SUB-LINEAR DC PHOTOCONDUCTIVITY OF THERMALLY EVAPORATED POLYCRYSTALLINE CDSE THIN FILMS

DHANESWAR KALITA

Abstract :CdSe thin films deposited on glass substrates are found to be polycrystalline having hexagonal type structure. The photoconductivity (σ_L)-bias voltage (V) characteristics show sub-linear behavior which is attributed to the defects of the films. A detailed study of conductivity – bias voltage curves in dark and under illumination clearly reveals the conduction mechanism is ohmic at low voltage whereas it is trap limited exponential conduction at higher voltage. The conduction mechanism from ohmic to exponential rise is explained on the basis of the exponential trap distribution in the CdSe thin film. The sub-linear characteristics of photoconductivity are characterized from the bias dependent dc photoconductivity data. The threshold voltage (V_t) from ohmic to exponential is totally independent of ambient temperature and intensity of external illumination. Trap depths were estimated from the plots $\ln\sigma_L$ vs. 1000 /T and then the relation with bias voltage was established. The calculated values of traps density has been co-related with bias voltage. The intensity of illumination dependent effective density of states and free to trap charge carriers were calculated at different bias voltage.

Keywords: Photoconductivity, native defect, Sub-linear conduction, effective density of states, trap centres, trap depth

1.   **Introduction** : Interest in nanometer-sized semiconductor crystals, in particular II-VI alloys, has rapidly increased over the recent years, because of their potential applications in optoelectronics and nonlinear optics [1]. CdSe is a compound semiconductor and is being regarded as a prominent member of II-VI group of semiconductors. The dark and photoconductivity of these films are highly influenced by grain boundary potentials which may be modified by externally applied fields. These defects characterized the electronic properties of the material as they give rise to charge center acting as donors or acceptors [2]2 In contrast to bulk crystals, a large fraction of the constituent atoms of CdSe thin films are located at the surface of isolated nanocrystals or within the grain boundaries of nanometer-sized polycrystalline materials. This leads to a variety of defects (dangling and wrong bonds, bond lengths longer or shorter than those in the bulk, surface oxidation etc.) and significantly affects electrical nanosized semiconductors [3]. 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 better understanding of conduction mechanism. In view of relatively lack of information regarding the optoelectronic properties of thermally evaporated thin films, an attempt has been made to make a quantitative and qualitative study of conduction properties under different applied bias and intensity of illuminating radiation.

Experimental

In a vacuum of 10^{-5} torr (using a HINDHIVAC vacuum coating unit), the thin films of CdSe has been deposited on to cleaned glass substrate. Glass slide substrates were first cleaned with detergent water, degreased with acetone and rinsed with deionized water in an ultrasonic cleaner for (30min), then immediately dried by

blowing air and wiped with soft paper. CdSe powder with high purity (99.999%) was used in the films preparation (from Koch Light Lab. U.K.). Tantalum was selected as boat material as it has a low partial pressure up to the evaporation temperature of the material. The sublimation temperature of the film material is achieved nicely by adjusting the heating current in the range 40-60 amp, at filament voltage 10 V. The source-to-substrate distance was measured as to be 10 mm. The film thickness was measured by using an interferometric method (Fizeau's method) for equal thickness. An ECIL electrometer amplifier (EA815) of input impedance of $10^{14}\Omega$ and higher was used to measure dark and photocurrents. To provide bias, a series of highly stable dry cells of emf 9 volt each were used. The sample, by placing in a suitable sample holder was kept suspended by thin enameled copper wires inside a continuously evacuated glass jacket. The entire experimental set up including the observer was housed in a suitably fabricated Faraday cage in order to avoid the pick-up noises. A set of CZ matel interference filters of different wavelengths starting from 300 nm to 10500 nm were used for monochromatic radiations and these were calibrated by using highly sensitive APLAB luxmeter. X-ray diffraction (XRD) of different CdSe films were carried out by using Phillips X-ray diffractometer (Xpertpro) using CuKα radiation which was operated at 40 keV and 30 mA. Surface morphology of the films were studied with the help of a scanning electron microscopy (Carl Zeiss, Sigma VP)

2.   Results and discussion

3.1 The structural analysis of the films

The XRD patterns of the CdSe film reveals that films grown at temperature 303K are polycrystalline and have a würtzite (hexagonal) ZnS type structure. The crystallites are preferentially oriented with the (002) plane parallel to the substrate, as shown on Fig. 1.

