

Electrode Effects on Aluminum Oxide Tunnel Junctions*

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The properties of evaporated $\text{Al-Al}_2\text{O}_3\text{-}M_x$ tunnel junctions have been investigated by systematic variation of the upper electrode metal (M_x) using comparison techniques on air-grown oxide layers of known uniformity. It was observed with the metals $M_x = \text{Ni, Cu, Al, Ag, Au, Sn, Sb, Pb, and Bi}$ that relative tunnel resistance increases with increasing atom size up to atomic radius approximately 1.6 \AA , leveling off thereafter. The effect of large differences in evaporation temperature for the different metals was found to be small, and the influence of atom size was shown to be correlated with the spinel-like structure of the oxide. Contrary to the assumptions of other workers, the upper metal-oxide transition zone was found to exert a powerful influence on the properties of the junction. The influence of electrode work function was investigated using barium, and an average decrease in resistivity of the order predicted by the Holm-Kirschstein equations for an ambient barrier height of 3 to 4 eV was observed.

INTRODUCTION

IN the past year there has been a considerable revival of interest in electron tunneling through thin insulating films, particularly for the study of the energy gap in superconductors,¹⁻³ and the construction of active devices to be used as emitters or amplifiers.^{4,5} The common element of these studies is a metal-oxide-metal sandwich in which the oxide serves as a spacer to position the electrodes within tunneling range ($<100 \text{ \AA}$), yet prevents any direct contact. Because of their uniformity and compactness, grown oxides on aluminum or tantalum are generally used, with the second electrode being evaporated onto the oxide surface. The ways in which the oxide barrier is affected by the choice of the covering electrode and its method of application are crucial to the interpretation of the observed behavior of such tunnel structures and to the comparison with theoretical prediction. This research reports the first quantitative measurement of such electrode effects.

The earliest reported observations of tunneling through thin layers were made by Holm and Meissner in 1932,⁶ and subsequently extended by Wendt⁷ and Dietrich.⁸ The attempts of these workers and more recently of Giaever and Fisher⁹ to fit their observations of the behavior of metal-insulator-metal tunnel junctions to the theoretical predictions¹⁰⁻¹² were only partially successful. As was predicted by Holm and Kirschstein¹⁰ the observed temperature dependence of the junction resistivity was small, for low voltages the resistivity was constant, and at higher voltages the resistivity decreased rapidly with increasing voltage until breakdown occurred. Giaever and Fisher also observed approximately exponential increase of junction resistivity with increasing barrier thickness, in accord with the theoretical calculations. The observed resistivity, however, was several orders of magnitude too low. This is partially related to the lack of adequate knowledge of the actual barrier thickness, electron mass, dielectric constant, and barrier work function. In addition, the influence of the physical properties of the electrode metals was not known. It was the purpose of the present investigation to systematically study the influence of the electrode metals for comparison with theoretical predictions, and, where possible, to test the proposals advanced by Giaever and his co-workers^{2,9} concerning the influence of evaporator source temperature and character of the metal-oxide interface regions adjacent to each electrode.

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¹ I. Giaever, *Phys. Rev. Letters* **5**, 147, 464 (1960).

² I. Giaever and K. Megerle, *Phys. Rev.* **122**, 1101 (1961).

³ J. Nicol, S. Shapiro, and P. Smith, *Phys. Rev. Letters* **5**, 461 (1960).

⁴ C. Mead, *Proc. Inst. Radio Engr.* **48**, 360, 1478 (1960); *J. Appl. Phys.* **32**, 646 (1961).

⁵ J. Spratt, R. Schwarz, and W. Kane, *Phys. Rev. Letters* **6**, 341 (1961).

⁶ R. Holm and W. Meissner, *Z. Physik* **74**, 715, 736 (1932); **86**, 787 (1933).

⁷ J. Wendt, *Philips Tech. Rev.* **5**, 238 (1940); *Physica* **8**, 233 (1941).

⁸ I. Dietrich, *Z. Physik* **132**, 231 (1952); **133**, 499 (1952).

⁹ I. Giaever and J. Fisher, *J. Appl. Phys.* **32**, 172 (1961).

