

Space charge limited conduction in CdSe thin films[†]

PRADIP KR. KALITA*, B K SARMA and H L DAS

Department of Physics, Gauhati University, Guwahati 781 014, India

*Department of Physics, Guwahati College, Guwahati 781 021, India

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Abstract. The current (I)–voltage (V) characteristics of thermally evaporated CdSe thin films having thickness in the range 850–3000 Å and deposited within the substrate temperature of 303–573 K show nearly linear dependence at low voltage and afterwards a non-linear behaviour at higher voltage range. A detailed study of I – V curves in dark and under illumination clearly reveals the mechanism as ohmic at low voltage and that of trap limited space charge limited conduction (SCLC) at higher voltage. The transition voltage (V_t) from ohmic to SCLC is found to be quite independent of ambient temperature as well as intensity of illumination. SCLC is explained on the basis of the exponential trap distribution in CdSe films. Trap depths estimated from the $\ln I$ vs $10^3/T$ plots are found to be within 0.60–0.37 eV. Using the relevant SCLC theory, the carrier concentration, n_0 , total trap concentration, N_t , and the ratio of free charge to trapped charge, q , have been calculated and correlated with ambient temperature and intensity of illumination.

Keywords. CdSe thin film; I – V characteristics; SCLC mechanism; localized traps.

1. Introduction

CdSe has emerged as a promising material in recent years because of its potential technological importance. It is widely preferred in fabrication of solar cells, photodetector, light emitting diodes and other opto-electronic devices owing to its high photosensitive behaviour compared to other II–VI materials (Sathyalatha *et al* 1989; Padmanabhasarma *et al* 1995). CdSe often possesses n -type conductivity in bulk as well as in thin film form (Oduor and Gould 1995). The native defects in excess Cd and Se vacancies thus play an important role in the determination of conduction processes in CdSe thin films (Raoult *et al* 1989; Oduor and Gould 1995; Nesheva 1996).

The current (I)–voltage (V) characteristics in thin films is an important tool for analysing the different conduction processes. Several workers (Gogoi and Barua 1982; Gould and Ismail 1992) studied the I – V curves in II–IV semiconductor films with a variety of methods and thereby determined the various physical processes viz. Schottky, Pool-Frankel and space charge limited conduction depending on the film growth and experimental ambient conditions. However, the work done so far in CdSe thin films in order to characterize the defect levels and their influence on the physical processes is insufficient for a better understanding of conduction mechanism. Most of the

investigations were carried out using sandwich type films compared to a lesser amount of work done using gap type films. Moreover, the gap type film configuration is more favourable for direct photoresponse study. Keeping in view of above aspects, SCL conduction process based on the experimental I – V characteristics in dark and under illumination in thermally evaporated CdSe films has been analysed and reported in this paper.

2. Experimental

Thin films of cadmium selenide were deposited on glass substrates by usual thermal evaporation technique (HINDHIVAC 12 A 4) at a vacuum $\sim 10^{-6}$ torr. High purity (99.999%) bulk CdSe powder obtained from Koch Light Lab, UK was used for deposition of films at substrate temperature (T_s) in the range 303–573 K. The film thickness (t) was measured with the help of a multiple beam interferometry method. Gap type film geometry with an effective gap of 3 mm between the electrodes was made to facilitate photoresponse study. Pure Al, Ag and In were taken for preparation of electrode films.

The current measurement was done by using a high impedance ($\sim 10^{14} \Omega$) ECIL electrometer amplifier with an accuracy of 3%. The film was kept inside a continuously evacuated glass chamber which along with other measuring equipments was again kept inside a shielding network in the form of a Faraday Cage during measurements. A 250 W quartz halogen bulb was used for white light illumination and the intensity of illumination was measured with the help of a sensitive Aplab luxmeter.

