Vacuum Evaporated CdSe Thin Films and its Some Spectral Response Characteristics

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Abstract. CdSe thin films deposited by means of thermal evaporation technique under a high vacuum of $10^{-5}$ Torr on properly cleaned glass substrates held at different elevated temperatures are of polycrystalline nature having hexagonal structure. For a typical Al/CdSe/Al gap type structure of such films the I-V characteristics are linear both under dark and under monochromatic illuminations for low bias voltages, but such curves show Poole-Frenkel type of conductivity under the same illuminations mainly for high bias regions. The photocurrents of the deposited CdSe films are of defect controlled type. The spectral response characteristics of the films at room temperature show a prominent peak along with some smaller peaks mainly in the longer wavelength side. The transport mechanism for the said films are generally a doubly activated process. From $\ln \sigma$ vs $1000/T$ plot dark and photo-activation energies along with the mobility activation energies are calculated for a few wavelengths close to the threshold wavelength. The photocurrent decay characteristics curves under room temperature environment basically exhibited two different decay times which actually corresponds to two distinct trap levels and the corresponding trap depths are calculated. From the transmission spectra, optical band gaps have been calculated for deposited films.

1. Introduction
In recent past much importance has been given in the field of II-VI class of semiconducting compounds because of their optoelectronic properties and applications. CdSe, a prominent member of this II-VI group of semiconductor, is actually a compound semiconductor. Because of its high photosensitive nature, it is widely preferred in the fabrication of different optoelectronic devices [1-3]. It has a suitable direct intrinsic band gap of 1.74eV [4] and often possesses n-type conductivity in bulk as well as thin film form [5]. Electrical and optical properties of semiconducting films are essential requirements for proper application in different optoelectronic devices and these properties are very sensitive to ambient conditions and deposition techniques used. Therefore 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 optoelectronic properties of CdSe thin films studied under both white as well as monochromatic illuminations and deposited by thermal evaporation technique have been reported.

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2. Experimental Details:
Thin films of CdSe of various thicknesses (t) within the range (1000-2500)Å are deposited at different substrate temperatures (T_s) with the help of Hind High Vacuum Coating Unit at a vacuum better than 10^{-5} Torr on chemically and ultrasonically cleaned high quality glass substrates, having pre-evaporated high purity aluminium electrodes, to obtain a gap type cell configuration of 10 mm x 7 mm geometry. A suitably designed and assembled multiple interferometer is used to measure the thicknesses of the films with an accuracy of ±15Å. An ECIL electrometer amplifier of input impedance of 10^{14}Ω and higher is used to measure dark and photocurrents. In order to provide bias a series of highly stable dry cells each of 9V are used. The entire experimental set up including the observer is housed inside a suitably fabricated Faraday Cage in order to avoid the pick-up noises. Filters of different wavelengths starting from 600 nm to 950 nm are used and these are being calibrated by using highly sensitive luxmeter. X-ray diffractograms of different CdSe films are taken using Phillips X-ray diffractometer (Xpertpro) using CuKα radiation. Surface morphology of the films is studied by using a scanning electron microscope (LEO 1430VP) with an accelerating potential of 18 KV.

3. Results and Discussions:
3.1 Structural characterization.
The X-ray diffraction profiles of CdSe thin films (figure 1) reveal that films grown at room temperature (RT) are amorphous and those grown at elevated Ts are polycrystalline having hexagonal type structure. In these films [002] plane is very clear and abundant [6]. However small percentage of orientation of [110], [112] & [100] plans are also observed depending upon Ts of deposition. The preferential orientation is thus [002] plan of crystallites with c-axis perpendicular to the surface of the substrates. With the increase of Ts the crystallinity of the films improve substantially. At higher Ts in the formation of the film, atoms possess greater mobility along direction parallel to the substrate surface which may contribute to improvisation of the crystallization processes.

