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Spectral response characteristics of photoelectronic properties of vacuum evaporated CdSe thin films

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CdSe thin films were grown by thermal evaporation technique under a vacuum of 10^{-6} torr on glass substrates held at different temperatures. On thermal annealing and subsequent aging the properties of the films become stable. The photocurrent of such films are of highly defect controlled type and the nature of photocurrent as a function of applied field exhibits two distinct conductivity regions. The spectral response of photocurrent revels a maximum peak at 725nm along with some smaller peaks. Growth and decay of photocurrent for such films are very fast and the decay is generally accompanied by along tail. The transport mechanism of the films is a double activation process.

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1. Introduction

In recent years much importance has been given towards the field of II-VI class of semiconductor compounds because of their photoelectronic properties and applications. Cadmium Selenide, a prominent member of this II-VI group of semiconductors, is actually a compound semiconductor. Because of its high photosensitive nature, it is widely preferred for the fabrication of different optoelectronic devices like thin film transistors, photovoltaic solar cells, photodetectors, light emitting diodes, filters etc [1,2,3]. It has a suitable direct intrinsic band gap of 1.74eV [4] and often possesses n-type conductivity in both bulk and thin film form [5]. Different methods like solution grown, vacuum evaporation etc for preparation of CdSe films have been reported by different workers [6,7]. Irrespective of preparation conditions such films are generally accompanied by different types of defects which are very much instrumental in effecting different electrical and optical properties of semiconductor films. Hence these properties are very sensitive to deposition conditions and techniques used. Electrical and optical properties are essential requirements for proper application in different optoelectronic devices. So study of such properties of the films with respect to their different growing as well as ambient conditions is a matter of profound importance. In this paper some photoelectronic properties of CdSe thin films deposited by thermal evaporation technique and studied mainly under monochromatic illuminations have been reported.

2. Experimental

Thin films of CdSe of various thicknesses were deposited at different substrate temperatures with the help of Hind High Vacuum Coating Unit at a vacuum of 10^{-6} torr on chemically and ultrasonically cleaned glass substrates. The prepared films were annealed at high temperature for definite interval of time and stored for ageing. High purity aluminium electrodes were vacuum evaporated on the already annealed and aged thin films to obtain a gap type cell configuration of 10mm x 7mm geometry. Thin tantalum boat of proper size and shape was used as source heater. The thicknesses of the films were measured by a suitably designed and assembled multiple beam interferometer with an accuracy of ±15Å. An ECIL electrometer amplifier (EA815) of input impedance of $10^{14}\Omega$ and higher was used to measurer dark and photocurrents. Filters of different wavelengths starting from 600 nm to 900 nm were used and these were calibrated by using highly sensitive APLAB luxmeter. To avoid pick-up noises a suitably designed Faraday Cage was used.

3. Results and discussions

Varition of dark current (I_D) with applied bias voltage (V) for the experimental CdSe thin films are linear (ohmic) within the entire range (+108V) to (-108V) of applied bias. For the low bias voltages of both polarities (below 72V), current under illumination (I_L) varies linearly with bias voltage. The present photoelectronic studies correspond to applied bias within this linear region only.

The experimental CdSe thin films are found to be highly photo sensitive and wide scale variation are observed in case of photocurrent I_{ph} (where $I_{ph}=I_L-I_D$) with intensity of illumination, Φ. It follows the relation

$$I_{ph}= C\Phi^{\gamma} \tag{1}$$

where C is a constant of proportionality and γ is the power factor. The plots of $\ln I_{ph}$ vs $\ln\Phi$, are linear under white as well as the monochromatic illuminations of different wavelengths (Fig 1), where the order of different wavelengths are in accordance with the spectral response characteristics of photocurrent for the said films. Here the photocurrent for the threshold wavelength of 725nm; also for several wavelengths close to it are higher than corresponding photocurrent for white light of same intensity. The plots yield that the values of γ is close to 0.5. Hence it is concluded that photoconductivity in these thin films are of defect control type. In these polycrystalline thin films plane photoconductivity is highly influence by primary defects, which are essentially localized in the grain boundaries and the surfaces [8]. The exponent γ states about the recombination process, whether it is mono-molecular or bimolecular. The distinction may be made with the help of a simple relation [9] given by

$$g = C_n(\Delta n^{2} + 2n_o\Delta n) \tag{2}$$

Here g is the generation rate, C_n is the capture coefficient. n_o is the density of thermally generated carriers and Δn is the carrier density. For bimolecular recombination process $\Delta n \gg n_o$,therefore