*Author for correspondence

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3. Results and discussion

3.1 I - V characteristics

Study on I - V characteristics is a matter of importance for properly analysing the conduction mechanism in films. A non-linear curve often may reveal the existence of different kinds of conduction mechanisms. In the present work the non-linear I - V characteristics of the films are examined and explained on the basis of SCL conduction. The I - V relationship shows an overall non-linear behaviour within the applied bias - 160 V- 160 V. The electrode-film contacts were examined with pre-evaporated Ag, Al, and In films which show identical non-linear behaviour and thereby rule out the possibility of electrode effect. Non-linearity is thus the manifestation of volume conductivity that can explore the feasibility of different conduction mechanisms (Khare *et al* 2000). The I - V characteristics in \ln - \ln scale for different CdSe thin films deposited at T_s within 303-573 K are depicted in figure 1. Another plot of I - V curves measured from 303-393 K for a film deposited at 423 K having thickness, 3000 Å, is shown in figure 2. Figure 3 represents the same characteristic of a film in dark and under different white light illuminations. Figures 1-3 clearly show two distinct slopes for each of the curves within the applied bias.

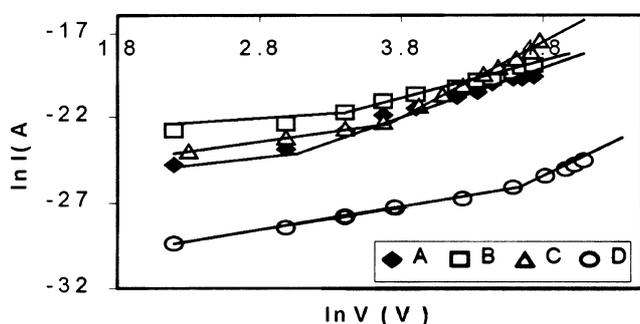


Figure 1. $\ln I$ - $\ln V$ characteristics of four CdSe films. A: 850 Å (t), 303 K (T_s); B: 1400 Å, 473 K; C: 2000 Å, 573 K and D: 3000 Å, 423 K.

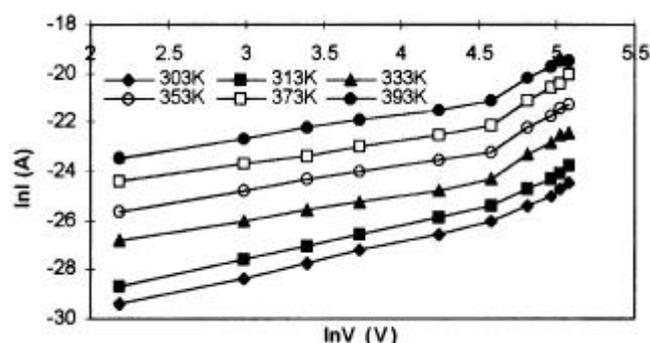


Figure 2. $\ln I$ - $\ln V$ characteristics for a CdSe film (D) measured at 303-393 K.

For lower applied bias the value of slopes are 1.25, 0.80, 1.25 and 1.38 whereas for higher bias the slopes change to 2.5, 2.8, 3.8 and 3.0 as shown in figure 1 for four CdSe films having thicknesses 850 Å, 1400 Å, 2000 Å and 3000 Å, respectively. Similar behaviour of changing slope with the increasing bias is also found when the current measurement is done at different ambient temperatures and white light illuminations (figures 2 and 3). Thus the I - V curves show two regions of conduction, viz. (i) nearly ohmic at lower bias and (ii) non-ohmic conduction at higher bias, in these CdSe films. For lower bias the injected charge carrier density is lower than the thermally generated carrier density and that leads to ohmic behaviour. At higher bias, as the slopes are > 2 it clearly suggests that the conduction in this region is dominated by trap limited space charge limited conduction mechanism (Devi and Prakash 1992, 1993; Oduor and Gould 1995; Goswami 1996). The transition voltage (V_t) at which the transition occurs from ohmic to SCLC is expected to depend on the film growth condition. It is evident from figure 1 that V_t changes with the change in film thickness as well as substrate temperature. However, it is found that V_t is quite invariant on increasing ambient temperature and intensity of illuminations. Similar characteristics of SCLC in II-VI films is also reported by other workers (Lhermitte *et al* 1975; El-Kadry *et al* 1995; Nesheva 1996).