![Figure 1. X-Ray Diffraction profiles for three CdSe thin films having thickness (t) nearly 2000Å, deposited at substrate temperatures (T_s) 473K, 423K and 300K (RT) respectively.](image1)

Figure 1. X-Ray Diffraction profiles for three CdSe thin films having thickness (t) nearly 2000Å, deposited at substrate temperatures (T_s) 473K, 423K and 300K (RT) respectively.
The film morphology under SEM studies (figure 2) shows that the films deposited at higher Ts are fairly uniform, polycrystalline and free from macroscopic defects like cracks or peeling. Therefore for the photoconductivity studies the quality of the such grown films are quite suitable.

![Figure 2. SEM of a CdSe thin film (t ~ 2000Å, T_s = 473K) Magnification 12.14 KX](image2)
3.2 I-V characteristics.
Variation of dark current \( (I_D) \) with applied bias voltage \( (V) \) for the considered CdSe thin films are linear (ohmic) within the entire range of applied bias. For the low bias voltages of both polarities, current under illumination \( (I_L) \) varies linearly with bias voltage and beyond this low voltage range \( I_L \) increases non-linearly with the applied bias (figure 3a). However at higher ambient temperatures the linear nature of the I-V curves becomes prominent in higher bias region also under illumination (figure 3b). Now when \( \ln J_{ph} \) (\( J_{ph} \) is the photocurrent density, photocurrent \( I_{ph}=I_{L}-I_D \)) is plotted against \( F^{1/2} \) (\( F \) being the field corresponding to the applied bias) the plots are found to be linear in the high field region (figure 4a).

\[
\sigma_{PF} = \frac{1}{2} \exp \left( \frac{\beta_{PF}}{kT} \right)
\]

where \( \sigma_{PF} \) is the low field current density, other symbols bear their usual significance. The \( \beta_{PF} \) is known as the Poole-Frenkel coefficient. Plot of \( \ln J_{ph} \) vs \( F^{1/2} \) gives a slope \( m = \beta_{PF}/kT \) from where the Poole-Frenkel coefficients can be obtained and these values of \( m \) are in the range \((4.4 - 4.9) \times 10^{-4} \text{ eV V}^{-1/2} \text{ m}^{1/2} \). These values of \( \beta_{PF} \) are higher than the same calculated theoretically which suggest the existence of some localized electric fields within the film having values higher than mean field \( F \). Such localized fields may be present due to different type of effects like band bending in the region of contacts due to difference in work function between the electrode metal and semiconductor while various localized environments of individual trapping centers in the grain boundary regions of the film are unlikely to result in an exactly linear variation of potential on a microscopic scale.

3.3 Intensity dependence of photocurrent.
The intensity \( (\Phi) \) dependence of photocurrent for the considered CdSe thin films follows the relation

\[
I_{ph} = C \Phi^r
\]
where \( C \) is a constant of proportionality and \( \gamma \) is the power factor. The plots of \( \ln I_{ph} \) vs \( \ln \Phi \), are linear under different monochromatic illuminations (figure 4b), where the order of different wavelengths are in accordance with the spectral response characteristics of photocurrent for the said film and here the photocurrent for the threshold wavelength of 725 nm and also for several wavelengths close to it are higher than corresponding current for white light of same intensity, which yields the values of \( \gamma \) in the range between 0.4–0.6. Hence it is concluded that photoconductivity in these thin films are of defect control type [9]. In these polycrystalline films photoconductivity is highly influence by primary defects, which are essentially localized in the grain boundaries and the surfaces [6]. The exponent \( \gamma \) states about the recombination process, whether it is monomolecular or bimolecular.

Figure 4. \( \ln J_{ph} \) vs \( F^{1/2} \) plot of a representative CdSe thin film \( (t \sim 2000\text{Å}, T_S = 473K) \) (a) under the monochromatic illuminations of various wavelengths and white light (WL) of intensity 60 lux (b) \( \ln I_{ph} \) vs \( \ln \Phi \) plot for the same CdSe film, \( \Phi \) is the intensity of illuminations.

