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Citation: Journal of Applied Physics 69, 6547 (1991); doi: 10.1063/1.348865
View online: http://dx.doi.org/10.1063/1.348865
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/69/9?ver=pdfcov
Published by the AIP Publishing
The anomalous photovoltaic effect in polycrystalline zinc telluride films


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(Received 26 March 1990; accepted for publication 2 January 1991)

The anomalous photovoltaic effect has been studied in polycrystalline ZnTe films. Increase of photovoltage on Te doping and a decrease on Zn doping is observed. The effect of phase transition, grain-boundary potential barrier, and surface space charge on the photovoltaic effect are reviewed and studied. Analysis of different experimental results reveals that the generation of emf in angularly deposited films on an insulating surface is mainly due to formation of $p-n$ or $p-p^+$ junctions at the grain boundaries and the surface band bending.

INTRODUCTION

Investigation of the anomalous photovoltaic effect in thin films of different materials deposited onto inclined substrates was made by many workers. Parameters affecting the value of photovoltage are studied, and different models are suggested by different workers to explain this effect. Out of them, the most popular interpretations of the anomalous photovoltaic effect in these films are (a) the Dember effect, (b) structural transition within the crystallites, (c) the $p-n$ or $p-p^+$ junction model, and (d) the surface band-bending model. Each of the models has been invoked to explain specific experimental results.

In our present study we have performed different experiments on polycrystalline ZnTe films to justify each of the models and have tried to separate the contribution of each of the effects to the net photovoltage. Though the net photovoltage of the films depends on the condition of deposition—and it is very difficult to maintain the identical deposition condition for all the sets of films, causing a lack of reproducibility of the results—effort has been given to maintain those conditions of deposition very close from set to set, and the correlation between the results and the parameters has been made from the observation of a large amount of data.

EXPERIMENTS

Thin films on ZnTe were deposited onto glass, polysilicon, and mica substrates by thermal evaporation with the help of a Hind Hivac vacuum coating unit (model 12-A4). The ZnTe bulk material was synthesized and placed in a quartz crucible kept inside a tungsten coil. Films of different thickness ($t$) were deposited at different substrate temperatures ($T_s$) where the evaporated ZnTe beams were coming to the substrates. Substrate temperature was maintained 623 K during film deposition. To study the effect of substrate temperature, the films of a particular thickness ($\sim 0.87 \mu$m) were deposited at different substrate temperatures ($T_s$) keeping the angle of deposition fixed ($\theta_D = 45^\circ$). The effect of angle of inclination of the substrates to the incident beam was studied by depositing the films at different $\theta_D$ keeping the other parameters at their optimized values. For Te doping, after the deposition of ZnTe films on glass substrates at $\theta_D = 45^\circ$ and $T_s = 623$ K, a thin layer of Te was deposited on the films followed by an aftergrowth baking at 400 K for 2 h without bringing the films outside. For Zn doping, same procedure has been followed as that of Te doping, but here the baking temperature was 430 K. The rate of deposition was maintained fixed ($\sim 120$ nm/min) for all the sets, and the vacuum inside the deposition chamber was $\sim 10^{-4}$ Pa.

For the measurement of open-circuit photovoltage ($V_{OC}$), the samples (films) of different lengths and different widths were taken. Silver paint was used as the ohmic contact. The samples were illuminated by a white light produced by a 600-W tungsten halogen lamp fed by a stabilized power supply. The open-circuit photovoltage and the short-circuit current of the films were measured by a Keithley electrometer amplifier (610 C). The intensity of illumination of the samples was measured by an Eppley calibrated thermopile. The scanning electron micrographs were taken by an electron microscope (Camscan Series 2DV). Transmission electron diffraction was taken by an electron microscope (JEOL, JEM 200CX). The spectral response of photovoltage was measured by an Oriel monochromator (7240).

