NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

-iii-

CHARACTERIZATION OF METAL OXIDE TUNNELING BARRIERS

Contents

ABSTRACT	v
I. INTRODUCTION	1
II. THE MODEL AND THEORY	4
A. Fowler-Nordheim Calculation	4
B. Calculation of the Tunnel Current	6
C. The Tunneling Probability and the Barrier	11
D. Approximation Methods	13
E. Choice of a Model Barrier and Method of Calculation	15
III. EXPERIMENT	21
A. Sample Preparation	21
B. Cryogenics	23
C. Electronics	23
D. Junction Quality	24
E. Junction Stability	27
IV. ANALYSIS	29
V. RESULTS	36
A. The Test Case: Aluminum-Oxide-Aluminum	36
B. Other Materials: Chromium and Vanadium	45
C. Discussion	50
VI. SUMMARY AND CONCLUSION	55
ACKNOWLEDGMENTS	58
APPENDIX A: Details of the Computer Calculation	59
APPENDIX B: The Logarithmic Derivative as a Means of Determining Barrier Heights	63

MASTER

APPENDIX C: Graphs for an Approximate Determination of	
Barrier Parameters	71
REFERENCES	78

CHARACTERIZATION OF METAL OXIDE TUNNELING BARRIERS

Duncan Eldridge McBride, Jr.

Department of Physics, University of California
and
Inorganic Materials Research Division
Lawrence Berkeley Laboratory,
Berkeley, California

ABSTRACT

We have developed a method of characterizing the barrier in a metal-insulator-metal tunneling junction on the basis of experimental current-voltage curves and a simple theoretical model. We are able to determine unambiguously the barrier height ϕ and barrier thickness S by, first, measuring the quantity $S\phi^{3/2}$ from the slope of the Fowler-Nordheim plot. Then experimental data are compared with a family of current-voltage curves calculated for various pairs of S and ϕ with $S\phi^{3/2}$ fixed at the measured value, and the pair which gives the best fit is determined. This procedure has been tested on the best understood tunneling barrier, that grown thermally on an aluminum film, and is found to give a barrier height of about 2.6 eV, in good agreement with independent measurements.

Our method also enables us to construct a qualitative description of the tunneling barrier which provides a context for the quantitative measurements. The barrier seems adequately described by a trapezoidal model, often with unequal sides but of nearly uniform height over the junction area. Although the barrier thickness is not uniform, the variation occurs on a microscopic scale in a well-prepared junction,

and the magnitude of the variation is a small fraction of the mean thickness.

We have also used the method to measure parameters of barriers grown thermally on chromium, thin film vanadium, and bulk vanadium, and we obtain barrier heights of 0.6 eV, 0.1 eV, and 0.2 eV respectively. The technique is a convenient one for the analysis of data from an experiment, and the results it gives are unambiguous, consistent, and provide a sensitive measurement of the characteristics of the barrier.

1. INTRODUCTION

When two metal electrodes are separated by a sufficiently thin insulating layer, electrons can transfer between them by the process of quantum mechanical tunneling. Tunneling has proved to be an extraordinarily useful technique for studying the electrodes; it has provided a wealth of information about electron interactions in metals, particularly superconductivity. More recently, attention has been turned to the nature of the insulating barrier, largely because of the discovery that tunneling electrons can excite molecular vibrational and rotational modes in the barrier,¹⁻⁵ and also because it has been discovered that more than one kind of barrier material can be formed on the same metal.⁶ In order to compare results of different experiments it is necessary to be able to confirm that they were done with the same barrier material. Likewise, in order to study the molecular modes, which appear as weak fine structure on the current-voltage graph of the junction, it is necessary both to be able to characterize the tunneling barrier in sufficient detail and to know as accurately as possible the junction's gross behavior on which the structure appears superimposed. Further, in any tunneling experiment it is useful to have some knowledge of the nature of the tunneling barrier.

This work describes a way of attacking these problems and presents results from junctions made by thermally oxidizing four different kinds of metal electrodes to form an insulating layer on them. The electrodes are bulk vanadium and thin film aluminum, chromium, and vanadium.

In section II we discuss the results of theoretical work which has been done to characterize the tunneling barrier. Most of the simple theory of tunneling between metals which are not superconducting was developed quite early, but it was necessary, until fast computers were available, to make rather severe mathematical approximations in order to make calculations possible. Since much of the intuitive thinking about tunnel junctions still depends on the approximations, they will be discussed briefly. In addition we discuss some of the general ideas which it is necessary to consider in constructing a model barrier for our calculations and, on the basis of these, present the model barrier and method of calculation which we employ throughout our analysis.

In section III we describe the preparation of our samples and the way in which our measurements are made. In addition, we discuss the criteria which we employ to verify that our samples are indeed tunneling junctions.

Section IV contains a description of our general method of analysis in which we combine the results of experiments with the theory described in section II to obtain values for the parameters of the theory for an experimental junction.

Our analysis is applied to specific junctions in section V. We begin by applying it to the most extensively studied kind of tunneling barrier, that grown thermally in air on an aluminum electrode. Barrier thickness and barrier height are obtained for a particular aluminum junction and compared to our own and other independent measurements of these parameters. The discrepancy between the average barrier

thickness determined from capacitance measurements and the thickness determined from tunneling leads us to modify the plane parallel geometry of our model to include a variation in the barrier thickness which is small compared to the mean thickness and occurs on a microscopic scale over the junction area. We briefly consider three alternate methods of determining barrier heights and note that all of them have given results consistent with our own. The analysis is then applied to barriers grown thermally on thin film chromium and thin film and bulk vanadium. Tentative suggestions are made relating the barrier heights we measure to the properties of the compounds which we suppose make up the insulating layers. Finally, on the basis of our analysis we outline the most complete description of a tunneling barrier which we think can reasonably be made based on macroscopic electrical measurements.

In an appendix a series of curves are presented which encompass a wide range of barrier heights and thicknesses for use in estimating barrier parameters without doing lengthy computer calculations.

II. THE MODEL AND THEORY

A tunnel junction is conventionally made by exposing a clean surface of either a relatively thick ($> 1000 \text{ \AA}$) evaporated metal film or a bulk ingot to a reactive atmosphere to form a thin ($10\text{--}30 \text{ \AA}$) insulating barrier. Usually the atmosphere is air or oxygen and the barrier is assumed to be an oxide. After suitable masking, a cross strip of metal is evaporated on top. The simplest useful model of this type of junction is that of two semi-infinite bulk electrodes which are free electron gas metals separated by a uniform thin insulating layer. A rather stylized schematic drawing of this is shown in figure 1. The potential barrier, of height ϕ and thickness S , is formed by the forbidden gap of the insulator, with filled valence band below and conduction band above. At nonzero bias (figure 1b) the Fermi levels of the metals are offset and a net tunneling current flows through the barrier.

This kind of model has been used since the very beginning of tunneling calculations, and in this section we explore some of the calculations which have been done on it.

A. Fowler-Nordheim Calculation

One of the earliest and most useful calculations was done by Fowler and Nordheim⁷⁻⁹ in 1928, in which they considered field emission of electrons from a metal surface in an intense electric field. Here, one electrode is a metal as before, but the other is replaced by the vacuum, and a barrier to the flow of electrons exists because of the work function of the metal, which produces a roughly triangular barrier for the electrons. This problem is the same as that of tunneling at

very high bias, in which the Fermi levels are offset by more than the barrier height, producing the same roughly triangular barrier through which the electrons can be thought of as being field emitted into the conduction band of the positively biased electrode.

By considering the transmission and reflection coefficients for electrons incident on such a barrier and the statistics of the electron gas, Fowler and Nordheim derive an expression for the field emission current in terms of barrier properties, under the assumption of low temperature ($kT \ll \phi$) and high voltage ($eV > \phi$). It is

$$I = CV^2 \exp \left[- \frac{4\sqrt{2m}}{3\hbar} \frac{S\phi^{3/2}}{eV} \right], \quad (1)$$

where C is a constant which depends on the metal, m is the free electron mass, $(-e)$ is the electron charge, and V/S is the electric field strength.¹⁰

The importance of this expression is its simplicity. The properties of the barrier are contained in a simple (albeit nonlinear) product in the exponent, and the whole expression has but one term. Thus dividing by V^2 and taking a logarithm gives

$$\ln \frac{I}{V^2} = \ln C - \frac{2}{3} \frac{\alpha}{e} S \phi^{3/2} \left(\frac{1}{V} \right), \quad (2)$$

where $\alpha = \frac{2\sqrt{2m}}{\hbar}$. Equation 2 implies that a graph of $\ln(I/V^2)$ versus $1/V$ will result in a straight line of slope $-\frac{2}{3} \frac{\alpha}{e} S \phi^{3/2}$, yielding an immediate measurement of the product $S\phi^{3/2}$.

In a tunnel junction the measurement is almost, but not quite, this simple. In the case of field emission almost no current is observed until the voltage is high enough to give the Fowler-Nordheim result,

and the barrier is always roughly triangular. This is not true in a tunnel junction. Instead, the barrier becomes triangular at high bias, and thus there is a gradual asymptotic approach to the Fowler-Nordheim behavior at voltages which are greater than the barrier height. (For an example, see figure 4, page 31).

B. Calculation of the Tunnel Current

A large part of the most general theory of tunneling between non-superconducting electrodes was worked out by Frenkel¹¹ in 1930 (although little was done with it until the 1960's). He considered exactly the model we have discussed, that of free electron gas metals separated by an insulator, and assumed the problem could be treated as one of independent electrons tunneling through a one-dimensional barrier. Thus transmission coefficients can be calculated using the one-dimensional single-particle Schroedinger equation. These coefficients can be cast in the form of a tunneling probability at a given energy, $D(E)$, which contains all the information about the assumed barrier geometry and which is voltage dependent. Then the product of this probability and the number density of electrons with a given energy $n(E)$ can be integrated to obtain the current.