3.2 Conduction mechanism

The conduction mechanism in compound thin films is mainly governed by the grain boundary defect states (Pawlikowski 1990; Kalita *et al* 1999). Native defects and their concentration is dependent on the film growth condition. Thus the defect states which effectively act as either trapping or recombination centres play an important role in determination of conduction mechanism in the films deposited at different growth conditions. At lower bias up to transition voltage (V_t), the current density (J) governed by the intrinsic free carrier density (n_0), in the film can be expressed as

$$J = n_0 m n_i / d, \quad (1)$$

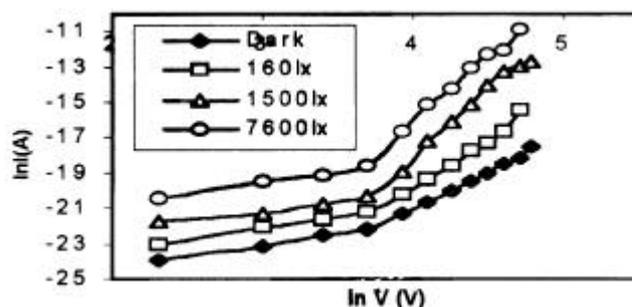


Figure 3. $\ln I$ - $\ln V$ characteristics for a CdSe film (C) in dark and under white light illuminations.

here d is the gap between the electrodes and m the electron mobility. It is established that CdSe in bulk and in thin film form always possesses n -type conductivity. Therefore, the hole transport is taken to be at minimum.

In the high bias region usually a slope of 2 indicates shallow trapping. However, in the present case as the slopes are > 2 , it clearly suggests that the SCLC is governed by the exponential trap distribution preferably with deep traps. Therefore, this trap limited SCLC current density is expressed as (Oduor and Gould 1995),

$$J = e m N_c (e/e N_0 k T_l)^l n^{l+1} / d^{2l+1}, \quad (2)$$

here N_0 is the trap density per unit energy range at conduction band edge, e the permittivity of the film taken as 5.76 (Sharma *et al* 1992) and l the ratio of (T_l/T) , here T_l and T are the characteristic temperature (Bak and Lipinski 1994) of energetic trap distribution and ambient temperature, respectively. Other parameters have their usual significance. The total trap concentration is given by

$$N_t = N_0 k T_l. \quad (3)$$

The injected carrier density becomes greater than the free carrier density at high bias which leads to SCLC conduction in the films. At transition voltage (V_t) where conduction changes from ohmic to SCLC, the injected carrier density is equal to free carrier density. Therefore, at transition voltage, n_0 is the measurement of normal volume generated free carrier density (Khare *et al* 2000). Assuming the earlier reported value of $m = 2.2 \times 10^{-8} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$ (Buragohain and Barua 1987) measured within ambient temperatures, 303–423 K and under illuminations, 3500–7000 lx for gap type CdSe film, n_0 is calculated from relation (1). Equating (1), (2) and (3), the total trap concentration, N_t , is determined as

$$N_t = (N_c/n_0)^{1/l} (e n_l / e d^2). \quad (4)$$

Here N_c is the effective density of states in the conduction band given by the relation

$$N_c = 2(2 p m_e k T / h^2)^{3/2}, \quad (5)$$

here the symbols have their usual meanings. m_e is the effective electron mass taken as $0.13 m_0$ for CdSe films (Oduor and Gould 1995). N_c increases with ambient temperature. Using (4) the corresponding density of total trap concentration is determined. If q be the fraction of total charge injected being available for conduction then it can be approximately related to n_0 as (Khare *et al* 2000)

$$n_0 = (e e_0 q n_l / e d^2). \quad (6)$$

Thus using (6) q can be estimated. The trap depth, E_t , is a function of q which can be expressed as