RESULTS

It has been observed that the open-circuit photovoltage of the films is proportional to their length. Figure 1 shows the variation of open-circuit photovoltage (per unit length) on the thickness of undoped ZnTe films where the
FIG. 1. Variation of photovoltage (per unit length) with thickness ($t$) of undoped ZnTe films deposited at $T_s = 623$ K and $\theta_D = 45^\circ$ ($L = 7000$ W m$^{-2}$).

substrate temperature ($T_s$) is maintained at 623 K and the angle of deposition ($\theta_D$) is kept at 45°. The intensity of illumination ($L$) is maintained constant (7000 W/m$^2$). From the figure it is clear that at this particular condition, the photovoltage is maximum for the film thickness $\approx 0.87$ μm. It is also observed that the open-circuit photovoltage maxima occur at different thicknesses for the films deposited at different substrate temperatures. The dependence of photovoltage on substrate temperature is shown in Fig. 2 for films of thickness $t = 0.78-0.85$ μm. The photovoltage is observed to be maximum for $T_s = 623$ K, where the films are stoichiometric$^{21}$ and the phase transition occurs.$^{22}$ Figure 3 shows the dependence of photovoltage on the inclination of the glass substrates to the incident beam of ZnTe vapor. Photovoltage is maximum for $\theta_D = 45^\circ$, which is also observed by Patel and Patel$^3$ for the polycrystalline films of ZnTe. Room-temperature (K1) measurement of the open-circuit photovoltage of the undoped films and films doped with Zn and Te at different light intensities ($L$) are shown in Fig. 4. It is seen that the $V_{OC}$ is proportional to $\ln L$ for lower values of intensities, but it saturates at higher intensities. The dependence of $V_{OC}$ on $L$ at low temperature (135 K) is shown in Fig. 5. Open-circuit photovoltage of these undoped and Zn- and Te-doped films are measured at different temperatures for a particular intensity of illumination ($L = 7000$ W/m$^2$) and is shown in Fig. 6. An increase of $V_{OC}$ for lower temperatures is observed for all the films, which is very similar to the observation of Goldstein and Pensak$^6$ for CdTe films and Patel and Patel$^3$ for ZnTe films.

From Figs. 5 and 6 it is clear that the open-circuit photovoltage of Te-doped films is higher than that of undoped films of the same set for all intensities and temperatures, whereas it is less for all intensities and temperatures for Zn-doped films of the same set. The temperature dependence of dark conductivity of those undoped and Te and Zn-doped films is measured. The magnitudes of the conductivities of undoped and Te-doped films at room temperature (295 K) are very close to each other and are about $8.3 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$, whereas the conductivity of Zn-doped films is about $3.8 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$. The spectral response of $V_{OC}$ for an undoped ZnTe film is shown in Fig. 7 in the range of 290–950 nm. The maximum of this curve occurred at 544 nm, which more or less agrees with the band gap. No polarity reversal is observed due to the change of wavelength. Polarity reversal is not observed (as observed by others)$^2$ on illuminating the back surface of
films at a particular intensity of illumination ($L = 7000 \text{ W/m}^2$) and is depicted in Fig. 11. The increase of this ratio with an increase of temperature is prominent for all the films.

In dry weather the photovoltage is retained for more than 15 days, but in moisture its quick degradation is observed. The films deposited on mica and polysilicon at $T_i = 623 \text{ K}$ and $\theta_i = 45^\circ$ showed less photovoltage than that of the films grown on glass substrates.

**DISCUSSION**

In this section we will first discuss the suitability of different proposed models to explain the mechanism of the generation of anomalous photovoltage in different materials in the light of different reported experimental results.

The difference of mobility between photogenerated electrons and holes can lead to a potential difference between the illuminated and nonilluminated faces of a semiconductor slab.\textsuperscript{24-26} This mechanism has been suggested as being responsible for the photovoltage in each microcrystallite of a polycrystalline film.\textsuperscript{7,8} The cancellation of consecutive Dember voltage is prevented by the presence of some unspecified layers of different properties at the crystallite interfaces. The difference of recombination rates at the opposite faces of a crystallite determines the direction of carrier drift and hence determines the polarity of resultant photovoltage.

In case of our ZnTe films, no photovoltage is observed to be produced near the metal-semiconductor contact or along the films between the illuminated and nonilluminated regions. Similar observation is made by other workers\textsuperscript{3,27-29} also. The above result leads to the conclusion that the photovoltaic effect is not due to the Dember effect.

