

Studies on photoelectrical, optical and galvanomagnetic properties of CdSe films

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CdSe films were deposited onto glass substrates by the hot wall technique at a system pressure of $\sim 10^{-6}$ torr. The optimum deposition conditions for obtaining device grade films were determined. Photoelectrical and optical properties of the films deposited at the optimum conditions were studied. Information on the refractive index and absorption coefficient were derived from the above measurements and the data were analysed in the light of the existing theories. Direct transitions corresponding to band gaps of 1.7 and 1.92 eV were obtained. Measurement of mobility of CdSe films as a function of temperature indicated ionized impurity scattering to be predominant in our temperature range of measurements. The scattering parameter and the effective mass m_e^* of carriers was determined from thermoelectric power measurements.

1. Introduction

Cadmium selenide has found its application in photoconductive devices [1] and thin film transistor [2]. Fabrication of high quality CdSe thin films for device applications requires a detailed knowledge of the dependence of the deposition parameters on the microstructures of the films produced. The performances of polycrystalline CdSe thin film devices were seen to depend critically on the preparation conditions and subsequent heat treatment [3]. Structural studies of CdSe films deposited onto different substrates were reported by us in our earlier communication [4]. Wurtzite hexagonal phase has been obtained by Naguib *et al.* [5] for films deposited onto glass substrate at temperature below 470 K. Photoconductivity of CdSe films and the effect of defect structure were studied by Sakalas [6]. Various deposition techniques such as evaporation [7], r.f. sputtering [8], molecular beam [9], etc. have been tried by different groups for the deposition of CdSe films. Electrical and photoelectrical properties for CdSe films and crystals were also reported by a few groups [7, 9, 10].

In this paper we report our studies on the photoelectrical and optical properties of CdSe films deposited onto glass substrates by the hot wall evaporation technique.

2. Experimental details

Cadmium selenide powder (99.999% Koch-Light Laboratories Ltd, UK) was evaporated from a quartz crucible heated by a specially prepared graphite heater. The hot wall arrangement used for deposition is very similar to that reported earlier for the deposition of CdSe films [11]. There were appropriate buffers inside the quartz crucible to ensure adequate mixing of the vapour before ejection. A quartz wool plug was placed at the neck of the quartz crucible to prevent the spattering or ejection of small grains of CdSe during depo-

sition. The rate of evaporation was always less than 0.5 nm sec^{-1} to allow sufficient time for the adatoms to orient themselves on the substrate before being buried by the incoming adatoms. The n-type conductivity of CdSe films is due to the existence of selenium vacancies [10, 12], which were reduced by providing an increased deposition flux rich in selenium by using a chimney (hot wall) at 520 K.

3. Results and discussion

3.1. Photoconductivity measurements

Photoelectrical properties of CdSe films deposited at various substrate temperatures (390–610 K) have been studied in detail. Variation of photoconductivity as a function of wavelength of the incident radiation measured at room temperature for three representative films deposited at 390, 470 and 550 K is shown in Fig. 1. It was observed that the dark conductivity and photoresponse depend on the deposition temperature of the CdSe films. The dark resistivity and photoresponse were always greater for films deposited at higher substrate temperatures. This may be due to the fact that photogeneration of carriers is assisted [12, 13] by the attainment of improved crystalline structure and stoichiometry with increase in substrate temperature as revealed by TEM and EDX studies reported in our earlier report [4]. It may also be observed that there is a peak in the photoresponse near about 630 nm as indicated in Fig. 1 which shifts towards higher wavelength for films deposited at higher substrate temperatures indicating that the centres of photosensitivity are intimately connected with the microstructure of the films [14].

