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Dark- and photoconductivity in doped and undoped zinc telluride films

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Abstract. Thin films of ZnTe are prepared under different conditions by a vacuum evaporation technique. Dark- and photoconductivity are measured at different temperatures. The effect of doping on conductivity is studied for BaF₂ (7 wt %), PbCl₂ (6 wt %) and In (6 wt %) dopants. The spectral response of photoconductivity and intensity variation of photocurrent in ZnTe films of different thickness is studied. The mechanism of conduction in those films is properly explained by considering different models. The variation of drift barrier height with film thickness, and hence the particle size, is studied. An exponential distribution of traps or impurity states within the bands is suggested for the films.

1. Introduction

Electrical conductivity measurements on ZnTe bulk materials or crystals have been carried out by several workers (Bube and Lind 1956, 1957, Boltkas *et al* 1956, Tubota *et al* 1961, Tittle *et al* 1964). Measurements of this parameter in ZnTe films in amorphous (Brown and Brodie 1972, Webb and Brodie 1979) or polycrystalline form (Kroger 1965, Senokosov and Usatyi 1979, Patel 1988) have also been extensively studied. It is a well established fact that ZnTe crystals in their undoped and doped states are generally of high-resistive p-type due to self-compensation (Kroger and Vink 1956, Tittle *et al* 1964). Tittle *et al* (1964) prepared an Al-doped solution grown ZnTe. They also tried to produce n-ZnTe by Ga, In, Br and I doping, but only the insulating crystals were produced. Bube and Lind (1957) investigated the photoconductivity in single crystals of ZnTe and revealed that the mechanism proposed for photoconductivity phenomena in CdS and CdSe may also be applied to ZnTe. The variation of electrical resistivity and photosensitivity in ZnTe films grown on glass substrates by vacuum evaporation have been explained by Patel (1988) on the basis of stoichiometric composition and crystallite size.

In the present study the dark- and photoconductivity of vacuum-evaporated ZnTe films deposited at room temperature and at 573 K substrate temperature are measured at different temperatures. The effect of doping with different materials like BaF₂, PbCl₂ and In on those parameters are studied.

Analysis of the electronic properties of ZnTe layers using only conductivity turned out to be complicated due to the variety of different effects that may be contributing to the measured values. Due to the high resistivity of the films no Hall or thermoelectric measurements could be performed to probe into the mechanism of electronic phenomena in these films properly. However, some measurements like photoconductivity and its spectral dependence and intensity variation of photocurrent are performed to explain the nature of trap distribution between the bands.

2. Experiment

Thin films of ZnTe are deposited on properly cleaned glass substrates by evaporating the bulk material from a quartz crucible placed inside a tungsten coil under a vacuum of the order of 10⁻⁴ Pa. The detailed description of the method of synthesis of the bulk material is given elsewhere (Pal and Saha 1985). Films of different thickness are deposited at room temperature (298 K). For doping, films of a particular thickness (≈ 600 nm) are deposited at a substrate temperature of 573 K, where the films are seen to be stoichiometric (Pal *et al* 1989). Fixed amounts of dopants like PbCl₂ (6 wt %), BaF₂ (7 wt %) and In (6 wt %) are deposited on the surface of the films. The films are subsequently annealed at 423 K for 6 h in vacuum for PbCl₂ and BaF₂ doping. For In doping, the same procedure is followed except that the annealing temperature is maintained at 400 K. The deposition rate for all the films is maintained fixed (~ 120 nm min⁻¹). The thickness of the films is measured by a surfometer (SF 101).

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The electrical conductivity measurement of the ZnTe films in dark and under illumination is carried out within the temperature range 140–373 K by a suitably designed cryostat. Of the various contact materials, aquadag (graphite paint), silver paint and electroless gold are observed to form ohmic contacts with the films. However, in the present study, graphite paint is used for ohmic contacts.

As the dark resistance of the ZnTe films is generally of the order of $10^8 \Omega$ at room temperature, and is higher at low temperatures, the two-probe method is used for measuring the resistivity/conductivity of the samples. The method of measuring photoconductivity has been described earlier (Pal *et al* 1990). The type of conduction in these films is measured by the hot-probe method.

