Letters to the Editor

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High-Voltage Photovoltaic Effect*

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VACUUM evaporated films of cadmium telluride have been prepared that show unusually high photovoltages across their ends. The effect is independent of the electrode material and the voltage is proportional to the length of the film. A value of one hundred volts/cm has been obtained in sunlight. Since the photovoltage of a single junction is limited by the band gap of the material (1.45 ev), it is concluded that the films consist of large numbers of junctions (or other photovoltaic elements) whose individual voltages add to produce the observed values. Photovoltages greater than band gap have been reported for films of PbS,[1,2] but with a maximum of 3 volts and only after some post-evaporation processing. No such processing is required for the CdTe films.

The presence of the effect depends on the angle, θ, of deposition of the vapor onto the substrate as shown in Fig. 1. Lines of constant θ are found to be equipotentials for photovoltage. No photovoltage exists in material deposited with $\theta=0$. The photovoltage increases rapidly with θ up to about 10 degrees and then very slowly up to 60 degrees, above which no measurements were taken. A second requirement for the effect is that the substrate be held at a temperature between 100 and 250°C during deposition. The pressure during evaporation, $\sim 10^{-5}$ mm, is maintained by an oil diffusion pump.

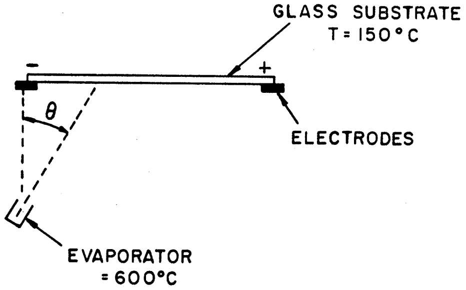

FIG. 1. Schematic diagram of evaporation arrangement for producing the high-voltage photovoltaic effect in films of CdTe. Polarity of the film is as indicated.

The rate of film formation is about 1000 A per minute. The films become photovoltaic when the thickness is sufficient to absorb some light, and the voltage increases to a maximum at approximately one micron. The effect occurs with Pyrex glass, fused quartz, and other substrate materials. The only requirement is that the substrate be more insulating than the films which, in the dark, have a resistance of the order of 10^{13} ohms per square at room temperature.

The electrical properties of the films and their response to light and temperature are reported in a following letter. Optical transmission measurements show that the fundamental absorption edge is 8300 A, the expected value for CdTe. X-ray studies by J. G. White of this Laboratory are consistent with the view that the films consist of crystallites whose size is comparable with the film thickness ($\sim 1\ \mu$). The crystallite (111) planes have a preferred orientation parallel to the substrate, regardless of the angle of deposition.

Although the effect has been found in every film made, the magnitude has not been reproducible within a factor of 10. An explicit model for the mechanism of the effect has not yet been established. An effect of comparable magnitude has been found in single-crystal zinc sulfide by another group in this laboratory. Further studies of the effect in both materials are under way.

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* This work was supported by the Evans Signal Corps Laboratories.

[1] Starkiewicz, Sosnowski, and Simpson, Nature **158**, 26 (1946).

[2] Berlaga, Rusmach, and Strakhov, Zhur. Tekh. Fiz. **25**, 1878 (1955).

Properties of Photovoltaic Films of CdTe†

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THIS letter describes some of the basic properties of a representative photovoltaic film of CdTe.[1] The film was deposited onto a Pyrex substrate: it was one-half cm long, one cm wide, and about one micron thick. The open-circuit voltages were measured with a bucking circuit and null detector.

Both the open-circuit photovoltage and the short-circuit photocurrent of the film cut off sharply at 8300 A. The photovoltage is strongly temperature-dependent as shown in Fig. 1. Figure 2 shows the light intensity dependence of the open-circuit photovoltage at four temperatures for a light source and filter combination which transmits light of wavelengths less than 6500 A. Analysis of these data has shown that the photovoltage has many of the important characteristics exhibited by that of a well-behaved p-n junction. The photovoltage saturates with light intensity at low temperatures, while at higher temperatures it follows

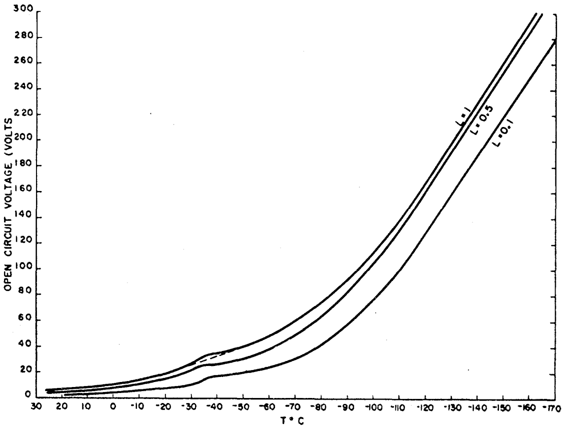

FIG. 1. Open-circuit photovoltage *vs* temperature at three relative light intensities. $L=1$ corresponds to a photon flux of the order of $10^{17}/\text{cm}^2$ sec.