The dependence of photoconductivity on temperature for films deposited at various deposition temperature were studied at a fixed wavelength of $\lambda = 630 \text{ nm}$ and in the temperature range of 180–340 K. Figure 2 shows a representative plot for the

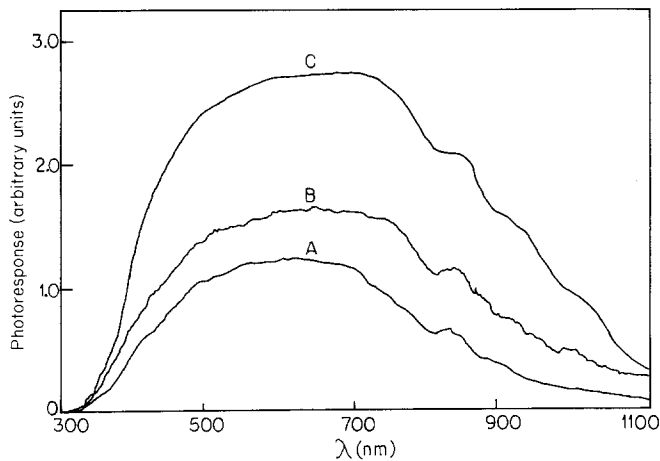


Figure 1 A representative plot of photoresponse of CdSe films with incident wave length (λ) deposited at three substrate temperatures: (A) 390 K, (B) 470 K, (C) 550 K.

above for a CdSe film ($0.6 \mu\text{m}$ thick) deposited at 550 K. The photoconductivity can be seen to increase with increasing temperature in our range of measurement which is true for all the films.

According to Petriz [15] the change in conductivity $\Delta\sigma$ due to irradiation of the films results from the changes in carrier concentration and effective mobility μ^* caused by the barrier modulation. $\Delta\sigma$ is given by the equation

$$\Delta\sigma = q\mu^*\Delta p + qp\Delta\mu^* \quad (1)$$

where

$$\mu^* = \mu \exp\left(-\frac{q\phi}{kT}\right) \quad (2)$$

$$\Delta\mu^* = -\frac{q\mu}{kT} \exp\left(-\frac{q\phi}{kT}\right) \Delta\phi \quad (3)$$

$\Delta\phi$ is the change in barrier height produced by light. From Equation 1 we can write:

$$\Delta\sigma = \Delta\sigma_0 \exp\left(-\frac{q\phi}{kT}\right) \quad (4)$$

where

$$\Delta\sigma_0 = q\mu \left(\Delta p - \frac{qp\Delta\phi}{kT} \right) \quad (5)$$

If the change in photoconductivity with temperature is dominated by the exponential term then Equation 4 indicates that the plot of $\log \Delta\sigma$ against $1/T$ should be a straight line (Fig. 2). The activation energies computed from the above plots are given in Table I. It can be observed that the films deposited at higher substrate temperature have higher activation energy. This is basically due to the fact that with increased deposition temperature the crystallinity and grain growth improves considerably [4].

We have also studied the rise and decay of monochromatic photoconductivity (Fig. 3). For this purpose a constant current source (Keithley 225) was used and the changes in resistance (ΔR) due to incident monochromatic radiation was observed. It was noted that photoresponse in CdSe films was independent of the constant current density ($180 \text{ nA} - 2 \mu\text{A cm}^{-2}$) used during the above measurements. Figure 3 shows the rise and decay of photoresponse of two representative CdSe films deposited at 390 and 550 K. The films deposited at higher substrate temperatures shows higher photoresponse which has also been reported by other workers [10] and discussed in the earlier section of this communication. The rise is quite faster than the decay. This seems to hold the