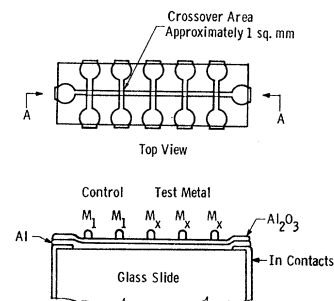


FIG. 1. Experimental test arrangement showing two cross stripes of cover electrode metal M_1 and three of M_x deposited on the same $\text{Al-Al}_2\text{O}_3$ base layer. The indium contacts extend around to the back of the slide for connection to the external measuring circuit.

¹⁰ R. Holm and B. Kirschstein, *Z. tech. Physik* **16**, 488 (1935); *Z. Physik* **36**, 882 (1935).

¹¹ An extensive review of theoretical work is provided by R. Holm in *Electric Contacts Handbook* (Springer-Verlag, Berlin, 1958), 3rd ed., paragraph 26 and Appendix III.

¹² W. Harrison, *Phys. Rev.* **123**, 85 (1961).

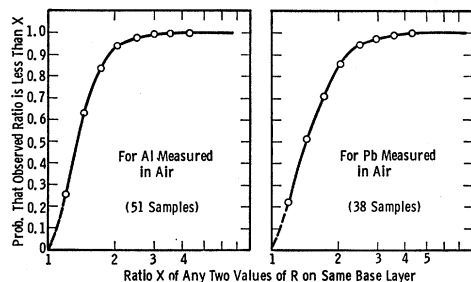


FIG. 2. Experimentally observed probability that the ratio of resistance of any two of five identical junctions formed on the same $\text{Al}-\text{Al}_2\text{O}_3$ base layer is less than some arbitrary number X .

EXPERIMENTAL TECHNIQUES

Aluminum oxide grown on evaporated aluminum layers was chosen as the oxide spacer because of its extensive use by other workers^{1-5,9} and ease of preparation. One of the two electrodes therefore will be aluminum, yielding an $\text{Al}-\text{Al}_2\text{O}_3-M_x$ structure. To study the effects of the physical properties of the electrode materials, the cover electrode (M_x) is varied while all other conditions are held constant, particularly the oxide thickness and junction area. These requirements are met by depositing several metal stripes across the same base layer as in Fig. 1, and measuring at low voltage (≈ 10 mv) the tunnel junction resistance obtained under the different cover metals. The experiments are conducted by comparison, the resistance of several $\text{Al}-\text{Al}_2\text{O}_3$ -Pb junctions, for example, being compared against several $\text{Al}-\text{Al}_2\text{O}_3$ -Al junctions, all formed on the same $\text{Al}-\text{Al}_2\text{O}_3$ base layer. The uniformity of this $\text{Al}-\text{Al}_2\text{O}_3$ base layer is consequently of prime concern.

The base layers were prepared by deposition of 1-mm wide stripe of 99.99% aluminum onto a 25- \times 75-mm microscope slide provided with indium solder contacts. The slightest visible imperfection or contaminant film on the slide caused serious deterioration in uniformity and therefore each slide was meticulously cleaned and inspected prior to evaporation. The pressure during evaporation was generally held in the 10^{-6} torr range by a liquid-nitrogen cold trap. (1 torr \equiv 1 mm Hg.) The details of the cleaning, masking, and evaporation procedures have been given previously by the author.¹³

The completed base layers were oxidized by storing for several days in dust-free containers in an air-conditioned room held at $22^\circ \pm 1^\circ\text{C}$. These preparation techniques yielded layers of dependable uniformity as illustrated by Fig. 2 for $\text{Al}-\text{Al}_2\text{O}_3$ -Al junctions. From Fig. 2 it is seen that 90% of all similar junctions formed on the same base layer differ in resistance by less than a factor of 2 due to uncontrolled causes. Therefore, for the ensuing measurements comparing different metals, any difference of resistance less than

ratio 2 was not considered conclusive. The uniformity was continuously monitored during all succeeding measurements and with the exception of barium, no significant deviations from this confidence level were observed.¹⁴

Measurements of junction resistance were made at 1-10 mv using four-terminal methods, so that lead and contact resistance errors were avoided. Contacts to the plate were included within the evaporator bell jar¹³ so that the junction resistance could be measured immediately after formation and monitored for unlimited periods thereafter under high vacuum ($< 5 \times 10^{-7}$ torr), or at any desired pressure up to 760 torr. These contacts also were used to monitor the resistance of the metal stripes during deposition so that evaporation rate and terminal electrode thickness could be approximately reproduced.