$$\Delta n = (g/C_n)^{1/2} \tag{3}$$

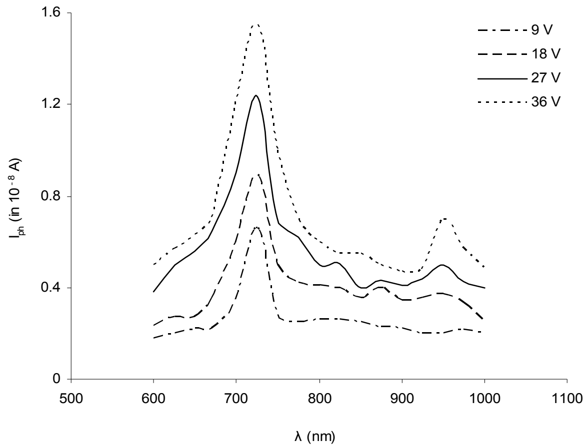

Figure 1 *$\ln I_{ph}$ versus $\ln\Phi$ plot for a CdSe thin film of $t = 2000Å$ and $T_s = 473K$*

which is proportional to $\Phi^{1/2}$, so photocurrent is directly proportional to square root of intensity of illumination.

The spectral response curves (Fig 2) for the studied films show a sharp peak at 725nm along with a few smaller peaks mainly in longer wavelength side. The position of this prominent peak is independent of applied bias or intensity of light. The maximum spectral sensitivity of CdSe films at 725nm corresponds to an optical energy gap of 1.71ev which is close to the band gap energy 1.74ev of CdSe at room temperature for a single crystal. It is observed that there is a decrease in the photocurrent for both wavelengths, shorter and longer than the band edge wavelength. For longer wavelengths it may be explained on the basic of high transmittance and low absorbance of light. Shorter wavelengths have higher photon energy are being strongly absorbed, so produces excitation only near the surface layer of the thin film. As the volume of this layer is small the concentration of free carriers in it becomes too high which causes sharp increase in the recombination rate and hence decreases the surface life time. Thus due to high surface recombination photocurrent is generally found to be smaller.

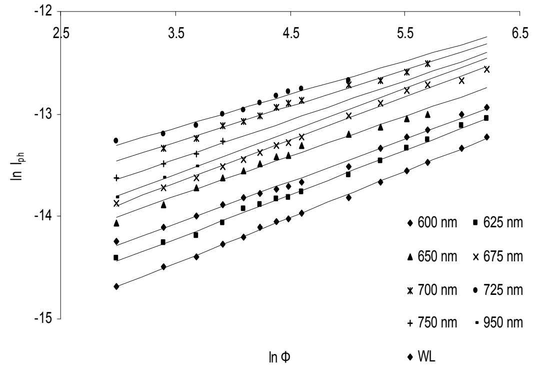

Figure 2 *Spectral response characteristics for a CdSe thin film ($t = 2000Å$, $T_s = 473K$) under applied bias conditions.*

The photocurrent at any instant of time during growth is given by the equation

$$I_t = I_o\{1-\exp(-t/\tau_r)\} \tag{4}$$

where I_o is the maximum photocurrent and τ_r is the growth time of photocurrent. With passes of time, the photocurrent reaches a steady state and when the light is turned off photocurrent decreases, because excess number of carrier decreases as a result off rapid recombination. The decay may be represented by the equation

$$I_t=I_o\{\exp(-t/\tau_d)\} \tag{5}$$

where τ_d is the photocurrent decay time. It is observed that grown CdSe thin films exhibit a rapid growth of photocurrent which is followed by an initial fast decay accompanied by a tail. (Fig 3) The fast decay is associated with free electron-hole recombination and the subsequent region is due to release of electrons from traps. Rise and decay times corresponding to different monochromatic illumination levels are presented in Table 1.