the mathematical expression describing the behavior of the open-circuit photovoltage developed at a *p-n* junction[2,3]:

$$\lambda V=\ln(KL+1). \tag{1}$$

Here λ is e/kT, V is the open-circuit voltage, L is the light intensity, and K is equal to the ratio of the short-circuit current and I_s, to the thermally-generated reverse saturation current, I_0. In addition, the short-circuit current of the CdTe film ($\sim 5\times10^{-10}$ amp at high light levels) varies linearly with light intensity and is relatively independent of temperature from -169°C to 150°C.

Assuming that the film is composed of a number of junctions (or other photovoltaic elements) arrayed in such a way that their individual voltages add, one can estimate the number of such elements, n, in two ways. In the first, Eq. (1) is rewritten for the case of n similar junctions in series, $(\lambda/n)V=\ln(KL+1)$, and n is calculated by fitting this equation to the data in Fig. 2. In the second, one compares the slope of the temperature dependence of the photovoltage of a single junction (measured on a single crystal of CdTe) to that of the film as given in Fig. 1. These estimates are listed in Table I under the headings n_λ and n_{slope}, respectively. Agreement between the two is seen to be good. Table I shows that n increases as the temperature decreases. This suggests a series of single photovoltaic junctions with a distribution of barrier heights. At low temperatures most of the junctions are contributing, while at higher temperatures a much smaller number are effective. Note that at low temperatures the linear density of junctions approaches 10^4 per cm, the linear density of crystallites.[1]

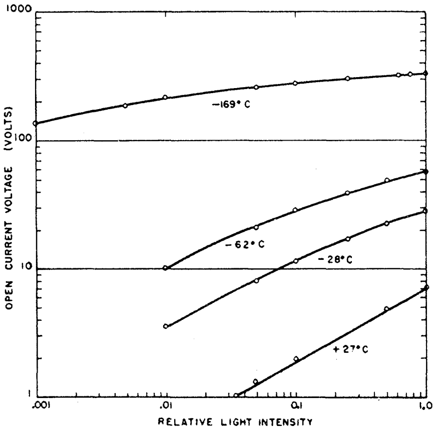

FIG. 2. Open-circuit photovoltage *vs* relative light intensity at four temperatures.

TABLE I. Summary of the important photovoltaic parameters at different temperatures assuming the film to be composed of an array of *p-n* junctions. The film resistance, photovoltage, and short-circuit current are given for light intensity $L=1$.

Temperature (°C)	n_λ	n_{slope}	Resistance (ohms)	Voltage (volts)	Short-circuit current (amp)
27	114	150	1.9×10^{10}	7.0	3.7×10^{-10}
−28	425	417	7.1×10^{10}	28.5	4.0×10^{-10}
−62	700	695	15×10^{10}	57.0	3.8×10^{-10}
−169	3680	1900	104×10^{10}	315.0	3.1×10^{-10}

While the short-circuit current and open-circuit voltage of the film behave as though they originate at *p-n* junctions, the film resistance is completely ohmic at all light intensities and temperatures. This means that if junctions cause the photovoltaic effects, then the film must contain either a series resistance much greater than the junction resistance or a shunt resistance much less than the junction resistance.[2] Our data do not distinguish between these two cases. A typical set of current-voltage curves is shown in Fig. 3. From these curves it was determined that the resistance as a function of light intensity is $R(L)=(1/L)\ln(KL+1)$, except at voltage saturation where it is linear. The same behavior is observed in films deposited at normal incidence which exhibit no net photovoltage. This indicates that the resistance is due to some property of the film itself and not merely to the presence of a photovoltage. Films having resistivities appreciably lower than those given in Fig. 3 ($\sim 10^7$ ohms/square) do not show a photovoltage. It is interesting to note that for all light intensities and temperatures, the film resistance is equal to the ratio of the open-circuit voltage to the short-circuit current.

Measurements similar to those described before were made on a film deposited onto a sapphire substrate and the same general behavior was found.

The magnitude of the observed photovoltages suggests that the effect stems from a system containing 10^2 to 10^4 photovoltaic elements per cm. While the experimental results discussed here suggest an equivalent circuit based on a series arrangement of *p-n* junctions, it should be emphasized that this is but one possible interpretation, at this time the most promising.

