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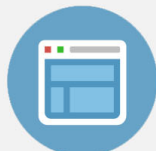
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# Anomalous photovoltage in Cd<sub>0.80</sub>Zn<sub>0.20</sub>Te thin films

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The mechanism of anomalous photovoltage in Cd<sub>0.8</sub>Zn<sub>0.2</sub>Te films is explained on the basis of the formation of junctions at the grain boundaries and the surface band bending. The role of atmospheric oxygen on the surface space charge and, indirectly, on photovoltage is demonstrated. The change of polarity with ambient temperature is explained as is the combined effect of the two models.

Anomalous photovoltage in CdTe,<sup>1-5</sup> ZnTe,<sup>6,7</sup> ZnS,<sup>8</sup> and other materials has been studied by numerous researchers using different models. Rejecting all other models, Pal *et al.*<sup>7</sup> have used *p-n* or *p-p*<sup>+</sup> junctions, surface space charge, and phase transition models for explaining this effect. They have explained almost all behavior relating to this effect by considering these three models. However, as far as we know, there is no such report on anomalous photovoltage in Cd<sub>1-x</sub>Zn<sub>x</sub>Te thin films. This article reports on the generation and behavior of anomalous photovoltage in vacuum evaporated Cd<sub>0.8</sub>Zn<sub>0.2</sub>Te thin films deposited normally on glass substrates.

Cd<sub>0.8</sub>Zn<sub>0.2</sub>Te thin films of different thicknesses were deposited on properly cleaned glass substrates at different substrate temperatures by a vacuum evaporation technique. Measurements of open circuit photovoltage, short circuit photocurrent, and their temperature variations were performed following the procedure of Pal *et al.*<sup>7</sup> Average grain size in the films was determined by a Camscan series II DV electron microscope. Scanning electron microscope (SEM) photographs of these films were taken after etching the upper surface of the films with bromine (1%)-methanol vapor in order to reveal the grains properly.

The open circuit photovoltage of the films is proportional to its length and no photovoltage is produced near the metal semiconductor contact (graphite paint is used for contacts) or along the films between the illuminated and nonilluminated regions.<sup>7</sup> The variation of the photovoltage with ambient temperature is depicted in Fig. 1. From this figure it can be seen that open circuit photovoltage is not only proportional to the film length but it also increases with film thickness. So, it appears that the open circuit photovoltage increases with the volume of the film. Recently we have observed that the hexagonal phase is prominent for films deposited at substrate temperatures higher than 375 K.<sup>9</sup> Generation of photovoltage in films deposited at higher substrate temperatures may indicate phase transition as the possible cause of such effect, but a similar effect is also observed for the films deposited at room temperature when the possibility of phase transition is at its least.<sup>9</sup> The nature of the variation of the photovoltage in films of different thicknesses deposited at room temperature as well as at a higher substrate temperature (575

K) supports the assumption of linear array of *p-n* or *p-p*<sup>+</sup> junctions<sup>1,6,7</sup> along the films. Since the conductivity ( $\sigma$ ) of the films is very low (it varies from 10<sup>-5</sup> to 10<sup>-6</sup>  $\Omega^{-1} \text{cm}^{-1}$  in the temperature range of 320–150 K), Hall measurement is very difficult to perform on these samples. However, from thermoelectric power measurements it can be seen that all the films are *p* type in nature and carrier concentration at 320 K is  $\approx 10^{15} \text{cm}^{-3}$  (taking  $m_h^* = 0.4m_0$  and the scattering factor  $r=2$ ).<sup>10</sup> Thus, the mobility ( $\mu$ ) of the majority carriers is estimated to be nearly 0.1  $\text{cm}^2/\text{V s}$  (using the equation:  $\mu = \sigma/nq$ ). To the best of our knowledge, the minority carrier diffusion length for Cd<sub>0.8</sub>Zn<sub>0.2</sub>Te is not known. But for *p*-type CdTe thin films the reported value of minority carrier diffusion length varies between 1 and 4  $\mu\text{m}$ .<sup>11</sup> The junctions are formed due to the nonuniform segregation of constituent elements towards the grain boundary and due to the separation of photogenerated carriers by the grain boundary potential. So the average diode size is approximately equal to the average grain size which varies from 1 to 10  $\mu\text{m}$  for different films as determined by SEM (a typical SEM photograph is shown in Fig. 2). Thus we observe that the average diode size is comparable to the diffusion length.