The occurrence of a phase transition at some elevated temperatures is well known for the films of several materials.\textsuperscript{5,22,23,30-35} The appearance of a hexagonal phase in CdTe at about $423 \text{ K}$ is reported by Saha et al.\textsuperscript{30} In ZnTe films this phase transition occurs at about $623 \text{ K}$.\textsuperscript{22} In both the samples the phase changes from cubic to hexagonal. Many workers\textsuperscript{9,10,12,24-37} have correlated the coexistence of both phases to the generation of photo emf in the films and bulk samples. According to their model, at each transition from cubic to hexagonal structure or vice versa, a barrier is formed at which the electron-hole pairs which are created by the light are separated and give rise to a voltage. Assuming the samples to be chemically uniform, the $p-n$ junction model is ignored to explain the observed high photovoltage. A band structure is modeled by Merz\textsuperscript{36} in which there are asymmetric barriers, all of which are alike, so that the voltage is added up. By analogy with the case of ZnS crystals, Semiletov\textsuperscript{37} offered the hypothesis that the reason for the appearance of photovoltage in CdTe films resides in a departure from the ideal regular arrangement of atomic layers, i.e., stacking faults and transition regions between the hexagonal and cubic packing and vice versa. In the case of ZnS, the open-circuit photovoltage appears across the direction perpendicular to (111)- or (0001)-type of planes, i.e., planes with the densest atomic packing. A similar explanation is given by El-Shazly et
for ZnSe films. The sign of the photovoltage is a strong function of crystallographic orientation and, hence, the permanent dipole moments of the hexagonal regions.

It is interesting to note that a similar photovoltaic effect has been observed in Si and Ge where such a structure transition is not possible and casts doubt upon the validity of the cubic-hexagonal structure transition model for the generation of the anomalous photovoltaic effect. We could not find any photovoltage in ZnTe films deposited normally onto glass substrates at $T_s = 623$ K where the phase transition occurs. We have detected the photovoltage in the films deposited angularly on the substrates kept even at room temperature (295 K) where there is no possibility of a hexagonal phase occurring. These results may lead to the violation of this hypothesis, but Saha et al. have obtained a photovoltage in CdTe films deposited at about 423 K for $\theta_p = 0^\circ$, which is in agreement with this phase-transition model, though the photovoltage is found to be very small.

Regarding the polarity of the observed photovoltage, Goldstein and Pensak have reported that a positive polarity would be developed at that end of the films which is far away from the crucible for CdTe films. A similar observation is made in Ge by Kallman et al. and Nakai, whereas the opposite polarity is observed at the far end by Novik for a single-crystal film of CdTe. For polycrystalline ZnTe films, Patel and Patel reported the positive polarity at the far end. Lyubin and Fedorova and Semiletov have observed and also suggested the 50% possibility of both the polarities at any particular end of the films as there are no factors which would stimulate the sequence of atomic layers on the film surface during deposition. A change of polarity with the change of $\lambda$ in CdTe films is observed by Semiletov and suggested a different structure in the surface layer than near the substrate. Korovon and Liubits have obtained a positive far end for a few polycrystalline films of Ge, whereas most of the films showed negative polarity at the farthest end. At about 123 K the polarity of first type changes to the second type. The change of polarity on exposing the films in air or on vacuum pumping is observed by Koronov and Liubits and Nakai.

In the case of our ZnTe films, 60% showed negative polarity at the farthest end and the rest showed opposite polarity. No change of polarity is observed for the change of wavelength of incident radiation ($\lambda$) (Fig. 7). By analyzing our observations and that of previous workers, we can say that the phase transition is one of the causes of the appearance of photovoltage, though we did not get any photovoltage in ZnTe films for $T_s = 623$ K and $\theta_p = 0^\circ$. If any photovoltage appears under such a condition, it should be taken to be due to the phase transition only. The contribution of the phase transition to the photovoltage in ZnTe films is so small that it could not be detected. The appearance of a weak photovoltage (-mV) in CdTe for the phase transition has already been reported in our previous publication. The change of polarity at low temperature and in air or in vacuum as seen by Koronov and Liubits and Nakai also suggests the contribution of another factor or factors along with the phase transition in
Starkiewicz, Soenowski, and Simpson\textsuperscript{43} have explained the anomalous photovoltage in PbS films assuming a distribution gradient of positive and negative impurity ions through the microcrystallites, with an orientation such as to give a nonzero photovoltage. The model of \textit{p-n} or \textit{p-p}+ junction array has been reported for CdTe by Adirovich, Rubinov, and Yuabov,\textsuperscript{14,15} Adirovich and Shakirov,\textsuperscript{16,17} and Karpovich and Shilova\textsuperscript{18} for Sb\textsubscript{2}S\textsubscript{3}, and by Patel and Patel\textsuperscript{1} for ZnTe films, but the mechanism by which such \textit{p-n} or \textit{p-p}+ junctions can be formed has not been properly explained, although a difference in mobility of impurities on either side of growing hillocks could be invoked.\textsuperscript{6,19} Goldstein and Pensak\textsuperscript{6} have explained the formation of such \textit{p-n} junctions due to the trapping of residual gases at the shadowed region during its formation. Johnson, Williams, and Mee\textsuperscript{2} have studied the same effect in CdTe films prepared by thermal evaporation in ultrahigh vacuum using very pure material. From their\textsuperscript{2} \textit{in situ} measurement, a large photovoltage is observed, which ruled out the concept of the adsorption of a foreign gas or residual gas as suggested by Goldstein and Pensak.\textsuperscript{6}