3. Results

The ZnTe films deposited in vacuum and exposed to the atmosphere after deposition are found to be p-type as determined by thermoelectric measurement (hot-probe method). The films doped with BaF_2 , $PbCl_2$ and In are also seen to be p-type. X-ray and electron microscopic studies have revealed that the films are polycrystalline and consist of particles of size ranging from 6 nm to 15 nm (Pal *et al* 1989). Figure 1(a) shows the variation of conductance with temperature in the dark and under illumination (1400 W m^{-2}) for a typical ZnTe film of 1200 nm thickness. In the low-temperature region the variation of conductance with temperature is very small, rather it is constant, and in the high-temperature region it increases sharply. Variation of a similar nature is also observed for the films under illumination. The conductivity of a polycrystalline semiconductor is given by (Sinha 1976)

$$\sigma = AN_v \exp\left(-\frac{q\phi_d + (E_F - E_V)}{kT}\right) \quad (1)$$

where $A = Lq^2/8\pi m^*kT$, L is the grain size, $N_v = (2\pi m^*kT/h^2)^{3/2}$, ϕ_d is the drift barrier height and m^* is the effective mass of the carriers. From the slope of the $\ln G$ versus $1/kT$ in the dark, the value of $\phi_d + (E_F - E_V)$ is calculated. Figure 1(b) shows the logarithmic variation of excess conductance (ΔG) of the film with temperature. From the figure it is clear that this curve follows the equation (Pal *et al* 1990)

$$\Delta G = B \exp\left(-\frac{q(\phi_d - \phi_{r0}) - (E_F - E_V)}{kT}\right) \quad (2)$$

where ϕ_{r0} is the recombination barrier height at $t = 0$, i.e. under illumination, and B is a constant. From the slope of the high-temperature region, the values of $\phi_d - (\phi_{r0} + E_F - E_V)$ are estimated for films of different thickness, assuming the variation of E_F with temperature to be very small. The estimated values of $\phi_d + (E_F - E_V)$ and $\phi_d - (\phi_{r0} + E_F - E_V)$ for films of different thickness are listed in table 1.

The variation of conductance with temperature for the undoped, BaF_2 -doped, $PbCl_2$ -doped and In-doped films

