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Temperature dependence of dc photoconductivity in CdTe thin films

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Abstract. The temperature dependence of dc photoconductivity in the measuring range 303–417 K has been studied in CdTe thin films having thickness $t < 4000$ Å. The photoactivation energy decreases in dark which is explained on the basis of grain boundary (GB) effect. The current lost to recombination at GB space charge region causes a negative effect on the photosensitivity of the films. A decrease in photosensitivity with increase in temperature is attributed to the reduction of photoexcitation process. It is observed that the minority carrier lifetime varies inversely with light intensity which supports the sublinear relationship of photoconductivity with the intensity of light and thereby confirms the defect-controlled photoconductivity in CdTe thin films.

Keywords. Cadmium telluride; photoconductivity; photosensitivity; grain boundary effect.

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1. Introduction

Cadmium chalcogenides and their ternary compound films have emerged as promising materials in recent times because of their successful application in the fabrication of solar cells and other opto-electronic devices. In a polycrystalline film like CdTe the photoconductivity processes are mainly governed by the inherent grain boundary states. Although several workers till date had formulated and studied the photoconductivity phenomena, it is realized that the temperature dependence of photoconduction mechanism is quite complicated to be fully understood [1–7]. Trapping centres increase the photosensitivity while the recombination centres decrease the sensitivity of the films [8]. The mutual cooperation of traps and recombination centres and their influence on the carrier lifetime depends on the intensity of illumination as well as on the ambient temperature. The carrier recombination at the grain bondaries thus plays a dominant role in determining the carrier transport mechanism. Keeping the above aspects in mind, an experimental study on photoconductivity processes in pure CdTe thin films has been undertaken and a brief report on the temperature dependence of dc photoconductivity in CdTe thin films has been presented in this paper. The effect of grain boundary scatterings and their influence in the minority carrier lifetime in determining the photosensitivity of the films has been highlighted.

2. Experimental procedure

CdTe thin films were deposited on clean glass substrates held at different temperatures by thermal evaporation method (HINDHIVAC 12 A4) at vacuum of the order of 10^{-6} torr. High purity (99.999%) bulk CdTe powder obtained from Kuch Light Lab. UK was used for deposition. A gap type film geometry with an effective gap of 3 mm between two pre-evaporated Al electrodes was used for the photoconductivity measurements. The thickness of the film was measured using multiple beam interferometry method with an accuracy of ± 20 Å. The substrate temperature as well as ambient temperature were measured by putting a cu-cons thermocouple behind the substrate in conjuction with a microvoltmeter. A 250 W quartz halogen bulb was used for white light illumination which is properly focused upon the film. The light intensity was measured with a sensitive Aplab luxmeter. The photocurrent as well as dark current were measured with the help of a high impedance ($\sim 10^{14}\ \Omega$) electrometer amplifier (ECIL 815) with an accuracy of ± 3%. The film was put inside a continuously evacuated glass chamber during current measurement. The whole measuring assembly was again put inside a properly grounded shielding network in the form of a Faraday caze to keep undesirable noise at minimum.

3. Results and discussion

3.1 *Structure*

CdTe thin films posses fcc zincblende structure when deposited at substrate temperature $T_s > 423$ K. Polycrystalline CdTe films show the most prominent reflection along [111] direction together with [220] and [311] reflections. Figure 1 shows XRD traces of the three CdTe films deposited at 473 K. The average grain size of the films corresponding to [111] direction is of the order of 260 Å. The results are in conformity with other workers [9–11]. Attempts are made to correlate photosensitivity with structure as presented in ref. [12]. The lattice constant of CdTe films estimated from the Nelson–Riley plots are found to be within 6.4999 Å to 6.5291 Å which deviated from its bulk counterparts. This lattice misfit with respect to bulk lattice constant indicates the existence of defects arising from vacancies and interstitials [13]. Thus these defect states are expected to play a leading role in photoconductivity process in thermally evaporated CdTe films.

