electrons into the conduction band. This process is known as the Poole-Frenkel effect.[13] If a Coulomb potential is assumed for the state, a volt-ampere characteristic of the form

$$J=G_0E\exp(\beta v^{1/2}-V)/kT \tag{3}$$

is obtained, where $J$ is the current density, $v$ the applied voltage, and $T$ the absolute temperature. The quantity

$$\beta=(q^3/\pi\epsilon d)^{1/2} \tag{4}$$

is larger than in the case of Schottky emission by a factor of 2 since the barrier lowering is twice as large due to the immobility of the positive charge. Here $d$ is the dielectric thickness and $\epsilon$ the permittivity of the dielectric.

The current is considered to be limited in all cases by bulk processes in the material and not by the electrodes. At higher temperatures, mechanism (a) would normally be expected to contribute much less current than (c), but if the work function of the positive electrode is

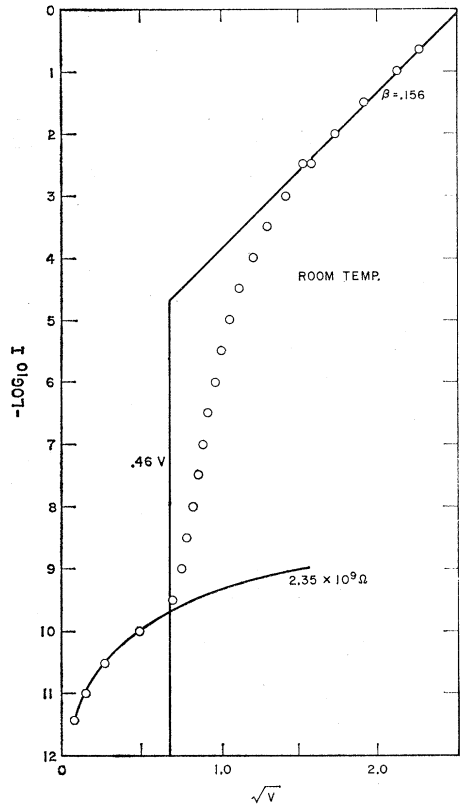


FIG. 4. Typical voltage-ampere characteristic of Ta-$Ta_2O_5$-Au diode. Note Ohmic region at low voltages and $\exp(v^{1/2})$ region at high voltages. Transition voltage (0.46 V) is difference in work functions. (110 Å oxide thickness.)

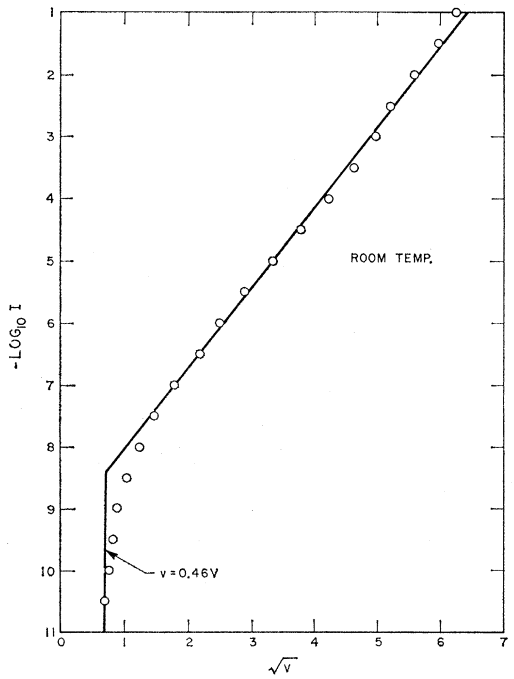


FIG. 5. Voltage-ampere characteristic for thicker film showing $\exp(v^{1/2})$ region and transition at 0.46 V. (870 Å oxide thickness.)

[10] N. F. Mott and W. D. Twose, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107.

[11] A. G. Chynoweth, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 4, p. 95.

[12] W. W. Piper and F. E. Williams, Phys. Rev. **98**, 1809 (1955).

[13] Ia. Frenkel, J. Exptl. Theoret. Phys. (U.S.S.R.) **8**, 1893 (1938).

higher than that of the negative one, (c) is effectively cut off by the negative electric field at applied voltages less than the difference in barrier heights and (a) may be observed.