However small percentage of orientation of [110] and [112] planes are also observed of the thermally deposited films The method used for sample preparation
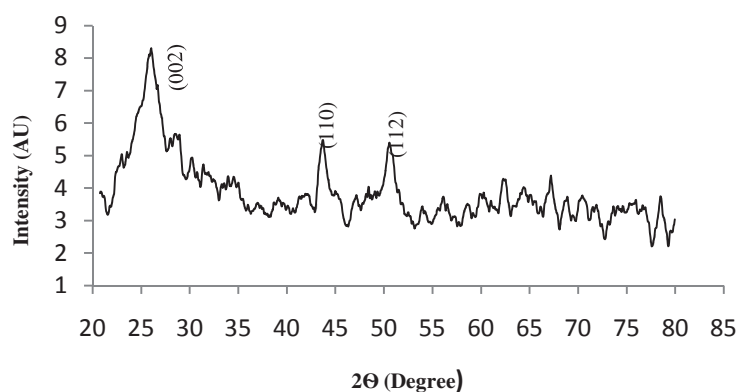

Figure 1. XRD plot of CdSe nanocrystal thin film deposited at 333K

takes into account the complete dissociation of the compound into Cd and Se molecules during the evaporation process and their recombination on the substrate to form CdSe films. It is observed that the inter planer distance for the deposited films changed with respect to the bulk one. The change may be due to the existence of some inherent defect states such as Se vacancies and Cd interstitials of the present study. These defect states plays important role in conduction process. No other phase except würtzite CdSe was identified in the XRD patterns. The sharp

absorption edge (corresponding to the forbidden energy gap) observed for CdSe film [4, 5] might indicate that the films have a stoichiometric composition [6]. The average size of the crystallite of CdSe thin film was found to be 129 nm determined by means of XRD.

3.2   SEM

Fig. 2 shows the presence of a homogeneous, adherent, fine grain polycrystalline surface morphology of CdSe thin film. The grains in the films are densely pack, well defined and having almost similar size [7]. The average size of the crystallites CdSe thin films determined by means of SEM image found to be 157 nm. No macroscopic defects like void, pinhole, peeling are seen from the SEM micrograph.
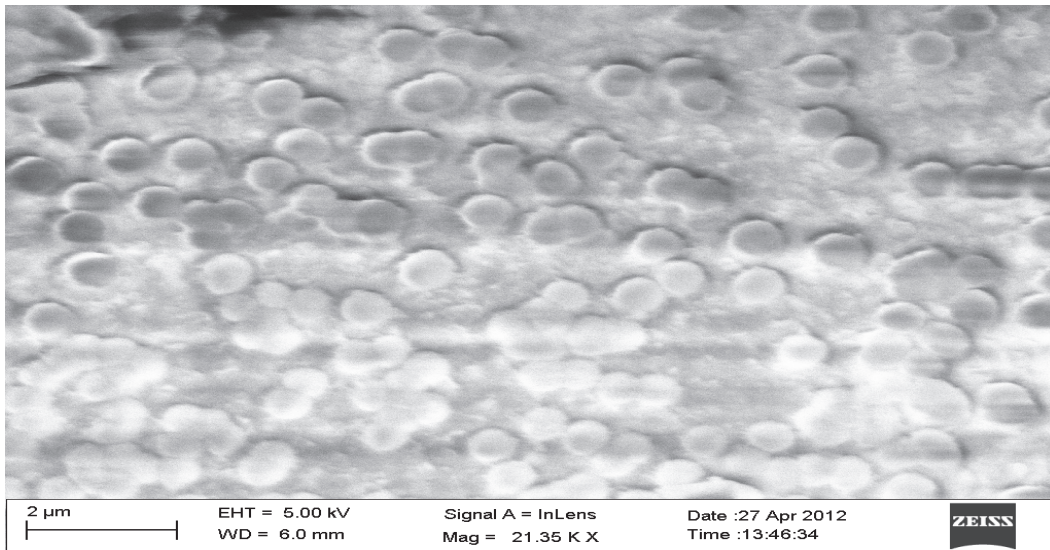