EXPERIMENTAL RESULTS

During preliminary measurements it was noted that junctions formed with some metals changed properties with time. Furthermore, variations in junction resistance of more than two orders of magnitude were observed when comparing cover metals possessing different evaporation temperatures, such as Al and Pb, for example. A number of experiments were made to establish the order of these effects and to provide a common basis of comparison for all of the layers.

Changes of Junction Resistance with Time

If the resistance of an $\text{Al}-\text{Al}_2\text{O}_3-M_x$ junction is monitored following its formation, the resistance is observed to change, even under a vacuum of less than 5×10^{-7} torr. For the metals $M_x = \text{Al}$, Sn, Cu, Ni, Ag, and Au, the resistance continually *increased* with time according to

$$R = k_1 \log(t + t_0) + k_2. \quad (1)$$

Figure 3 shows an $\text{Al}-\text{Al}_2\text{O}_3$ -Al junction typical of the

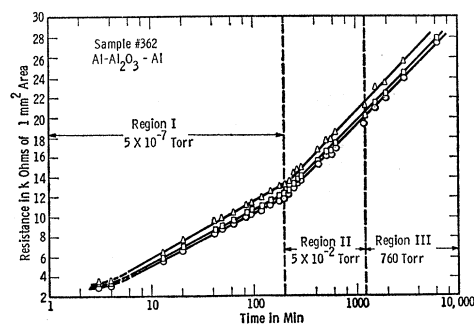


FIG. 3. Change in tunnel resistance with time for three $\text{Al}-\text{Al}_2\text{O}_3$ -Al junctions formed on the same $\text{Al}-\text{Al}_2\text{O}_3$ base layer. Applied voltage (10 mv) was disconnected between measurements. System pressure was varied by successively shutting off diffusion and fore pumps.

¹³ R. Handy, Ph.D. dissertation, Electrical Engineering Department, Northwestern University, 1961 (unpublished).

¹⁴ The number of samples used for each group of tests is noted on the appropriate figures.

behavior observed for Al and Sn. The time scale is divided into three regions corresponding to different system pressure during measurement. It is seen that there is a change in slope associated with an increase of ambient pressure from $\approx 5 \times 10^{-7}$ torr to $\approx 5 \times 10^{-2}$ torr, indicating that the constants in Eq. (1) are pressure dependent for some metals. Additional increase in pressure to 760 torr did not result in any further increase in slope, suggesting that the rate mechanism is already saturated at $\approx 5 \times 10^{-2}$ torr for Al and Sn. With Cu, Ni, Ag, and Au, pressure effects were much smaller and in contrast to Al and Sn were not consistently observed.

$M_x = \text{Pb, Bi, and Sb}$ formed a second group of metals exhibiting different behavior. For lead a small (<20%) but consistent decrease in resistance with time was observed. Sb and Bi also showed only comparatively small changes in resistance, but lacked the consistency of direction observed for lead. No pressure effects were observed.

Effects of Evaporation Temperature

When Al- and Pb-covered junctions were compared on the same base layer, it was consistently found that

$$(R_{\text{Pb}})_{\text{AV}} \approx 1.3 \times 10^2 (R_{\text{Al}})_{\text{AV}} \quad (2)$$

An explanation of this type of phenomena was proposed by Giaever and Megerle² based upon the observation that the evaporation temperature¹⁵ of Al (1150°C) was higher than of Pb (718°C). They presumed that metals of higher evaporation temperature and hence higher kinetic energy would penetrate further into the oxide as they condensed and effectively reduce the thickness of the oxide layer. From the Holm-Kirschstein

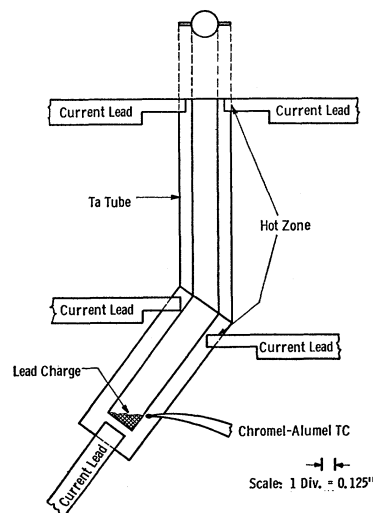


FIG. 4. Source for multiple-temperature lead evaporation. Made from 0.002-in. Ta sheet welded into the shape of a hollow tube closed at the lower end. Lead vaporized in lower section passes through hot zone before escaping at top to deposit on sample.