## ROOM TEMPERATURE

Figure 4 shows a typical volt-ampere characteristic of a Ta-$Ta_2O_5$-Au device at room temperature. The high current asymptote has been calculated from Eq. (1), the only adjustable constant involved being the vertical position of the curve. An applied bias of 0.46 V, (the difference between the Ta and Au vacuum work functions) is shown as the vertical asymptote. At lower voltages the characteristic is Ohmic over several decades. The existence of an Ohmic characteristic up to many times $kT/q$ would rule out any mechanism involving the barriers and conduction band. If the 0.46-V asymptote is due to a difference in barrier heights, it would be expected to be independent of oxide thickness but quite dependent upon the positive electrode material. Experimentally, the vertical asymptote is constant over more than an order of magnitude variation in oxide thickness. This fact is illustrated in Fig. 5 where a quite thick film exhibits the same asymptote. The asymptote should be larger if a higher work function material is used. Figure 6 shows the volt-ampere characteristic of a diode made with a platinum positive electrode. Again the vertical asymptote corresponds closely with the difference in work functions. The difference in material can also be examined in the

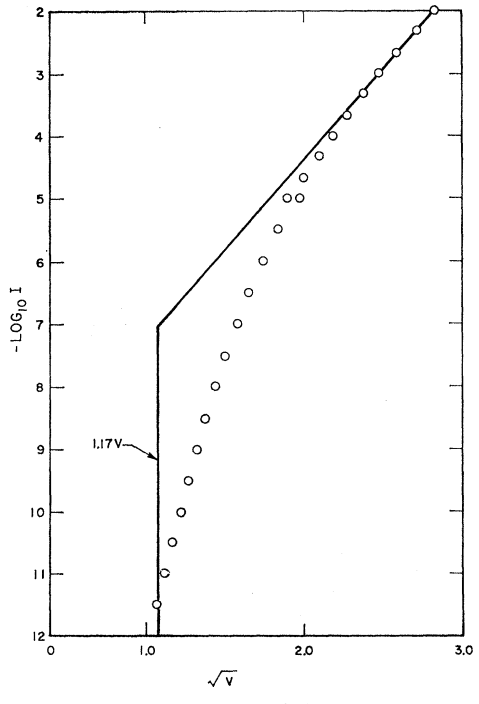


FIG. 6. Voltage-ampere characteristic of Ta-$Ta_2O_5$-Pt diode showing transition at higher voltage. 1.17 V is the difference in work functions.

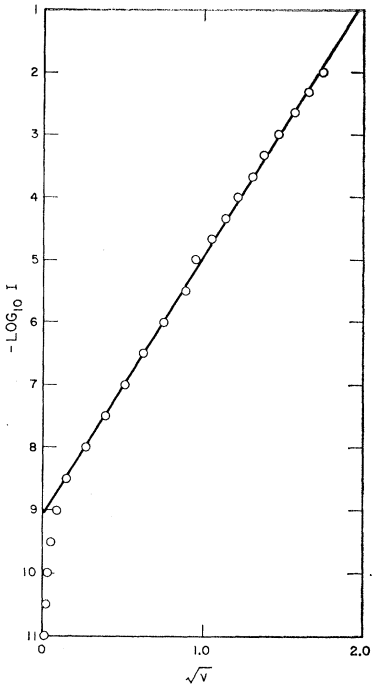


FIG. 7. Voltage-ampere characteristic of Ta-$Ta_2O_5$-Al diode showing transition at 0 V. The Al has a lower work function than the Ta.

opposite extreme, i.e., a material with a lower work function than Ta. The vacuum work function of Al is approximately 0.38 V lower than that of Ta, and hence no drop in current would be expected until zero voltage was approached. That this is indeed the case is shown in Fig. 7. It was not possible to obtain reproducible data on these units in the reverse direction at room temperature due to drift of the characteristic.

The values of $\beta$ calculated from Eq. (4) are very close to the slopes of the experimental curves. The remarkable extent to which this agreement is true is illustrated in Fig. 8. The observed $\beta$ values are obtained from the

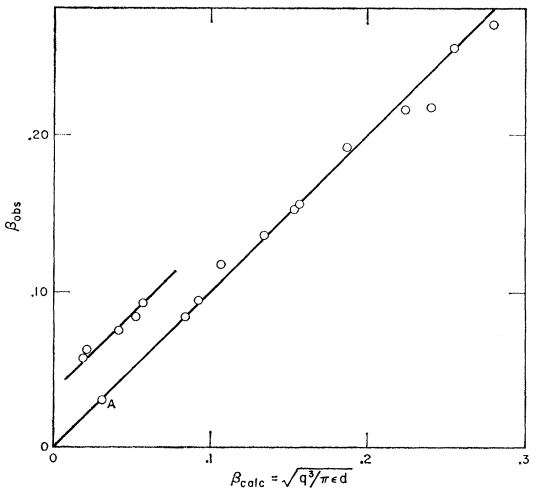


FIG. 8. Comparison of observed and calculated log$I$ vs $v^{1/2}$ slopes points below $\beta_{calc}=0.08$ correspond to upper branch of Fig. 1.