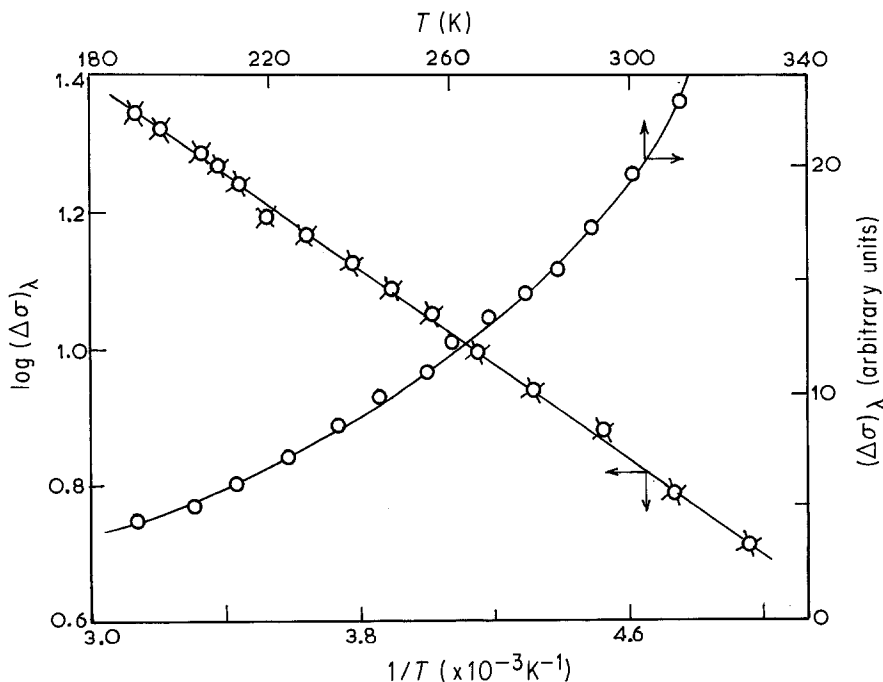


Figure 2 Temperature dependence of monochromatic photoconductivity $(\Delta\sigma)_{630 \text{ nm}}$ of a representative CdSe film deposited at 550 K.

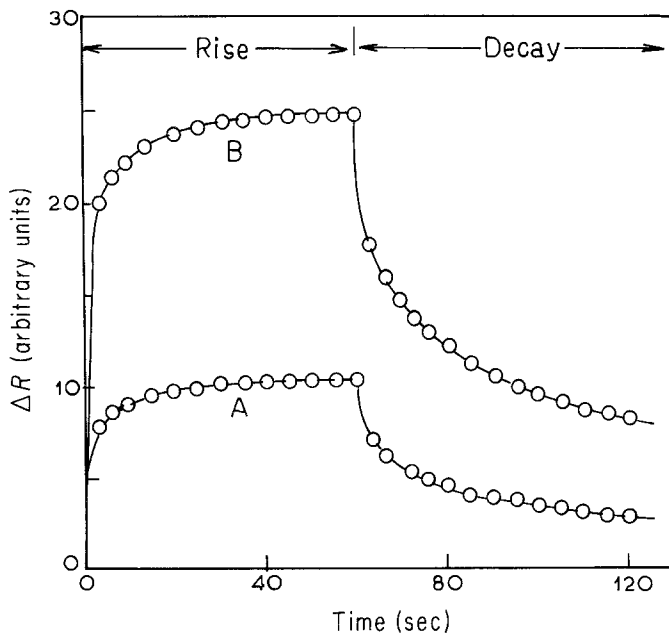


Figure 3 Rise and decay of sheet resistance (ΔR) of two representative CdSe films deposited at (A) 390 K, (B) 550 K.

power law expression:

$$\Delta R \propto t^{-m} \quad (6)$$

where ΔR is the change in resistance at time t .

Figure 4 shows the plot of $\log \Delta R$ against $\log t$ which is a straight line in the time domain used in this experiment. The magnitude of m is always less than unity and is lower for rise than that for decay for any particular film. This means that photoconductive decay is always slower than the rise.

3.2. Optical measurements

The optical absorption of CdSe films were recorded by a spectrophotometer (Hitachi 330) as a function of wavelength (400–2000 nm). Figure 5 shows a representative plot for CdSe films deposited at 390, 550 and 610 K. At the absorption edge [16–18]

$$\alpha = \frac{1}{t} \ln \left(\frac{I_0}{I} \right) \quad (7)$$

where I_0 and I are the reference and measured intensities, t being the thickness of the film.