3.4 Spectral response characteristics.

The spectral response curves (figure 5a) for the said film at RT show a sharp peak at 725nm along with a few smaller peaks mainly in longer wavelength side. But with the increase in ambient temperature the sharpness of these peaks decreases (figure 5b). 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 RT for a single crystal. This is due to direct transition of electrons from valanced band (VB) to conduction band [10]. 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 basis of high transmittance and low absorbance of light. Shorter wavelengths have higher photon energy are being strongly absorbed, so they produce 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 smaller.
3.5 Temperature dependence of conductivity.

The plots of $\ln \sigma$ vs $1000/T$ for the considered film, both under dark and under illuminations show two distinct conductivity regions (figure 6). Thus the conductivity $\sigma$ cannot be represented by a single exponential form, so the transport mechanism is assumed to be a double activated process of the form

$$\sigma = \sigma_0 \exp(-E_1/kT) + \sigma_0' \exp(-E_2/kT)$$

where $k$ is the Boltzmann constant. $E_1$, $E_2$ and $(\sigma_0)$, $(\sigma_0')$ are the activation energies and electrical conductivities corresponding to lower and higher temperature regions respectively. For the experimental film, activation energies ($E_a$) and mobility activation energies ($E_{ma}$) are calculated. From the plot of figure 6a, the calculated values of $E_a$ under dark has been found to be 1.17eV for high temperature region and 0.572 eV for low temperature region, which are in agreement with the already reported values [4]. Under illumination of the monochromatic radiations in the high temperature region $E_a$ and $E_{ma}$ ranges are observed as (0.98 – 0.72)eV and (0.192 – 0.44)eV respectively whereas in the low temperature region their ranges are (0.48 – 0.31)eV and (0.09 – 0.26)eV respectively.

3.6 Growth and decay of photocurrent:

It is observed that as-deposited CdSe thin film exhibit a rapid growth of photocurrent which is followed by a initial fast decay accompanied by a long tail. (figure 7) The fast decay is associated with free electron-hole recombination process and the subsequent region is due to release of electrons from traps.
The trap depth $E$ below the bottom of the conduction band (CB) or the top of the VB has been calculated (table 1) by using the decay law

$$I(t) = I_0 \exp(-pt)$$  \hspace{1cm} (4)

where $p$ is the probability of escape of an electron from the trap per second and is given by [11]

$$p = S \exp(-E/kT)$$  \hspace{1cm} (5)

Using these two relations, the equation for trap depth become

$$E = kT[\ln S - \ln\{(\ln I_0/I)/t\}]$$  \hspace{1cm} (6)

where $T$ is the ambient temperature in K. $I_0$ is the photocurrent at the termination of illumination, $I_t$ is the photocurrent at any instant $t$ after termination of illumination. $S$ is the frequency factor which is defined as the number per second that the quanta from the lattice vibrations attempt to eject the electron from trap, multiplied by the probability of transition of the ejected electron to the conduction band [12] and is given by [13]

$$S = N_{\text{eff}} V_{\text{th}} \sigma$$  \hspace{1cm} (7)

where $N_{\text{eff}}$ is the effective density of states in the conduction band, here it is assumed that at comparatively low temperature the number of occupied energy in the CB i.e. $n$ is identical with $N_{\text{eff}}$ [14]. Now

$$n = \sigma / e \mu$$  \hspace{1cm} and  \hspace{1cm} $$S_t = \pi r^2$$  \hspace{1cm} (8)

where $\sigma$ is the conductivity corresponding to photocurrent $I_0$, $\mu$ is the mobility of electrons in CdSe sample which is taken as 540 cm$^2$V$^{-1}$ sec$^{-1}$ [14]. $S_t$ is the capture cross section of electron at temperature $T$ and $r$ is the radius of capture center. It is calculated by putting coulomb energy of interaction of an electron with the corresponding trap equal to the thermal energy of the electron at $T$ [13]. In other words

$$\frac{e^2}{\epsilon e} = kT$$

So

$$S_t = \pi e^3 / k^2 T^2 \epsilon^2$$  \hspace{1cm} (9)