The presence of humps in the  $V_{oc}$  vs  $T$  curves at about 190 K supports the notion of contributions by other factors, along with the effect of junctions in the net photovoltage.<sup>7,12,13</sup> In Fig. 3, the variation of photovoltage with temperature is shown for a film deposited at a substrate temperature of 475 K. Curves I, II, and III indicate the results of successive runs of measurements performed on the same film without changing the vacuum condition (10<sup>-1</sup> Pa). After keeping the sample in the vacuum for 2 h the measurements were started and results of the first thermal cycle (from 150 to 320 K) were recorded and is shown as curve I. Each cycle of the measurements took nearly 5 h and the time interval between two successive cycles of measurements was 2 h. A change in the polarity of the photovoltage with the change of ambient temperature is clearly observed for this film. The temperature at which polarity changes shifts towards the lower temperature for successive runs. Such results support the theory of surface band bending in air exposed films. If the films are exposed to air for a whole day, the films then regain their

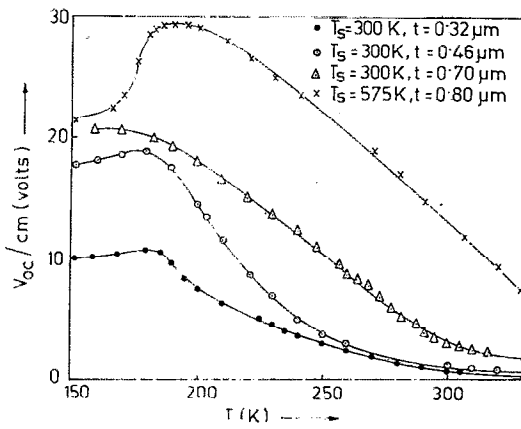


FIG. 1. Photovoltage (per cm) vs temperature ( $T$ ) for  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  films of different thicknesses ( $t$ ) and deposited at different substrate temperatures ( $T_s$ ) ( $L=7000 \text{ W cm}^{-2}$ ).

initial photovoltage and similar characteristics are obtained in repeated measurements. On exposing the film to air, an accumulation layer is produced near the surface of the film due to adsorption of oxygen. So there is a surface band bending, the space charge depth being of the same order as the size of crystallites in the films. Now, if the film surface is illuminated, electron-hole pairs are generated due to high optical absorption in the surface region. So there will be a reduction in the surface band bending, which gives rise to photovoltage.<sup>2</sup>

Considering all the experimental observations, we can conclude that the main contribution to the net photovoltage arises from the junction elements and the surface space charge. In the  $p$ - $n$  or  $p$ - $p^+$  junction model, each of the junctions acts as a diode, and under illumination follows the relationship

$$J = J_0 \exp(qV/KT - 1) - J_L, \quad (1)$$

where the notations bear their usual meanings. Since the particle size of the  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  films is very small and the photovoltage per cm is small, we can simplify Eq. (1) and write the expression for photovoltage per junction as

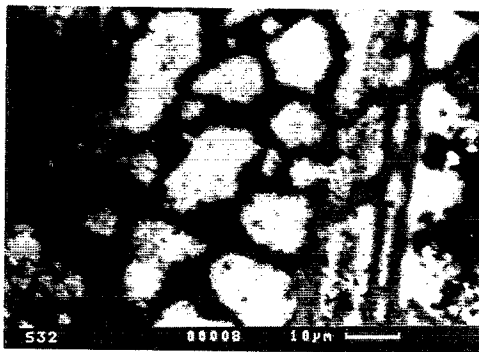


FIG. 2. SEM photograph of a  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  thin film  $0.80 \mu\text{m}$  thick deposited at a substrate temperature  $T_s=575 \text{ K}$ .

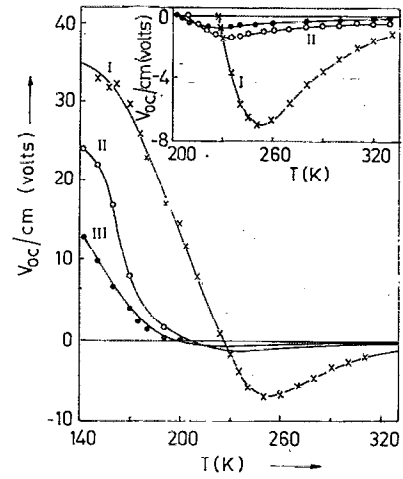


FIG. 3. Temperature variation of photovoltage (per cm) for  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  film  $0.85 \mu\text{m}$  thick deposited at  $475 \text{ K}$  ( $L=7000 \text{ W m}^{-2}$ ). Curves I, II, and III show the results of successive runs. The inset shows the amplified portion of the negative half.