To be more precise, let us define E as the energy of an electron above the bottom of the conduction band on the left of the barrier in figure 1 and $D(E_x)$ as the probability that an electron of energy $E_x = \frac{1}{2} m v_x^2$ will tunnel through the barrier. The number of electrons per unit area and time tunneling from left to right can be written as

XBL 733-5840

Fig. 1. A schematic one-dimensional representation of the band structure of a tunnel junction in the neighborhood of the barrier region. At zero bias (a) the Fermi levels (ϵ_f) in the two metals are at the same energy. The barrier is formed by the forbidden gap of the insulator, with conduction band (c) above and valence band (v) below. The barrier is of height ϕ and thickness S . At some nonzero bias (b) the Fermi levels in the metals are offset by eV , where V is the bias voltage. The barrier tilts due to the voltage drop across it.

$$N_{LR} = \int_0^{\infty} v_x n(v_x) D(E_x) dv_x = \frac{1}{\Omega} \int_0^{\infty} n_L(v_x) D(E_x) dE_x, \quad (3)$$

where $n_L(v_x) dv_x$ is the number of electron per unit volume on the left with x-component of velocity between v_x and $v_x + dv_x$. In addition,

$$n_L(v) dv_x dv_y dv_z = \frac{2\Omega^4}{h^3} f(E) dv_x dv_y dv_z, \quad (4)$$

where $f(E)$ is the Fermi-Dirac function. Thus

$$n_L(v_x) dv_x = \frac{2\Omega^4}{h^3} \int f(E) dv_y dv_z \quad (5)$$

and, substituting, we obtain

$$N_{LR} = 2 \left(\frac{\Omega}{h} \right)^3 \int dE_x \int dv_y dv_z D(E_x) f(E). \quad (6)$$

The probability for tunneling from right to left is the same $D(E)$. One way of seeing this, as Duke¹² points out, is to note that the one-electron Schrodinger equation is invariant under time reversal. Then the number of electrons flowing from right to left is

$$N_{RL} = \int_{v_x^0}^{\infty} v_x n_R(v_x) D(E_x - eV) dv_x, \quad (7)$$

where v_x^0 is defined by $\frac{1}{2}\Omega(v_x^0)^2 = eV$. Then

$$N_{RL} = \frac{1}{\Omega} \int_{E_x^0}^{\infty} n_R(v_x) D(E_x - eV) dE_x = \frac{1}{\Omega} \int_0^{\infty} n_L(v'_x) D(E'_x) dE'_x, \quad (8)$$

which is in the same form as N_{LR} . The only difference is the fact that the Fermi level has been shifted by eV and $f(E)$ must be replaced by $f(E+eV)$. Upon doing this we obtain

$$N_{RL} = 2 \left(\frac{D}{L} \right)^j \int dE_x \int dv_y dv_z D(E_x) f(E+eV) . \quad (9)$$

Therefore we obtain the same argument for $D(E)$ in both N_{LR} and N_{RL} and the net flow of electrons is simply $N = N_{LR} - N_{RL}$. The current density is just Ne ; from equations 6 and 9,

$$J = 2e \left(\frac{D}{h} \right)^3 \int dE_x \int dv_y dv_z D(E_x) [f(E) - f(E+eV)] . \quad (10)$$

If we define

$$v_r^2 = v_y^2 + v_z^2 \quad (11)$$

and

$$E_r = \frac{1}{2} m v_r^2 , \quad (12)$$

then equation 10 can be written in cylindrical coordinates as

$$J = \frac{4\pi me}{h^3} \int dE_x \int dE_r D(E_x) [f(E) - f(E+eV)] . \quad (13)$$

This in turn can be expressed as

$$J = \int_0^\infty dE_x D(E_x) N(E_x) , \quad (14)$$

where

$$N(E_x) = \frac{4\pi me}{h^3} \int_0^\infty [f(E) - f(E+eV)] dE_r . \quad (15)$$

The integral for $N(E_x)$ can be done exactly (e.g., by parts) to give

$$N(E_x) = \frac{4\pi me k_B^{-1}}{h^3} \ln \left[\frac{1 + \exp[(E_f - E_x)/k_B T]}{1 + \exp[(E_f - E_x - eV)/k_B T]} \right] , \quad (16)$$

which has a $T=0$ limit of

$$N(E_x) = \begin{cases} \frac{4\pi m e^2 V}{h^3} & ; E_x < \epsilon_f - eV \\ \frac{4\pi m e}{h^3} (\epsilon_f - E_x) & ; E_f > E_x \geq \epsilon_f - eV \end{cases} \quad (17)$$

Then equation 14 can be written in a form useful for computation as

$$J = \frac{4\pi m e}{h^3} \left\{ eV \int_0^{\epsilon_f - eV} D(E_x) dE_x + \int_{\epsilon_f - eV}^{\epsilon_f} (\epsilon_f - E_x) D(E_x) dE_x \right\} \quad (18)$$

at $T=0$. Although our derivation has been semiclassical, Duke¹¹ shows that the thick barrier limit ($D \ll 1$) of the coherent elastic tunneling current in the transfer Hamiltonian scheme is exactly this expression except perhaps for a constant of normalization. By writing equation 18 we have reduced the problem, within the framework of our general assumptions, to that of defining and calculating the tunneling probability $D(E_x)$.

C. The Tunneling Probability and the Barrier

The probability D implicitly contains all the information about the tunneling barrier, and in order to construct a model for the potential and calculate the probability we must consider what we know about experimental barriers. Unfortunately not a great deal is known about the details of either the physics or the chemistry of the barrier, but we can make some general statements. The barrier is made by admitting air, oxygen, or nitrogen into the vacuum chamber in which the fresh metal surface has been prepared. The gas presumably diffuses into and reacts with the metal, forming a thin film on the surface which is an insulator and which is relatively impermeable to further diffusion of the gas, thus limiting the thickness of the layer formed. The insulating film is thought to be amorphous or polycrystalline, and it is probably inhomogeneous, with a progression from pure metal deep inside the electrode to a rather highly oxidized state at the surface. The compound formed is conventionally assumed to be an oxide (usually the common bulk oxide) when the barrier has been formed in air or oxygen, although this usually cannot be confirmed.

Ideally the barrier would be marked by a sharp transition on the surface of the oxidized film at which the band structure changed from that of a metal to that of an insulator, the forbidden gap of which forms the barrier. Actually we know from the manner in which the insulator grows that the transition is in fact not sharp. There might even be more than one distinct compound in the barrier region and therefore more than one gap as a function of depth from the surface.

Many barrier profiles have been proposed to take account of these factors, although considerations of computational simplicity seem to have been as important. Duke¹⁴ gives a comprehensive list with references. The most common choice is one form or another of the trapezoidal profile, a simple example of which has already been shown in figure 1.

Once a basic barrier profile has been chosen it can be modified by the interaction of the potentials in the metals and the insulator. In addition to the uniform-field voltage drop across the barrier due to biasing the junction, there may be charge imbalances which distort the barrier. For example, this would cause a barrier which would otherwise be rectangular at zero bias to become a more general trapezoid. Further, there has been discussion of the effects of electric field penetration into the metal electrodes. Ku and Ullman¹⁵ have concluded that this has a significant effect on the apparent barrier thickness. In a more recent calculation, however, Theophilou and Modenos¹⁶ show that, under a different set of assumptions, the effect is negligible. The matter is not yet fully resolved. Finally, the barrier profile has often been corrected by the inclusion of the image potential of the electrodes in the barrier. For a plane parallel geometry this tends to make all barriers more or less parabolic in shape. For a barrier which is not uniform in composition or thickness the effect of the image potential is difficult to estimate.

D. Approximation Methods

Once a model is chosen which allows a tunneling probability to be computed, either analytically or numerically, equation 18 may be evaluated to give the current density as a function of voltage. Both the calculation of the probability and the current have traditionally involved approximations and, although some of them are now largely of historical interest, we consider here briefly a few of their qualitative features.

The tunneling probability D can be calculated exactly for a number of simple barriers by solving the Schrodinger equation for a particle of a given energy incident on the barrier. However, the WKB approximation¹⁷ has almost universally been used, largely because it is simple and because one does not like to have to perform a further integral (for the current density) over the horrendous functions one usually obtains in an exact calculation of the probability. In the WKB approximation the tunneling probability is given as

$$D(E_x) \propto \exp \left\{ -\alpha \int_{S_1}^{S_2} \left[\epsilon_f + \phi(x) - E_x \right]^{1/2} dx \right\}, \quad (19)$$

where $\phi(x)$ is the barrier profile, S_1 and S_2 are the classical turning points for an electron of energy E_x , and α is $2\sqrt{2m}/\hbar$ as defined in equation 2.

Further, the WKB approximation is probably a good one in most cases. Gundlach and Simmons¹⁸ have shown that for a trapezoidal barrier the functional form of the tunneling probability is accurately approximated as long as the barrier is sufficiently thick and high

$(S\phi^{1/2} \gtrsim 6 \text{ \AA} (\text{eV})^{1/2}$, where S is the barrier thickness and ϕ the barrier height). This is true in spite of the fact that, of all simple barriers, the trapezoidal barrier shape most severely violates the assumption, made in deriving the WKB approximation, that the potential does not change too rapidly as a function of position. The results of their comparison made between the exact and WKB probabilities show that the calculated probabilities differ by a multiplicative factor which depends on the details of the barrier but which is almost independent of bias voltage. This is probably true for other barrier shapes as well, and the WKB probability, which is much simpler to compute and express, can thus be used as long as the correction factor is either known or unimportant.

Further approximations have traditionally been made in the calculation of J from equation 18. One, associated with Simmons,¹⁹⁻²¹ in effect replaces the actual model barrier with an effective square barrier whose height is a function both of the model barrier shape and bias voltage. The integrals for the probability and the current can then be done by retaining only the most significant terms. The other, associated with Stratton,^{21,22} takes advantage of the fact that tunneling takes place predominantly at high electron energies (E_x near E_f) because the barrier is lower there and, at high biases, thinner as well. Thus the WKB exponent is expanded around the small parameter $\epsilon_x \equiv (E_f - E_x)$ and integrated term by term. In practice only the first two terms are retained.

Neither of the methods of approximation for the current integral is very satisfactory. It is difficult to tell exactly how serious the

approximations are, although the unphysical discontinuities which appear at voltages equal to the barrier height do not instill confidence. Further, the expressions obtained in trying to write an approximate analytic formula for the current are so unwieldy that algebraic and computational errors seem inevitable and in fact apparently have occurred²³ in most published versions of the approximations. Fortunately, modern computers almost entirely eliminate the need for the approximations, although they may be useful for studying the dependence of current on a parameter over a limited range of values (e.g., J on V near $V=0$).

E. Choice of a Model Barrier and Method of Calculation

It is apparent that, from a theoretical point of view, the nature of the tunneling current-voltage curves (for example) can be exactly predicted only after the barrier is sufficiently well understood. However, it is useful to consider what can be said about the barrier based on experimental current-voltage curves and other measurements. Here we are attempting to obtain information about a cause from its effects, and finally we can only make a description of the cause plausible, not certain. We may construct a description which accounts for the effects but which corresponds in only a vague way to the cause itself. Yet, even though a description is not an explanation, it is useful from an experimental point of view to have the order of classification which a description allows even if the description is based on an inadequate view of the situation.

It is in this spirit that we attempt to characterize the tunnel barrier of a metal-insulator-metal junction. The theory we have

presented to this point is elementary, and we are not able to make a definitive test of its adequacy. Any model barrier we pick to use with the theory is at best tentative and certainly too simple. Rather, we wish to see if, using this theory and a simple barrier model, we can construct a description of a tunnel barrier which will allow us to classify experimental barriers on the basis of their measured characteristics with sufficient sensitivity to be useful experimentally. If we are successful we can then try to relate the properties we have assumed in the model to the properties we know from other measurements on actual barriers, being pleased with successes and using major discrepancies to refine the model while realizing that a realistically simple model and theory cannot account for minor disagreements.