3.2 *Space charge effects*

The space charges exist not only at the electrode–film interface but also at the film–substrate interface as well as along the grain boundaries in the film. The film–substrate interface which is usually only a few atomic spacing may effect grain boundaries (GB) in the deposited CdTe films. Those atomic layers primarily may contain residual oxides, reaction products of the film with the substrates [14] etc. In the present work high quality glass was used as substrate which serves as an atomically smooth and inert material. The glass substrates with the pre-evaporated Al electrodes were sufficiently heated at high vacuum prior to the deposition of films to eliminate the oxide formation if any on the electrode surface as well as the undesired surface layers of various orgin over the bared substrate

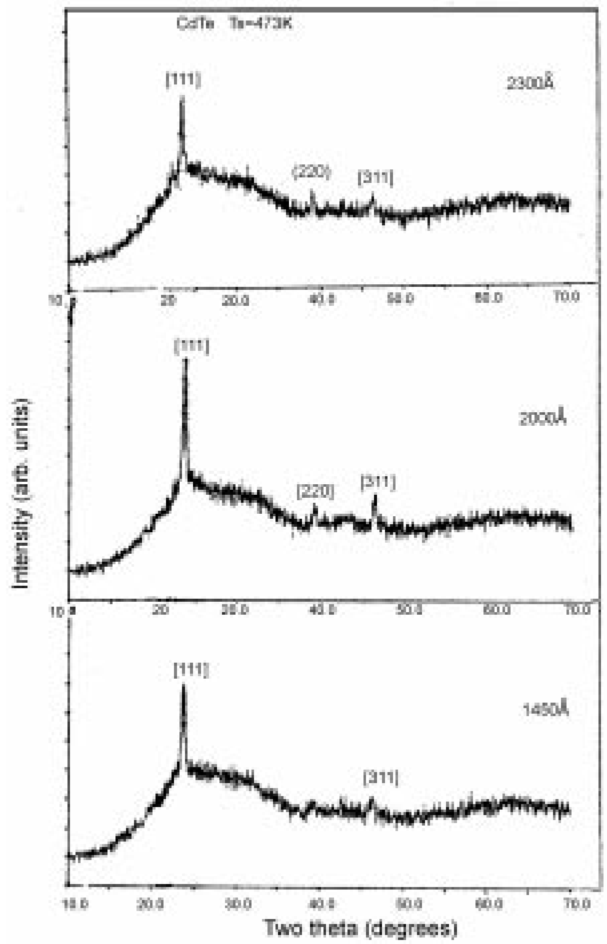

Figure 1. XRD traces of three representative CdTe films deposited at 473 K.

surface. The adhesion of film to the substrate was examined which was found to be better enough. Therefore, it clearly supports the non-existence of physical barrier at CdTe film–substrate interface [8].

After deposition of film the power law of *I–V* characteristics [15] in dark and under external illuminations has been examined and it was found to be unity within the applied bias of 0–120 V. This clearly reveals that there is no accumulation of charges injected from the electrodes to yield space charge limited current. Ohmic behaviour also rules out the presence of potential surface barrier at the electrode–film interface. However, as the film thickness $t < 4000$ Å, the size effect and the effect of microstrain developed modified to some extent by the surface states [8] are also important. The surface states can influence the intergrain boundary cores apart from the grain boundary state originated from the incomplete bonding, i.e., the native defects itself. It is observed that the films are subjected to strain $(2.76 \times 10^{-3}–7.26 \times 10^{-3})$ and have relatively smaller grain size D (260 Å) which clearly indicates the increase in density of grain boundary states as reported in earlier communication [12]. In these smaller grained films, therefore, the physiochemical imperfections like the screening charges developed along the grain boundaries near the surface may play an additional important role in the determination of recombination mechanism under illumination together with those screening charges of various origins developed at GBs in the volume.