¹⁵ L. Holland, *Vacuum Deposition of Thin Films* (John Wiley & Sons, Inc., New York, 1960), pp. 110-114.

equations¹⁰ for low voltage,

$$\sigma = (2.66 \times 10^{11}) \left(\frac{A^2}{1+AB} \right) \exp(AB) \text{ ohm cm}^2, \quad (3)$$

$$A = s - 7.2/\phi, \quad B = 0.928(4 - 10/s\epsilon_r)^{1/2},$$

where ϕ = barrier height in volts, s = barrier thickness in angstrom units, and ϵ_r = relative dielectric constant, the reduction in thickness required to produce this change is only a few angstrom units, and thus their explanation seemed entirely reasonable. This order of change, however, is large enough to mask the observation of any effects due to electrode work function or density of states, and therefore it was experimentally tested.

A special two-zone source was constructed, Fig. 4, in which lead could be vaporized in the lower zone and accelerated in the upper zone. The temperature of the two zones could be independently controlled so as to give the effect of projecting the lead vapor onto the sample at an energy corresponding approximately to the temperature of the upper zone,^{16,17} and at the same

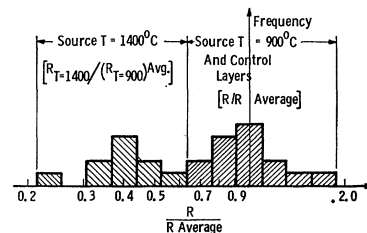


FIG. 5. Shift in tunnel resistance caused by different source temperature for lead cover electrode. (24 samples.)

time maintain a reasonable evaporation rate. The source was dimensioned so that the lead vapor was required to make many collisions with the walls of the upper hot zone before escaping. By this means, a number of experiments were made in which stripes were deposited on the same base layer with the upper zone held at 900° and at 1400°C. In addition, a number of control plates were made at constant source temperature to insure that this source shape did not in itself introduce any unusual spread in the data. The results are plotted in Fig. 5. It is immediately seen that a downward shift in junction resistance is observable, but that it is much smaller than had been anticipated. Evidently then, temperature effects alone are not sufficient to account for the large differences in resistance previously observed [Eq. (2)]. To remove any doubt as to the energy increase experienced by the lead vapor in the upper zone, the effective path length

¹⁶ R. Fraser, *Molecular Rays* (Cambridge University Press, New York, 1931), Chap. 1 and 3; and *Molecular Beams* (Methuen and Company, Ltd., London, 1937), Chap. 1.

¹⁷ N. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1956), Chap. 1.

was increased by adding five more kinks in the tube and the experiments repeated. The results remained essentially the same.

Correlation with Atom Size

As a further confirmation of the fact that source temperature exerts little influence on the junction resistivity, comparison tests were made between $M_x = \text{Ag}, \text{Al},$ and Au . These metals have many common physical properties such as atom size, crystal lattice, high conductivity, etc., but different evaporation temperatures, 1047, 1150, and 1465°C, respectively. The variation between junctions of any of these three cover metals deposited on the same base layer did not differ significantly from the random control variations of Fig. 2.

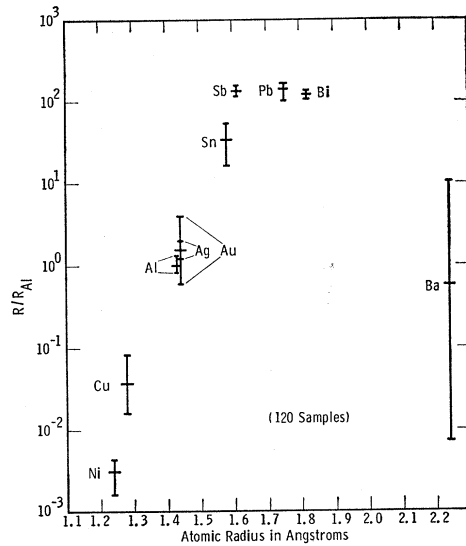


FIG. 6. Variation in relative tunnel resistance as a function of the atomic radius of the cover-electrode metal. The tunnel resistance for the various metals is compared with equivalent $\text{Al}-\text{Al}_2\text{O}_3-\text{Al}$ junctions on the same base layer as a reference. (120 samples.)