$$V_{oc} = \frac{KT}{q} (J_L/J_0) = \frac{KT}{q} (I_{sc}/I_0), \quad (2)$$

and the total photovoltage per cm becomes

$$V_{Toc} = \frac{nKT}{q} (I_{sc}/I_0), \quad (3)$$

where  $n$  is the number of junctions per cm,  $I_{sc}$  is the short circuit current,  $V_{oc}$  is the open circuit photovoltage, and  $I_0$  is the thermally generated reverse saturation current. With the lowering of ambient temperature, the carrier concentration decreases ( $10^{12} \text{ cm}^{-3}$  at  $150 \text{ K}$ ) and thus  $I_0$  also decreases. As  $I_0$  decreases and the number of junctions per cm  $n$  increases with the lowering of temperature due to the reduction of the shorting of elements,<sup>1,14</sup> ( $I_0/n$ ) decreases sharply (Fig. 4). Since the photovoltages developed up on illuminating, the front and rear faces of the films are not

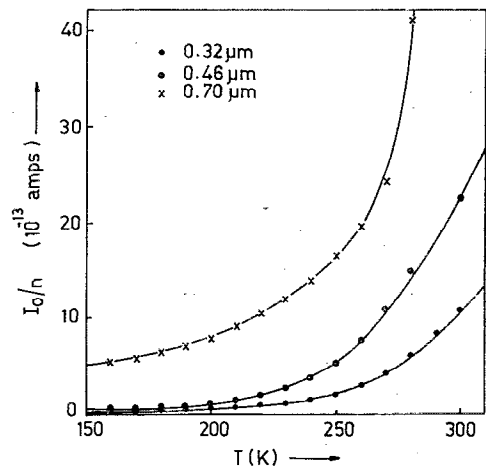


FIG. 4.  $(I_0/n)$  vs  $T(K)$  for  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  films deposited at  $300 \text{ K}$  having different thicknesses ( $L=7000 \text{ W m}^{-2}$ ).

the same, the photovoltage is not due only to junctions. The surface photovoltage seems to contribute along with the junction photovoltage. On exposing the film to air, an accumulation layer is produced near the surface of the film due to the adsorption of oxygen, whereas at the rear surface, i.e., at the film glass interface, there is a possibility of the formation of a depletion or inversion layer. The surface photovoltage developed on one face may be an additive to the junction photovoltage, and the photovoltage developed on the other surface may be of lesser magnitude or opposite in polarity, depending on the nature of the interface layer. Here it should be noted that the surface is, in general, parallel to the bulk of the film; grain boundaries are more sensitive to the ambient than the bulk due to less binding energy in the grain boundary region. Therefore, the formation of the accumulation layer or the inversion layer takes place more efficiently at the grain boundaries. The surface contribution is not always an additive to the bulk contribution, and it depends on the nature of the surface layer, the polarity of the bulk contribution, and the contribution of the rear face (film glass interface) of the sample.<sup>2</sup>

Results of continuous measurements done on the film deposited at 475 K are shown in Fig. 3. The diodes or junctions in the films are formed at the grain boundaries due to nonuniform segregation of constituent elements towards the grain boundaries. For angularly deposited films such directional segregation of the elements causes a more specific orientation in polarity of the diodes (depending upon their mobilities and the nature of the substrates<sup>1,7,12</sup>) and, of course, some random orientation of the diodes. For normal deposition of films, though randomness is very high, even then, on the average, we could detect a specific directional polarity in these films. Continuous vacuum pumping causes the reduction of adsorbed oxygen and hence the depth of the accumulation layer, whereas such

evacuation does not affect the junction much. Therefore, a reduction of photovoltage in the positive side and a shift of temperature when the polarity change occurs in Fig. 3 are not surprising.

In conclusion, we can say that the generation of photovoltage in  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$  thin film is due to the cumulative effect of  $p-n$  or  $p-p^+$  junctions at the grain boundaries and to surface band bending. The temperature dependence of  $(I_0/n)$  for the films supports the additional array of junction elements in the films. The polarity of photovoltage is highly dependent on the chemical composition of the opposite sides of the grain boundaries, on the nature of the surface states of the two faces of the films, and also on the proportion of contribution from these effects. Oxygen plays a vital role in controlling the surface space charge layer and, hence, the magnitude and polarity of photovoltage.

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