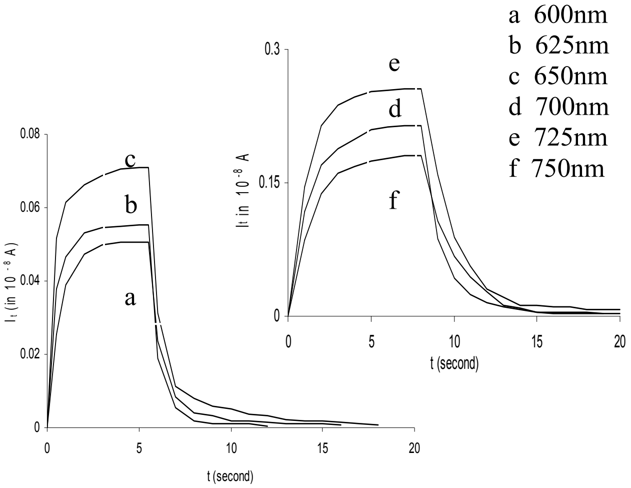

***Figure 3**. Growth and decay of photocurrent for a CdSe thin film (t = 2000Å, T_s= 473K) under different monochromatic illuminations.*

***Table 1** Rise & decay time for a CdSe thin film (t = 2000Å, T_s = 473K) under different monochromatic illuminations*

λ nm	600	625	650	700	725	750
τ_r sec	3.5	3	2.5	2	1.7	2.2
τ_d sec	2.5	2	2	1.7	1.5	1.8

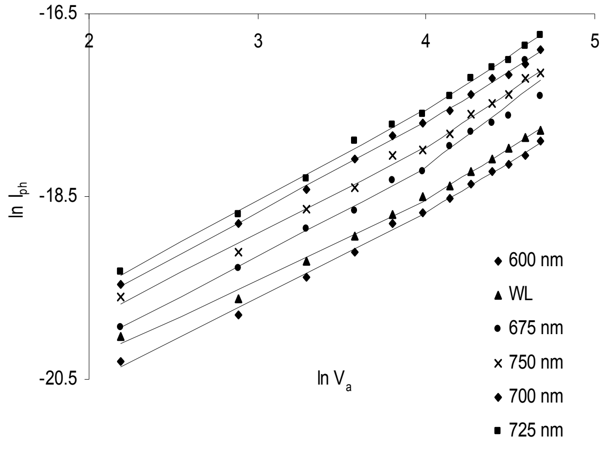

***Figure 4** lnI-lnV curve for a CdSe thin film (t = 2000Å, T_S = 473K) under different monochromatic as well as white light (WL) illuminations.*

Beyond the low voltage range (above 72V) I_L increases nonlinearly with the applied bias. These linear and non-linear regions are clearly shown in the I-V characteristics plots (Fig 4). Again when $\ln J_{ph}$ (J_{ph} is the photocurrent density) is plotted against $F^{1/2}$ (F is the field corresponding to the applied bias) the plots are found to be linear in the high field regions (Fig 5). Plots in the high field region are in accordance with the Poole-Frenkel function given by equation (16). This clearly shows that in high field region the conduction mechanism is of Poole-Frenkel type. This type of conductivity mainly depends upon the grain boundary potentials, so may be modified by externally applied fields.

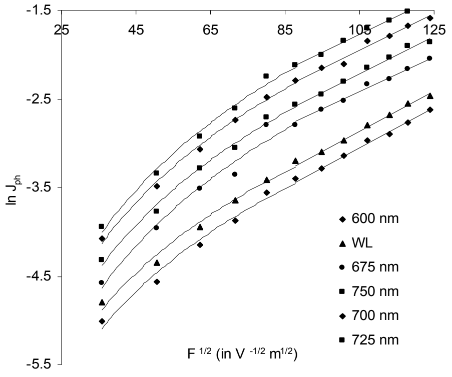

***Figure 5** $\ln J_{ph}$ versus $F^{1/2}$ plot of the same CdSe film (t = 2000Å, T_S = 473K) under different monochromatic as well as white light (WL) illuminations.*

The Poole-Frenkel effect is the lowering of built-in potential barriers inside a sample while interacting with an applied electric field [10]. At a metal insulator interface the potential step changes smoothly as a result of image force. The force arises because the metal surface becomes polarized (positively charged) by escaping electrons, which in turn exerts an attractive force $e^2/16\pi\varepsilon_o\varepsilon^*x^2$ on the electron. So the potential energy of the electron due to image force is

$$\Phi_{im} = - e^2/16\pi\varepsilon_o\varepsilon^*x \qquad (6)$$

where x is the distance of the electron from the electrode surface, ε^* is the frequency dependent dielectric constant. Image force effects play an important role in the conduction process when the current is electrode limited. The potential energy of an electron in a Coulombic field is given by

$$\Phi_{cf} = -e^2/4\pi\varepsilon_o\varepsilon^* x \tag{7}$$

which is four times that due to image force effects. When an electric field exists at a metal insulator interface, it interacts with the image force and lowers the potential barrier. The change $\Delta\Phi_s$ in the barrier height due to interaction of the applied field with the image potential is given by

$$\Delta\Phi_s = (e^3/4\pi\varepsilon_o\varepsilon^*)^{1/2}F^{1/2} = \beta_s F^{1/2} \tag{8}$$