$$q = (N_c/N_t) (\exp(-E_t/kT)).$$

A plot of $\ln I$ vs $10^3/T$ in the SCLC region thus can measure the trap depths (Goswami 1996). Figure 4 shows $\ln I$ vs $10^3/T$ plots for a representative CdSe thin film

when the bias voltage are applied above transition voltage. All curves either measured in dark or under white light illumination have a single slope each and the slope decreases with increasing bias and intensity of illumination. The trap depths corresponding to slopes for different CdSe films are calculated which are found to be within 0.60–0.37 eV. These trap depths are in conformity with the earlier reported works (Yodogawa *et al* 1973; Raoult *et al* 1989; Sathyalatha *et al* 1989). The photocurrent measured in the same film shows a sublinear relationship with the intensity of illumination (figure 5). Hence it supports the defect controlled SCLC dominated by those deep trapping states.

The calculated values of free carrier density, n_0 , total trap density, N_t , ratio of injected charge to trapped charge, q , and the trap depths are systematically represented in tables 1 and 2. It is seen that the fraction of free carriers for conduction (q) and the corresponding free carrier density increases with increasing ambient temperature and intensity of illumination where the total trap density decreases. This is predominantly due to thermal ionization and minority carrier recombination with the trapping centres. In pure compound film like CdSe, the grain boundary core contains a large number of defects due to

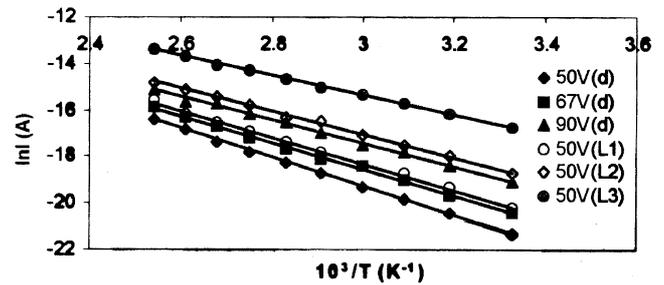


Figure 4. $\ln I$ – $\ln 10^3/T$ plots for CdSe film (C) measured in dark (d) and under illuminations (L_1 : 160 lx; L_2 : 1500 lx and L_3 : 7600 lx). Biases are applied above V_t .

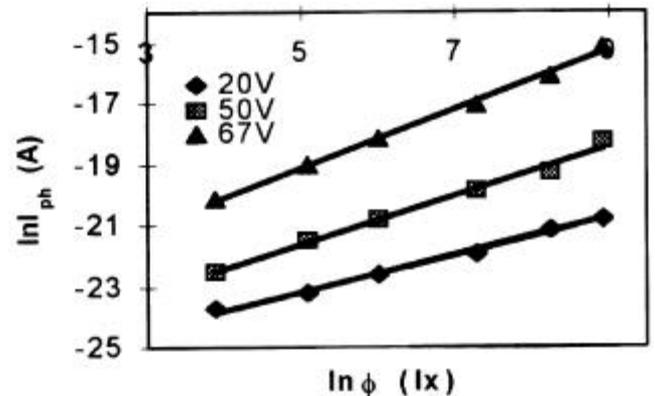


Figure 5. $\ln I_{ph}$ – $\ln f$ characteristics for CdSe film (C). Photocurrent $I_{ph} = (I_l - I_d)$, here I_l total current under illumination and I_d , dark current.

Table 1. The calculated values of l , n_t , n_0 , N_t and q for CdSe films.