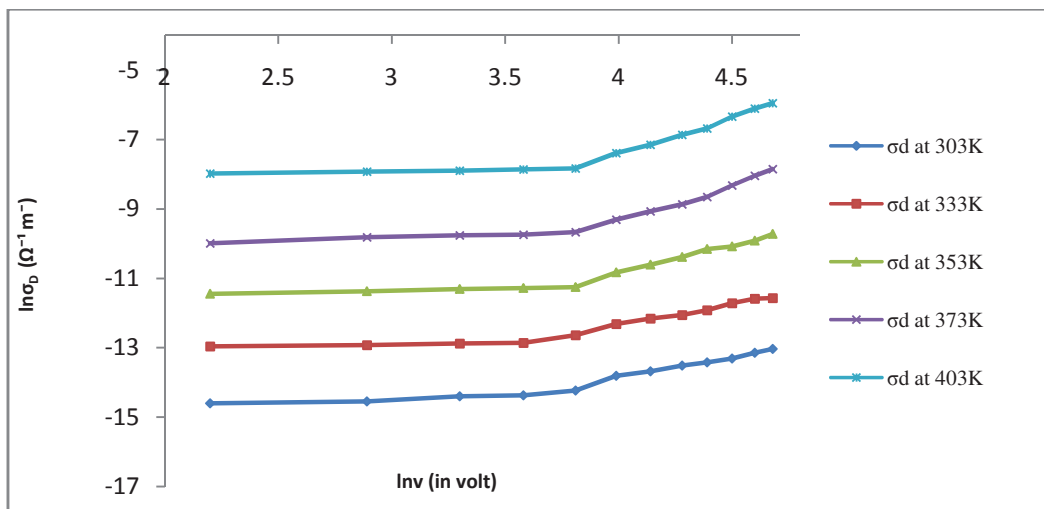Fig. 2. SEM micrograph of CdSe nano crystal thin film deposited at 333K.

Fig. 3. σ_D – lnV characteristics of CdSe nanocrystsalline thin film deposited at 303K and measured at temperatures 303K, 333K, 353K, 373K and 403K.

3.3   conduction mechanism

The conductivity (σ) − bias voltage (V) characteristics of CdSe thin films are a matter of important for properly analyzing the conduction

mechanism. lnσ-lnV characteristics under dark of the considered CdSe thin film deposited at 303K temperature are found to be linear within the range of specified applied bias voltage. This confirms that under dark, the contact electrodes of CdSe thin film are ohmic within that range of applied bias. But dark conductivity ($\sigma_{D)}$ – bias voltage (V) curves at high voltage are non-linear. The temperature dependent dark conductivity of CdSe thin film against bias voltage is shown in fig. 3.