At lower energy, beyond the absorption edge, the absorption coefficient (α) was calculated from the expression [16]

$$\alpha = \frac{1}{t} \ln \left(\frac{A}{T} \right) \quad (8)$$

where

$$A = 16n_a n_g (n^2 + k^2) / [(n_a + n)^2 + k^2] \times [(n_g + n)^2 + k^2] \quad (9)$$

$$T = \frac{C_1}{C_2} \left(1 - \sqrt{\frac{T_{\max}}{T_{\min}}} \right) \left(1 + \sqrt{\frac{T_{\max}}{T_{\min}}} \right)^{-1} \quad (10)$$

with

$$k = \frac{\alpha \lambda}{4\pi} \quad (11)$$

$$C_1 = (n + n_a)(n + n_g) \quad (12)$$

$$C_2 = (n - n_a)(n_g - n) \quad (13)$$

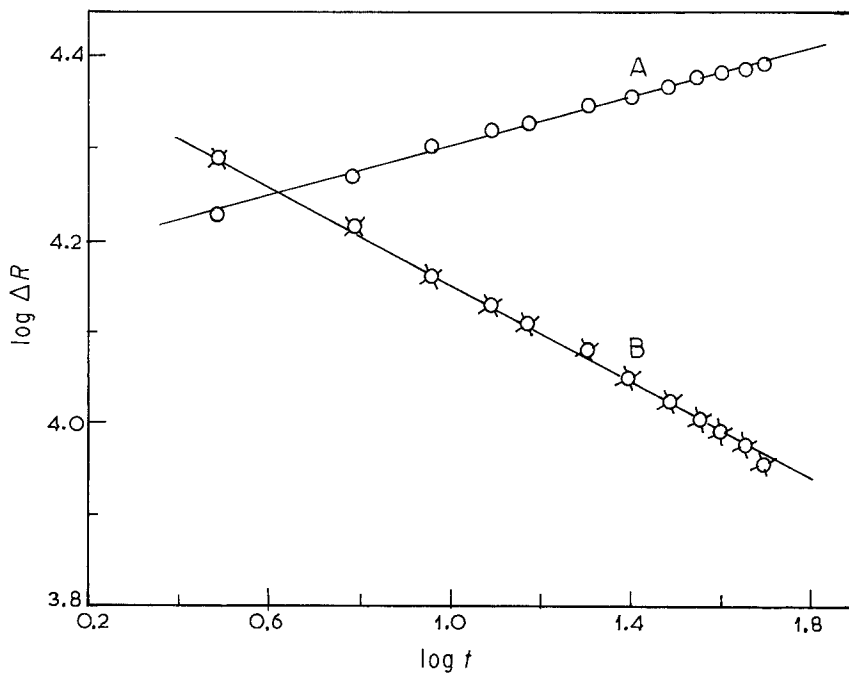


Figure 4 Plot of $\log \Delta R$ against $\log t$ for a CdSe film deposited at 390 K during (A) rise and (B) decay.

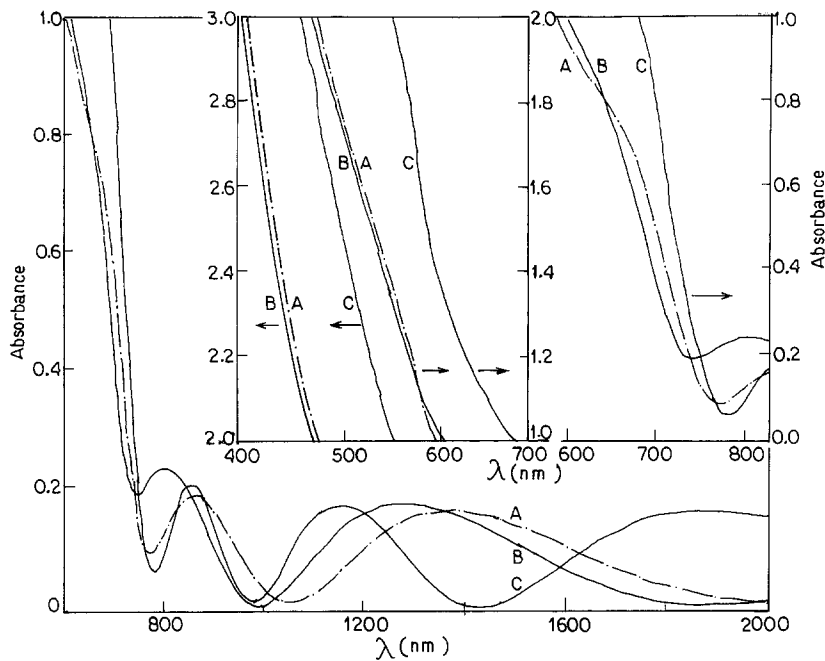
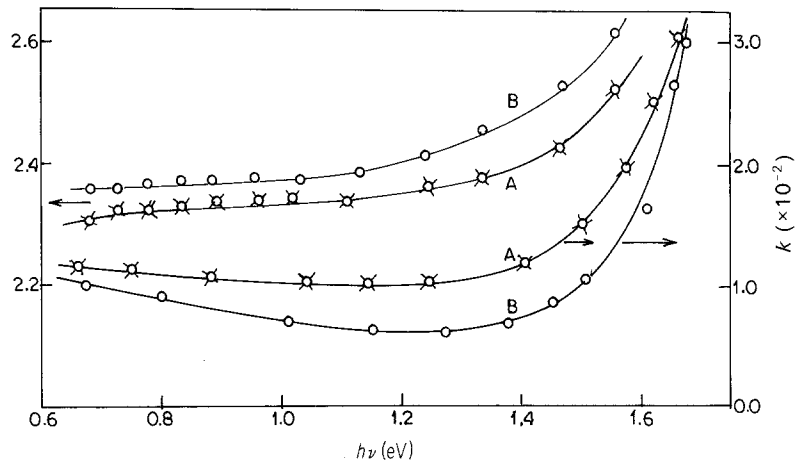


