Dielectric Breakdown in Cadmium Sulfide

RICHARD WILLIAMS
RCA Laboratories, Princeton, New Jersey
(Received September 26, 1961)

The dielectric breakdown field strength for CdS has been measured by a technique employing blocking contacts on conducting crystals. Values obtained with different crystals are in the range 0.9×10^6 to 2.5×10^6 volts/cm. Experiments in which carriers are injected by intermittent illumination show that impact ionization does not occur during breakdown. A variety of evidence is presented indicating that breakdown is due to internal field emission.

THE phenomenon of electronic breakdown has been studied for many insulating and semiconducting solids. In the interpretations of the results, discussion has centered around two basic electronic mechanisms: impact ionization and internal field emission.[1-3] The characteristic feature of extensive work with alkali halides is that the breakdown process may be satisfactorily interpreted by assuming that the currents responsible for the breakdown result from the multiplication of free carriers by impact ionization. Free carriers acquire sufficient energy in the high field present in the crystal to create hole-electron pairs by ionization across the band gap. The internal field emission process suggested by Zener[4] has been generally recognized as inadequate to interpret the experiments on alkali halides. More recently, detailed investigation of the current-voltage characteristics of back-biased *p-n* junctions in silicon and germanium has revealed considerable complexity in the breakdown process and has shown that more than one mechanism may be operative in a given material.[5-7] For silicon *p-n* junctions having thicknesses greater than about 0.1 μ, the breakdown was an avalanche due to multiplication of carriers by impact ionization in the high field at the junction. For junctions 400 A thick the breakdown involved both impact ionization and internal field emission. Thus, a change of the effective specimen thickness changes the mechanism of breakdown. The transition is completed in the now familiar tunnel diode where, with junctions only 100 A thick, large internal field emission currents flow with very low applied voltages.

Recently a technique has been developed for producing high electric fields of known magnitude and distribution in single crystals of CdS.[8] Some preliminary experiments on dielectric breakdown were reported in this reference. In what follows, the same experimental technique is applied to a study of the mechanism of the breakdown in CdS single crystals.

DESCRIPTION OF METHOD

The method is similar to that used to obtain high fields in *p-n* junctions in that the field is due to space charge of ionized electron donor centers within the crystal and appears across a narrow region about a micron thick.[8] It differs from the use of *p-n* junctions in that the space-charge region of ionized donors is not produced at a *p-n* junction but by means of a blocking contact. The blocking contact is provided by an aqueous electrolyte solution in contact with the surface of the crystal.

Vapor grown crystals of CdS were used.[9] They had *n*-type conductivity due to halogen donors and contained from 10^{16} to 5×10^{17} free carriers/cm^3. An ohmic contact of gallium-indium alloy was made to one end of the crystals which were in the shape of long thin ribbons. The blocking contact was made by immersing the other end several mm deep into a 0.1 molar KCl solution. A sheet platinum electrode, 3 cm square and well separated from the crystal, connected the external circuit to the solution. External voltage was applied with the positive terminal going to the crystal. It has been shown by field-effect measurements that, for a given applied voltage, the field within the crystal for this situation is described quantitatively by the simple Mott-Schottky equation for a uniform volume distribution of donors.[8] The field is perpendicular to the surface and exists wherever the surface is in contact with the electrolyte. Ordinarily the space-charge region is not thick enough to fill the crystal so there remains a high-conductivity strip down the interior. For this reason there is little potential drop along the length of the crystal and nearly all occurs across the space-charge region near the surface. The magnitude of the field is a linear function of distance, rising from zero at the inner boundary of the space-charge region to a maximum value at the surface of the crystal. Thus the maximum field at the surface is twice the average field across the space-charge region. In specifying the breakdown field strength in this work, it is the maximum field which is used.

[1] R. Stratton, in *Progress in Dielectrics* (John Wiley & Sons, Inc., New York, 1961), Vol. 3, pp. 235–292.
[2] W. Franz, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), pp. 155–263.
[3] H. Fröhlich and J. H. Simpson, *Advances in Electronics*, edited by L. Marton (Academic Press Inc., New York, 1950), Vol. 2, pp. 185–217.
[4] C. Zener, Proc. Roy. Soc. (London) **A145**, 523 (1934).
[5] K. G. McKay and K. B. McAfee, Phys. Rev. **91**, 1079 (1953).
[6] K. G. McKay, Phys. Rev. **94**, 877 (1954).
[7] A. G. Chynoweth and K. G. McKay, Phys. Rev. **106**, 418 (1957).
[8] R. Williams, Phys. Rev. **123**, 1645 (1961).
[9] The crystals were grown in this laboratory by S. M. Thomsen and C. Busanovich.