The rise of conductivity is expressed as

$$\sigma_D = \sigma_o \exp(-E_a / KT) \quad (1)$$

Where E_a is the activation energy measured from the bottom of the conduction band. The non-linear behavior of photoconductivity, σ_L, calculated from photocurrent (where photocurrent, $I_{ph} = I_L - I_D$, I_L is the current under illumination and I_D is the current at dark) vs. bias voltage (V) characteristics shown in fig. 4(a) and fig. 4(b), are examined and explain on the basis of defect controlled mechanism of as grown CdSe nanocryalline thin film at temperatures 303K and 403K. The conduction mechanism in CdSe like compound semiconductor thin films are mainly governed by the grain boundary defect states [8].
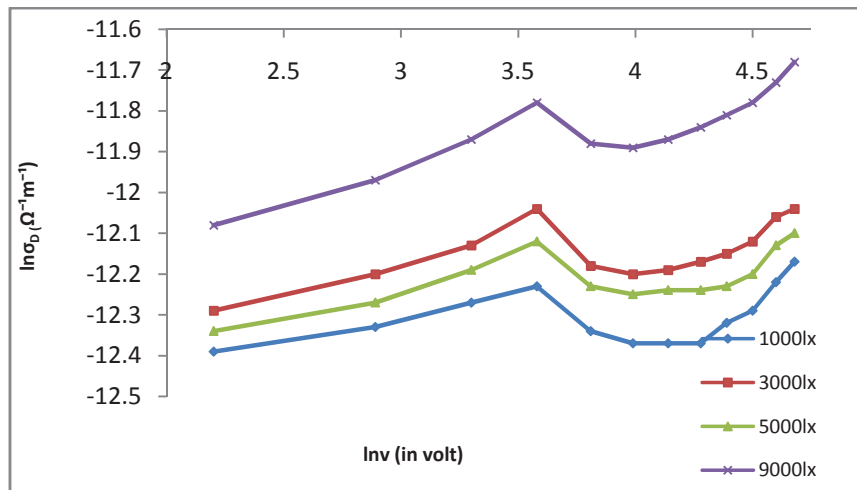

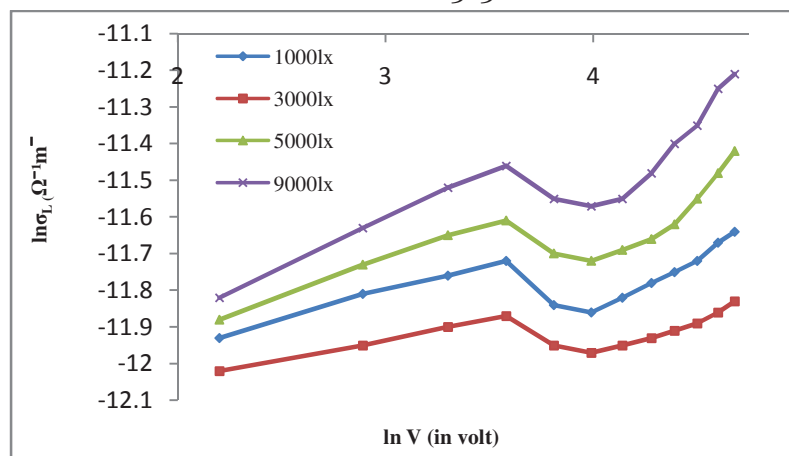Fig. 4(a). lnσ$_L$−lnV of CdSe nanocrystalline thin films deposited at 303K and photoconductivity measured at 303K.

Fig. 4(b). σ$_L$− lnV of CdSe nanocrystalline thin films deposited at 303K and photoconductivity measured at 403K.

The defect states which effectively act as either trapping centres or recombination centres plays an important role in determining conduction mechanism in CdSe thin films. The $\ln\sigma_L - \ln V$ characteristics are observed linear and symmetrical only for low bias voltages, i.e. in the low field region where conduction mechanism is ohmic in nature. At lower bias up to a certain voltage, known as threshold voltage, (V_t), the current density (J) in presence of light, govern by the intrinsic free carrier density (n_L), in the CdSe film that can be expressed as [9]

$$J = n_L \, \mu n L \, V_t / d \qquad (2)$$

Where d is the gap between the electrodes and μ_{nL} is the electron mobility. Beyond this low voltage range the photoconductivity increases nonlinearly with the applied bias. The photoconductivity of CdSe thin film under different illuminating intensities can be expressed as