The Poole-Frenkel attenuation of a Coulombic barrier, $\Delta\Phi_{PF}$, in a uniform electric field is twice that due to the Schottky effect at a neutral barrier

$$\Delta\Phi_{PF} = (e^3/\pi\varepsilon_o\varepsilon^*)^{1/2}F^{1/2} = \beta_{PF} F^{1/2} \tag{9}$$

This result was first applied by Frenkel to the host atoms in bulk semiconductors and insulators [10].

The observed conductivity in thin film insulators is due to extrinsically rather than intrinsically bulk generated carriers. The intrinsic current density in a semiconductor is given by

$$I = e\mu N_c F\exp(-E_g/2kT) \tag{10}$$

where e is the electronic charge, μ is the mobility, F is the field in the semiconducting material, N_c effective density of states in the insulator, E_g is the energy gap.

Frenkel argued that in the presence of uniform field the band gap energy E_g in a solid is lowered by an amount given by equation (9). Thus conductivity is obtained by substituting ($E_g - \Delta\Phi_{PF}$) for E_g in equation (10). Hence

$$I/F = e\mu N_c \exp\{-(E_g-\Delta\Phi_{PF})/2kT\}$$

or

$$I/F = e\mu N_c \exp(-E_g/2kT)\exp(\beta_{PF}F^{1/2}/2kT)$$

So the field dependent conductivity is of the form

$$\sigma = \sigma_o \exp(\beta_{PF}F^{1/2}/2kT) \tag{11}$$

where

$$\sigma_o = e\mu N_c \exp(-E_g/2kT)$$

Equation (11) may be written in the form

$$J = J_o \exp(\beta_{PF}F^{1/2}/2kT) \tag{12}$$

Here σ_o is the low field conductivity and $J_o = \sigma_o F$ is the low field current density. Because of image force lowering of the barrier, the electrode-limited current doesn’t saturate according to the Richardson law,

$$J = AT^2\exp(-\Phi_o/kT) \qquad (13)$$

where $A = 4\pi em(kT)^2/h^2$

It rather obeys the Richardson Schottky law

$$J = AT^2\exp\{-(\Phi_o-\Delta\Phi_s)/kT\}$$

$$= AT^2\exp(-\Phi_o/kT)\exp(\beta_s F^{1/2}/kT) \qquad (14)$$

Although $\Delta\Phi_{PF} = 2\Delta\Phi_s$, the coefficient of $F^{1/2}$ in the exponential is the same as for both Richardson-Schottky (at neutral contact) and Poole-Frenkel current density versus electric field characteristics, i.e.

$$\beta_{PF} = 2\beta_s \qquad (15)$$

Mead suggested [10] that since the traps abound in an insulator and that a trap having a Coulombic type barrier would experience the Poole-Frenkel effect at high fields, there by increasing the probability of escape of an electron immobilized therein, the current density in thin film insulators containing shallow traps is given by

$$J = J_o\exp(\beta_{PF}F^{1/2}/kT) \qquad (16)$$

In this case the coefficient of $F^{1/2}$ is twice that in equation (12). Mead first reported the field dependent conductivity apparently in the form given by (16) and it is the usual form of Poole-Frenkel equation associated with thin film insulators, rather than that given by (12).

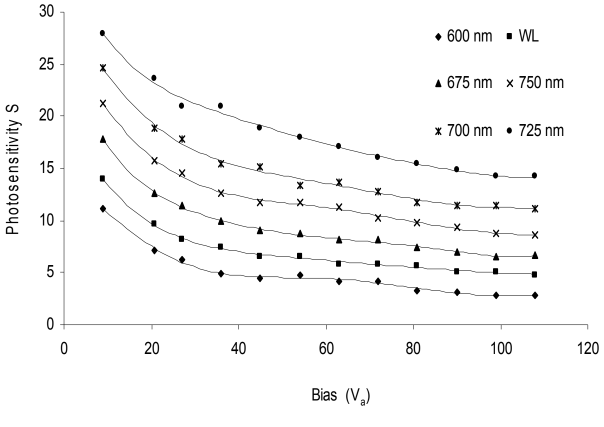

Figure 6 *Variation of photosensitivity (S) with applied bias under white as well as different monochromatic illuminations for a CdSe thin film (t = 2000Å, T_S = 473K).*

