

INTRINSIC FIELDS IN THIN INSULATING FILMS BETWEEN DISSIMILAR ELECTRODES

John G. Simmons

Burroughs Laboratories, Burroughs Corporation, Paoli, Pennsylvania

(Received 15 November 1962)

The fact that a large intrinsic field can exist in a thin insulating film sandwiched between electrodes having different work functions appears to have been neglected by some authors.¹⁻⁵ The field F_i within the insulator, which arises because of the contact potential difference between the two electrodes, is given by

$$F_i = (\Psi_2 - \Psi_1) / es, \tag{1}$$

where s is the thickness of the insulating layer, Ψ_1 and Ψ_2 are the work functions of the electrodes, and e is electronic charge. The effect of F_i is to produce an asymmetrical potential barrier between the two electrodes [as indicated in Fig. 1(b)].

Intrinsic fields are considerable in tunnel junctions in which the insulator is very thin ($<100 \text{ \AA}$). For example, in an Al-Al₂O₃-Au junction in

which the insulator film is 30 \AA thick,

$$\Psi_2 - \Psi_1 = 0.74 \text{ eV.}$$

Therefore,

$$F_i = \frac{1}{30}(0.74 \times 10^8) = 2.47 \times 10^6 \text{ volts/cm.}$$

This intrinsic field is critically close to the dielectric strength of even the best insulator.

Because of its magnitude, the field should be manifested under voltage breakdown conditions; that is, the junction should exhibit polar dielectric strength characteristics. This assertion is supported by considering the effect of the polarity of the voltage applied to the electrodes of two identical tunnel junctions as the voltage is gradually increased. If a gradually increasing voltage is applied across the electrodes of one of the junctions, with the electrode of lower work function negatively biased, then the initial increase in voltage decreases the intrinsic field F_i to zero. Further increase of potential gradually increases the field in the insulator until a critical field F_d in the opposite direction is attained, causing the junction to break down. The breakdown voltage V_1 under these conditions is given by

$$V_1 = (F_d + F_i)s. \tag{2}$$

If a voltage bias of opposite polarity is now applied to the second junction, increasing the potential between the electrodes gradually increases the field in the insulator from the intrinsic value F_1 until the breakdown field F_d is attained, causing destruction of the junction. In this case, there is no field reversal. The breakdown voltage V_2 under these conditions is

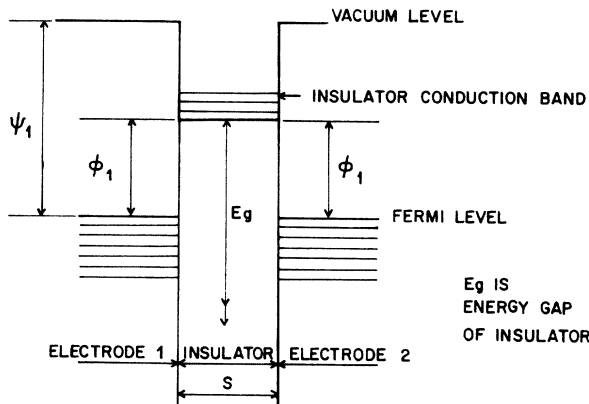
$$V_2 = (F_d - F_i)s. \tag{3}$$

The difference $\Delta V (= V_1 - V_2)$ in the breakdown voltages can be expressed in terms of the work functions of the electrodes as follows:

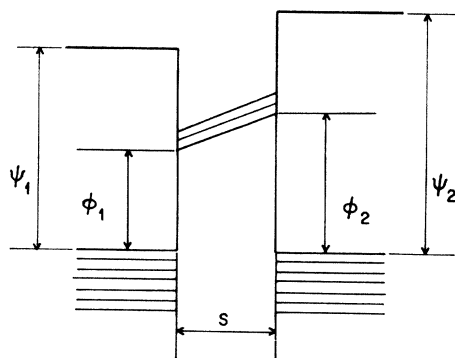
$$\Delta V = V_1 - V_2 = 2F_i s = 2(\Psi_2 - \Psi_1) / e. \tag{4}$$

The difference ΔV should be observed quite readily in tunnel junctions, since breakdown here occurs at low voltages.