In order to establish the controlling mechanism which accounts for the observed variations in junction resistance between other metals, junctions covered with $\text{Ni}, \text{Cu}, \text{Ag}, \text{Al}, \text{Au}, \text{Sn}, \text{Pb}, \text{Bi},$ and Sb were compared against each other and related to aluminum as a reference. The results were plotted in Fig. 6 as a function of the atomic radius of the various metals. It is seen that the junction resistance increases steadily with increasing atom size up to atomic radius approximately 1.6 Å, leveling off thereafter. The differences in electrode work function are not sufficient to account for the differences in junction resistivity. The size of the deposited atoms, therefore, appears to be the factor controlling the penetration of the metal atoms into the oxide film, and hence junction resistivity.

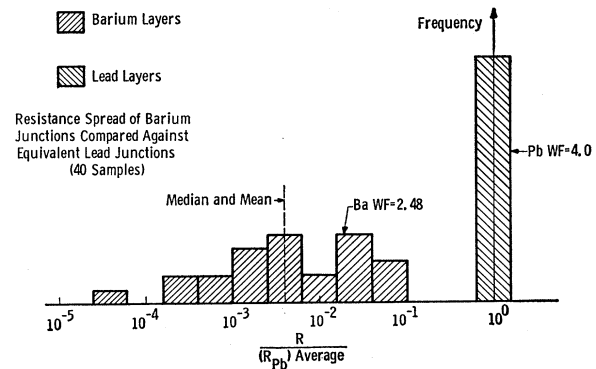


FIG. 7. Resistance spread of barium junctions compared with equivalent lead junctions. (40 samples.)

Work Function Effects

In order to have any hope of observing effects on junction resistivity due to the work function of the electrode metal, the difference in work function between the two electrode cover metals to be compared must be at least 1.0 eV and preferably greater. In addition, the metal atoms should be large to take advantage of the saturation effect for atomic radius greater than 1.6 Å, (Fig. 6). Barium (work function = 2.48 eV, atomic radius = 2.25 Å) meets these requirements and has the additional advantage that Al is known to reduce BaO to Ba metal and Al_2O_3 .¹⁸ It thus seemed unlikely that Ba would reduce Al_2O_3 .

The results of comparison tests between Ba and Al, and Ba and Pb cover electrodes are plotted in Fig. 7 using equivalent Pb layers as a common reference. The data spread among the barium layers is considerably larger than had been experienced with any other metal. Nevertheless, the barium junctions show a consistently smaller average resistance than the lead comparison layers,

$$(R_{\text{Ba}})_{\text{av}} \approx 4 \times 10^{-3} (R_{\text{Pb}})_{\text{av}}, \quad (4)$$

and in fact, this difference is just of the order which would be expected from the Holm-Kirschstein equations [Eq. (3)].

Temperature Effects and Junction Asymmetry

In addition to the high-vacuum low-voltage measurements described above, a number of samples were further tested at higher voltages in a dry helium atmosphere for temperature variations between 300° and 77°K. A standard method of measurement was applied, using a 0.05-cps positive and negative going triangular wave to trace out the $I-V$ characteristics on an $X-Y$ recorder. The ratio of resistance increase from room temperature to liquid nitrogen temperature was typically about 1.4, which is similar to the observations of Giaever and Fisher.⁹ All of the junctions

¹⁸ M. Knoll, *Materials and Processes of Electron Devices* (Springer-Verlag, Berlin, 1959), p. 436.

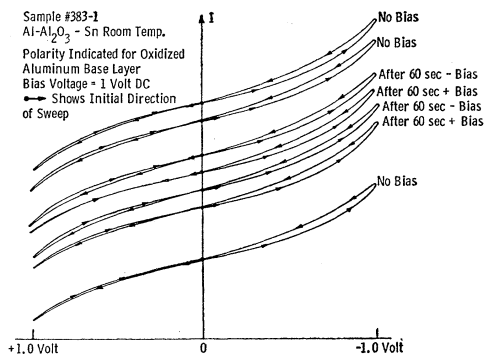


FIG. 8. Room temperature current voltage characteristics of an $\text{Al-Al}_2\text{O}_3\text{-Sn}$ tunnel junction using $\pm 1.0\text{-v}$ 0.05-cps sweep immediately following various conditions of dc bias. The zero point of the current scale was shifted for each test to avoid overlapping of the trace.

exhibited at least some asymmetry, and several metals ($M_x = \text{Ag, Au, Sn}$) showed the change in direction of rectification with temperature observed by Giaever and Fisher for some of their Al junctions. In addition, these same samples could be made to exhibit either direction of rectification, or none at all by simply adjusting the applied voltage. These effects were notably absent on the 23 aluminum samples tested in this manner, which always showed forward conduction when the oxidized aluminum base layer was positive.