Figure 5 Variation of the optical absorbance ($\log I_0/I$) with the wavelength of incident photon for three CdSe films deposited at (A) 390 K, (B) 550 K, (C) 610 K.

Figure 6 Variation of refractive index (n) and extinction coefficient (k) with incident photon energy ($h\nu$) for representative CdSe films deposited at (A) 390 K, (B) 610 K.



$T_{\max}(\lambda)$ or $T_{\min}\lambda = (I/I_0)$ at minima or maxima of the envelopes of the absorption traces. n , n_a and n_g are the refractive indices of film, air and glass respectively.

The refractive index (n) and thickness (t) were calculated from

$$n^2 = \left(\frac{n_a^2 + n_g^2}{2} + 2n_a n_g T' \right) + \left[\left(\frac{n_a^2 + n_g^2}{2} + 2n_a n_g T' \right)^2 - n_a^2 n_g^2 \right]^{1/2} \quad (14)$$

and

$$t = \frac{N_0}{2(n_1 \bar{\nu}_1 - n_2 \bar{\nu}_2)} \quad (15)$$

where

$$T' = \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} \quad (16)$$

TABLE I Value of activation energy and value of m for three representative CdSe films

Deposition temperature (K)	Activation energy (eV)	Value of m during rise	Value of m during decay
390	0.048	0.13	0.26
470	0.058	0.08	0.31
550	0.072	0.06	0.36

N_0 being the number of oscillations between two extrema and n_1 and n_2 represent the refractive indices of the film at the wave number $\bar{\nu}_1$ and $\bar{\nu}_2$ respectively. The variation of refractive index n and extinction coefficient k with incident photon energy are shown in Fig. 6. Refractive index (n) rises slowly with increasing $h\nu$ in our range of measurement. The absorption coefficient (α) was calculated at different values of $h\nu$. It was observed that the graphical representation (Fig. 7) of $\alpha^2 = f(h\nu)$ yields two straight parts indicating two direct optical transitions. The optical band gap (E_g) in CdSe films were determined from the spectral dependence of absorption coefficient (α). Now [17]

$$\alpha \sim (h\nu - E_g)^{m'} \quad (17)$$

where m' correspond to the values $\frac{1}{2}$, 2 and $\frac{3}{2}$, 3 for allowed direct, indirect and forbidden direct, indirect transitions, respectively.