Thus our plan is to take the simple theory and its underlying assumptions as a beginning, pick a simple but reasonable model for the barrier, and find a way to relate a comparison of experimental data and calculations as sensitively as possible to the properties of the model barrier. Finally, we attempt to use the properties of the model to discern some of the physical and chemical properties of the actual barrier, admitting that we must be most tentative here.

For the model barrier we have chosen to start with that shown in figure 1: a potential barrier which is uniform in height and width over the junction area and, at zero bias, has a square profile. It is characterized by two parameters, height ϕ and width S . At a non-zero bias the barrier tilts, becoming trapezoidal, since the voltage drop appears entirely across the barrier and we assume it to be uniform. This is the simplest model of a barrier which yields

interesting results. It cannot be expected to reproduce fine structure in the tunnel current and may, in fact, introduce some artificial structure because of the discontinuous potential changes at the edges of the barrier.

Further, we have chosen to ignore all the modifications to the basic barrier shape discussed previously, at least for the moment. We shall account for barrier distortion (here, tilt at zero bias, with the barrier of unequal height on the two edges) in a satisfactory way at a later stage. Field penetration into the electrodes is an open question, but we have arrived at a consistent model without needing to consider it. Image potential corrections play an unknown role, but one which is apparently not of major importance. In any case it is impossible to correct for them in anything but a plane geometry, and we certainly do not have that here because of the variation in oxide thickness which must occur. This variation itself will be dealt with at a later stage as well. For now we take a barrier which is uniform in width and height.

The tunneling probability can be calculated exactly for the trapezoidal barrier,²⁴ but the result does not invite further computation because it is a complicated set of Airy functions and their derivatives. Therefore we use the WKB approximation as a sufficiently accurate approximation¹⁸ to the functional form of the probability.

For our trapezoidal barrier, figure 1, the function $\phi(x)$ in the WKB exponent of equation 19 is $\phi - Vx/S$ if the coordinates of the barrier edges are taken to be 0 and S, respectively. The classical turning points may be determined by inspection of figure 1 and a straightforward

integration of equation 19 results in

$$D(E_x) \propto \begin{cases} \exp \left[-\frac{4}{3} \frac{\sqrt{2m} S}{h} \frac{(\epsilon_f + \phi - E_x)^{3/2} - (\epsilon_f + \phi - E_x - V)^{3/2}}{V} \right]; & E_x < \epsilon_f + \phi - V \\ \exp \left[-\frac{4}{3} \frac{\sqrt{2m} S}{h} \frac{(\epsilon_f + \phi - E_x)^{3/2}}{V} \right]; & E_x > \epsilon_f + \phi - V \end{cases} \quad (20)$$

Since all our experiments were done at 4.2°K or below we can safely use the zero-temperature form of the tunneling current given by equation 18. (For a 1 volt barrier height $k_B T / e\phi \lesssim 3 \times 10^{-4}$). It is

$$J = \frac{4\pi me}{h^3} \left\{ eV \int_0^{\epsilon_f - eV} D(E_x) dE_x + \int_{\epsilon_f - eV}^{\epsilon_f} (\epsilon_f - E_x) D(E_x) dE_x \right\} \quad (21)$$

Using D given by equation 20 in equation 21, we can calculate the tunneling current as a function of voltage for any S and ϕ . The calculation is a rather long but straightforward numerical integration which we carried out without further approximation on a CDC 7600 computer. The program and sample tabular results are reproduced in Appendix A.

We still need a way of relating the calculations to experiments we do. While it might be possible merely to compare calculated and experimental curves until a fit is found, this has not proved feasible. The primary difficulty is that, without the knowledge of more than a general range of reasonable barrier parameters, the fit obtained is

not very sensitive to the choice of the parameters. We need to have an idea of where to start which will restrict our choice of parameters and, we hope, eliminate all but one suitable fit.

The high-voltage asymptotic behavior of the tunnel current as a function of voltage gives us exactly the necessary constraint on our choice of S and ϕ . As we wrote it in equation 2, the Fowler-Nordheim relation predicts that a graph of $\ln I/V^2$ vs $1/V$ is asymptotic at high voltages (small $1/V$) to a straight line of slope $-\frac{2}{3} \alpha S \phi^{3/2}$. Thus for a particular junction the product $S \phi^{3/2}$ is fixed once the Fowler-Nordheim plot is made, and therefore we need to consider in our calculations only those values of S and ϕ which give the proper product; geometrically put, we have picked a line of possible values out of an entire plane of values of S and ϕ .

There is one potentially complicating factor to this simple measurement of $S \phi^{3/2}$. The quantity α , which is equal to $2\sqrt{2}m/h$, contains the electron mass, and if there are any effective mass corrections we need to know their effects in order to obtain $S \phi^{5/2}$. Basavaiah, Eldridge, and Matiso²⁵ have suggested that in lead-oxide-lead junctions it may be necessary to define a tunneling effective mass m^* of approximately $0.5 m$, where m is the free electron mass, in order to obtain agreement between the trapezoidal barrier model and experiment. While we cannot duplicate their experiment directly because it involves the use of a sophisticated ellipsometer to monitor the oxide growth, we obtain a satisfactory picture of a junction using the free electron value which occurs naturally in our simple model, and we know of no compelling theoretical reason for assuming otherwise.

Thus from a set of experimental data we can determine the product $S\phi^{3/2}$ from the slope of a Fowler-Nordheim plot. With $S\phi^{3/2}$ fixed at this value a family of current-voltage curves can be generated from equations 20 and 21 by use of different pairs of S and ϕ . Then the experimental data can be compared to each member of the calculated family to obtain a fit which will determine S and ϕ for a particular barrier.

III. EXPERIMENT

A. Sample Preparation

Experimental work was carried out on barriers grown on four kinds of metal substrates: bulk vanadium and thin films of aluminum, chromium, and vanadium.²⁶ All the films were fabricated by electron beam evaporation of high purity metals in an ion-pumped vacuum chamber at pressures of approximately 10^{-7} torr. Evaporation was done through aluminum masks onto a standard 1 in. by 3 in. glass microscope slide at room temperature. The film strips were 5 cm long, 2000 Å thick, and either 0.125 mm (Al) or 0.25 mm (Cr and V) wide. The bulk vanadium junctions were made on 2 gm ingots which were first melted in a vacuum of 10^{-7} torr and allowed to cool, and then the desired junction area was masked with GE 7031 insulating varnish.

Oxidation of the samples was carried out in laboratory air. The aluminum strips were removed from the evaporation chamber and immediately placed on a ceramic support in a glass dessicator jar which had about 100 ml of distilled water in the bottom. The jar was sealed and two heat lamps (standard 250 watt infrared flood lights) were placed about 5 feet from it. The temperature inside the jar after several hours was in the neighborhood of 30-35°C and the humidity close to 100%, although care was taken to prevent water droplets from dripping or condensing on the slide. In general, 6 to 8 hours under these conditions would result in finished junctions (using an aluminum cross strip) with low-bias resistances of 0.5 to 1.0 megohm; 15 to 18 hours would result in resistances of 10 to 30 megohms, too great for easy measurement. The

final resistance could not be predicted exactly from oxidation time, but, except for occasional shorted junctions, junction resistance scaled with junction area, which ranged from 0.015 to 0.05 mm² on the same slide.

The chromium films were placed in an oven and oxidized for approximately 30 minutes at 200°C. Both types of vanadium samples were oxidized in air in an oven at 120°C for approximately 20 minutes. The order of magnitude low voltage resistances obtained in the finished junctions were 20 k Ω for chromium, 10 k Ω for bulk vanadium, and 1 k Ω for vanadium film.

After oxidation the samples were returned to the vacuum chamber and cross strips of silver, aluminum, or lead, approximately 2000 Å thick, were evaporated on top. Five junctions were made simultaneously on the film samples; it was possible to make only one junction at a time on the bulk vanadium.

Following completion of the sample it was installed in a sample holder and electrical leads were attached with silver paint to pads about 5 mm in diameter at each end of the metal strips. The pads were of the same material and thickness as the strips but merely much wider to provide good contact to the leads.

B. Cryogenics

Within 30 to 60 minutes after completion of the final deposition the sample, mounted on the sample holder, was installed in a standard 2-liter glass cryostat in an atmosphere of helium gas and cooled to 77°K with liquid nitrogen in the outer jacket of the cryostat. Then liquid helium was admitted to cool the sample to 4.2°K. It could be cooled further by pumping on the helium bath with a large mechanical pump ($\sim 10^5$ liters/sec) through a network of vacuum valves that permitted a variable pumping rate. In fact most of the measurements were carried out at about 1.2°K in order to observe the superconducting characteristics of the lead, vanadium, and aluminum electrodes. The temperature of the helium bath was determined by measuring the pressure of the helium gas above it using a standard manometer.

C. Electronics

Current was fed to the junction from a sawtooth signal generator through a large resistor. For the vanadium and chromium junctions the resistor was large enough to give a constant current source at all biases. For the aluminum junctions the resistor was only 3 to 5 times the low-voltage resistance. However, this does not affect the measurement of the current-voltage curves.

Measurements were carried out in a 4-terminal configuration. The voltage across the junction was measured using a high input impedance amplifier (100 M Ω) driving the horizontal axis of an X-Y recorder. Current was measured using another amplifier which amplified the voltage across a 1 k Ω resistor in series with the junction and drove the vertical axis of the recorder.

When the resistance dV/dI was needed to observe the phonon structure in the lead or vanadium electrodes, a standard ac modulation technique²⁷ was used. Superimposed on the current fed to the junction was a small constant ac signal at a frequency of a few hundred hertz. The voltage which appeared across the junction at this frequency was synchronously detected with a lock-in amplifier and, if we assume that the current modulation dI is constant, the voltage modulation dV is proportional to the resistance dV/dI . Here a constant current source for both the dc sweep and ac modulation is necessary, and high enough resistances were employed to achieve this.

Capacitance measurements were carried out on most high resistance junctions by using an ac capacitance bridge and subtracting the capacitance of the leads. The capacitance of these junctions is considerable; a 0.015 mm^2 aluminum-oxide-aluminum junction has a typical capacitance of about 100 pf.

D. Junction Quality

The verification of junction quality is of great importance in a tunneling experiment because tunneling is only one of the possible mechanisms of current transport in a junction and because junction fabrication techniques are not yet sufficiently exact to assure a good junction. In many of our junctions one of the electrodes was a superconductor, usually lead, and in these it was possible to observe the current which flowed through the junction at voltages below the superconducting energy gap and at temperatures well below the superconducting transition temperature of the film. This is considered²⁸ to be the most satisfactory method of

verifying that the predominant transport mechanism is indeed tunneling. Our data were taken from junctions which had satisfactorily low excess currents below the gap; most junctions had currents in the range of 0.005 to 0.001 of the normal state current at 1.2°K.

A further test of junction quality is to observe the lead phonon structure in the junction conductance. Figure 2 shows a graph of conductance versus voltage for an aluminum-oxide-lead junction made in the standard way and measured at about 1.2°K. This can be compared with figure 19 in McMillan and Rowell's review article Tunneling and Strong Coupling Superconductivity,²⁹ although McMillan and Rowell's curve is for a lead-insulator-lead junction. M. D. Jack³⁰ has done a calculation in which he has shown that the conductance change in figure 2 due to the phonons is of the correct magnitude to within the uncertainty of the superconducting energy gap in the aluminum film.