From our experimental observations, we also support the formation of \textit{p-p}+ junctions in ZnTe films, which explains the appearance of photovoltage in ZnTe films deposited at room temperature. The formation of junctions at the interfaces of the crystallites is logical as the grain-boundary potential separates the carriers generated by light. The junctions can also be formed due to nonuniform segregation of constituent elements toward the grain boundary. This nonuniformity increases with the increase of the inclination of the substrates to the incident beam. The trapping of residual gas at the shadowed region of the hillocks is the secondary cause of junction formation. For low-resistance material or low-resistance substrates, the junction elements become shorted, causing the reduction of net photovoltage. The elements can also be shorted by annealing at higher temperatures, which is very clear from the micrographs of Patel and Patel.\textsuperscript{3} The occurrence of less photovoltage in the ZnTe films grown on a polysilicon wafer of less resistance is due to this shorting effect. The algebraic sum of the photovoltage of each unshorted element gives the net photovoltage.

According to the surface band-bending model, in the small inclined crystallites the presence of a surface charge can lead to a space charge extending through the whole crystallite. The space charge can be modified by illumination of the surface by highly absorbed radiation. In the

![FIG. 6. Photovoltage (per unit length) vs temperature (T) for undoped (▲), Zn-doped (×), and Te-doped (●) ZnTe films (t=0.5 μm).](image-url)
absence of illumination, no potential difference exists between the two points of opposite faces in the microcrystallite. On illumination of the front surface by highly absorbed radiation, the space charge and band bending are reduced by the generation of electron-hole pairs. If the optical absorption depth is much less than the space-charge depth, then, because of the inclined form of the crystallite, the charge is reduced more at the point which is nearer to the region of high optical absorption. The sign and magnitude of the surface charge probably depend on surface crystallography, chemical composition, and defect structure. The change of polarity with an increase of wavelength according to this model is due to an increase of the penetration depth of the light. For front-face illumination, much of the long-wavelength radiation penetrates into the region of the rear face and the resulting emf is the difference of the front- and rear-face contribution. If the rear-face contribution dominates over the front-face contribution, no change of polarity is observed on the variation of the wavelength for rear-face illumination. The above explanation also gives the reason for the change of polarity on rear-face illumination. The development of photovoltage in single crystals can be explained by the surface band bending. In the case of our ZnTe films, no change of polarity is observed on rear-face illumination. Similar obser-
FIG. 10. ($qI_0/nkT$) vs intensity of illumination ($I$) for undoped (□), Zn-doped (×), and Te-doped (○) ZnTe films (t=0.5 μm) measured at room temperature (295 K).

FIG. 11. ($I_o/nT$) vs $T/K$ for undoped (□), Zn-doped (×), and Te-doped (○) ZnTe films (t=0.5 μm) measured at room temperature (295 K).

*Figures and text from the document.*

Evans also made by many workers.\textsuperscript{3,4,41} Though this model explains many experimental observations, the results of the effect of moisture and other ambient atmospheres are contradictory\textsuperscript{2,44-46} and it cannot explain the change of polarity at low temperature as observed by Korovin and Liubits.\textsuperscript{27} However, the effect of surface modification on photovoltage is obvious and can be explained according to the surface space charge and, hence, the surface band bending.