From Equation 17 we can obtain a set of values (m' , E_g) from the plots of $\alpha^{1/m'}$ against $h\nu$ as discussed in detail in our earlier work on ZnTe films [19]. The band gap was obtained by extrapolating the linear portion of the above plot to $\alpha^{1/m'} = 0$. Then, depending on the nature of transition in the films, a single set of values

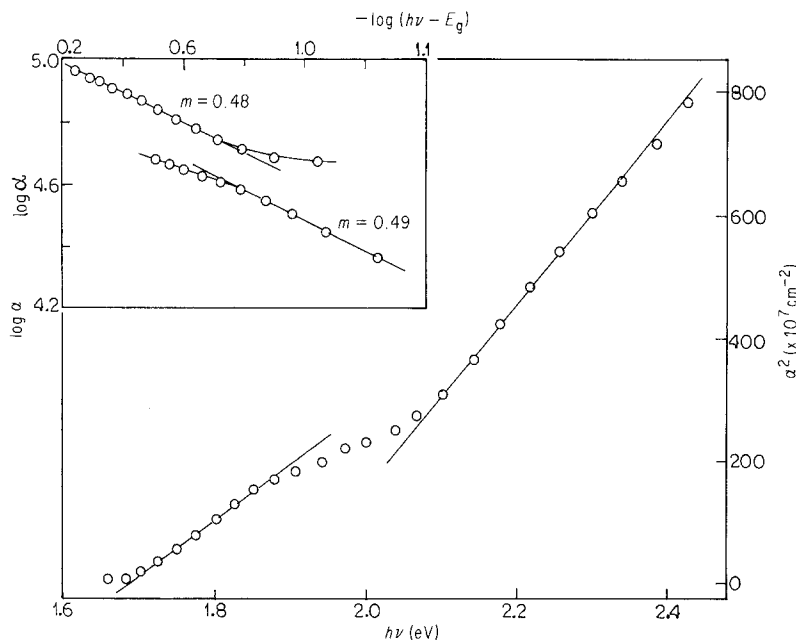


Figure 7 Plot of α^2 against incident photon energy ($h\nu$) for a representative CdSe film (390 K) indicating $E_{g_1} = 1.69$ eV and $E_{g_2} = 1.91$ eV. The inset indicates the value of m' obtained from the variation of $\log \alpha$ with $\log(h\nu - E_g)$ assuming $E_g = 1.69$ eV (E_{g_1}) and 1.91 eV (E_{g_2}) at lower and higher energy regions.

(m' , E_g) obtained as above, will indicate a linear fit of the plot (Fig. 7) $\log \alpha$ against $\log(h\nu - E_g)$. In fact, for direct transitions the best linear fit was obtained for $m' = 0.48$ and $m' = 0.49$ (Fig. 7) corresponding to energy gaps $E_{g_1} = 1.69$ eV and $E_{g_2} = 1.91$ eV at lower and higher incident photon energies. The two energy gaps E_{g_1} and E_{g_2} for different films are given in Table II. The energy gap E_{g_1} is in good agreement with the works of El-Shazly *et al.* [20] but E_{g_2} is much lower than their reported value 2.12 eV.

3.3. Thermoelectric power measurements

The thermoelectric power (TEP) measured in the temperature range (280–400 K) indicated that the electrons are carriers in CdSe films which was also supported by Hall effect measurements. The TEP (S) may be expressed as [21, 22]

$$S = -\frac{k}{e} \left[A + \ln \left(\frac{N_c}{N} \right) \right] \quad (18)$$

where A is the thermoelectric counterpart of the Hall

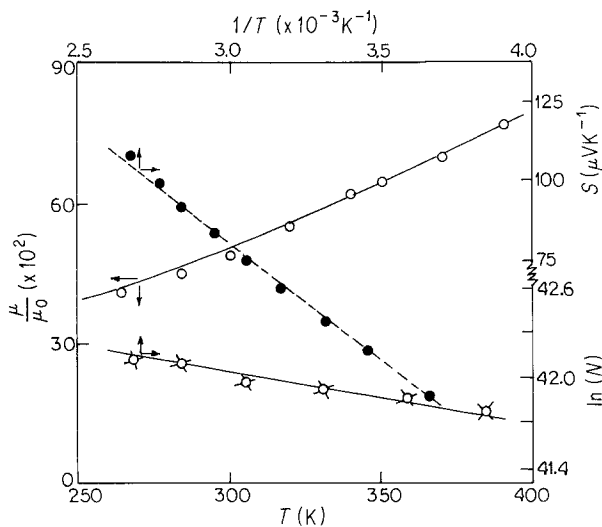


Figure 8 A representative plot of the variation of thermoelectric power (S), mobility (μ) and $\ln(N)$ with temperature for films deposited at 470 K. (O) experimental μ/μ_0 , (—) theoretical μ/μ_0 , (---●---) thermoelectric power S , (—○—) $\ln(N)$.