For the highest resistance samples, particularly aluminum, it was impossible to investigate the first few millivolts of the current-voltage curve, and thus we had to infer junction quality more indirectly. Usually junction resistance scaled with junction area, and the few junctions which departed from this pattern were rejected. The method of junction preparation for aluminum described in section III-A seems to have been highly reliable. In the lower resistance junctions, such as that shown in figure 2, where we could judge quality directly, it produced uniformly satisfactory junctions, except for a few junctions which were shorted. Thus we may have some confidence that most of the high resistance junctions were similarly good, since they were prepared in the same way except for being oxidized longer. Further, the fact

XBL738-1692

Fig. 2. Conductance-voltage curve for an aluminum-oxide-lead junction made in the standard manner, showing the conductance changes due to the lead phonons.

that we obtain results which are consistent from junction to junction argues that there was little significant variation in the quality of our junctions.

E. Junction Stability

Tunnel junctions often tend to be unstable. While we did not do any systematic study of junction aging, no change was observed in the gross characteristics of several aluminum-oxide-aluminum and chromium-oxide-silver junctions which had been stored for several months at room temperature between the times two sets of data were taken. On the other hand, we did observe two effects of bias on aluminum junctions. First, data were taken on most junctions to as high a bias voltage as possible: that is, until the junction either shorted or suddenly changed its resistance irreversibly. We think these effects are caused by junction heating, and this is another reason junctions were run in a bath of liquid helium. However, pumping the bath below the λ -point of helium seemed to have no further effect on the amount of power a junction could dissipate before failing. Second, on several of the highest resistance junctions (10-20 M Ω) on which we attempted to take data, the resistance showed a slow bias-dependent increase as data were being taken. That is, a particular current would be put through the junction and then removed. If the same current were again applied, the voltage across the junction would be greater, and this process could be repeated many times while the resistance seemed to approach some limit asymptotically. However, if the current were set to a new, higher value, the whole process would begin again. Since the field strength in the junction was then 0.1 to 0.5 V/A it is not unreasonable

to suppose that the increase in resistance was due to an electrochemical effect within the barrier. Data from these junctions were discarded, and junctions with resistances in the range 0.5 to 1.0 $M\Omega$ did not show this behavior.

IV. ANALYSIS

In this section we demonstrate our method of combining experimental results with the theory described in section II to obtain values for the parameters of the theory for an experimental junction. We begin by making a Fowler-Nordheim plot of the data and, if we have data to a high enough voltage, we obtain a straight line asymptote as predicted by equation 2. For example, figure 3 shows a Fowler-Nordheim plot for an aluminum junction, together with the asymptote. It yields a value for $S\phi^{3/2}$ of 79 Å (eV)^{3/2}. Next a family of calculated current-voltage curves is generated from equations 20 and 21 by using different values of S and ϕ for each, chosen so that the product $S\phi^{3/2}$ is kept constant. To continue the example, part of the family for $S\phi^{3/2} = 79$ is shown in figure 4. Then the experimental data are compared with each member of the calculated family until one is found which most closely matches the data. Since a relatively small change in the barrier parameters assumed for the calculation results in a considerable change in both the shape and magnitude of the calculated curves, the fit is a sensitive one. Figure 5 shows a comparison of experimental data and the calculated curve with which we obtained the best fit for $S\phi^{3/2} = 79$, giving $S = 20$ Å and $\phi = 2.50$ eV. Figure 6 shows the same data compared with the next member of the family, with $S = 22$ Å and $\phi = 2.35$ eV. The fit of the latter is obviously much poorer, and it is shown merely to illustrate the sensitivity of the method.

In doing the fitting in figures 5 and 6 the vertical axis of the calculated curves has been relabeled by adding an arbitrary constant to the logarithm of the current so that the curves lie approximately

XBL 733-5841

Fig. 3. A Fowler-Nordheim plot for an aluminum-oxide-aluminum junction.

Since $I \propto V^2 \exp \left[-\frac{4\sqrt{2m}}{3h} \frac{S\phi^{3/2}}{eV} \right]$ for large V , the data points asymptotically approach a straight line toward the left of the graph. The slope of the line gives a value for $S\phi^{3/2}$ of $79 \text{ \AA (eV)}^{3/2}$.

XBL 733-5842

Fig. 4. A family of calculated curves for various values of S with the product $S \phi^{3/2}$ fixed at $79 \text{ \AA} (\text{eV})^{3/2}$. The shape of the curve is a sensitive function of S , permitting an unambiguous determination of parameters by comparing this family to the experimental data.

XBL 733-5843

Fig. 5. The curve from figure 4 which gave the best fit for the particular junction with $S\phi^{3/2} = 79 \text{ \AA}(\text{eV})^{3/2}$ plotted on top of the experimental data. The agreement is excellent over five orders of magnitude of current. The slight hump in the data points near $V = 1$ volt is not understood.

XBL733-5841

Fig. 6. The same data as that shown in figure 5 compared with the calculated curve for a value of S which is 10% away from the best fit. The magnitude of disagreement illustrates the sensitivity of our technique for determining barrier parameters.

on the experimental data. This is equivalent to allowing an arbitrary constant multiplying equation 21. It is therefore the shape of the calculated curve and not its absolute magnitude that we compare with the data.

This procedure is necessary because the absolute current through a tunnel junction apparently cannot be calculated adequately in the coherent-elastic-tunneling scheme used to derive equation 21. First, there is an uncertainty in the multiplicative factor which should precede the WKB tunneling probability. For a trapezoidal barrier Gundlach and Simmons¹⁸ show that this is between 1 and 10. Second, there is the possibility of other, parallel tunneling processes. Duke³¹ discusses one which has the same functional form as the current described by equation 21 and therefore will produce a total current which is that of equation 21 multiplied by some constant. Finally there is the correction to the model used to derive equations 20 and 21 which takes account of the nonuniformity of the barrier thickness. It is difficult to know how to account for this quantitatively, since it depends on the details of the nonuniformity.

Practically we have decided to allow an arbitrary constant factor multiplying equation 21 in order to bring the calculations into rough agreement with the data, and we attach no physical significance to its value. With the graphs for data and calculations plotted on semilog paper it is easy to slide them up and down on top of each other until a reasonable fit is obtained, and this is equivalent to the multiplication we have described. The value of the multiplicative constant appears to vary from one type of sample to another, although it appears roughly

the same for the limited range of barrier parameters we have observed in each type of sample. For the aluminum sample shown in figure 5 it is experimentally 7.9×10^7 , while that calculated from the constants in equation 21 (including conversion of the dimensions of the integrals from electron volts to joules) is about $3.6 \times 10^6 \frac{\text{C(sec)}^3}{\text{m}^4 (\text{kg})^2}$, a factor of 22 smaller. For the vanadium and chromium samples to be discussed later (figures 7, 8 and 9) the experimental value is about 10^2 or 10^3 , while the calculated value is on the order of 10^4 larger.

While we have chosen largely to ignore this point in our analysis, and, as can be seen from figure 5 and later figures, we obtain good sensitive fits with reasonable barrier parameters, it is the least tidy part of the analysis. It certainly points to the inadequacy of our model in some respects. However, it is puzzling why the experimentally measured current should be greater than predicted in the case of aluminum junctions, yet considerably less in the case of chromium and vanadium junctions. We proceed with our analysis using the shape of the curves as the important criterion, since it appears that equation 21 does describe relative currents quite accurately.

V. RESULTS

A. The Test Case: Aluminum-Oxide-Aluminum

The barrier grown thermally in air on an aluminum electrode was chosen to test our method of analysis because it has been the most extensively studied kind of tunneling barrier.³²⁻³⁵ In addition, junctions made this way are relatively easy to fabricate with a variety of counterelectrodes, and they are relatively rugged and stable.

The fit shown in figure 5 for aluminum-oxide-aluminum is excellent over the whole range of tunnel current, and from it we can assign an effective tunneling thickness of 20 Å and an effective tunneling barrier height of 2.50 eV to this particular junction. We obtain similar fits for other aluminum junctions with thicknesses in the range 12-22 Å and barrier heights of 2.50-2.75 eV. All these measurements were made with the oxidized electrode biased negative.

1. Barrier Thickness

The parameters S and ϕ which we determine can of course be measured in other ways. A measure of barrier thickness can most simply be obtained by measuring the capacitance of the junction and its area. By assuming a value for the dielectric constant, a thickness can then be derived. The film thickness can also be measured by ellipsometry, with identical results,³⁶ although we have not performed this measurement ourselves. Capacitance and ellipsometry measurements always give a measure of barrier thickness greater than the thickness determined from tunneling measurements. For example, capacitance measurements on the aluminum junction discussed above, together with an assumed static dielectric constant of 8.8,³⁷ yield a barrier thickness of 33 Å.

While both the thickness measurements we have obtained, one from tunneling, one from capacitance, are reasonable values and correspond roughly to what has been obtained previously,³³ they differ by a large enough amount so that the difference cannot be ignored or readily explained away. For example the dielectric constant we have assumed is the value for bulk amorphous Al_2O_3 and it may not be exactly correct in this case. However, the value necessary to put the capacitance measurement in agreement with the tunneling measurement is much too low. A more reasonable explanation leads us to a refinement in our model for the barrier. In both the tunneling and capacitance calculations we have assumed a plane parallel geometry for the junction. As we have indicated in section III, this is certainly not the case in a real junction. The grown oxide does not cover the oxidized electrode in a layer uniform on the scale of a few angstroms, and thus there are some areas which are thinner and some which are thicker.

We can obtain an idea of how these nonuniformities must be distributed from the work of Dynes and Fulton³⁸ on Josephson junctions. Using the Josephson interference pattern they have shown that current flow is distributed almost uniformly over the area of a thermally oxidized tin-insulator-tin junction. It is likely that our junctions, oxidized in a similar way, have a similarly uniform current density distribution over the junction area. Thus the difference in thickness measurements in our junction is probably not due to only a small number of thin spots in the oxide, or to thin edges. However, the Fourier transform technique which Dynes and Fulton used is limited in resolution by the number of lobes of the Josephson interference pattern which can be

measured. Their measurements effectively average the current density over strips of about 0.01 mm by 0.2 mm on a junction 0.2 mm square. Thus their experiment could not resolve a variation in barrier thickness which occurred over distances much smaller than 0.01 mm.

In fact, there must be some variation in the thickness of the oxide layer, since thermal growth certainly cannot produce an oxide a few atomic layers thick which is uniform in thickness to within a single atomic layer. This variation apparently occurs on a scale small enough so that no macroscopic region of the junction carries a predominantly larger current than any other. The sample can be thought of schematically as a set of microscopic plane tunnel junctions, with the same barrier height but with barrier thickness distributed about a mean, which are connected in parallel and arranged randomly over the actual junction region.