The measurements made were: breakdown field strengths for a number of crystals, pre-breakdown currents as a function of field and the shift of optical absorption edge as a function of field up to the breakdown field strength. In addition, the behavior of light-injected carriers was studied in an attempt to observe impact ionization multiplication of these carriers during breakdown.

EXPERIMENTAL RESULTS

When a steadily increasing voltage is applied to the blocking electrode, the current flow is less than 10^{-8} amp/cm^2 and roughly constant until, near the breakdown field strength, it rises rapidly with increasing voltage. If the field is increased much further, the currents become large enough to destroy the surface of the crystal. For this work it was arbitrarily specified that breakdown occurred at that voltage where the current density reached 10 μa/cm^2. Since the current is a steeply rising function of voltage, the numerical value of breakdown field strength is not very sensitive to the value of current density chosen to specify breakdown. However, the fact that breakdown is defined by choosing a fixed current density in this way can lead to certain apparent effects which will be discussed later. A recorder tracing of pre-breakdown current vs applied field was given in reference 8.

The breakdown field strengths for several different crystals are shown in Fig. 1. Each point represents a different crystal. It is seen that there is a systematic trend of breakdown field strength with bulk free-carrier density. The significance of this will be taken up in the ensuing discussion.

Values of the breakdown field strength range from 1×10^6 to 2.5×10^6 volts/cm. These values are of the right magnitude to be due to internal field emission. The theoretical treatment best applicable is that due to Franz.[10] His equation for the probability, w, that an electron will tunnel from valence band to conduction band within an insulator in an electric field, F, is

$$w=AF^{10/3}\times10^{\alpha},$$

where (1)

$$\alpha=-1.75\times10^7E_g^{\frac{3}{2}}(m^*/m)^{\frac{1}{2}}/F.$$

A is a quantity independent of field with order of magnitude unity. E_g is the band gap in ev (2.44 ev for CdS). m^*/m is the electron effective-mass ratio, 0.2 for CdS.[11] Franz gives the criterion that breakdown occurs when the field is large enough to make the quantity in the exponent equal to about 15. Thus for CdS the critical field is 2.0×10^6 volts/cm which is in good agreement with the data. It is more difficult to obtain an estimate of the field required to produce breakdown by the alternative impact ionization theory. Fröhlich's theory[3] indicates that a somewhat higher field strength around 8×10^6 volts/cm is required.[8] More recent treatments are more elaborate, and a numerical value applicable to CdS cannot readily be obtained from them.[1]

[10] W. Franz, reference 2, p. 215.

[11] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

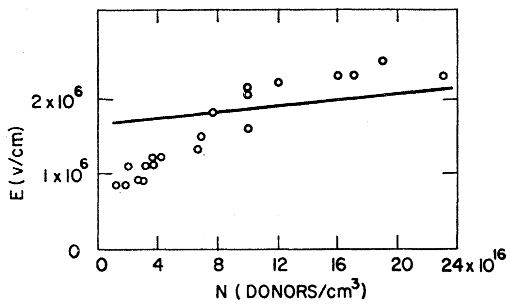

FIG. 1. Breakdown field strengths for several different crystals having different donor concentrations.

PRE-BREAKDOWN CURRENTS

Pre-breakdown currents were measured as a function of electric field and compared with theory. For convenience, we make the approximation that the theoretical variation of internal field emission current with field is given by replacing F in Eq. (1) by the maximum field which occurs at the surface, F_m. A more detailed analysis, taking proper account of the fact that the field is a function of position within the crystal, shows that this is a good approximation. Since the average field is V/λ and F_m is twice the average field, we have[8]

$$F_m=2V/\lambda=5.6\times10^{-4}N^{\frac{1}{2}}V^{\frac{1}{2}}\text{ volts/cm,} \qquad (2)$$

where V = applied voltage, N = number of ionized donor centers/cm^3, and λ = thickness of space-charge region.