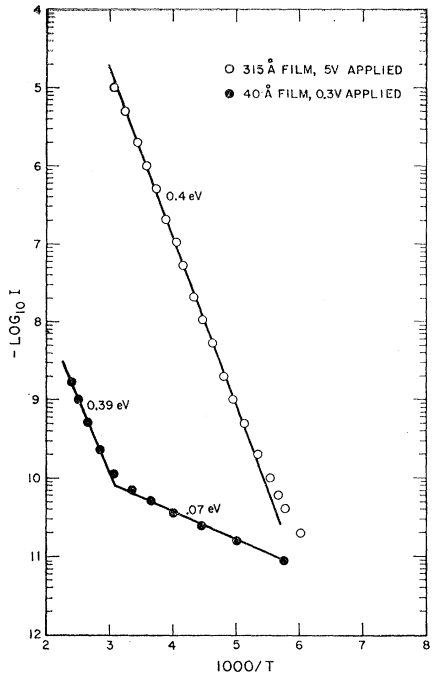


FIG. 9. Log$I$ vs $1/T$ plot of two Ta-$Ta_2O_5$-Au diodes of different thicknesses. Note change in activation energy of lower curve.

slope of the log$I$ vs $v^{1/2}$ plots at both 300 and 195°K. In all cases the agreement in values at the two temperatures is excellent. Calculated values are obtained from the capacitance and area of the device corrected for anomalous capacitance effect. For calculated values of $\beta$ above 0.08 (corresponding to the lower branch of Fig. 1) a dielectric constant of 21 was used. Points below 0.08 (corresponding to the upper branch of Fig. 1) were computed on the basis of a dielectric constant of 27. Several interesting features are apparent. In the majority of the thicker films, some mechanism (perhaps concentration of the field in small regions of the material due to a change in the structure of the films) has raised the experimental $\beta$, while preserving the rate of variation with thickness. In one case, however, (labeled A in the figure) the shift in the observed value has not occurred and the observed value is again in good agreement with the calculated one.

The activation energies of processes (a) and (c) can be determined in the conventional manner as shown in in Fig. 9. At moderate temperatures process (a) (Ohmic characteristic) exhibits a very low activation energy of 0.07 eV (suggesting the electron hopping from one trap to the other with low mobility). At higher temperatures, the activation energy increases in a way very characteristic of impurity conduction processes.[10]

Process (c) (log$I \propto v^{1/2}$) exhibits a much larger activation energy, that of the sample shown being approximately 0.4 eV which leads to $V \approx 0.6$ eV from Eq. (3). These values can vary by nearly a factor of two between samples. Both of the samples shown gave lower than average activation energies.

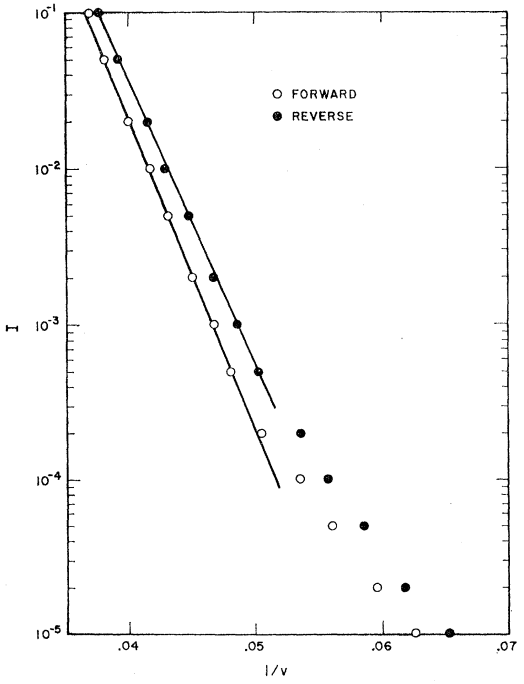


FIG. 10. Fowler-Nordheim type plot of Ta-$Ta_2O_5$-Au diode at 77°K. Note similarity in slopes of forward and reverse biased curves.

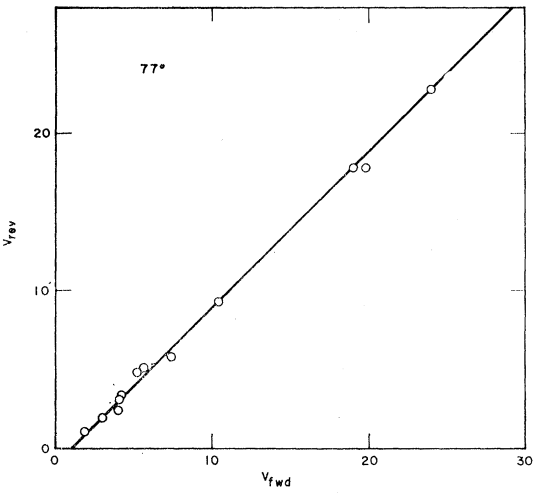


FIG. 11. Comparison of voltage required for 1 mA in forward and reverse direction. The straight line shown is predicted by a bulk mechanism.