Figure 8 shows the behavior typically exhibited by $M_x = \text{Ag, Au, and Sn}$ junctions. Figure 9 shows a representative Al junction which happens to be deposited on the *same* base layer as the Sn junction in Fig. 8. The several curves represent the behavior of a relaxed junction, and of the same junction following various polarities of dc bias. In order to be able to distinguish between the various curves, the zero point of the current scale was shifted each time. The Al-covered junction exhibits a form of hysteresis, the return sweep always following a locus of higher current than the up-sweep, and is relatively unaffected by biasing. The Sn-covered junction of Fig. 8, however, shows a loop whose shape depends upon the polarity of the sweep voltage. By biasing the sample, half of the loop can be made to open or close. If the samples are cooled to liquid nitrogen temperature, the loops disappear and a common direction of rectification is observed for all metals (oxidized Al base layer positive for forward conduction). The loops are obviously not due to the capacity of the sample.

DISCUSSION

The experiments made to test the influence of cover-metal evaporation temperature clearly show that the differences in kinetic energy of the condensing atoms are not in themselves sufficient to account for the observed differences in relative junction resistance. The correlation between atom size and relative junction

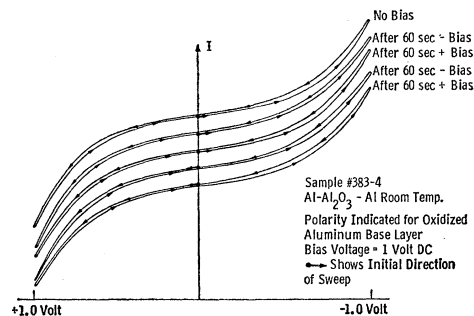


FIG. 9. Room temperature current-voltage characteristics of an $\text{Al-Al}_2\text{O}_3\text{-Al}$ tunnel junction using $\pm 1.0\text{-v}$ 0.05-cps sweep immediately following various conditions of dc bias. The zero point of the current scale was shifted for each test to avoid overlapping of the trace.

resistance, however, suggests that the reduction in resistance does take place because of penetration of the condensing atoms into the oxide, reducing the effective barrier thickness. The atom size is the controlling parameter for this process; the smaller the atom the further it will diffuse into the oxide. The failure of the metals of atomic radius greater than 1.6 \AA ($M_x = \text{Pb, Sb, Bi}$) to show progressively higher resistance with increasing radius is most interesting, since it suggests that they do not diffuse into the oxide. This in turn permits several conclusions to be drawn concerning the nature of the oxide layer itself.

Thin aluminum oxide layers grown in air at low temperature are known to be amorphous,^{19,20} showing no evidence of crystalline hydrate. This means that the oxide is not crystalline, but it does not say that it is completely lacking in order. Rather, the ordering scheme varies throughout the layer in a random way. Crystalline Al_2O_3 on the other hand is known to have a cation deficient spinel structure.²¹ That is, for the 32 oxygen anions close packed in the unit cell there exist 24 available interstitial cation sites of which only $21\frac{1}{2}$ are filled with aluminum ions. There exists, therefore, an average of $2\frac{2}{3}$ vacant cation sites per unit cell distributed randomly throughout the crystal, which favors diffusion of cations in the crystal. Thus a wide range of metals can form mixed spinels with Al_2O_3 , such as MgAl_2O_4 . Magnesium, whose atomic radius is 1.6 \AA , is the largest atom known to form a spinel with Al_2O_3 .²¹

It might be expected that the amorphous oxide would possess a similar, but less well-ordered anion structure, with possibly even more unoccupied cation sites. If this is the case, one would anticipate that the diffusion of the vapor atoms into the oxide film would be negligible for atoms of atomic radius greater than

¹⁹ D. Eley and P. Wilkinson, *Proceedings of the International Conference, September, 1959* (John Wiley & Sons, New York, 1959), p. 508.

²⁰ R. Hart, *Proc. Roy. Soc. (London)* **A236**, 68 (1956).