The photosensitivity is defined as

$$S = I_{ph} / I_D = (I_L - I_D) / I_D \qquad (17)$$

The increase of both I_D and I_{ph} for the experimental film with applied bias, when the ambient temperature is the room temperature, is mainly due to enhancement of transit time and consequent reduction of recombination rate and probability of trapping of the carriers. The photosensitivity S, given by equation (17), is seen to decrease with increasing bias (Fig 6) for a film grown at elevated T_s under white and different monochromatic illuminations of constant intensity. The variation of S for different wavelength is due to corresponding impurity level contributions.

The variation of dark conductivity, $\sigma_{D,}$ and conductivity under illumination, $\sigma_{L,}$ of CdSe thin films are studied as a function of ambient temperature within the range from room temperature to 500K. Both I_D and I_L are found to be increase exponentially with temperature. ln σ_D (or ln σ_L) as a function of 1000/T, are plotted in Fig 7. From the plots it is observed that, films are characterized by double activation regions in the above range of temperature.

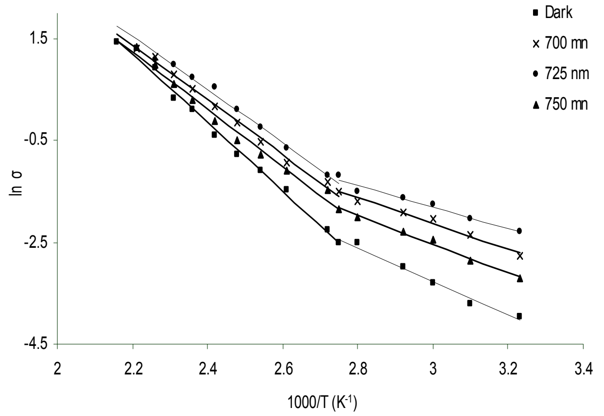

***Figure** 7 ln σ_D (or ln σ_L) versus 1000/T for a CdSe thin film (t = 2000Å, T_s = 473K) at dark and under different monochromatic illuminations*

Grain boundaries in polycrystalline films contain a large number of defects which results in the formation of energy states within the band gap. They act as effective carrier traps and after trapping carriers, the states become charged and there by give rise to some potential barriers. The barriers localized at the grain boundaries modulate the conductivity in the films. The current carriers have to pass through a number of such grain boundary potential barriers.

For uniform grain boundary structure with identical barrier, the conductivity may be expressed as

$$\begin{aligned} \sigma &= nq\mu^* \\ &= nq\mu_o \exp(-q\Phi_b / kT_o) \end{aligned} \tag{18}$$

where n is the majority carrier concentration and μ* is the effective mobility given by [11]

$$\mu^* = \mu_o \exp(-q\Phi/kT_o) \tag{19}$$

Considering only one type of carrier dominating the conduction process, the carrier density may be written as

$$n = 2(2n_d)^{1/2}(2\pi m_e^* kT/h^2)^{3/4}\exp(-\Delta E/kT) \tag{20}$$

So the dark conductivity

$$\sigma_D = nq\mu^* = (\sigma_o)_D \exp(-\Delta E/kT) \qquad (21)$$

where $(\sigma_o)_D = 2q\mu_o (2n_d)^{1/2} (2\pi m_e^* kT/h^2)^{3/4} \exp(-q\Phi_D/kT_o)$, ΔE is the donor or acceptor level activation energy, Φ_D is the barrier height in dark, which is greater than the same under illumination i.e. Φ_L. n_d is the donor level concentration.

σ_D increases primarily due to increase in thermally generated carriers, thus the activation process is dominated by the term $\exp(-\Delta E / kT)$ in equation (21). In this case, the effective barrier modulation is small. Therefore, with respect to the carrier activation process, determined by the temperature dependent exponential term $\exp(-\Delta E / kT)$, the mobility term may be taken to be effectively independent of temperature [12].