To verify (4), various tunnel structures were fabricated using Al-Al₂O₃ as the basic structure,



(a)



(b)

FIG. 1. Shape of potential barrier between (a) similar electrodes, and (b) dissimilar electrodes.

with counterelectrodes of Al, Au, Sn, and Be. The junctions were fabricated as follows. Cr-Au contacts, suitably arranged to facilitate four-probe measurements, were evaporated onto four carefully cleaned glass substrates in a vacuum $<10^{-7}$ Torr. Next, ten aluminum strips $\frac{1}{16}$ in. wide were evaporated onto each substrate. The surfaces of the strips were then oxidized by exposure to dry oxygen at atmospheric pressure for a period of four hours. Finally, a counter-electrode $\frac{1}{16}$ in. wide was deposited across the aluminum strips, each substrate having a counter-electrode of different material, thus providing four different sets of tunnel junctions. It is important to note that the junctions were made under identical conditions, and without being exposed to the atmosphere at any time during fabrication. This was accomplished by using a multiple-heater turret⁶; this apparatus also eliminated troublesome angle-of-incidence problems.

The tunnel voltage-current characteristics exhibited by the symmetrical structures (Al-Al₂O₃-Al) were almost independent of polarity; slightly greater currents (~4%) were obtained when the oxidized aluminum electrode was positively biased. These essentially nonpolar characteristics were to be expected from the symmetry of the potential barrier [as shown in Fig. 1(a)]. The asymmetric structures (Al-Al₂O₃-Au, Al-Al₂O₃-Sn, and Al-Al₂O₃-Be) exhibited polar characteristics, with the greatest value of current occurring when the aluminum electrode was positively biased. These results suggested that the barrier was asymmetric, thus indicating that a field existed in the insulator.

The junctions were tested to destruction with the oxidized aluminum electrode of successive junctions biased alternately, first positively, then negatively. The breakdown voltage for a given type of junction and polarity of bias was extremely consistent, never varying by more than 3%. The experimental mean values of ΔV for the junctions are compared with the theoretical values of ΔV in Table I (where ψ_1 refers to the work function of aluminum, and ψ_2 to the work function of the counterelectrode material).

The reproducibility of the above results suggests that this technique is a good method of determining the work function of thin films, with respect to some standard—in this case, aluminum. In particular, the technique facilitates work function comparison measurements at low temperatures, where work function measurements are difficult to make using more standard techniques. Using the results of the experiment described

Table I. Comparison of experimental and theoretical values of ΔV .

Junction	Experimental ΔV (volts)	Theoretical ^a $\Delta V = 2(\psi_2 - \psi_1)/e$
Al-Al ₂ O ₃ -Al	0 ± 0.02	0
Al-Al ₂ O ₃ -Au	1.21 ± 0.03	1.48
Al-Al ₂ O ₃ -Sn	0.67 ± 0.03	0.60
Al-Al ₂ O ₃ -Be ^b	-0.37 ± 0.03	-0.32

^aPreferred values of work function, Handbook of Chemistry and Physics (Chemical Rubber Publishing Co., Cleveland, Ohio, 1961-62), 43rd ed., p. 2594.

^bAluminum has a greater work function than beryllium; hence $\psi_2 - \psi_1$ is negative.

here, and assuming the work function of Al to be 4.08 eV, the work functions of Al, Sn, and Be are calculated to be 4.69, 4.42, and 3.89 eV, respectively.

A knowledge of the difference in work function of the electrodes facilitates computation of the difference in barrier height at the respective metal-insulator interfaces [Fig. 1(b)] for

$$\begin{aligned}\varphi_2 &= \varphi_1 + eF_i s, \\ &= \varphi_1 + (\psi_2 - \psi_1).\end{aligned}\quad (5)$$

As a result of (5), a knowledge of the height of either of the barriers permits a complete determination of the potential barrier (neglecting the image potential, which is a simple superposition problem).