$$\sigma_L = e \, (n_L\mu_{nL} + h_L\mu_{hL}) \qquad (3)$$

Where n_L and h_L are the number of electron and hole concentration under illumination along with hole mobility μ_{hL}. The sub-linear behavior of photoconductivity indeed always indicates the existence of high defect density in the films. The defect act as traps states (centres) situated at different energy states within the forbidden gap and there by influence largely the photo response performance. The initial linear rise of photoconductivity in presence of external illuminating radiation is due to increase of intrinsic charge carriers. At threshold voltage, however, after equilibrium a slow retrapping process starts where the holes from valence band are traps as holes centres. Therefore, an equivalent number of electrons are added to these hole centres from the conduction band that result a fall down conduction on further increase of bias voltage and intensity of illumination. Thereafter further increase of bias voltages attributes to the ionization of shallow and deep holes traps which withdraw the corresponding number of electrons from conduction band and increase the conductivity exponentially [10,11].

The conduction mechanism beyond threshold voltage is governed by exponential traps distribution preferably with deep traps. Therefore the current density in this region can be expressed as [12]

$$J = e\mu_{nL}N(\epsilon/eN_p \, kT)^x \, V_t^{1+x}/d^{2x+1} \qquad (4)$$

Where N is the effective density of state, N_p is the trap density per unit energy range at conduction band edge, ϵ the permittivity of the film taken as 5.76 [13] and x is the ratio of characteristic temperature of trap distribution to ambient temperature.
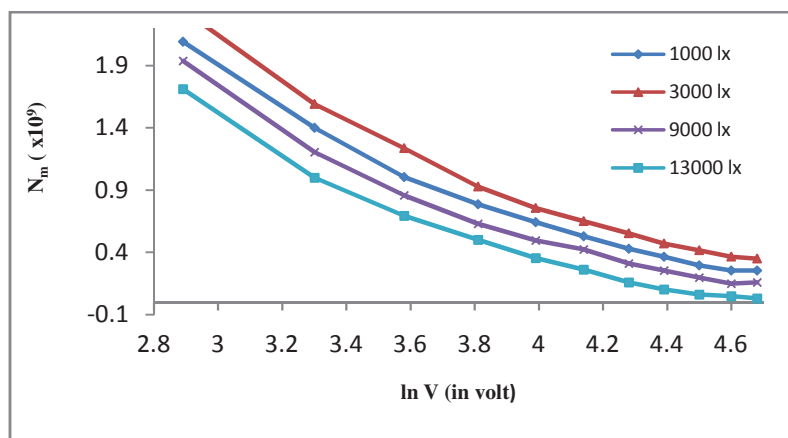

Fig. 5. $N_m - \ln V$ characteristics of CdSe nanocrystalline thin film deposited at 303K and measured at intensity of illuminations 1000lx, 3000lx, 9000lx and 13000lx.

1000lx		5000lx		9000lx	
N_b (cm^{-3}) (10^{14})	N_a (cm^{-3}) (10^{14})	N_b (cm^{-3}) (10^{14})	N_a (cm^{-3}) (10^{14})	N_b (cm^{-3}) (10^{14})	N_a (cm^{-3}) (10^{14})
1.17	1.29	1.74	2.02	2.54	2.63
1.27	1.28	1.84	2.11	2.63	2.61
1.34	1.36	1.95	2.19	2.69	2.67
1.43	1.44	2.04	2.26	2.88	2.92
1.49	1.61	2.4	2.42	3.02	3.13
	1.89		2.63		3.37
	2.04		2.79		3.78

The effective density of states can be calculated from the photoconductivity data by using the relation [14]

$$n_L = \sigma_L / e\,\mu_{nL} \qquad (5)$$

Where $\mu_{nL} = 580 \times 10^{-4}$ cm^{2}V^{-1}s^{-1} [15]. In this case, it is assumed that at comparatively low temperatures, the number of occupied energy levels under illumination in the conduction band i.e. n_L is identical with N. The calculated values of N before and after V_t are denoted by N_b and N_a which are listed in table. From the table it is clear that N_b increases linearly whereas a non-linear increasing nature is observed for N_a.