The pre-exponential field dependence in Eq. (1) is ignored since, typically, the magnitude of the field changes by less than twenty percent for the current range measured. Thus the exponential term in Eq. (1) becomes 10^{α}, where

$$\alpha=-5.3\times10^{10}/(NV)^{\frac{1}{2}}. \qquad (3)$$

The current is proportional to this term and for a given crystal, with N known, we then have a theoretical slope for the line obtained by plotting $\log_{10} i$ vs $1/V^{\frac{1}{2}}$. A typical plot for a CdS crystal is shown in Fig. 2. Data for four crystals, including this one, are given in Table I. The data plotted in this way were all fairly good straight lines as in Fig. 2 though there is considerable scatter in comparing theoretical and observed slopes. On the average, the observed slope is about one third the theoretical slope with the current rising *less steeply* with voltage than the theory predicts. Thus there is a rather rough agreement between theory and experiment if the pre-breakdown currents are interpreted as being due to internal field emission. This may be compared with the results of McKay and McAfee who measured pre-breakdown currents in Ge and Si where the break-

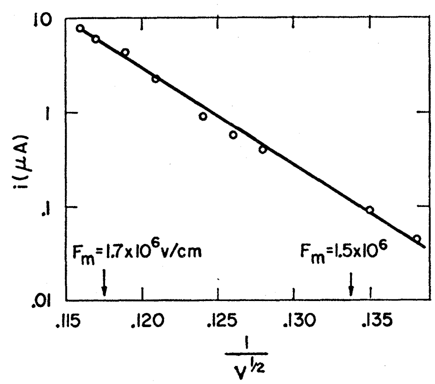

FIG. 2. Breakdown current-voltage data for a crystal having a donor density of $1.0\times10^{17}/cm^3$.

down was due to impact ionization.[7] In their experiments, the breakdown current was found to rise much *more steeply* with field than the internal field emission theory predicts. In silicon, for instance, when their data are plotted in the same way as was done here, the observed slope is more than 15 times as large as the theoretical slope. They obtained similar results with germanium. Thus in cases where it is definitely established that breakdown is due to impact ionization, it is also found that the pre-breakdown current-voltage slopes are more than an order of magnitude greater than those predicted by the internal field emission equation. Conversely, where internal field emission was found in back-biased silicon *p-n* junctions[6] the current-voltage curve was "soft." The current rose less steeply than the equation predicts. For these reasons we take the rough agreement between theory and experiment obtained here as partial evidence that the breakdown is due to internal field emission. Unfortunately, the impact ionization theory is sufficiently complicated[1] that a similar comparison with these data cannot be readily made.

ATTEMPTS TO OBSERVE IMPACT IONIZATION DIRECTLY

A significant feature of the evidence that breakdown in silicon and germanium occurs by impact ionization is the direct observation of multiplication of light-injected carriers in *p-n* junctions biased near the breakdown voltage.[5–7] Illuminating with a constant light intensity, there is a constant photocurrent through the back-biased junction which is independent of voltage for low bias voltages. As the breakdown voltage is reached, the carriers passing through the junction are multiplied by impact ionization and an increased current results. The same technique was applied here in an attempt to observe multiplication of light-injected carriers as breakdown occurs. The electrode arrangement used here is especially well adapted to this experiment, since the surface of the crystal may be illuminated with strongly absorbed light through the transparent electrolyte. Light of 4500-A wavelength from a monochromator was used. The absorption constant for this wavelength is about 10^5 cm^{-1} which guarantees that most of the light is absorbed within 0.1 μ of the surface of the crystal. At the breakdown voltage the thickness of the space-charge region is typically 1 micron so the light is absorbed well within the high-field region. To separate the current due to light-injected carriers from the rising dark current which occurs at breakdown an intermittent illumination was used. This was obtained with a rotating sector turning at 10 rps. Applied voltage was increased at a uniform rate with a battery box and a Helipot driven by a 10-rpm motor. Applied voltage was displayed on the horizontal axis of an oscilloscope trace and the current through the crystal was displayed on the vertical axis. The applied voltage increased by about 100 volts per minute. Results may best be explained by reference to Fig. 3 which is typical of many traces obtained. At low voltages there are two horizontal traces. The upper trace is the current through the crystal while the intermittent light is on and the lower trace is that while the light is off. When the light is off, the current is several orders of magnitude smaller than when the light is on (in the low-voltage region). The slight displacement of the lower trace from the bottom line of the reticle is for convenience in viewing and is not a true measure of the current for the lower trace. Since the horizontal motion of the trace across the screen is slow compared with the period of the rotating sector, both traces appear continuous. The photocurrent in the low-voltage range corresponds to one electron per incident photon within the absolute accuracy of the monochromator calibration (i.e., to within a factor of 2). If multiplication of the light-injected carriers began at some voltage there would be an increase in the vertical separation between the two traces. It is seen that there is *no* such increasing separation as the voltage increases and passes through the breakdown range. The dark current increases manyfold with no observable multiplication of the light-injected carriers. Identical results were obtained with many crystals having various carrier densities spanning the entire range shown in Fig. 1. Some crystals were mounted so that the light was incident on the

TABLE I. Theoretical and experimental slopes for pre-breakdown current-voltage data.