The width (w) of GB is usually equal to a few lattice spacing only whereas the space charge region on either side of GB core is relatively wider. In dark the charges in GB is counterbalanced by the charges in the space charge regions on both sides of GB. However, under illumination the photogenerated minority carrier holes try to cross over the GB and their distribution near the GB causes the corresponding Fermi level not to remain flat as shown in figure 2a and 2b. The minority carriers effectively recombine with the trapped majority carrier electrons in the space charge region and results in an additional current loss apart from the current lost due to the recombination at the GB interface as well as at bulk [16]. The current lost due to the recombination in GB space charge region is prominent in smaller size crystallites which increases the grain boundary recombination velocity at the edge of depletion region, as well as an increment of the difference of electron and hole quasi-Fermi levels ΔE_{F} and a decrease in effective diffusion length. It is observed that the power factor γ for photocurrent light intensity characteristics measured for deposited CdTe films is slightly less than 0.5 as depicted in table 1. This change may be attributed to the additional current lost due to the recombination at GB space charge region caused by the GB states originated from the physiochemical imperfections.

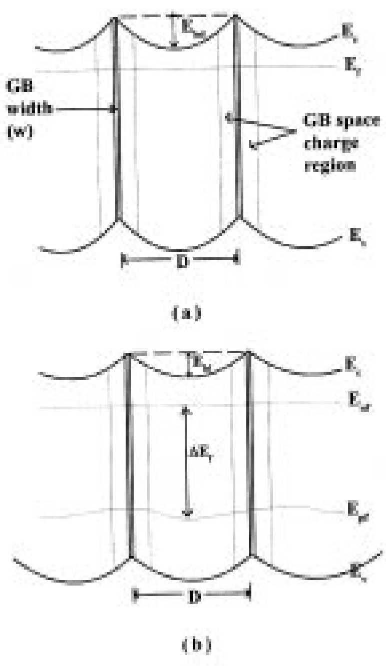

Figure 2. A systematic representation of GB space charge region in dark (**a**) and under illumination (**b**) (refs [6,16]).

Table 1. Variation of γ values correspond to the change of photoconductivity with light intensity at different temperatures.

		γ values at different ambient temperatures					
t (Å)	T_s (K)	303 K	316 K	328 K	351 K	381 K	403 K
1450	473	0.44	0.42	0.40	0.36	0.34	0.31
2300	473	0.46	0.43	0.40	0.35	0.30	0.28
3000	573	0.50	0.47	0.42	0.35	0.30	0.25

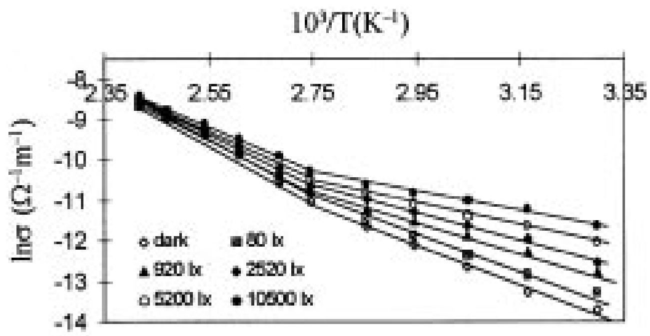

Figure 3. $\ln\sigma$ vs. $10^3/T$ plots for a CdTe film (2000 Å) deposited at 473 K.

3.3 *Measurement of photoconductivity*

CdTe films deposited at $T_s \geq 473$ K posses photosentivity. As the absorption coefficient is nearly inversely proportional to thickness, the film thickness is maintained at $t < 4000$ Å to make a better absorption of incident light upon films. The *I–V* characteristics of CdTe films measured at different ambient temperatures (T) in dark and under illumination are found to be ohmic. Ohmic nature thereby confirmed the measurement of bulk limited photoconductivity properties in these films. The dark conductivity of as-grown CdTe films measured at room temperature is $\sim 10^{-6}\ \Omega^{-1}\ \mathrm{m}^{-1}$. The dark conductivity as well as the photosensitivity increases with increasing T_s in the range of 303–573 K [12].