The intrinsic field is an important consideration in the design of the thin film devices proposed by Mead.^{2,7} The maximum energy E_m with which an electron can be injected from the emitter to the base is given by

$$\begin{aligned}E_m &\simeq e(F_d + F_i)s, \\ &= eF_d s + \psi_b - \psi_e,\end{aligned}\quad (6)$$

where ψ_b is the work function of base material, and ψ_e is the work function of emitter material. Thus, using an emitter of lower work function than the base (that is, where $\psi_b - \psi_e > 0$) permits higher maximum electron injection energies than if the electrodes are of the same work function (where $\psi_b - \psi_e = 0$). The advantage of this principle has been neglected in the device proposed by Spratt *et al.*,¹ who injected electrons from an emitter of high work function into a base of lower work function.

The author wishes to acknowledge stimulating discussions with various members of the Burroughs Laboratories staff, and to thank, in particular, W. W. Allen, who measured the characteristics of the junctions, and G. J. Unterkofler, who fabricated the devices.

¹J. P. Spratt, R. F. Schwarz, and B. M. Kane,

Phys. Rev. Letters **6**, 341 (1961).

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

³H. Kanter and W. A. Feibelman, Twenty-Second Conference on Physical Electronics, Massachusetts Institute of Technology, March, 1962 (unpublished).

⁴R. M. Handy, Phys. Rev. **126**, 1968 (1962).

⁵C. A. Mead, Phys. Rev. Letters **6**, 545 (1961).

⁶J. G. Simmons and D. Moister, Rev. Sci. Instr. **33**, 978 (1962).

⁷C. A. Mead, Proc. I.R.E. **48**, 359 (1960).

PHOTOGENERATION OF FREE CARRIERS IN ORGANIC CRYSTALS VIA EXCITON-EXCITON INTERACTIONS*

M. Silver

Army Research Office, Durham, North Carolina

and

D. Olness, M. Swicord, and R. C. Jarnagin

Physics and Chemistry Departments, University of North Carolina, Chapel Hill, North Carolina

(Received 13 November 1962)

Although it has been suggested before¹ that the interactions between two excitons may be responsible for the photogeneration of free carriers in organic crystals, it is only recently that a theoretical calculation of this process has been made by Choi and Rice.² These very beautiful calculations were motivated by the results reported by Northrop and Simpson.¹ These experiments, however, cannot be unambiguously interpreted as being due to this bimolecular process since the current increased only linearly with intensity under uv excitation. Indeed, the transient current measurements of Kepler³ rule out the possibility of free exciton-free exciton interactions when the crystals are excited with strongly absorbed light. Thus, until now there is no experimental evidence in the literature to support such a suggestion.

In this note, we wish to present some results which for the first time not only support the exciton-exciton theory, but also yield a bimolecular rate constant in good agreement with that calculated by Choi and Rice.²

We observe a current which increases with the square of the light intensity and also increases with temperature in the superlinear region. Bube⁴ observed superlinear currents in CdSe and CdS and has attributed this effect to the action of different recombination centers. Our results cannot be so interpreted in any obvious way, because of our observed temperature dependence.

We have investigated transient photocurrents in the direction perpendicular to the *ab* plane in anthracene. Crystals obtained from the Harshaw Company as well as ultrapure Kodak crystals were used. The hole lifetime in all samples was greater than 100 microseconds. The crystals were cleaved in air and etched and polished using benzene. Blocking, electrolytic and pressed metal evaporated Vycor electrodes were employed. (The pressed electrodes were used to make temperature-dependent measurements.) The results were essentially independent of the electrode material. We used a dc applied voltage and excitation by a high-intensity microsecond flash of weakly absorbed light; i.e., light of wavelengths longer than 4150 Å. Only the light between 4150 Å and 4550 Å is involved, because the signal obtained from wavelengths longer than 4550 Å was reduced tenfold from that obtained from wavelengths longer than 4150 Å, while the intensity was reduced by only 30%. The transient pulse obtained from weakly absorbed excitation is quite different from that obtained from strongly absorbed light. These results are shown in Fig. 1. It is clear from the shape of these transients that with strongly absorbed light, carriers are generated at or near the illuminated surface while with high-intensity weakly absorbed light, carriers are generated approximately uniformly throughout the bulk, as well as at the surface of the sample. The bulk generation is inferred from