Carrier density N/cm^3	Theoretical slope Eq. (3)	Observed slope	Ratio of theoretical to observed slope[a]
1.0×10^{17}	170	95	1.8
2.9×10^{16}	248	45	5.5
6.8×10^{16}	203	56	3.6
1.6×10^{17}	132	91	1.4

[a] Average value of the ratio of theoretical to observed slope is 3.1. All slopes are negative. The signs have been omitted for convenience.

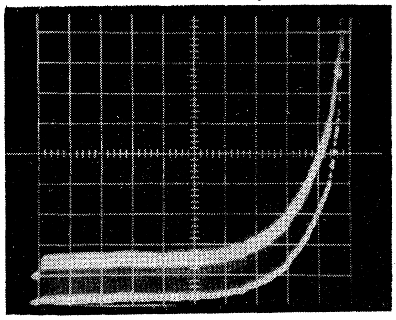

FIG. 3. Current-voltage curve showing behavior of light-injected carriers during breakdown. Horizontal scale 10 v/cm. Vertical scale 3 μa/cm.

broad faces, and others were mounted so that the light was incident on the narrow edges to be sure that data were available for all the crystal faces on which breakdown might occur. In no case was any multiplication of the injected carriers observed. The breakdown fields obtained for the illuminated crystals fall nicely among the data of Fig. 1 indicating that the breakdown process is very likely identical in the light and in the dark. There seems to be no question that the injected carriers were present in the high-field region where breakdown occurred so it must be concluded that breakdown does *not* take place by impact ionization of carriers in the high-field region. This, of course, does not preclude the possibility that impact ionization occurs in CdS under other circumstances; e.g., where the effective specimen thickness is much greater.

SHIFT OF OPTICAL ABSORPTION EDGE PRIOR TO BREAKDOWN

In fields slightly below that necessary to cause breakdown by internal field emission there is a shift of the optical absorption edge of the material due to the field. This has been analyzed by Franz and is due to a precursor of internal field emission in which the wave function for an electron in the valence band has an exponential tail extending into the forbidden energy gap.[12] According to Franz's theory, the effect in CdS should become observable when fields between 10^5 and 10^6 volts/cm are present. For an exponential band edge, which is a good approximation for CdS, the band edge is predicted to shift to longer wavelengths by an amount proportional to the square of the field. This has been reported earlier[13] for CdS, and some data from the present work are shown in Fig. 4. This is representative of data obtained with four different specimens and for all of these a good proportionality was found between shift of the band edge and the square of the field. The agreement is somewhat surprising, since the Franz theory applies to a crystal in a uniform field while, in the present experiment, the field is a function of position within the crystal. In addition, the thickness of the space-charge region and therefore the effective specimen thickness vary with field. The situation does not yield to a simple analysis under these circumstances. What is significant here is that what is very probably the expected precursor to breakdown by internal field emission is actually observed as the precursor to the experimentally observed breakdown and that the magnitudes of the fields involved are those which theory predicts. A similar analysis is used in the theoretical treatment of both effects. For this reason, the relative fields at which the two effects are predicted to occur have a significance apart from possible absolute errors in the theory or in its application to a particular substance as done here.

DISCUSSION AND CONCLUSIONS

The failure to detect impact ionization during breakdown suggests that the breakdown is due to the alternative process of internal field emission. In this process the electrons might originate from the valence band, from deep traps, or from the electrodes. The magnitude of the breakdown field strength and the other observations are in accord with the hypothesis that the actual process is internal field emission from the valence band to the conduction band.

In Fig. 1 there is an apparent trend of the breakdown field strength with the carrier density of the crystal used. It is believed that this is not a real trend in the breakdown field strength but is a consequence of two features of the present experiments. These features are: (1) the definition of breakdown, which specifies that breakdown occurs when a fixed current density is reached, and (2) the fact that the thickness of the space-charge region varies with donor concentration. It is very likely that, in these experiments, the significant difference between crystals having different carrier densities is that the carrier density determines the thickness of the space-charge region, which is the effective specimen thickness. At the breakdown voltage, the space-charge region is thickest for specimens with low carrier density. Thus the breakdown field strength is smallest for the specimens with the greatest effective

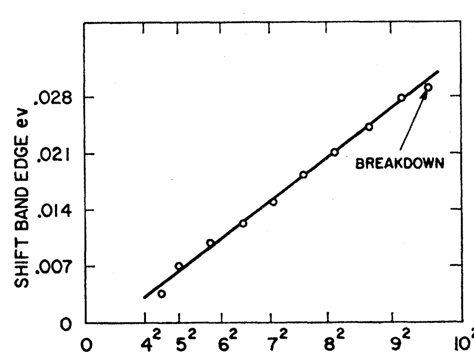

FIG. 4. Shift of band edge vs square of applied field in CdS.