A stable high voltage (24 V) was applied across the films during photoconductivity measurement when the ambient temperature is increased in the range of 303–403 K. Figure 3 shows the $\ln\sigma$ vs. $10^3/T$ plots in dark and under different white light illuminations for a representative CdTe thin film. The activation energies in dark and under illumination were calculated from the slopes of the curves. Table 2a shows the systematic representation of dark activation energies (ΔE_{D}) and photoactivation energies (ΔE_{L}) for different CdTe films deposited at different growth conditions. It is clearly seen that the photoactivation energies decrease over dark with increasing white light intensity. This decrease of photoactivation energy at higher illumination level is primarily attributed to the lowering of intercrystalline grain boundary potential barrier height. It is expected that the potential barrier, in fact, greatly influences the carrier mobility and thereby controls the photosensitivity.

Polycrystalline film contains a large number of grains and grain boundaries (GB). The constituent atoms in GBs are disordered. Therefore, a large number of defects arise due

Table 2. (**a**) Activation energies of CdTe films in dark and under white light illuminations (ΔE). (**b**) Power factor α and β correspond to variation of mobility activation energy with ϕ.

		Temp.	(a) Activation energies in eV						(b) Power factor	
t (Å)	T_s (K)	range (K)	Dark	80 lx	920 lx	2520 lx	5200 lx	10,500 lx	β	α
2000	473	303–365	0.39	0.35	0.32	0.28	0.23	0.19	0.39	−0.61
		365–417	0.59	0.58	0.56	0.54	0.506	0.43	0.50	−0.50
2300	473	303–345	0.31	0.17	0.14	0.10	0.08	0.06	0.12	−0.88
		345–417	0.59	0.55	0.52	0.465	0.41	0.30	0.39	−0.61
2000	523	303–393	0.43	0.46	0.41	0.39	0.36	0.29	0.44	−0.56
3000	573	303–393	0.45	0.435	0.39	0.35	0.30	0.22	0.60	−0.40

to incomplete atomic bonding which form energy states within the band gap. The defect states effectively act as carrier traps and after trapping they are charged thereby creating a potential barrier across GB. Considering a uniform grain boundary structure with an average barrier height E_{bd}, the dark conductivity in the film is expressed as

$$\sigma_{\mathrm{D}} = N_{\mathrm{c}} e \mu_0 \exp[-(\Delta E + E_{\mathrm{bd}})/kT] = N_{\mathrm{c}} e \mu_0 \exp[-\Delta E_{\mathrm{D}}/kT] \quad (1)$$

where N_{c} is the density of the carriers and μ_0 the mobility in the grain. The dark conductivity increases due to the thermally generated carriers from traps along with the contraction of band gap. The contribution to the activation process is expected to be more from carrier modulation (ΔE) than from the barrier modulation in dark. It is established that CdTe films are *n* type when deposited at $T_{\mathrm{s}} \geq 473$ K. Thus the electron trapping centres arising from the excess Cd and/or Te vacancies limit the conductivity process [4]. In the present work the rise of temperature from 303 to 417 K does not activate the intrinsic process. The dark activation energies (ΔE) are determined for the extrinsic regions of $\ln\sigma$ vs. $10^3/T$ plot as shown for a CdTe film (figure 3). Thus the calculated ΔE_{D} is primarily due to the thermal excitation from the imperfection levels. Similar dark activation energies are also reported by other workers in thermally evaporated CdTe films [11,17,18]. When the film is illuminated by light, the conductivity of the film may enhance due to the increase in excess carriers and/or decrease in barrier height depending upon the incident photon energy [7,19]. In the present work the number of photons falling per second on an effective film area 4×3 mm^2 between the electrodes is found to be within 1.7×10^{15}–2.3×10^{17} corresponding to white light intensity range 80 lx–10,500 lx, which is expected to be strong enough to cause a partial depletion of grains [20]. Thus the change in conductivity due to carrier modulation from the excess photogenerated carriers is insignificant relative to those remaining thermally generated carriers. Hence the conductivity under illumination increases primarily due to the enhancement of carrier mobility resulting from barrier modulation. The total photoconductivity in the films for partially depleted grains can be expressed as