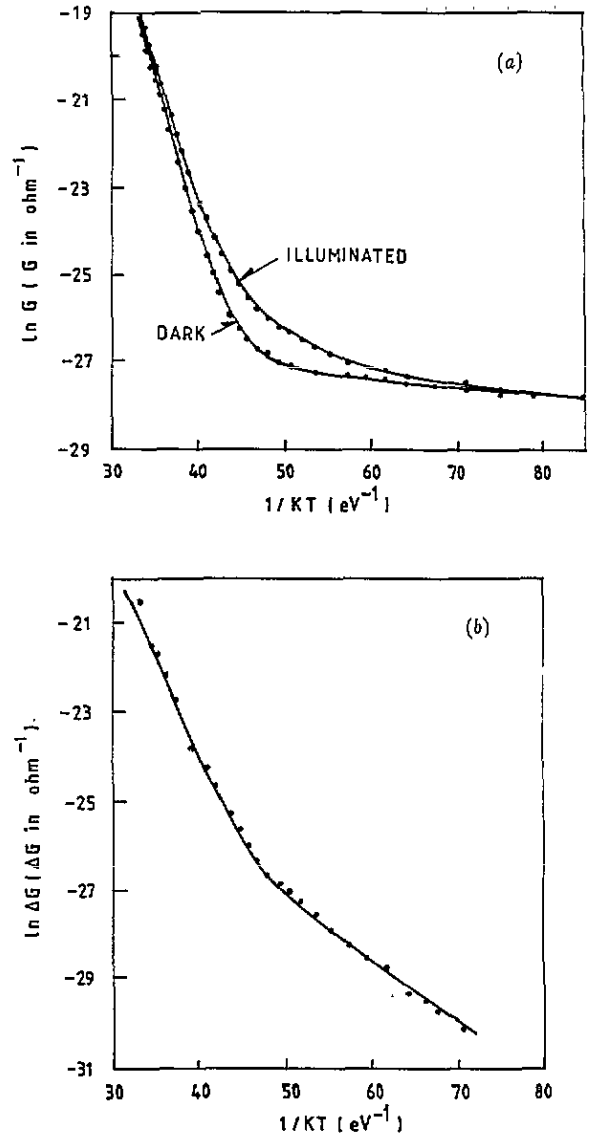
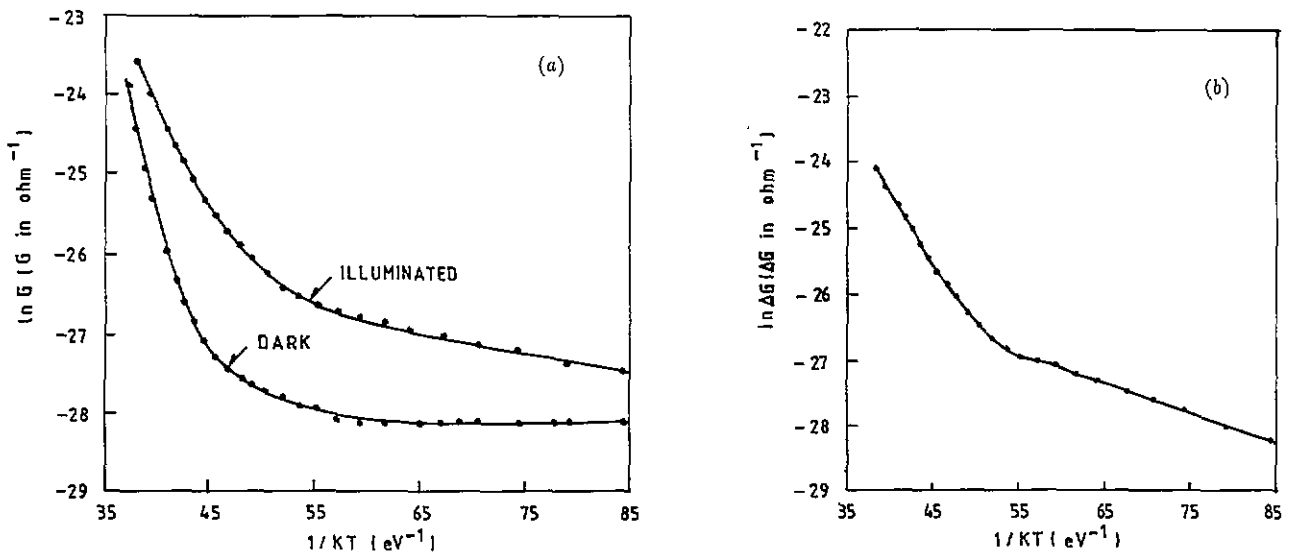


Figure 1. (a) Temperature variation of dark- and photoconductance of a typical ZnTe film (1200 nm) deposited at RT (298 K). (b) Temperature variation of excess conductance of a typical ZnTe film (1200 nm) deposited at RT (298 K).

deposited at 573 K. is measured in the dark and under illumination. The variation of these parameters for all the films is almost the same. Figure 2(a) represents the variation of conductance in the dark and under illumination for a typical BaF_2 -doped ZnTe film. The variation of excess conductance with temperature for the film is depicted in figure 2(b). The values of $\phi_d + (E_F - E_V)$ and $\phi_d - (\phi_{r0} + E_F - E_V)$ for those films at room temperature are given in table 1. The photorelaxation time constant τ_{r0} is estimated at different temperatures from the photodecay curves, and the values of $\phi_{r0} + (E_F - E_V)$ for the films are estimated from the $\ln \tau_{r0}$ versus $1/kT$ curves (Pal *et al* 1990). By manipulating the estimated values of $\phi_d + (E_F - E_V)$, $\phi_d - (\phi_{r0} + E_F - E_V)$ and $\phi_{r0} + (E_F - E_V)$ the values of ϕ_d , ϕ_{r0} and $E_F - E_V$ were estimated and presented Pal *et al* (1990), where it was shown that the values of ϕ_d and ϕ_{r0}

Table 1. Different electrical parameters of ZnTe films deposited at RT (room temperature, 298 K) (undoped) and at 573 K (undoped and doped).