factor r and N_c is the effective density of states given by

$$N_c = 2 \left(\frac{2\pi m_c^* kT}{h^2} \right)^{3/2} \quad (19)$$

The carrier concentration (N) may be expressed as

$$N = N_c \exp \left(-\frac{E_f}{kT} \right) \quad (20)$$

where E_f is the distance of the Fermi level from the bottom of the conduction band. A plot of S against reciprocal temperature ($1/T$) indicated (Fig. 8) a straight line. From the slope and intercept of the above plot E_f and A were determined to be 0.03 and 3.8 eV respectively. Using this value of A , the scattering parameter s ($\tau \sim E^{-s}$) was calculated as -1.3 . This indicated ionized impurity scattering to be predominant in CdSe films. This is in good agreement with $s = -\frac{3}{2}$, reported in the literature for ionized impurity scattering.

3.4. Hall effect measurements

The Hall mobility in CdSe films was measured by the four probe technique. The mobility increased with temperature (Fig. 8) according to

$$\mu = \mu_0 T^{n'} \quad (21)$$

The value of n' varied from 1.2 to 1.5 in our films. The

TABLE II Energy gaps corresponding to two direct transitions ($m' = \frac{1}{2}$) for representative CdSe films

Deposition temperature (K)	Film No.	E_{g_1} (eV)	E_{g_2} (eV)	$E_{g_2} - E_{g_1}$ (eV)
390	6B	1.69	1.91	0.22
	6D	1.69	1.92	0.23
	10A	1.68	1.91	0.23
480	7B	1.68	1.90	0.22
	9B	1.70	1.92	0.22
550	11C	1.69	1.91	0.22
	11E	1.70	1.92	0.22
610	9E	1.70	1.91	0.21

theoretical plot of μ/μ_0 against T supports ionized impurity scattering [23] in our temperature range of measurements. The carrier (electron) density (N) was determined from Hall effect measurements with

$$N = \frac{r}{R_H e}$$

where r is given by

$$r = \frac{\Gamma(\frac{s}{2} - 2s)\Gamma(\frac{s}{2})}{[\Gamma(\frac{s}{2} - s)]^2} \quad (22)$$

For ionized impurity scattering r was calculated as 1.9 using $s = -1.3$, obtained from TEP measurements. From the intercept of the plot of $\ln(N)$ against T^{-1} (Fig. 8), the effective mass was determined as $m_e^* = 0.13 m_e$. This is in good agreement with that obtained by other workers [24].

4. Conclusion

Cadmium selenide films were found to be n-type with Hall effect and thermoelectric power (TEP) measurements. It was observed that the variation of Hall mobility ($10\text{--}30 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$) with deposition temperature ($390\text{--}550 \text{ K}$) to be negligible whereas the carrier concentration varied from 5×10^{18} to $4 \times 10^{17} \text{ cm}^{-3}$ in the same temperature range. The experimental $\mu\text{--}T$ plot showed a good agreement with the theoretical plot indicating that ionized impurity scattering might be the most predominant scattering mechanism above room temperature (300 K). The scattering parameter s ($\tau \sim E^{-s}$) determined from our TEP measurements was found to be -1.3 , which also supported ionized impurity scattering in CdSe. The effective mass m_e^* calculated from TEP measurements assuming ionized impurity scattering agrees extremely well with the value ($0.13 m_e$) published earlier for CdSe.

Studies on photoconductivity of CdSe films showed higher photoresponse for films deposited at higher substrate temperature (T_d). The rise and decay studies on monochromatic photoconductivity indicated $\Delta R \sim t^{-m}$, where m varied from 0.26 to 0.36 with variation of T_d from 390 to 550 K. From optical transmittance measurements, direct transitions corresponding to band gaps of 1.70 and 1.92 eV were observed.

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