This distribution of thicknesses affects the tunneling current and junction capacitance in different ways, because of their different dependence on thickness. The capacitance varies as $1/S$, while the tunneling current very crudely can be approximated by an exponential e^{-S/S_0} , where S_0 (although voltage dependent) is a characteristic length on the order of 1 Å. Therefore a distribution of thicknesses has a much larger effect on the tunneling current than on the capacitance of the junction, and this effect tends to make the apparent tunneling thickness smaller than the capacitative thickness.

We can get a quantitative estimate of this variation by assuming a Gaussian distribution³⁹ and asking what standard deviation is necessary, assuming a mean thickness of 33 Å, to match the tunneling curve which

we calculated by assuming a thickness of 20 Å and a plane geometry. Let us approximate the dependence of current on barrier thickness by the simple exponential

$$I \sim e^{-S/S_0} \quad (22)$$

and define S_m as the mean barrier thickness, σ as the standard deviation around the mean, and t as the thickness of the equivalent plane barrier. Then we can obtain an equation for σ in terms of S_m , S_0 , and t by equating the current through a barrier of mean thickness S_m and deviation σ to that through a plane barrier of thickness t . Using the usual expression for a weighted average

$$\bar{I} = \int \rho(S) I(S) dS \quad (23)$$

and letting $P(S)$, the probability of a given thickness occurring, be given by

$$P(S) = \frac{1}{\sqrt{2\pi} \sigma} \exp \left[-\frac{(S-S_m)^2}{2\sigma^2} \right], \quad (24)$$

we obtain

$$I \sim \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} \exp \left[-\frac{(S-S_m)^2}{2\sigma^2} \right] e^{-S/S_0} dS = e^{-t/S_0}. \quad (25)$$

The integral in this equation is the current through a barrier with a distribution of thicknesses about the mean S_m ; the term on the right is that through a plane barrier of thickness t .

One potential difficulty must be noted before we can simplify equation 25. It is not meaningful to consider a value of S less than zero in doing the integral, since this corresponds to a barrier with

negative thickness. However, if S_m is sufficiently large and σ sufficiently small the contribution from the region $S < 0$ will be negligible and, as we shall see (equation 26 below), the problem is merely a conceptual one.

By completing the square in the exponent of the integrand in equation 25, the equation can be written as

$$\frac{1}{\sqrt{2\pi} \sigma} \left[\int_{-\infty}^{\infty} e^{-\frac{1}{2\sigma^2} (S - S_m + \frac{\sigma^2}{S_o})^2} dS \right] \exp \left[-\frac{S_m - \frac{\sigma^2}{2S_o}}{S_o} \right] = e^{-\frac{t}{S_o}}. \quad (26)$$

The integral in brackets is just another Gaussian and, since it is properly normalized, unity. By taking the logarithm of both sides of the rest we obtain

$$S_m - \frac{\sigma^2}{2S_o} = t, \quad (27)$$

or

$$\sigma^2 = 2S_o(S_m - t). \quad (28)$$

An estimate for the value of S_o can be made by noting that in the high voltage (Fowler-Nordheim) region

$$\frac{1}{S_o} = \frac{2\alpha\phi^{3/2}}{3 \text{ eV}} \quad (29)$$

which for $\phi = V = 2$ volts has a value of about 1 A^{-1} . Using this value and $S_m = 33 \text{ A}$ and $t = 20 \text{ A}$, we obtain a value of $\sigma = 5 \text{ A}$.

While the calculation is oversimplified, the estimate we make is useful, and a more detailed calculation is probably unwarranted. A deviation of 5 Å is small and entirely reasonable and gives us an idea of the scale on which the thickness variations in the junction occur. The capacitance is hardly affected by a variation of thickness with this distribution; an almost exact calculation can be done⁴⁰ which shows the capacitance increases by about 3%.

In this way we conclude that a thermally oxidized tunneling barrier is microscopically nonuniform and that the capacitatively determined thickness is to a good approximation the mean thickness of the insulating barrier. The thickness derived from tunneling measurements is, however, the thickness which must be used to determine a barrier height from a Fowler-Nordheim value of $S\phi^{3/2}$, not the capacitative thickness, which results in a considerable underestimate of ϕ .

2. Barrier Height

The most convincing independent measurement of barrier height is obtained from photoemission over the barrier.⁴¹ In this experiment the junction is irradiated with photons through one of the electrodes, which is made sufficiently thin to pass most of the light incident on it. Electrons are photoexcited, primarily in the thin electrode,⁴¹ and those excited by photons of energy greater than the barrier height can flow through the conduction band of the insulator to the other electrode, inducing a photocurrent in parallel with the tunneling current. The photon energy below which no photoresponse is observed is taken as the barrier height.

Unfortunately attempts to observe a photoresponse in our junctions have been unsuccessful, and the reasons for this are still not understood. However, Mead⁴² has told us that their photoresponse measurements required a powerful light source, large aperture optics, and a great deal of fiddling with equipment and junctions before any photoresponse at all was observed. In particular, they were able to see a photocurrent only in junctions whose barriers were formed at high temperatures (several hundred degrees Celsius) in a nitrogen atmosphere; they were not able to obtain a response with any junctions whose barriers were formed at room temperature.

Gundlach and Hölzl³² do report a value for the barrier height determined from photoresponse in thermally oxidized aluminum-oxide-aluminum junctions; they obtain a value of about 2.4 eV for a junction in the direction corresponding to the oxidized electrode being negatively biased.

Gundlach⁴³ has developed another technique for determining barrier heights from the derivative of the logarithm of the tunneling current with respect to voltage $d \ln I/dV$ (logarithmic derivative). He noted that in the Simmons approximation for a trapezoidal barrier this quantity exhibits a discontinuity and peak at a voltage corresponding to the barrier height and, although the discontinuity is an artifact of the approximation, the logarithmic derivative of the current obtained from equation 21, using a trapezoidal barrier model, does contain a pronounced peak at a voltage approximately corresponding to the barrier height as well. Further, Gundlach and Hölzl³² have observed this peak experimentally in aluminum-oxide-aluminum junctions at about 2.6 volts with the oxidized electrode negative.

Our calculations and experience have shown that, while it is sometimes useful, this peak is not an unambiguous indicator of junction barrier height. A more complete discussion of our calculations can be found in Appendix B. To summarize them briefly, the peak is highly model dependent, in that we can produce it in a calculation at a voltage anywhere from 25% below to 40% above the actual barrier height used merely by changing the shape of the model barrier slightly, and for some barrier profiles it does not occur at all. The latter behavior will be illustrated by our chromium and vanadium junctions discussed later in this section. For a trapezoidal barrier with parameters which correspond roughly to those of aluminum, the peak occurs about 10 to 20% above the actual barrier height. If it is possible to obtain data to this voltage and if there are reasons to believe the trapezoidal model is reasonably good, then the peak can be used as an indicator of barrier height, as in the case of Gundlach and Hölzl's junctions. However, for the junction whose data are shown in figure 5 we estimate that the peak would occur between 2.8 and 3 volts and that the junction would then be dissipating about 200 watts/cm^2 . Our highest data point, limited by junction burnout, is 2.7 volts, and the logarithmic derivative is still rising.

There is one further way of obtaining an estimate of the barrier height from experimental data. If the calculation of the tunneling current is done for a nonzero temperature, rather than for $T = 0$ as we have done, the temperature dependence of $J(V, T)$ will be found to be greatest at $V \approx \phi$.⁴⁴ The physical origin of this effect is that an increase in temperature effectively removes electrons from a region

where the barrier is high and thick to a region where the barrier is both lower and thinner. At $V \approx \phi$ the effect is a maximum. The usual measure of this is to plot

$$\hat{j}(V, T_1, T_2) = \frac{J(V, T_1) - J(V, T_2)}{J(V, T_2)} \quad (30)$$

as a function of bias for fixed T_1 and T_2 . As with the peak in the logarithmic derivative, this effect is somewhat model dependent, although apparently less so. However, there may also be effects due to changes in the properties of the insulator with temperature which confuse the interpretation of the method. As an indication of this, the magnitude of the temperature dependence predicted from the finite-temperature version of the theory in section II is always much smaller than that observed. Chang, Stiles, and Esaki³⁴ have used the method to estimate the barrier height of an aluminum-oxide-aluminum junction and report a value of about 2.3 eV.

We have discussed briefly three other methods of estimating barrier heights in tunnel junctions. The results they have given other workers for junctions which are similar to ours are consistent with our estimates, although a little lower. The most satisfactory of the four for measuring the barrier height alone is photoresponse, although it appears to be a difficult experiment which is not suitable for routine use. The three tunneling methods all require high-voltage data. However, with our method we have been able to obtain estimates of parameters in junctions for which neither of the other two could be used because of lack of data to quite a high enough voltage. Here the voltage difference

is small but the current difference is enormous. All three methods are more or less model dependent, but seem to give reasonably consistent results, to judge by those for aluminum.

Having a measure of the barrier height can not only allow us to compare tunnel junctions, but it can also suggest something about the properties of the barrier material. In figure 1 we show the Fermi level half way between the valence and conduction bands in the insulator. This is true for an insulator without impurities in our simple model and predicts that the tunneling barrier is just one-half the optical band gap in the insulator. While nothing is so simple for a real junction, there seems to be a remarkably close correspondence in the aluminum oxide barrier. Our values of ϕ lie between 2.5 and 2.75 volts, while half the band gap in amorphous Al_2O_3 is between 2.5 and 3 volts.^{45,46}

B. Other Materials: Chromium and Vanadium

We have applied the method developed above for aluminum junctions to determine parameters for barriers grown thermally on thin film chromium and on thin film and bulk vanadium. Representative values of $S\phi^{3/2}$ for these junctions are 2.75 for barriers on bulk vanadium, 0.52 for barriers on thin film vanadium, and 5.9 for barriers on thin film chromium. Figure 7 shows data taken from a junction made on bulk vanadium with a lead counterelectrode, together with the calculated curve from the family with $S\phi^{3/2} = 2.75$ which gives the best fit to the data. The fit is quite good, and from it we can assign a thickness parameter of 25 Å and a barrier height of 0.23 eV to this junction. In figure 8 we show data from a similar junction made on thin film vanadium.

XBL 736-6342

Fig. 7. Experimental data and calculated curves for a tunneling barrier grown on a piece of bulk vanadium. The ϕ is almost as good as that shown in figure 5.

XBL 736-6341

Fig. 8. Experimental data and calculated curves for a tunneling barrier grown on a vanadium film. The fit is not as good as that in figure 5, and therefore three calculated curves are shown, bracketing the barrier parameters, S between 14 and 20 $\text{\AA}$ and ϕ between 0.087 and 0.111 eV.