Film	Thickness (nm)	$\phi_d + (E_F - E_V)$ (eV)	$\phi_d - (\phi_{r0} + E_F - E_V)$ (eV)
Undoped ZnTe ($T_s = RT$)	420	0.51	0.32
Undoped ZnTe ($T_s = RT$)	630	0.80	0.45
Undoped ZnTe ($T_s = RT$)	870	0.95	0.50
Undoped ZnTe ($T_s = RT$)	1020	0.78	0.64
Undoped ZnTe ($T_s = RT$)	1200	0.68	0.34
Undoped ZnTe ($T_s = 573$ K)	600	0.96	0.32
ZnTe, doped with BaF_2 ($T_s = 573$ K)	660	0.50	0.21
ZnTe, doped with $PbCl_2$ ($T_s = 573$ K)	630	0.43	0.26
ZnTe, doped with In ($T_s = 573$ K)	620	0.73	0.24


Figure 2. (a) Temperature variation of dark- and photoconductance of a BaF_2 - (7 wt %) doped ZnTe film (660 nm); $T_s = 573$ K. (b) Temperature variation of excess conductance of the BaF_2 - (7 wt %) doped ZnTe film (660 nm); $T_s = 573$ K.

varied with the variation of film thickness, whereas the value of $E_F - E_V$ remained almost fixed (~ 0.05 eV).

The conductivity of the undoped films ($T_s = 298$ K) is very low (e.g. $\sigma = 2.36 \times 10^{-5} \Omega^{-1} m^{-1}$, $4.52 \times 10^{-5} \Omega^{-1} m^{-1}$ and $8.55 \times 10^{-5} \Omega^{-1} m^{-1}$ for 420 nm, 1020 nm and 1200 nm films respectively). The ZnTe films deposited at $T_s = 573$ K are seen to be stoichiometric (Pal *et al* 1989) with conductivity of the order of $1.4 \times 10^{-5} \Omega^{-1} m^{-1}$. No improvement of conductivity has been observed on BaF_2 ($\sigma = 2.2 \times 10^{-5} \Omega^{-1} m^{-1}$) or $PbCl_2$ ($\sigma = 4.5 \times 10^{-5} \Omega^{-1} m^{-1}$) doping; only in In-doped films has a one order increase of conductivity ($\sigma = 3.3 \times 10^{-4} \Omega^{-1} m^{-1}$) been noticed. Due to the high resistivity of the films accurate thermoelectric power and Hall measurements could not be performed.

Figure 3 shows the logarithmic variation of photocurrent with intensity of illumination for the films of different thickness. It is seen that the $\ln i_{ph}$ versus $\ln L$ plots are straight lines with different slopes. The variation of i_{ph} with L follows the relation (Rose 1963, Sinha 1976)

$$i_{ph} = A \left(\frac{LN_V^{T/T_1}}{CT_1} \right)^{T/(T+T_1)} \quad (3)$$

where T_1 is the formal parameter that can be adjusted to fit the curves with equation (3); $A = Sq\mu\zeta$, S is the area of cross section of the sample, q is the electronic charge, L is the light intensity, μ is the mobility of the carriers, C is a constant, ζ is the applied field and T is the ambient temperature. Though the equation is deduced for homo-

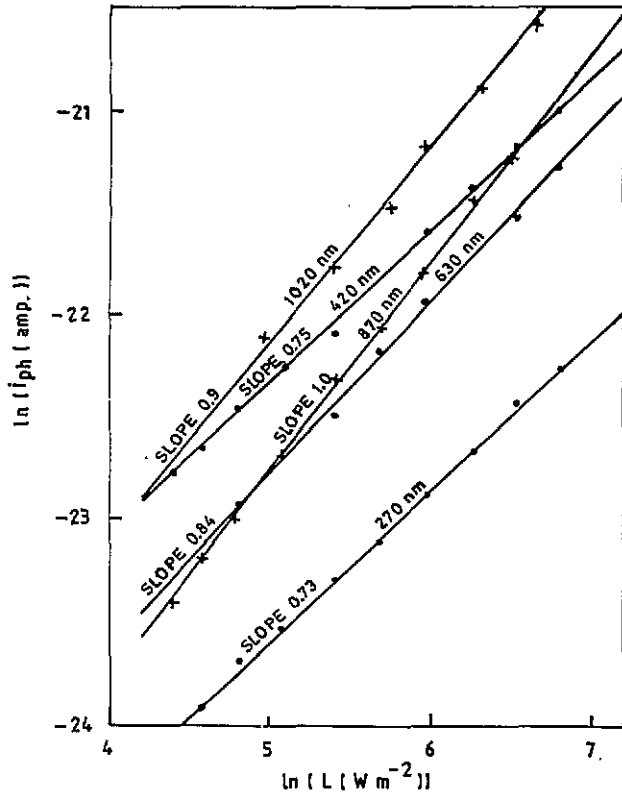


Figure 3. $\ln i_{ph}$ versus $\ln L$ for ZnTe films of different thickness.