²¹ R. Evans, *Introduction to Crystal Chemistry* (Cambridge University Press, New York, 1939), p. 104, 206 ff.

magnesium (1.6 \AA), and that penetration should increase steadily for atoms of atomic radius less than 1.6 \AA with a corresponding rapid drop in relative junction resistance. This is exactly what was observed (Fig. 6).

The shift in junction resistance to be expected from the use of a barium-cover electrode can be estimated by using the published curves of the Holm-Kirschstein equation¹¹ or Appendix I of reference 13, for a work function difference of

$$\frac{1}{2}(\varphi_{\text{Al}} + \varphi_{\text{Pb}}) - \frac{1}{2}(\varphi_{\text{Al}} + \varphi_{\text{Ba}}) \\ \approx \frac{1}{2}(4.2 + 4.0) - \frac{1}{2}(4.2 + 2.48) = 0.76 \text{ ev}, \quad (5)$$

an ambient barrier height of 4 ev, and the observed resistivity for the Pb-covered junctions of approximately $5 \times 10^9 \text{ ohm-cm}^2$. This estimate yields the theoretical value

$$R_{\text{Ba}} \approx 7 \times 10^{-3} R_{\text{Pb}} \quad (6)$$

for the relative junction resistance which is comparable with the observed value of 4×10^{-3} from Eq. (4). The use of the Holm-Kirschstein equations for such an estimate requires the assumption that the oxide layer in this case is *not* thoroughly doped by the electrode metals, so that the conduction band²² of the aluminum oxide is at least 3–4 ev above the Fermi level of the metal electrodes. If the oxide is thoroughly doped by donor metals, and consequently the barrier height reduced to about 1 ev, for example, by depressing the conduction band of the oxide, then the junction properties will be almost independent of the electrode work function. If such a thoroughly doped barrier is present, one would also expect to observe a strong dependence of barrier height and hence tunnel resistance on temperature. This, however, was not observed. The unexpected spread in the barium data and the lack of adequate knowledge of the barrier height or shape is disturbing, and therefore these observations are presented as suggestive but not conclusive evidence that an electrode work function effect indeed exists, and that its magnitude is correctly predicted by the Holm-Kirschstein equations.

The Holm-Kirschstein derivation¹⁰ implies a dependence of tunnel current on the density of states in the electrode metals, and this is observed when the electrode metals are superconducting.^{1–3} Harrison,¹² however, has pointed out that this dependence should not carry over into normal metals. In those cases (e.g., Pb and Bi)

where the difference in density of states is large and the influence of other factors small, there is no substantial difference in low-voltage resistivity (Fig. 6). This supports Harrison's conclusion that the tunnel current between normal metals is independent of the density of states.

In explaining their observations of the dependence of rectification direction on temperature, Giaever and Fisher⁹ constructed a model based upon the assumption that the upper (evaporated) metal-oxide interface is relatively abrupt, and that the temperature dependence of rectification direction arises entirely from a more gradual interface region near the parent aluminum electrode. The results of the present investigation indicate that this is not the case.

The penetration of the smaller atoms into the oxide layer in itself suggests a gradual upper transition region. The changes of resistance with time are of the order of the asymmetry observed, and the sensitivity of the rate of change to ambient pressure suggests that these changes are taking place at the upper oxide-metal interface closest to the atmosphere. Finally, the evidence from the sample used in Figs. 8 and 9 again suggests the importance of the upper oxide-metal interface in determining junction properties. These cover metal electrodes were deposited on the *same* base layer, yet the Al- Al_2O_3 -Sn junction of Fig. 8 showed changes in rectification direction with both temperature and voltage, while the Al- Al_2O_3 -Al junction of Fig. 9 did not. The differences in properties must therefore stem from the upper metal-oxide interface.

SUMMARY

The effect of electrode work function was tested using barium and a decrease in tunnel resistance appropriate to an ambient barrier height of 3 to 4 ev was observed. It is not certain at present whether the barrier is actually this high and hence this work is being continued. It is important to recognize however that the tunnel structure is strongly affected by the character of *both* metal-oxide transition regions. The properties of the upper transition region are influenced in a quantitatively predictable fashion by the atom size of the electrode cover metal and the spinel-like structure of the oxide.

ACKNOWLEDGMENTS

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²² Whether it is even legitimate to speak of the "band structure" of a material which is only 10 to 30 atom layers thick is a moot point.