In this case three calculated curves have been drawn, bracketing the data, because the deviation from any one of the curves is larger than that in figures 5 or 7. The middle curve (B) seems to be the most reasonable since the deviation from it is on the whole the smallest. It was calculated with a barrier thickness of $17 \text{ \AA}$ and a barrier height of 0.097 eV . Figure 9 shows data from a junction made on chromium. Again, three calculated curves have been drawn, bracketing the data. The middle one (B) allows us to assign a barrier thickness of $13 \text{ \AA}$ and a barrier height of 0.59 eV ; the parameters assumed in the other two curves in figure 9 differ only slightly.

The deviations of the data from the calculated curves which occur in figures 7, 8 and 9 are probably due to the fact that the model used in the calculations is oversimplified. In fact, the deviations are reproducible from sample to sample and even resemble each other from one type of junction to another. That is, after the best fit is made to the experimental data, deviations regularly occur in two places: the current at low voltages is slightly too small and the current at intermediate voltages is slightly too large. No better fit can be obtained to the data shown, the deviations fortunately are small, and we can tightly bracket the range of possible values of the parameters we determine.

We know of no other measurements of barrier parameters in chromium and vanadium oxide junctions. We have calculated the logarithmic derivative $d \ln I/dV$ for the data shown in figures 7, 8 and 9 in an attempt to check our own measurements. For the thin film chromium and vanadium junctions there is no definite peak in the derivative; it

XBL 736-6340

Fig. 9. Experimental data and calculated curves for a tunneling barrier grown on a chromium film. The fit is not as good as that in figure 5, and therefore three calculated curves are shown, bracketing the barrier parameters, S between 12 and 14 $\text{\AA}$ and ϕ between 0.56 and 0.62 eV.

decreases monotonically. In both cases, however, there may be a weak broad shoulder at approximately the proper bias voltage, although its amplitude is less than the scatter in the data. In the case of bulk vanadium there is a small but definite peak at about 0.2 volts, which is consistent with our measurements.

C. Discussion

The results we have shown so far have been obtained for particular junctions with the oxidized electrode negative in each case. However, from the analysis of many samples it is possible to draw some more general conclusions about the barriers of the tunnel junctions we have made.

First, the barrier height we measure is practically the same from sample to sample for a barrier grown in the same way on the same material, and therefore we conclude that we are measuring an intrinsic property of the material. Our range of measurements has been 2.50-2.75 eV for aluminum, 0.52-0.60 eV for chromium, 0.20-0.25 eV for bulk vanadium, and 0.090-0.110 eV for thin film vanadium. The barrier thickness, on the other hand, varies considerably from sample to sample, and its value means little except for the individual sample.

Second, when data are used from the opposite bias polarity, that with the oxidized electrode positive, for a particular sample, the thickness parameter we measure is almost exactly the same as that measured with the electrode negative, but the barrier height we measure is often different. In the case of aluminum junctions it corresponds to that obtained previously by other workers (e.g., reference 32), roughly 2 eV, for the oxidized electrode positive. Chromium-lead

junctions show a similar asymmetry, but in both bulk and thin film vanadium-lead junctions the current-voltage curves are virtually symmetric in bias polarity, and this results in the same measure of barrier height. By comparing our results with those from photoemission and logarithmic derivative measurements on asymmetric barriers, we judge that we are measuring the barrier height at whichever electrode is negatively biased (in our sharp barrier model). Thus although the model we use is exact only for a symmetric barrier, it seems to give reasonable estimates of the barrier heights of asymmetric barriers as well.

One remarkable fact emerges when results are compared for barriers grown on the two types of vanadium. Even though the base metal is the same and the barriers were formed under identical conditions, the barrier heights differ by more than a factor of two. This is a property common to all the barriers we have grown on each type of vanadium base. The reasons for it are not understood. However, there is one condition which is likely to account for the difference. Oxygen is highly soluble in vanadium, and the evaporated films probably contain a significant amount of dissolved oxygen. Because the vanadium-oxygen system is so complex⁴⁷ this may result in different nonstoichiometric versions of the same oxide or two entirely different oxides in the two types of junction. In addition the presence of different amounts of oxygen in the vanadium may make the metal-barrier interface quite different in the two cases.

Up to this point we have avoided specifying what the insulating compounds are which make up the barrier. We have made no direct study

of the question, although techniques (Auger and ESCA spectroscopy, most notably) are becoming available and can do exactly this. It is now a question of major importance in the study of the tunneling barrier and should be pursued. It is conventionally assumed that the common oxide of the metal which forms the base makes up the barrier in junctions thermally oxidized in air. Therefore for a barrier grown on an aluminum film the material would be Al_2O_3 , and, in comparing the barrier height to the optical band gap in Al_2O_3 , we obtained a reasonable agreement. However, the situation is almost certainly more complicated than that suggested by our model—a homogeneous layer of pure Al_2O_3 with sharp boundaries between the aluminum electrodes. In particular, there is likely to be a gradual progression from pure aluminum deep inside the oxidized electrode to a rather highly oxidized state at the surface of the counterelectrode, although there may be regions where there is a specific compound. The most highly oxidized state is also likely to be the best insulator.

In the case of chromium the insulator is almost certainly Cr_2O_3 , since it is the only common oxide which grows on pure chromium under oxidation conditions similar to those we used.⁴⁸⁻⁵⁰ Further, the other common oxide, CrO_2 , is metallic. However, the barrier height we obtain for a chromium junction, about 0.6 eV, is only about one-quarter of the optical gap in Cr_2O_3 .

Before discussing this difference we consider vanadium. The vanadium-oxygen system is extremely complicated. About ten oxides and two stable solid solutions have been reported in bulk; these are reviewed by Adler⁴⁷ and Stringer.⁵¹ In addition, the oxides have

considerably different electron transport properties. In particular, most of them show in bulk a sharp metal-semiconductor transition. The common oxide which does not is V_2O_5 . The transition was not observed in any of our junctions except a few whose oxide was reduced at high temperatures in an atmosphere of carbon monoxide before depositing the top electrode.⁵² This was done to produce a different oxide, and data from these junctions has been excluded from the present analysis. The transition observed in these reduced junctions was that corresponding to V_2O_3 ,⁵² which suggests that the original oxide was a higher oxide. V_2O_5 is the likely candidate, and it has the further attraction of being the best insulator of the group; the other common oxides are probably not good enough insulators to account for the junction resistances we observe. The other possibility which has been suggested⁵³ is one of the so-called Magnéli phases, V_3O_5 , about which little is known. While any statement about the insulator is speculation, if the barrier were V_2O_5 the barrier heights we measure, 0.1 eV (film) or 0.2 eV (bulk) would be only a small fraction of the optical gap, 2.5 eV.⁵⁴

If the oxides on vanadium and chromium are indeed V_2O_5 and Cr_2O_3 it is possible to account for the abnormally low barrier height by noting that these two oxides in bulk are both oxygen-deficient n-type semiconductors.^{47,54} That is, oxygen vacancies occur in the compounds, leaving two extra electrons which attach themselves loosely to Cr^{3+} and V^{5+} ions, resulting in Cr^{2+} and V^{4+} donors. These donors, which would not be ionized at the temperature at which our experiments were done, lie approximately 0.6 eV⁴⁷ below the conduction band in the case of chromium and 0.2 eV⁵⁴ below the conduction band in the case of

vanadium. At zero temperature the Fermi level lies half way between the conduction band and the donor level, resulting in a barrier height of half the donor depth. While this explanation is based on an oversimplified model and a guess about the oxides, it goes remarkably far towards accounting for the abnormally low barriers.

VI. SUMMARY AND CONCLUSION

We have described a method for obtaining a set of characteristic parameters for the barrier in a tunnel junction from the experimental current-voltage curves by use of a simple model for the barrier. The general method is to determine the combination of parameters $S\phi^{3/2}$ for a particular junction from a Fowler-Nordheim ($\ln I/V^2$ vs $1/V$) plot of the experimental data. Then, using a trapezoidal barrier profile which is rectangular at zero bias and the WKB approximation to calculate the tunneling probability, we compute the tunneling current from equation 21. This is done for several values of S and ϕ with the product $S\phi^{3/2}$ held equal to the experimentally determined one. Experimental data are then compared to the calculated curves and barrier parameters are assigned based on the curve to which the data corresponds most closely.

We have tested the method with high quality aluminum-oxide-aluminum junctions using one bias polarity, and we obtain fits to data which are both excellent over a large range of current and voltage and highly sensitive to the choice of barrier parameters. In addition, the method is more generally applicable than the model might suggest, since, for barriers which are not rectangular at zero bias, the barrier thickness we determine seems to be independent of polarity and the barrier height seems to be equal to those determined by others for the corresponding polarity.

Further, from our analyses has emerged a description of the insulating tunnel barrier which we believe to be as detailed as is reasonable to consider from an analysis based on macroscopic properties (e.g., tunnel current and capacitance). While we have at times gone beyond

this description to speculate about some of the details of the barrier materials and the way they grow, this speculation relies on information which is less certainly known, and it is not at all necessary for the analysis we have presented. The trapezoidal model seems to be a reasonably adequate description of the barrier. The barrier heights on the two sides of the barrier are often unequal, producing a potential profile with a tilt at zero bias, but the barrier height does not appear to vary to any significant extent over the junction area. The barrier thickness is not uniform, but the variation, which is on a microscopic scale, can be approximated, at least for the purposes of calculation, by a Gaussian distribution with a standard deviation which is a small fraction of the mean.

Within the framework of this simplified description of the barrier our analysis provides a convenient, consistent, and sensitive way to determine barrier parameters of high resistance tunnel junctions. We have been able to achieve this sensitivity and the good agreement between our measurements and those of others largely because of the way in which we have combined experimental data and theoretical calculations. By using the Fowler-Nordheim graph to limit our choice of possible values of S and ϕ before doing any calculations, we have avoided the problem which others have had who have tried to fit tunneling data and calculations without first knowing something of the parameters involved: A fit can then be obtained with quite a wide range of parameters, most of them reasonable. By initially restricting our choice we obtain parameters which are virtually unique for a particular junction.

We illustrate the use of our method of analysis with three other types of tunneling barriers: those grown thermally on thin film chromium, thin film vanadium, and bulk vanadium, and we consider briefly what guesses can be made about the composition of the barrier materials based on our analysis. Finally, in Appendix C we have graphed a series of curves with different values of $S\phi^{3/2}$ for use in estimating barrier parameters without doing lengthy computer calculations.

ACKNOWLEDGMENTS

I wish to thank Professor Gene Rochlin for introducing me to tunneling and for his generous and enthusiastic support throughout my research. Professor Paul Hansma made the suggestion that led to the beginning of the present project, and he has provided much invaluable advice and guidance along the way. For this and for permission to use his chromium and vanadium data I am grateful. Thanks are due to Professor L. M. Falicov for assistance and stimulation during the course of the project. I thank Professor G. A. Somorjai for helpful discussions of the chemistry of the oxide layer, and Professors A. F. Kip and John Clarke for their counsel and advice.

This work was done under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory.