Now when the film is illuminated by white or monochromatic light the photoconductivity increases over the dark values. The total conductivity under external illumination may be expressed as

$$\sigma_L = nq\mu^* = (\sigma_o)_L \exp(-\Delta E/kT) \qquad (22)$$

where $(\sigma_o)_L = 2q\mu_o (2\pi kT/h^2)^{3/2} (m_e^* m_h^*)^{3/4} \exp(-q\Phi_L/kT_o)$

Thus the change in conductivity with temperature may be either due change in carrier density or mobility or of both of these parameters.

The grain boundary potential barrier, Φ_b, can be expressed as [13]

$$\Phi_b = (Q_t - \Delta P_t) / 8\varepsilon\varepsilon_o \Delta n \qquad (23)$$

where Δn is the photo generated carrier density, which is greater than the density of majority carrier traps, Q_t localized at the grain boundaries, ε and ε_o are the dielectric constants of the material of the film and free space respectively. ΔP_t is the density of trapped minority carriers under illumination in the depletion region. It may be noted that ΔP_t increases with the illumination level.

Of the photo generated carriers, which are in excess to the thermal equilibrium carriers at any temperature, a part is responsible for enhancement of conductivity (photoconductivity) and the other part goes to neutralize some fraction of the corresponding localized charges in the depletion region between the grains. This results in the reduction in the grain boundary potential barrier Φ_b. Thus one gets $\Phi_D > \Phi_L$ where, as already mentioned, Φ_D and Φ_L are the grain boundary potential barriers under dark and under illumination respectively. Due to reduction of barrier height the effective mobility μ^* under illumination gets enhanced. This is known as the barrier or mobility modulation process.

As a result of this mobility activation, due to illumination, the current density under illumination gets enhanced over the corresponding dark values. From equation (19) the effective mobility under dark and illumination can be written as

$$\mu_D^* = \mu_o \exp(-q\Phi_D/kT_o) \qquad (24a)$$

$$\mu_L^* = \mu_o \exp(-q\Phi_L/kT_o) \qquad (24b)$$

The change in mobility due to illumination is given by

$$\Delta \mu^* = \mu_L^* - \mu_D^* \qquad (25)$$

Since $\Phi_D > \Phi_L$, $\mu_D^* < \mu_L^*$, $\Delta\ \mu^*$ is positive.

At any temperature $\sigma_L > \sigma_D$ and in the $\ln\sigma$ versus 1000/T plots in the both activation regions $(\text{slope})_L < (\text{slope})_D$. The decrease in slope under illumination is due to mobility activation process.

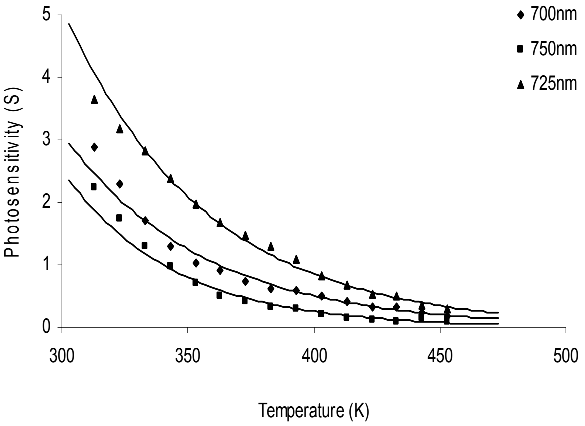

Figure 8 *Variation of photosensitivity (S) with ambient temperature under different monochromatic illuminations for a CdSe thin film (t = 2000Å, T_s = 473K).*

The variation of photosensitivity with ambient temperature for a CdSe thin film of thickness 2000Å and deposited at T_s = 473K are depicted in Fig 8. The photosensitivity is found to be maximum for the film, at room temperature condition under different monochromatic illuminations and decreases rapidly with ambient temperature showing there by that there is an exponential like decrease of photosensitivity with ambient temperature. Similar type of observation of temperature dependence of photosensitivity was also reported by other worker [14].

4. Conclusions

Photoconductivity of CdSe thin films deposited by the technique of thermal evaporation at higher substrate temperature is basically controlled by the grain boundary defects. The photocurrent is dependent on the wavelength of excitation and increases towards the band edge of wavelength. They are characterized by Poole-Frenkel type of conductivity and barrier modulated photoconductivity. Films exhibit a rapid growth & decay of photocurrent and because of the presence of trapping centers the decay becomes slow afterwards. The transport mechanism of the films is governed by a double activation process.

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