t (Å)	T_s (K)	Measured at	V_t (V)	l	n_0 (m ⁻³)	N_t (m ⁻³)	q
850	303	RT (303 K)	20	1.5	5.47×10^{21}	2.85×10^{27}	7.72×10^6
1400	473	RT (303 K)	30	1.08	1.90×10^{22}	5.44×10^{27}	1.78×10^7
2000	573	RT (dark)	50	2.8	6.06×10^{21}	1.04×10^{27}	4.27×10^6
		160 lx (w.l.)	50	3.9	1.73×10^{22}	4.68×10^{26}	1.21×10^7
		1500 lx (w.l.)	50	4.2	2.66×10^{22}	3.92×10^{26}	1.87×10^7
		7600 lx (w.l.)	50	7.8	2.12×10^{23}	1.98×10^{26}	1.50×10^8
3000	423	RT (303 K)	97	2.0	3.73×10^{16}	2.17×10^{30}	10.55
		313 K	97	2.0	6.67×10^{16}	1.68×10^{30}	19.10
		333 K	97	2.63	1.94×10^{17}	1.56×10^{29}	56.45
		353 K	97	2.75	6.14×10^{17}	8.16×10^{28}	1.78×10^2
		373 K	97	2.7	1.75×10^{18}	6.38×10^{28}	5.09×10^2
		393 K	97	2.7	5.02×10^{18}	4.38×10^{28}	14.6×10^2

RT, room temperature; w.l., white light.

dangling bonds that give rise to large number of localized states. These localized states act as carrier trapping centres and after trapping the injected charge from electrodes they become charged and thereby expected to build up a space charge. This build up of space charge by inherent native defects then play a key role in determination of SCLC process. At low field, the rate of carrier injection is small and therefore the current is entirely governed by the intrinsic free charge carrier density. When the bias is applied beyond V_t , the rate of injected charge density increases and exceeds the thermally generated free charge carrier density. As the ambient temperature is increased from room temperature, this consequently leads to an increase of probability of thermal ionization of trapping centres. Therefore, the probability of trapping of injected charge with increasing temperature decreases. N_t then decreases and there is an increase in q with temperature. It is observed that trap depth decreases on increasing T_s and t as shown for film (C) (table 2). At high T_s and t the film grain size becomes higher which effectively reduces the inter grain boundary defect states and thereby decreases trap depth. The calculated values of the parameters and their varying nature are well in agreement with the results reported by other workers (Chan and Hill 1976; Buragohain and Barua 1987; Sathyalatha *et al* 1989).

The SCLC conduction under external illumination may also be due to the injected charge density from electrodes as in dark. When the film is illuminated by light, additional photo-excited carriers are generated in the films. The current under illumination at any temperature increases over dark owing to additional photogenerated majority carrier electrons as well as the contribution from barrier modulation by minority carrier holes. It is seen that the sublinear behaviour of photocurrent on light intensity for applied voltage around V_t (figure 5) clearly reveals the cooperation of traps and recombination centres (Rose 1956). In the presence of light the quasi fermi levels pull towards the respective band edge. The trapping centres

Table 2. Estimated trap depths found from 4 CdSe films.

Film	Bias applied (V)	E_t (eV)	Light (lx)	E_t (eV)
A	30	0.53		
B	45	0.60		
C	50	0.51	160	0.48
	67	0.49	1500	0.40
	90	0.42	7600	0.37
D	123	0.58		

then effectively act as recombination centres and recombine with the photogenerated minority carrier holes. This in turn reduces the grain boundary potential barrier heights and contribute to the enhancement of film conductivity (Kalita *et al* 1999). The total trap density and corresponding trap depth under illumination thus decreases owing to recombination with minority carriers.

4. Conclusions

The I - V characteristics of CdSe thin films have been examined in dark at different temperatures and under illuminations. The I - V curves show nearly ohmic behaviour at low bias and SCLC at high bias range. The transition voltage from ohmic to SCLC is independent of ambient temperature and intensity of illumination. The defect states in the films form space charge on trapping the injected charge from electrodes and thereby determine the SCLC process. A slope > 2 in the high bias region confirms the SCLC governed by the exponential trap distribution preferably with deep traps. Trap depths are calculated within 0.60–0.37 eV. The ratio of injected charge to free charge, q , the free carrier electron density (n_0) increase with the increase of ambient temperature and intensity of illumination whereas the total trap density, N_t , decreases. A decrease in trap depth with increasing T_s and t is also due to the reduction of total grain boundary trap density in the films. The defect controlled SCLC is

also supported by the sublinear behaviour of $\ln I_{ph} - \ln f$ characteristics in the films.

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