## LOW TEMPERATURES

At 77°K the volt-ampere characteristic becomes very nearly independent of temperature, as shown in Fig. 1. A Fowler-Nordheim type plot of a typical unit in both the forward and reverse directions is shown in Fig. 10. It will be noted that the slopes of the two curves are

nearly identical. We have noted that the barriers are approximately 0.5 V different in height, which is probably a large fraction of their total height. If the barriers were the rate-limiting step in the tunneling process, one would expect a very strong asymmetry in the characteristic on this account. The symmetry of the characteristic is strong evidence that the current is bulk controlled rather than electrode controlled.

Another rather conclusive evidence for the bulk process is in the voltage required for a given current in the forward and reverse directions. Plotted in Fig. 11 are the forward and reverse voltages for a number of units of different thicknesses. The straight line with unity slope and intercept at twice the difference in work functions is to be expected from a bulk field ionization process. The curve for electrode tunneling would be steeper by the ratio of the barrier heights.

The value of $V$ as calculated from Fig. 10 is about twice that obtained from the temperature data in Fig. 9 but detailed comparison is difficult due to the uncertainties in $m^*$ and $V_g$ in Eq. (2).

## CONCLUSIONS

This author can see no way in which the usual electrode-controlled processes can be made to explain the observed experimental characteristics. Although all of the work reported here has been done with tantalum oxide films, many other films exhibit very similar characteristics and the above considerations undoubtedly apply in some cases. It should be emphasized that with the experimental evidence at hand, it is impossible to establish a complete model of the current flow processes in these films. However, it is believed that the mechanisms proposed are the rate-limiting processes involved and should be carefully considered in the construction of any complete analysis.

## ACKNOWLEDGMENTS

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# Wave-Number-Dependent Dielectric Function of Semiconductors*

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Expressions for the wave-number-dependent dielectric function are derived for various models of a semiconductor. The calculation is carried out for the diagonal part of the dielectric function at zero frequency. It is found that calculations based on plane wave models (such as the free electron model) give poor results for small values of the wave number due to neglect of both Bragg reflections and Umklapp processes. We use instead an isotropic version of the nearly free electron model in which dielectric function depends on only one parameter $E_g$ representing an average energy gap that can be determined from optical data. It is noted that for small wave numbers Umklapp processes give the major contribution to the dielectric function, whereas for large wave numbers normal processes dominate. The dielectric function is evaluated numerically for a value of $E_g$ appropriate to Si.

## I. INTRODUCTION

THE interaction between an external electric field and the electrons in a solid can be described by the relationship

$$V(\mathbf{r},t)=\int\int \mathcal{K}(\mathbf{r},\mathbf{r}';t-t')V_{\text{ext}}(\mathbf{r}',t')d\mathbf{r}'dt',$$

where $V_{\text{ext}}$ is the potential due to the external field, $V$ is the total microscopic potential, and $\mathcal{K}$ describes the response of the solid to $V_{\text{ext}}$. For the case of a solid with a periodic lattice we can write

$$\mathcal{K}(\mathbf{r},\mathbf{r}',t-t')=\int\int d\omega d\mathbf{q}\sum_{\mathbf{K}}\mathcal{K}(\mathbf{q},\mathbf{q}+\mathbf{K};\omega)e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')-i\mathbf{K}\cdot\mathbf{r}'-i\omega(t-t')},$$

where $\mathbf{K}$ is a reciprocal lattice vector. A general discussion of the inverse dielectric function, $\mathcal{K}$, has been given by Falk.[1]

The formalism can be used to treat the screened electron-electron interaction in the crystal by letting $V_{\text{ext}}$ be the coulomb potential of the electron in the solid. Hubbard[2] has used the dielectric function to derive expressions for the ground-state energy of a medium, Quinn and Ferrell[3] have shown how $\mathcal{K}$ can be used in computing quasi-particle energies, and Phillips[4] has shown how it can be employed in forming a screened exchange operator.

Calculating $\mathcal{K}(\mathbf{q},\mathbf{q}+\mathbf{K};\omega)$ for arbitrary $\mathbf{K}$ and $\omega$ is generally very difficult. However, under certain circum-

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