$$\sigma_{\mathrm{L}} = N_{\mathrm{c}} e \mu_0 \exp[-(\Delta E + E_{\mathrm{bl}})/kT] = N_{\mathrm{c}} e \mu_0 \exp(-\Delta E_{\mathrm{L}}/kT). \quad (2)$$

Here $\Delta E_{\mathrm{L}} = (\Delta E + E_{\mathrm{bl}})$ is the observed photoactivation energy where E_{bl} is the barrier height under illumination. The photogenerated minority carriers crossover the GB interface and rapidly recombine with the majority carrier traps. This causes a reduction of barrier height and consequently increases the carrier mobility. Thus the reduction of barrier height is attributed to the mobility activation process. The mobility activation energy can be expressed as

$$\Delta E_n = \Delta E_{\rm D} - \Delta E_{\rm L} = (E_{\rm bd} - E_{\rm bl}).$$

It is realized that the mobility activation energy depends on the lifetime of minority carriers which in turn is dependent on the intensity of light as well as temperature. The relationship between photoconductivity and the mobility activation energy can be expressed using eqs (1) and (2) as

$$\sigma_{\rm L}/\sigma_{\rm D} = \exp(\Delta E_\mu/kT). \tag{3}$$

Slater formulated the temperature dependance of photoconductivity relationship as [19]

$$\sigma_{\rm L}/\sigma_{\rm D} = \exp(c\tau\phi/kT). \tag{4}$$

From relations (3) and (4)

$$\Delta E_\mu = c\tau\phi \tag{5}$$

where c is a constant. This shows that ΔE_n is directly proportional to minority carrier lifetime (τ) and intensity of light (ϕ). Moreover τ is dependent on ϕ and if it varies with a power α as, $\tau\alpha\phi^\alpha$ then the dependence of ΔE_n on ϕ can be expressed as

$$\Delta E_\mu \alpha \phi^{1+\alpha} \quad \text{or} \quad \Delta E_\mu \alpha \phi^\beta. \tag{6}$$

From the slopes of $\ln\Delta E_\mu$ vs. $\ln\phi$ plots as depicted in figure 4 for a representative film, the values of α and β are determined and shown in table 2b. It is clearly seen from figure 4 that the mobility activation energy due to lowering of barrier height is relatively more at low temperature region than at high temperature region when the film is illuminated by relatively low intensity light. The difference in lowering process for both regions decreases when the light intensity is sufficiently large. However, the rate of increase of ΔE_μ with light intensity as defined by power β is relatively less at low temperature region compared to high temperature region. At low temperature the rapidity of decrease of minority carrier

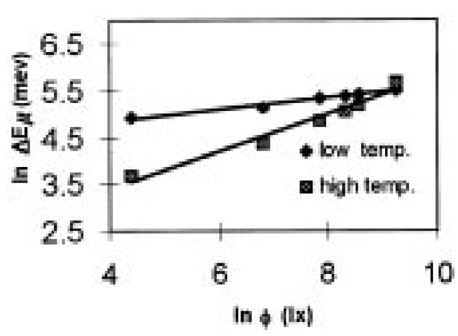

Figure 4. $\ln\Delta E_\mu$ vs. $\ln\phi$ plots at low (303–345 K) and high (345–417 K) temperature regions for a CdTe film (2300 Å) deposited at 473 K.

lifetime with light intensity as defined by the power factor α is more. This clearly signifies that the grain boundary scattering mechanism is predominant in the lowering of potential barrier height at low temperature regions as in the present work around room temperature 303 K. At high temperature region, a relatively small value of α clearly indicates that the minority carrier lifetime is affected due to the onset of a different kind of scattering [22]. In fact the dependence of τ on ϕ in the entire range of ambient temperature supports the sublinear relationship of photoconductivity with light intensity as discussed in §3.4.