Table: Calculated value of effective of density of states before (N_b) and after (N_t) of V_t of as grown CdSe thin film at intensity of illumination 1000lx, 3000lx and 5000lx at temperature 303K.

The total trap concentration (N_m) of CdSe thin films can be calculated from the relation given bellow

$$N_m = (N/n_L)^{1/x}(\epsilon V_t / ed^2) \qquad (6)$$

In fig. 5., the plots of N_m vs. lnV reveal that N_m abruptly reduces against the increase of applied bias voltage.

The injected carrier density under illumination becomes greater than free carrier density at voltage higher than Vt. At V_t, where conduction changes from ohmic to exponential, the injected carrier density is equal to free carrier density. So, at V_t, n_L becomes the normal volume generated free carrier density.
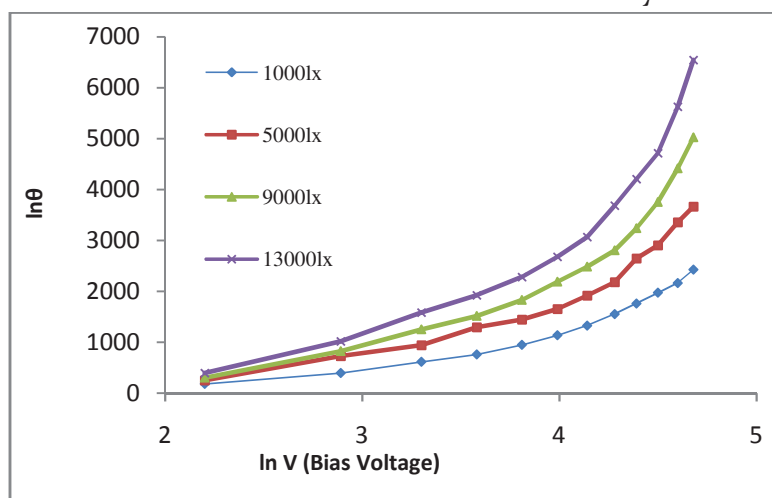

Fig. 6. $\ln\psi$ – ln V plots of nanocrystal CdSe thin film measured at intensity of illumination 1000lx, 5000lx, 9000lx and 13000lx

The ratio of free to trapped injected charges at different trap centres, ψ in the conduction process can approximately be related with n_L as [16]

$$n_L = (\epsilon\epsilon_o\psi V_t/ed^2) \qquad (7)$$

Using relation (7), ψ can be calculated. The plots of $\ln\psi$ vs. $\ln V$, where V is bias voltage (shown in fig. 6.) reveal ψ linearly increases with the increase of bias voltage up to V_t but it bear an exponential rise after V_t.