APPENDIX A

Details of the Computer Calculation

The following pages contain a listing and sample tabular results of the computer program used to calculate the tunneling current given by equation 21. The method used is an adaptive Simpson's rule numerical integration, which proved to be sufficiently fast and accurate. If the integration interval is divided into n segments of length z , then the integral can be approximated by

$$\int_a^b f(x) dx = \frac{b-a}{n} \left[\frac{1}{4} f(b) + \frac{1}{3} f(b-\frac{z}{2}) + \frac{11}{12} f(b-z) + f(b-2z) + \dots \right. \\ \left. \dots + f(b-(n-2)z) + \frac{11}{12} f(a+z) + \frac{1}{3} f(a+\frac{z}{2}) + \frac{1}{4} f(a) \right] \quad (31)$$

Computation was done to about 3 digit accuracy. On a CDC 7600 computer with the Berkeley RUN76 compiler, computation of a 100-point current-voltage table with this program required about 1 second of central processor time.

TUNN

```

PROGRAM TUNN( INPUT,OUTPUT)
COMMON D,V,EF,PHI
DIMENSION AJ(100)
DIMENSION DJ(100)
DIMENSION VX(5)
DIMENSION AX(5)
      dco READ 1,D,PHI,VTOP,IEND
      1  FORMAT (3F10.4,110)
16      EF=6.
17      VP=VTOP/100.
21      V=-VP
22      PRINT 4,D,PHI
      4  FORMAT(11H1CURRENT,D=,F10.1,SH PHI=,F10.3///)
32      DO 1000 J=1,100
34      V=V+VP
35      BINT=0.
36      N=16
37      STORE=DEX(EF-V)
44      50  FN=N
45      A=(EF-V)/FN
50      X=EF-V
51      AINT=DEX(X)/4.
54      X=X-A/2.
57      AINT=AINT+DEX(X)/3.
64      X=X-A/2.
66      AINT=AINT+11.*DEX(X)/12.
73      L=N-1
76      DO 10 I=3,L
77      X=X-A
100     DX=DEX(X)
102     AINT=AINT+DX
104     IF(DX/STORE-.0000001 )11,11,10
107     10  CONTINUE
112     X=X-A
113     AINT=AINT+11.*DEX(X)/12.
120     X=X-A/2.
123     AINT=AINT+DEX(X)/3.
130     X=X-A/2.
132     AINT=AINT+DEX(X)/4.
137     11  AINT=AINT*(EF-V)/FN
142     IF(AINT)20,30,20
143     20  ABINT=ABS(AINT)
145     IF(ABS(ABINT-ABS(BINT)))/ABINT-.001 ) 30,30,40
153     40  N=2*N
154     BINT=AINT
156     GO TO 50
      C
      C SECOND INTEGRAL*****
      C
156     30  BINT=0.
157     CINT=0.
157     N=16
161     STORE=DEX(EF)
163     120  FN=N
164     A=V/FN
166     X=EF

```


TURN

```

167      IF(V)60,60,70
170      HINT=((EF-X)/4.)*DEX(X)
175      X=X-A/2.
200      BINT=BINT+((EF-X)/3.)*DEX(X)
207      X=X-A/2.
211      BINT=BINT+((EF-X)/12.)*DEX(X)
220      L=N-1
223      DO 80 I=3,L
224      X=X-A
225      DX=DEX(X)
227      BINT=BINT+(EF-X)*DX
233      IF(DX/STORE-.0000001 181,81,80
236      CONTINUE
241      X=X-A
242      BINT=BINT+((EF-X)/12.)*DEX(X)
251      X=X-A/2.
254      BINT=BINT+((EF-X)/3.)*DEX(X)
262      X=X-A/2.
264      BINT=BINT+((EF-X)/4.)*DEX(X)
273      81 BINT=BINT+V/FN
275      IF(BINT)90,60,90
276      90 ABINT=ABS(BINT)
300      IF(ABS(ABINT-ABS(CINT))/ABINT-.001 160,60,123
306      123 N=2*N
307      CINT=BINT
311      GO TO 120
311      60 AJ(J)=V*ABINT+BINT
315      1000 CONTINUE
317      DO 100 I=1,20
320      DO 101 J=1,5
326      L=I+(J-1)*20
331      QTEMP=L-1
332      VX(J)=QTEMP*1000.*VP
334      101 AX(J)=AJ(L)
337      100 PRINT 2,(VX(K),AX(K),K=1,5)
2      FORMAT(5(F10.1,E14.5))
356      600 IF(IEND)700,800,700
357      700 CONTINUE
360      ENQ

```

DEX

```

FUNCTION DEX(X)
COMMON D,V,EF,PHI
IF(V)1,1,2
TERM=EF+PHI-X
TR1=TERM**1.5
IF(TERM-V)3,3,4
TR2=(TERM-V)**1.5
GO TO 5
3      TR2=0.
4      5 COEFF=(2.*1.025*D)/(3.*V)
27     DEX=EXP(-COEFF*(TR1-TR2))
35     RETURN
35     1 DEX=EXP(-1.025*D*(EF+PHI-X)**.5)
47     RETURN
47     END

```


APPENDIX B

The Logarithmic Derivative as a Means of Determining Barrier Heights

Gundlach⁴³ has proposed a technique for determining the barrier height of a tunnel junction by the observation of a peak in the logarithmic derivative $d \ln I/dV$ of the tunnel current. In the Simmons approximation for a trapezoidal barrier an analytic expression may be obtained for this quantity, and it contains a discontinuity which results in a peak at a voltage corresponding to the barrier height. The discontinuity is an artifact of the approximation, since the actual current in a tunnel junction does not show a discontinuity in slope, but in a numerical calculation for the same model a definite peak remains, displaced to a somewhat higher voltage than the barrier height.

Gundlach⁴³ saw the peak in experimental data from aluminum-oxide-aluminum and aluminum-oxide-magnesium junctions, and since then he and Hölzl,³² and Basavaiah, Eldridge, and Matisoo²⁵ report data which also exhibits a peak of this kind. We were unable to obtain data to a high enough voltage from our aluminum junctions to confirm its existence for our junctions, although the derivative rises steeply at a high voltage, as it would just below the peak. However, our chromium and vanadium data show virtually no sign of a peak except for some junctions made on bulk vanadium, which show a small peak.

In addition to the fact that we sometimes did not see the peak, we were concerned about its dependence on the trapezoidal barrier model,

both because it was said to measure the height of the sharp barrier at the metal-insulator interface, which is highly model dependent, and because in the calculations the assumed barrier height apparently differed from the position of the peak by a small but unknown amount. We therefore have done a set of calculations on the trapezoidal model and two others which, while far from exhaustive, suggest some of the strengths and limits of the method. Our calculations are to some extent complementary to Gundlach and Hölzl's,³² to which we shall refer as well.

For the trapezoidal barrier model they have shown that a peak always occurs, and that its position is relatively insensitive to the barrier thickness, energy difference between the top of the valence band and the Fermi level, and the dielectric constant of the insulator. For a limited range of barrier heights corresponding to reasonable parameters for aluminum junctions, the peak occurs from 10 to 20% above the barrier height assumed for a trapezoidal barrier. For example, figure 10 shows the logarithmic derivative from a calculation made with a trapezoidal barrier of height 2.5 eV and thickness 20 Å which is square at zero bias. The peak is evident and rather sharp, and it occurs at about 2.75 volts, or 10% above the assumed barrier height, which is marked with an arrow.

This difference is not itself independent of barrier parameters, however. Figure 11 shows the logarithmic derivative for exactly the same barrier profile but with parameters at the opposite extreme, a barrier height of 0.097 eV and a barrier thickness of 17 Å. Here the peak is relatively broader, and it occurs at 0.138 volts, about

XBL 738-1693

Fig. 10. Logarithmic derivative of the tunnel current calculated for a trapezoidal barrier like that shown in figure 1. The peak occurs at 2.75 volts, 10% above the 2.50 eV assumed barrier height, marked with an arrow.

Fig. 11. Logarithmic derivative of the tunnel current calculated for a trapezoidal barrier as in figure 10, but with a much lower barrier height. The peak is now at 0.138 volts, about 40% above the 0.097 assumed barrier height, marked with an arrow. The minimum which occurs near the arrow is not significant.

40% higher than the assumed barrier height. (The fact that the minimum occurs at almost the assumed height is clearly fortuitous.) We have made no attempt to be more systematic in investigating the shift in the peak since we make little use of the effect, but we must conclude that the position of the peak cannot be predicted even with a trapezoidal model of known barrier height.

In order to check to what extent the peak in the logarithmic derivative is dependent on the particular barrier shape chosen, we picked two other shapes which were reasonably easy to calculate: the half (truncated) parabola and the full parabola.

The half parabola, whose profile is shown in the inset to figure 12, is a shape which is not too different from the trapezoidal barrier used in the rest of our calculations. In particular, it has a sharp edge of height ϕ at one edge of the barrier, and this height is what the peak in the logarithmic derivative is supposed to represent. If the voltage drop across the barrier is taken to be linear, the profile can be written as

$$\phi(x,V) = -\frac{\phi}{2} x^2 - \frac{V}{S} x + \phi \quad . \quad (32)$$

The WKB integral can be done exactly and the results, using the parameters $S = 20 \text{ \AA}$ and $\phi = 2.5 \text{ eV}$, are shown in figure 12. There is still a peak, but here it occurs at about 1.9 volts, 25% below the assumed barrier height.

An additional barrier profile was tried, that of a full parabola, shown in the inset to figure 13. This does not have the sharp barrier edge of the trapezoid or half parabola. If the maximum height at zero

XBL 738-1695

Fig. 12. Logarithmic derivative of the tunnel current calculated for a half parabolic barrier as shown in the inset. The peak still occurs but is shifted to 1.9 volts, 25% below the 2.50 eV assumed barrier height, marked with an arrow.

bias is taken as ϕ and the voltage drop is again linear, then the profile can be written as

$$\phi(x,V) = -\frac{4\phi}{S^2} x^2 + \frac{1}{S}(4\phi-V)x \quad . \quad (33)$$

For the same barrier parameters as before, $S = 20 \text{ \AA}$ and $\phi = 2.5 \text{ eV}$, the logarithmic derivative is shown in figure 13. There is absolutely no peak or shoulder on the curve, and above 1 volt it is exactly linear.

We make no claim that either of these barrier profiles is likely to describe a real tunnel junction; we have merely carried out a mathematical exercise. However, the half parabola is not far from a trapezoid with a low edge, and if image potentials are added to a plane junction with a trapezoidal barrier profile, the resulting profile can be roughly approximated by a parabola.¹⁹

Rather, what this analysis shows is that, if a peak is seen in the logarithmic derivative, its position is near but not necessarily equal to the barrier height. The actual barrier height cannot be determined merely from the peak, however, because its position is highly model dependent. When compared with independent measurements, as has been possible in the case of aluminum-oxide-aluminum junctions, where the trapezoidal model seems to work reasonably well, it can be used with some confidence as a check on barrier heights of individual junctions. For a new junction material, other measurements are needed as well. When a peak is not observed, as in the case of our chromium and vanadium junctions, it suggests that the trapezoidal model is not entirely correct, but it can say nothing about the actual barrier height or, as far as our calculations have shown, about what profile it is appropriate to use.