3.4 *Photosensitivity*

Photosensitivity is an effective parameter in determining photoconductivity. In defect controlled photoconductivity, the photosensitivity is largely influenced by the native as well as foreign imperfections which either act as trapping or recombination centres within the forbidden gap. In the present work the photosensitivity at a particular ambient condition is defined as

$$S = (\sigma_{\mathrm{L}} - \sigma_{\mathrm{D}})/\sigma_{\mathrm{D}}. \tag{7}$$

Using eqs (1) and (2), photosensitivity can be expressed as

$$S = \sigma_{\mathrm{ph}}/\sigma_{\mathrm{D}} = \exp(\Delta E_{\mu}/kT) - 1. \tag{8}$$

Equation (8) clearly reveals that the photosensitivity is a function of mobility activation energy. In the present work the photosensitivity is found to be dependent on substrate temperature as well as on the ambient temperature. At high $T_{\mathrm{s}} \geq 473$ K the flms possess less grain boundary defect states owing to higher crystallite size [4,5]. Thus the dark conductivity as well as photosensitivity increase because of increase of carrier mobility. The mobility activation process corresponding to the lowering of barrier height may be a function of ambient temperature as well as the substrate temperature apart from the intensity of illumination. For simplicity the photosensitivity can be written as

$$S = \sigma_{\mathrm{ph}}/\sigma_{\mathrm{D}} = \exp(\Delta E_{\mu}/kT) - 1 = 1 + (\Delta E_{\mu}/kT) - 1$$

or

$$\sigma_{\mathrm{ph}} = \sigma_{\mathrm{D}}(\Delta E_{\mu}/kT). \tag{9}$$

Considering the effect of temperature on the photoexcitation process, the mobility activation energy can be written as [3]

$$\Delta E_{\mu} = f(T)\phi^{\gamma}. \tag{10}$$

Here $f(T)$ is a function of temperature which measures the effect of photoexcitation process in lowering the potential barrier height at a particular temperature T when the film is illuminated by light intensity ϕ. The photoconductivity then can be expressed as

$$\sigma_{\mathrm{ph}} = \sigma_{\mathrm{D}} f(T)\phi^{\gamma}/kT$$

and taking ln,

$$\ln\sigma_{\rm ph} = \ln[\sigma_{\rm D} f(T)/kT] + \gamma \ln\phi.$$

Thus from the slopes and intercepts of $\ln\sigma_{\rm ph}$ vs. $\ln\phi$ plots as depicted in figure 5 for a representative CdTe film, the values of γ and $f(T)$ are calculated respectively for the operating temperature in the range 303–403 K. The γ values for the three CdTe films are represented in table 1 which show a decreasing trend with increasing ambient temperature. However $\gamma < 1$ at any temperature and thereby it indicates the predominance of bimolecular recombination process in the films. The trapping centres are converted into recombination centres under illumination which shorten the free lifetime of carriers. This results in a sublinear relationship of photocurrent–light intensity characteristics [21]. This sublinear relationship is found to be independent of film growth as well as ambient condition (table 1) which confirmed the defect controlled photoconductivity in CdTe films.