Considering all the experimental observations and the existing models, we can say that the phase transition is one of the causes of producing photovoltage in both the films and bulk samples, but the effect is very small. The main contribution to the net photovoltage arises from the junction elements, p-p\textsuperscript{+} in the case of ZnTe films and the surface space charge. In the case of a single crystal, the photovoltage is due to this last factor only. In the p-n or p-p\textsuperscript{+} junction model, each of the junctions acts as a diode and under illumination follows the equation

$$J = J_0 \exp \left( \frac{qV}{kT} - 1 \right) - J_L,$$

where the notations bear their usual meanings. Since the particle size of the ZnTe films is very small\textsuperscript{22} and the photovoltage per centimeter is small, we can simplify (1) and write the expression of photovoltage per element as
\[ V_{OC} = \frac{kT}{q} (I_L/I_0) = \frac{(kT/q)}{(I_{SC}/I_0)}, \]  
and the total photovoltage per centimeter is
\[ V_{TOC} = (nkT/q) (I_{SC}/I_0), \]
where \( n \) is the number of junction elements per centimeter, \( I_{SC} \) is the short-circuit current, \( V_{OC} \) is the open-circuit voltage, and \( I_0 \) is the thermally generated reverse saturation current. The plots of \( qI_0/(nkT) \) vs \( L \) for the undoped and Zn- and Te-doped films are shown in Fig. 10. From the figure, the constancy of \( I_0 \) with \( L \) and an increase of \( I_0 \) for Zn doping is clear. This indicates that the barrier potential height decreases on Zn doping. The reverse situation is observed on Te doping where the barrier height is increased. Therefore, an increase in photovoltage in Te-doped films is perhaps due to an increase of barrier height caused by the segregation of doped impurities at the grain boundaries during the process of annealing of the films in vacuum. With a decrease of temperature as \( I_0 \) decreases and \( n \) increases due to reduction of shorting of elements, \( I_0/(n) \) decreases sharply (Fig. 11). As the photovoltages developed on illuminating the front and rear face of the films are not same, the photovoltage is not due to junctions only. Te doping on the front and back surfaces of the films separately caused an increase of photovoltage on the corresponding face illumination. Therefore, the surface photovoltage seems to contribute significantly along with the junction photovoltage. On exposing the films in air, an accumulation layer is produced near the surface of the films due to adsorption of oxygen, whereas at the back surface, i.e., at the glass film interface, there is a possibility of the formation of a depletion or inversion layer. The surface photovoltage developed on one face is additive to the junction photovoltage, and the photovoltage developed at the other face may be less in magnitude or of opposite polarity, depending on the nature of the interface layer. So, in such a case, it may be subtractive. The increase of photovoltage on rear-face illumination for the films deposited on a predeposited Te layer may be due to the conversion of the surface layer (i.e., film-glass interface) to an accumulation layer, causing the development of photovoltage of the same polarity as that of the junction photovoltage. The reduction of photovoltage upon exposing the films to a moist atmosphere supports our view regarding the contribution of surface photovoltage to the total photovoltage of the films. It is known that water vapor helps to produce an inversion layer on the surface that changes the existing accumulation layer and results in the reduction of the effective photovoltage due to subtraction of two photovoltages.

**CONCLUSIONS**

Comparison of different experimental observations of different workers leads to the conclusion that the generation of photovoltage in angularly deposited films is the cumulative effect of a phase transition, \( p-n \) or \( p-p^+ \) junctions at the grain boundaries, and surface band bending.

The light intensity and temperature dependence of the photovoltage of all the doped and undoped films are consistent with the assumption that the films consist of an additive array of photovoltage elements (i.e., \( p-p^+ \) junctions in the case of ZnTe films).

The constancy of \( qI_0/(nkT) \) with intensity of illumination and its different values for undoped and Zn- and Te-doped films justifies the assumption of the role of barrier height on photovoltage.

The polarity of photovoltage cannot be predefined. It is highly dependent on the orientation of the crystallites, the chemical composition of both of the sides of the grain boundaries, and the nature of the surface states of both of the faces of the films, and also on the proportional contribution of all three effects.

The contribution of these three effects does not always produce photovoltage in the same direction, and their contributions are not same at all wavelengths of radiation and at all temperatures. That is why sometimes the change of polarity is observed due to a change of wavelength and change of temperature.

24. H. Dember, Phys. Z. 32, 856 (1931).