XBL738-1696

Fig. 13. Logarithmic derivative of the tunnel current calculated for a full parabolic barrier as shown in the inset. There is no peak whatsoever in the function, nor is there any evidence of a departure from linearity above about 1 volt.

APPENDIX C

Graphs for an Approximate

Determination of Barrier Parameters

Figures 14 a-f show families of curves for various S- ϕ pairs for six different values of $S\phi^{3/2}$. We present these as a rough guide for determining barrier parameters when more exact information is unavailable or unnecessary. For each value of $S\phi^{3/2}$ the family includes more than the full range of barrier thicknesses which might reasonably be expected in oxidized barriers, along with enough values so that interpolation is possible. The graphs have been accurately scaled to 1 cm per division to facilitate use.

Because the voltage (horizontal) scale is different for the different members of figure 14, they bear a superficial resemblance to each other. However, curve shapes are actually quite different between the various families, and we have been able to find no means of parameterizing the curves into one universal family.

XBL 737- 6452

Fig. 14a. Computer generated current-voltage curves for $S\phi^{3/2} = 2.0$. The axes have been scaled so that one division is one centimeter. The curves in figures 14a through 14f can be used for quickly approximating barrier parameter of a new material.

XBL737-6453

Fig. 14b. Curves for approximating barrier parameters for a junction with $S\phi^{3/2}$ near 4.0.

XBL 737-6454

Fig. 14c. Curves for approximating barrier parameters for a junction with $S\phi^{3/2}$ near 8.0.

XBL 737- 6455

Fig. 14d. Curves for approximating barrier parameters for a junction with $S\Phi^{3/2}$ near 16.

XBL737-6456

Fig. 14e. Curves for approximating barrier parameters for a junction with $S\phi^{3/2}$ near 32.

XBL 737-6457

Fig. 14f. Curves for approximating barrier parameters for a junction with $S\phi^{3/2}$ near 64.

REFERENCES

1. R. C. Jaklevic and J. Lambe, Molecular Vibration Spectra by Electron Tunneling, Phys. Rev. Letters 17, 1139 (1966).
2. R. C. Jaklevic and J. Lambe, Molecular Vibration Spectra by Electron Tunneling, Phys. Rev. 165, 821 (1968).
3. D. J. Scalapino and S. M. Marcus, Theory of Inelastic Electron-Molecule Interactions in Tunnel Junctions, Phys. Rev. Letters 18, 459 (1967).
4. A. L. Geiger, B. S. Chandrasekhar, and J. G. Adler, Inelastic Tunneling in Al-Al-Oxide-Metal Systems, Phys. Rev. 188, 1130 (1969).
5. J. Klein, A. Léger, M. Belin, D. Défourneau, and M. J. L. Sangster, Inelastic Electron Tunneling Spectroscopy of Metal-Insulator-Metal Junctions, Phys. Rev. B7, 2336 (1973).
6. For example, different forms of nickel oxide have been observed under different oxidation conditions. See J. G. Adler and T. T. Chen, Tunneling in Ni-NiO Structures, Solid State Communications 9, 501 (1971) and D. C. Tsui, R. E. Dietz, and L. R. Walker, Multiple Magnon Excitation in NiO by Electron Tunneling, Phys. Rev. Letters 27, 1729 (1971). There is considerable literature on other materials.
7. L. Nordheim, Zur Theorie der thermischen Emission und der Reflexion von Elektronen an Metallen, Z. Physik 46, 833 (1928).
8. R. H. Fowler and L. Nordheim, Electron Emission in Intense Electric Fields, Proc. Roy. Soc. (London) A119, 173 (1928).
9. L. W. Nordheim, The Effect of the Image Force on the Emission and Reflexion of Electrons by Metals, Proc. Roy. Soc. (London) A121, 626 (1928).

10. If the field is set up by another electrode (as it is in the case of a tunnel junction), then S is the electrode spacing.
11. J. Frenkel, On the Electrical Resistance of Contacts between Solid Conductors, Phys. Rev. 36, 1604 (1930).
12. C. B. Duke, Tunneling in Solids (Academic Press, New York, 1969) p. 52.
13. *ibid*, pp. 215-20.
14. *ibid*, p. 33.
15. H. Y. Ku and F. G. Ullman, Capacitance of Thin Dielectric Structures, J. Appl. Phys. 35, 265 (1964).
16. A. K. Theophilou and A. Modinos, Metallic-Field Effect and its Consequences in Field Emission, Field Ionization, and the Capacitance of a Capacitor, Phys. Rev. B6, 801 (1972).
17. David Bohm, Quantum Theory (Prentice-Hall, New York, 1951) pp. 264-95.
18. K. H. Gundlach and J. G. Simmons, Range of Validity of the WKB Tunnel Probability, and Comparison of Experimental Data and Theory, Thin Solid Films 4, 61 (1969).
19. John G. Simmons, Generalized Formula for the Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film, J. Appl. Phys. 34, 1793 (1963).
20. John G. Simmons, Electric Tunnel Effect between Dissimilar Electrodes Separated by a Thin Insulating Film, J. Appl. Phys. 34, 2581 (1963).
21. Thomas E. Hartman, Tunneling Through Asymmetric Barriers, J. Appl. Phys. 35, 3283 (1964).

22. R. Stratton, Volt-Current Characteristics for Tunneling through Insulating Films, J. Phys. Chem. Solids 23, 1177 (1962).
23. C. B. Duke, Tunneling in Solids (Academic Press, New York, 1969) p. 64.
24. K. H. Gundlach, Zur Berechnung des Tunnelstroms durch eine Trapezförmige Potentialstufe, Solid-State Electronics 9, 949 (1966).
25. S. Basavaiah, J. M. Eldridge, and J. Matisoo, Tunneling in Pb/PbO/Pb Junctions, Bull. Am. Phys. Soc. 18, 462 (1973).
26. The present author carried out all the analysis of data presented here, but he is indebted to Dr. Paul Hansma for allowing access to his data from chromium and vanadium junctions prepared for other purposes: See G. I. Rochlin and P. Hansma, Tunneling Through Cr_2O_3 by Means of Cr- Cr_2O_3 -Metal Junctions, Bull. Am. Phys. Soc. 15, 332 (1970); G. I. Rochlin and P. K. Hansma, Electron Tunneling in Cr- Cr_2O_3 -Metal Junctions, Phys. Rev. B2, 1460 (1970); P. K. Hansma and G. I. Rochlin, Observation of Phonon Structure in the Tunneling Density of States of Superconducting Vanadium, Bull. Am. Phys. Soc. 17, 46 (1972).
27. G. I. Rochlin, Determination of the Anisotropy of the Energy Gap in Superconducting Pb by Superconductive Tunneling, Phys. Rev. 153, 513 (1967).
28. C. B. Duke, Tunneling in Solids (Academic Press, New York, 1969) p. 92.
29. W. L. McMillan and J. M. Rowell, Tunneling and Strong-Coupling Superconductivity, in Superconductivity, R. D. Parks, ed. (Marcel Dekker, New York, 1969) p. 597.

30. M. D. Jack, private communication.
31. C. B. Duke, Tunneling in Solids (Academic Press, New York, 1969) pp. 220-22.
32. K. H. Gundlach and J. Hölzl, Logarithmic Conductivity of Al-Al₂O₃-Al Tunneling Junctions Produced by Plasma- and Thermal Oxidation, Surface Science 27, 125 (1971).
33. S. R. Pollack and C. E. Morris, Electron Tunneling Through Asymmetric Films of Thermally Grown Al₂O₃, J. Appl. Phys. 35, 1503 (1964).
34. L. L. Chang, P. J. Stiles, and L. Esaki, Electron Tunneling between a Metal and a Semiconductor: Characteristics of Al-Al₂O₃-SnTe and -GeTe Junctions, J. Appl. Phys. 38, 4440 (1967).
35. C. B. Duke, Tunneling in Solids (Academic Press, New York, 1969) pp. 90-91 (an extensive bibliography of work done to 1969).
36. S. Basavaiah, private communication.
37. AIP Handbook, 3rd edition (American Institute of Physics, New York, 1972).
38. R. C. Dynes and T. A. Fulton, Supercurrent Density Distribution in Josephson Junctions, Phys. Rev. B3, 3015 (1971).
39. A Poisson distribution is probably a more reasonable one, but a Gaussian distribution was chosen as an approximation in order to simplify the calculations.
40. The Gaussian was truncated by multiplying it by $\exp(1/S^4)$ in calculating the capacitance in order to remove the singularity at $S=0$. For standard deviations which are a small fraction of the mean, this does not appreciably affect the normalization, and

the value of the capacitance calculated is insensitive to the form of the cutoff as long as it goes to zero sufficiently fast for small S .

41. G. Lewicki, J. Maserjian, and C. A. Mead, Barrier Energies in MIM Structures from Photoresponse: Effect of Scattering in the Insulating Film, J. Appl. Phys. 43, 1764 (1972).
42. C. A. Mead, private communication.
43. K. H. Gundlach, Eine Methode zur Bestimmung der Austrittsarbeit Metall-Metalloxyd aus Tunnelstrommessungen an Sandwichschichten, in Basic Problems in Thin Film Physics, R. Nedermayer and H. Mayer, eds. (Vandenbrock and Rupprecht, Göttingen, 1966) p. 696.
44. J. G. Simmons, Generalized Thermal J-V Characteristic for the Electric Tunnel Effect, J. Appl. Phys. 35, 2655 (1964).
45. V. A. Fromichev, Fiz. Tverd. Tela. 8, 2892 (1966)
[English Translation: Investigation of the Energy Structure of Al and Al_2O_3 by the Method of Ultralong-Wavelength X-ray Spectroscopy, Sov. Phys. Solid State 8, 2312 (1967)].
46. Alvin M. Goodman, Photoemission of Holes and Electrons from Aluminum into Aluminum Oxide, J. Appl. Phys. 41, 2176 (1970).
47. David Adler, Insulating and Metallic States in Transition Metal Oxides in Solid State Physics, Frederick Seitz, David Turnbull, and Henry Ehrenreich, eds. (Academic Press, New York, 1968) p. 1.
48. Robert M. Hill and Charles Weaver, The Optical Properties of Chromium, Trans. Faraday Soc. 54, 1140 (1958).
49. Julius Cohen, Tunnel Emission from Chromium Oxide Structures, J. Appl. Phys. 36, 1504 (1965).

50. O. Kubaschewski and B. E. Hopkins, Oxidation of Metals and Alloys (Academic Press, New York, 1968).
51. J. Stringer, The Vanadium-Oxygen System—A Review, J. Less-Common Metals 8, 1 (1965).
52. Paul Hansma, private communication based on unpublished work.
53. G. A. Somorjai, private communication.
54. T. Allersma, R. Hakim, T. N. Kennedy, and J. D. Mackenzie, Structure and Physical Properties of Solid and Liquid Vanadium Pentoxide, J. Chem. Phys. 46, 154 (1967).