The calculated values of $f(T)$ are plotted against the corresponding temperature T as shown for a representative CdTe film (figure 6). It clearly reveals that $f(T)$ decreases sharply at high temperature region which signifies that the effect of photoexcitation process in lowering the potential barrier is reduced towards high temperature and thereby cause a decrease in photosensitivity (figure 7). A decrease of γ values with increase in temperature is thus also attributed to the poor sensitivity (table 1). The experimental observations of photosensitivity as shown in figures 6 and 7 therefore confirm the simultaneous validity of eqs (8) and (1). It is noted that the power β is attributed to the overall dependence of lowering of barrier height on light intensity taking into account the continuous variation of

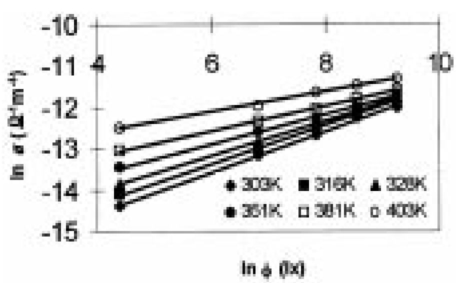

Figure 5. Photoconductivity vs. light intensity characteristics at different ambient temperature for a CdTe film (3000 Å) deposited at 573 K.

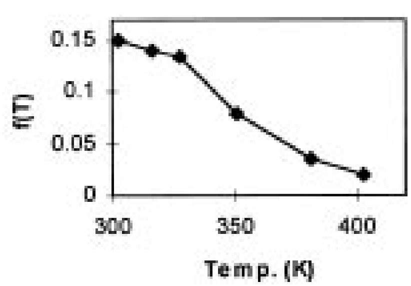

Figure 6. Variation of $f(T)$ with temperature for a representative CdTe film (2000 Å) deposited at 473 K.

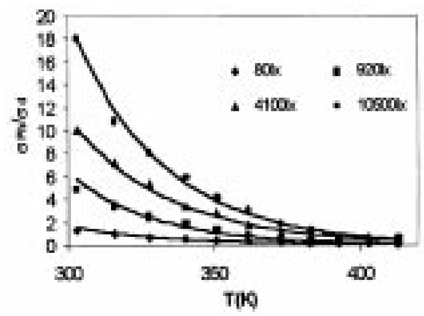

Figure 7. Variation of photosensitivity (σ_{ph}/σ_D) with ambient temperature for a representative CdTe film (2300 Å) deposited at 473 K.

temperature. However, γ corresponds to the dominant effect of light intensity at a particular temperature. The idea of dependence of photosensitivity on grain boundary barrier height is also supported by other workers [3,23].

4. Conclusions

CdTe thin films deposited at $T_s \geq 473$ K are found to be polycrystalline having fcc zincblende structure. The deviation of lattice constant measured for deposited films over the bulk counterparts clearly indicates the existence of defects owing to the dangling bonds. Although there is no pronounced surface barrier present in the films as confirmed by *I–V* characteristics, the surface states, however, influence the GB states and increase the GB defect density for smaller thickness films. The charges in GB is counterbalanced by the space charges on both sides of GB in dark. But under illumination due to minority carrier recombination with the trapped majority carriers in GB space charge region, an additional current is lost which is clearly reflected in photocurrent–light intensity characteristics of the films. The GB defects give rise to potential barriers which limit the photoconductivity mechanism in CdTe films. The existence of such defects is confirmed by the dark activation energies that appeared in the extrinsic region of temperature dependence of dc photoconductivity as well as the sublinear dependence of photoconductivity on light intensity in the films. The observed photoactivation energies are found to decrease over dark which is attributed to the mobility activation process owing to the lowering of grain boundary barrier height under illumination. In fact the lowering of potential barrier height is a function of temperature as well as the intensity of illumination. The lowering is more at low temperature and that causes maximum photosensitivity at room temperature. However, the rate of lowering is less for low temperature region compared to high temperature region. The photoexcitation process in lowering of barrier height is considerably reduced on increasing ambient temperature and thereby it causes a decrease in photosensitivity by reducing carrier mobility at high temperature. The minority carrier lifetime is found to be nearly inversely proportional to the light intensity in the entire temperature range 303–417 K which supports the bimolecular recombination of carriers and thereby the sublinear photoconductivity observed in CdTe films.

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