geneous material (Rose 1963) and may not be rigidly applicable for polycrystalline thin films which consist of large number of grains, it is observed that the present experimental results follow the above-mentioned equation within the experimental accuracy. The values of the slopes of those $\ln i_{ph}$ versus $\ln L$ curves for ZnTe films of different thickness are calculated, and from them the values of T_1 are estimated. It is seen that the slopes vary from 0.5 to 1.0. The values of T_1 are found to be positive for all the films. The spectral response curve of photocurrent for the films of 420 nm, 630 nm and 870 nm thickness deposited at room temperature (298 K) are shown in figure 4. A relatively sharp peak occurred at about 550 nm, which more or less corresponds to the bandgap of ZnTe. A relatively broad peak is observed at higher wavelengths. A red shift of both the peaks with the increase of film thickness is observed.

4. Discussion

Various models have been proposed by different workers for the understanding of the basic mechanism of conductivity and photoconductivity (Volger 1950, Simpson 1951, Moss 1953, Slater 1956, Petritz 1956, Acharya 1971). According to Moss (1953) and Simpson (1951), the observed change in conductivity is due to the change in carrier density in the crystallites under illumination. In this process, the mobility of the carriers under illumination needs to be considered as unaffected and also the presence of various trapping and recombination states of

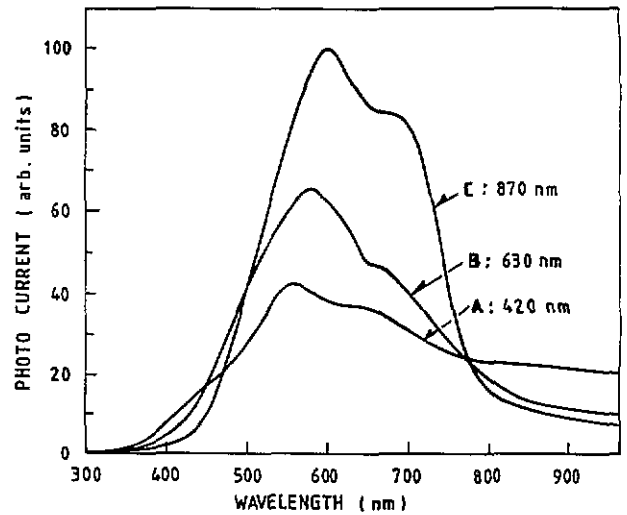


Figure 4. Spectral dependence of photocurrent for ZnTe films of different thickness deposited at RT (298 K).

appropriate capture cross section needs to be assumed in the films. Slater (1956) considered the lowering of intercrystallite potential barriers due to photoexcitation, enabling the free carriers to flow easily from grain to grain. The 'majority carrier model' developed by Petritz (1956) combines the concept of both the carrier theories and suggests that the primary photoeffect is due to increase in majority carriers in the individual crystallites. Volger (1950) pointed out that inhomogeneity in the films may affect the observed experimental results and proposed a geometric model for the study of an inhomogeneous sample consisting of highly conducting grains separated by thin layers of lower conductivity. According to the model proposed by Petritz (1956) the $\ln G$ versus $1/kT$ plot should be a straight line over the entire range of temperature. But in the case of ZnTe films in this investigation, it is seen that these plots are not straight over the entire range of temperature. In the lower range of temperature, the exponential curve tends to flatten out (figures 1(a) and 2(a)). Such a very low variation of conductivity at comparatively low temperatures can be explained by considering the shunt path (Slater 1956, Mahlman 1956, Acharya 1971, Sinha 1976) consisting of barriers in the samples. The carrier concentration in the shunt path is independent of temperature and the temperature variation of conductance in the low-temperature region is essentially due to the variation of mobility of the carriers.

The observed variation of photocurrent with light intensity (L) can be expressed as $i_{ph} \propto L^x$. From the plots of figure 3 (i.e. $\ln i_{ph}$ versus $\ln L$) it is seen that the slope values lie between 0.5 and 1.0 and the values of T_1 (equation (3)) are positive. Though equation (3) was deduced for homogeneous material (Rose 1963), it is seen to be valid for the films in the present investigation, and from the results it may be concluded that on the average the distribution of traps or impurity states within the bandgap is exponential in nature (Rose 1963).