[12] W. Franz, Z. Naturforsch **13a**, 484 (1958).
[13] R. Williams, Phys. Rev. **117**, 1487 (1960).

thickness. This relation between breakdown field strength and specimen thickness is also found in cases where the breakdown is due to impact ionization. In that case it is because electron avalanches are more likely where the electrons have a greater distance to travel within the crystal. Here the explanation must be different and the trend shown in Fig. 1 can be at least partly explained by considering the effect of variations in thickness of the space-charge region on the internal field emission current. Qualitatively, this is most easily understood by considering two crystals which have two greatly different carrier densities. With a blocking contact, a bias is applied to each such that the value of the electric field at the surface is the same for each crystal. In the crystal having the lower donor density the space-charge region, throughout which the electric field occurs, will be considerably thicker than in the other crystal. If the electric field is sufficient to cause internal field emission then this will be taking place throughout a larger volume of the crystal since the high field exists in a larger volume of the crystal. Therefore, though the maximum field at the surface is the same for both crystals, there will be a larger internal field emission current in the crystal having the lower donor density. In this work, the breakdown was defined as having occurred when the breakdown current reached a fixed value. The result is to make the apparent breakdown field strength smaller for crystals with lower donor densities. This is in qualitative agreement with the observation. A quantitative evaluation of this idea may be made by integrating the standard tunneling equation in the form given by Chynoweth.[14] The result gives the theoretical line of Fig. 1. (Details are given in the appendix.) It is seen that this effect is large enough to be significant though exact agreement with the data is still not obtained.

ACKNOWLEDGMENTS

I am indebted to M. Lampert and A. Rose for valuable discussions and suggestions.

APPENDIX

Variation of Apparent Breakdown Field Strength with Effective Specimen Thickness

The internal field emission equation is given by Chynoweth[14] in the general form:

$$j = AF^n e^{-B/F}, \tag{4}$$

where j is the internal field emission current density for a uniform field, F; A and B are constants for a given material; and n is an integer equal to 1, 2, or 3 in the several versions of the theory, depending on the model or approximations used. For simplicity the value $n=1$ is used here though the other values of n give nearly the same numerical result.

In the present experiments F is not uniform but is a known function of position within the crystal, e.g.,

$$F = F_m(x/\lambda), \tag{5}$$

where F_m is the maximum value of the field at the surface, λ is the thickness of the space-charge region, and x is the coordinate of distance within the space-charge region. $x=0$ at the inner edge of the space-charge region and $x=\lambda$ at the surface of the crystal.

For an element of thickness dx at position x, the element of field emission current density is

$$dj = (AF_m x/\lambda) e^{-B\lambda/F_m x} dx. \tag{6}$$

The total field emission current is obtained by integrating Eq. (6) over the volume included by the space-charge region:

$$j = \int_{x=0}^{x=\lambda} dj = (AF_m^2 \lambda/B) e^{-B/F_m}. \tag{7}$$

Dielectric breakdown is defined as occurring when j reaches some arbitrarily chosen value. Once this value is chosen, then for each value of λ there is a value of F_m specified by Eq. (7) and this is the breakdown field strength for that particular value of λ. Thus the relation between any two values of λ and the corresponding breakdown field strengths given by Eq. (7) is

$$\ln\lambda_1 - B/F_m(1) = \ln\lambda_2 - B/F_m(2). \tag{8}$$

[The range of field strengths considered here is small enough that the pre-exponential dependence of Eq. (7) on F_m may be ignored.] This equation was used to obtain the theoretical line in Fig. 1. The experimental value of B was used taken from the average for the data in Table I. This value was 1.0×10^7 volts/cm which is about one third the theoretical of B calculated from the appropriate quantities by which it is defined.

[14] A. G. Chynoweth, in *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 4, pp. 95–124.

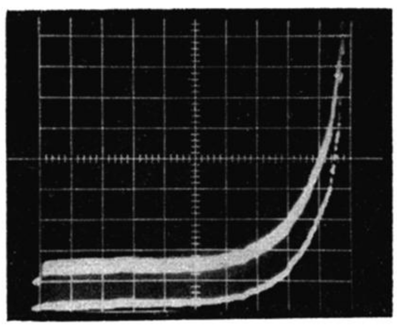

FIG. 3. Current-voltage curve showing behavior of light-injected carriers during breakdown. Horizontal scale 10 v/cm. Vertical scale 3 μa/cm.