The location of the photovoltaic elements is at present unknown. They may, for example, be associated

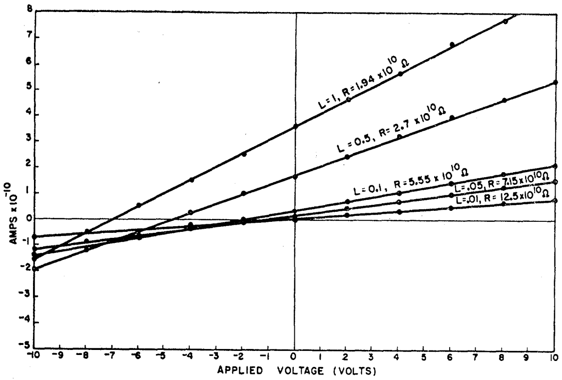

FIG. 3. Current through film *vs* applied voltage. Relative light intensities and corresponding film resistances are as shown. Intercepts on the ordinate and the abscissa are the short-circuit current and the open-circuit voltage, respectively.

with the space charge layers at grain boundaries. Whatever their location, however, the crystallographic ordering process which produces the additive arrangement of these elements is a major factor yet to be explained.

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† This work was supported by the Evans Signal Corps Laboratories.

[1] L. Pensak, Phys. Rev. **109**, 601 (1958), preceding letter.

[2] M. B. Prince, J. Appl. Phys. **26**, 534 (1955).

[3] J. J. Loferski, J. Appl. Phys. **27**, 777 (1956).

New Phenomenon in Narrow Germanium *p-n* Junctions

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IN the course of studying the internal field emission in very narrow germanium *p-n* junctions, we have found an anomalous current-voltage characteristic in the forward direction, as illustrated in Fig. 1. In this *p-n* junction, which was fabricated by alloying techniques, the acceptor concentration in the *p*-type side and the donor concentration in the *n*-type side are, respectively, 1.6×10^{19} cm^{-3} and approximately 10^{19} cm^{-3}. The maximum of the curve was observed at 0.035±0.005 volt in every specimen. It was ascertained that the specimens were reproducibly produced and showed a general behavior relatively independent of temperature. In the range over 0.3 volt in the forward direction, the current-voltage curve could be fitted almost quantitatively by the well-known relation: $I=I_s[\exp(qV/kT)-1]$. This junction diode is more conductive in the reverse direction than in the forward direction. In this respect it agrees with the rectification direction predicted by Wilson, Frenkel, and Joffe, and Nordheim 25 years ago.[1]

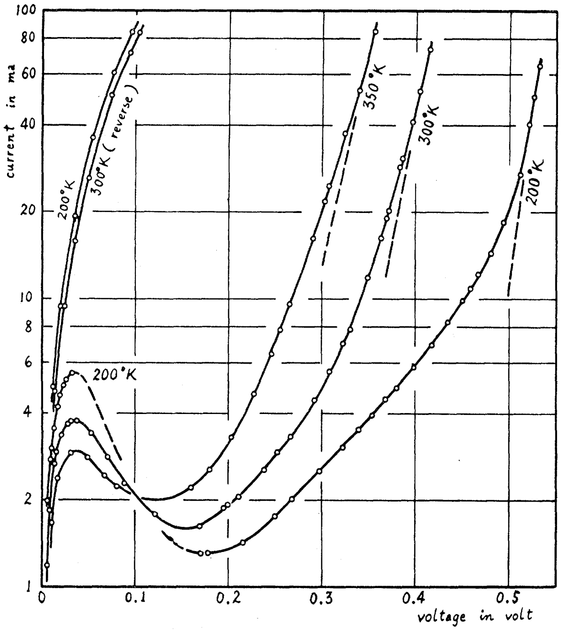

FIG. 1. Semilog plots of the measured current-voltage characteristic at 200°K, 300°K, and 350°K.

The energy diagram of Fig. 2 is proposed for the case in which no voltage is applied to the junction, though the band scheme may be, at best, a poor approximation for such a narrow junction. (The remarkably large values observed in the capacity measurement indicated that the junction width is approximately 150 angstroms, which results in a built-in field as large as 5×10^5 volts/cm.)[2] In the reverse direction and even in the forward direction for low voltage, the current might be carried only by internal field emission and the possibility of an avalanche might be completely excluded because the breakdown occurs at much less than the threshold voltage for electron-hole pair production.[3] Owing to the large density of electrons and holes, their distribution should become degenerate; the Fermi level in the *p*-type side will be 0.06 ev below the top of the valence band, E_v, and that in the *n*-type side will lie above the bottom of the conduction band, E_c. At zero bias, the field emission current $I_{v\rightarrow c}$ from the valence band to the empty state of the conduction band and the current

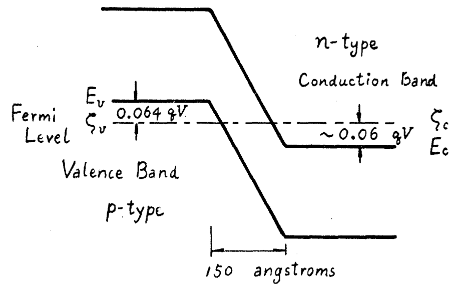

FIG. 2. Energy diagram of the *p-n* junction at 300°K and no bias voltage.