From the slopes in the comparatively high-temperature region of $\ln G$ versus $1/kT$ plots in the dark, the

values of $\phi_d + (E_F - E_V)$ are calculated, and their variation with film thickness is shown in figure 5. As the variation of $E_F - E_V$ with film thickness, and hence with the particle size, is small (Pal *et al* 1990), we can assume that this variation (figure 5) corresponds to the variation of barrier height (ϕ_d) with film thickness and hence the particle size (Pal *et al* 1989).

From the spectral response of photocurrent, it is seen that a peak appears more or less at the band edge ($E_g = 2.26$ eV) and another peak appears at the longer wavelengths. The broadening of the second peak (i.e. peak at the higher wavelength) indicates the presence of multiple trap levels within the bandgap. As the thickness of the films increases, both the peaks shift towards the higher wavelengths. This may be because, as the film thickness increases (up to 870 nm) barrier height (figure 5) increases. It is known that the barrier height is mainly governed by the carrier concentration and crystallite size. With the increase of barrier height, its modulation by illumination also increases. For thinner films ϕ_d is expected to be less because $L_c P < Q_t$ (Seto 1975, Kumar *et al* 1982). Here L_c is the crystallite size, P is the carrier concentration and Q_t is the trap density per unit area at the crystallite boundaries. The modulation of mobility of the carriers is also expected to be less in these films. The main contribution to modulation of the barrier is the modulation of carrier concentration. With the increase of film thickness, barrier height is expected to increase. The criterion for the maximum barrier height is given by (Seto 1975, Kumar *et al* 1982) $\phi = eL_c^2 P / 8\epsilon$. When $L_c P > Q_t$, the magnitude of barrier height will start decreasing with film thickness. It is observed that the barrier height (ϕ) increases monotonically with film thickness and shows a maximum at a thickness of 870 nm. With the increase of thickness (up to 870 nm), the modulation of intercrystallite barrier height with illumination will increase, which in turn will cause an increase of the magnitude of mobility. The shift of the peaks in the spectral response curve is due to such a modulation of mobility.

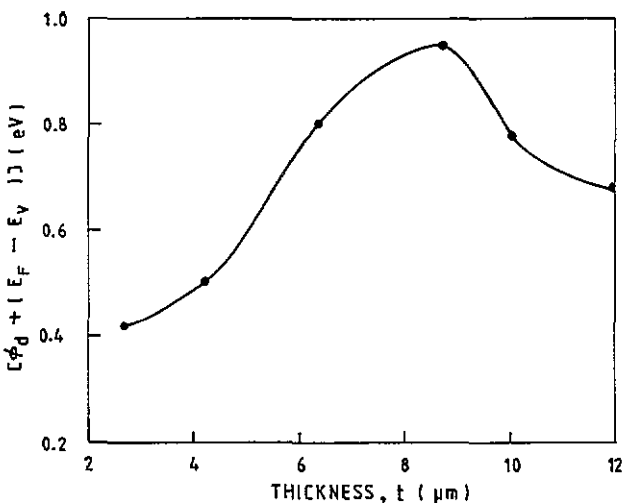


Figure 5. Plot of $\phi_d + (E_F - E_V)$ versus film thickness for ZnTe films deposited at RT (298 K).

5. Conclusions

The temperature variation of conductance curves for ZnTe films has two distinct regions, one is the lower-temperature region where the variation is small and the other is the higher-temperature region where this parameter increases sharply with temperature. The first region can be explained by considering a 'shunt path' model and the second region can be explained by considering the electronic processes within the grains.

The barrier height of the sample increases with the film thickness, and hence the particle size, up to a certain value and then decreases, which is a very common phenomenon for most of the semiconducting films. Though the doping of BaF₂ (7 wt %) and PbCl₂ (6 wt %) has little impact on the electrical properties of ZnTe thin films, In has a marked effect on them. Both ϕ_d and ϕ_{r0} vary with the variation of film thickness as well as doping materials.

Sublinear variation of photocurrent with illumination intensity indicates the non-uniform distribution of trap states within the bandgap.

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