At $300K$  \hspace{1cm} $$S_t = 10^{-10} / \epsilon^2 \text{ cm}^2$$ [15]

where $\epsilon$ is the dielectric constant of CdSe sample which is taken to be 5.76 [1]. Taking the effective mass of an electron $m^*$ as 0.13$m_e$ [14], the thermal velocity of an electron $v_{\text{th}}$ is calculated by using the relation

$$v_{\text{th}} = \sqrt{(2kT/m^*)}$$  \hspace{1cm} (10)
Figure 8. ln(I/I₀) vs time t plot for the same film (t ~ 2000Å, Tₘ = 200°C) (a) under different monochromatic illuminations of constant intensity (b) under illumination of 725nm of different intensities.

Table 1. Calculated values of trap depths (a) under different monochromatic illuminations of constant intensity (b) under monochromatic illumination of 725nm of different intensities, for the same CdSe film.

| Illumination Intensity | Wave-length | $\sigma$ $\Omega^{-1}$ cm$^{-1}$ in 10$^3$ | N$_{eff}$ cm$^{-3}$ in 10$^{10}$ | S Sec$^{-1}$ in 10$^6$ | E$_1$ (in eV) | E$_2$ |
|------------------------|-------------|---------------------------------------------|-------------------------------|---------------------|-------------|------|
| 50 lux                 | 700nm       | 0.41                                        | 4.50                          | 2.69                | 0.39        | 0.42 |
| 700nm                  | 0.35        | 3.77                                        | 2.25                          | 0.39                | 0.39        | 0.42 |
| 725nm                  | 0.43        | 4.63                                        | 2.76                          | 0.40                | 0.40        | 0.43 |
| 30 lux                 | 725 nm      | 0.30                                        | 3.3                           | 1.97                | 0.39        | 0.42 |
| 40 lux                 | 725 nm      | 0.39                                        | 4.28                          | 2.55                | 0.40        | 0.43 |
| 60 lux                 | 0.57        | 6.21                                        | 3.71                          | 0.41                | 0.41        | 0.43 |

3.7 Study of optical properties:
Optical absorbance and transmittance of CdSe thin films deposited at different Ts are studied in order to ascertain the nature of optical transitions. To calculate the values of the absorption coefficients for different wavelengths of light near the absorption edge the following relation [16] has been employed

$$\alpha = \ln T / t$$  \hspace{1cm} (11)

where T is the transmittance and t is the thickness of the film. Both direct and indirect transitions between valanced band and conduction band may be considered as allowed or forbidden depending upon the values of transition probability $p$ in the following relation [17].

$$\alpha = A (hv - E_g)^p$$  \hspace{1cm} (12)

where $p$ has discrete values like 1, 2, 3 2 or more depending upon whether the transition is direct, indirect, allowed or forbidden. This can be ascertained from the plots of $\alpha^2$, $\alpha^{-2}$ etc against photon energy hv. $E_g$ is the width of the forbidden gap.
Figure 9 shows the plot of $\alpha^2$ vs energy $h\nu$ for the representative CdSe film, which is found to be linear. This means the optical transitions take place directly and the values of direct optical band gap obtained from it (1.61 eV) is found to be quite lower than that calculated by electrical method using the thermal excitation which is considered to be less reliable because of the fact that in polycrystalline thin films transport phenomenon are strongly influenced by crystalline size and the characteristics of grain boundaries [6]. This evaluated value of direct optical band gap is found close to those reported values [6]. Variation in evaluated values of optical band gap has been observed for different CdSe thin films, that may be due to their different growing conditions.

4. Conclusions.
CdSe thin films deposited at higher substrate temperatures by the technique of thermally evaporated are of polycrystalline nature. Such films are found to be characterized by Poole-Frenkel type of conductivity and barrier modulated photoconductivity. Photoconductivity of these polycrystalline films are basically controlled by the grain boundary defects. The photocurrent is dependent on the wavelength of excitation and increases towards the band edge of wavelength. Rise and decay processes are effectively governed by different kinds of traps.

5. References

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