The trap depth (E_t) bellow the conduction band is given by the expression as

$$\Psi = (N/N_m) \exp (-E_t/kT) \qquad (8)$$

The slopes of the plots $\ln\sigma_L$ vs. $1000/T$, after V_t, as shown in fig. 7, give the respective trap depth of CdSe thin films. A trap is emptied by the absorption of optical illumination of different intensity and by the utilization of bias voltage. Therefore, the trap depth can be calculated from the spectrum of photoconductivity decay curve [17].
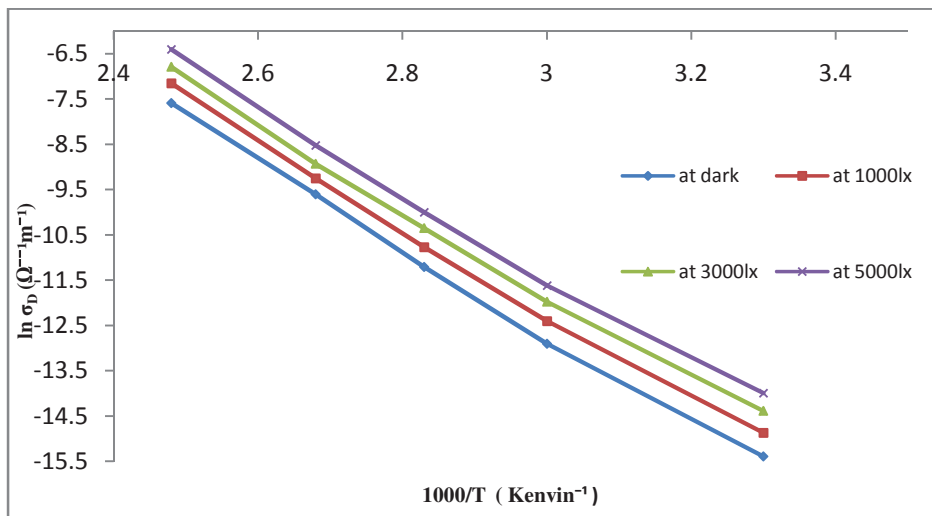

Fig. 7. Plots $\ln\sigma_L$ vs. $1000/T$ of CdSe nanocrystalline thin film at dark and under illumination of intensity 1000lx, 3000lx, 5000lx.
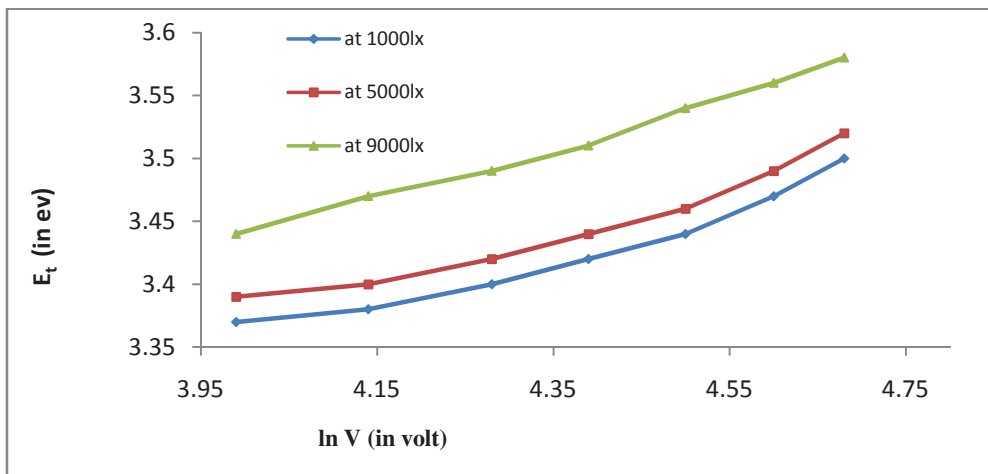

Fig. 8. E_t – $\ln V$ characteristics of CdSe nanocrystalline thin film deposited at 303K and trap depth measured at intensity of illumination 1000lx, 5000lx and 9000lx

The depth E_t, which a trap is required to possess in order that an electron may be trapped in it, varies depth to depth. Therefore the number of traps in which an electron spends a mean time, t, will vary with bias voltage and therefore, σ_L, varies with bias voltage

Fig. 8. Shows the variation of trap depth energy with bias voltage. It is clear from the figure that trap depths are not single valued but varies over a range with bias voltage.

3.   Conclusion : Thermally evaporated CdSe thin films onto glass substrate are of polycrystalline in nature. Such films are highly resistive and resistivity changes with applied bias. At low bias voltage photoconductivity observed linear whereas it becomes exponential after a certain bias voltage, known as threshold voltage. Photoconductivity of these polycrystalline films are basically controlled by native defects which act as trapping centres. The threshold voltage (V_t) from ohmic to exponential is totally independent of ambient temperature and intensity of external illumination. Traps are exponentially distributed in conduction band with different trap depths. After threshold bias, the number of trap density decreases abruptly with the increase of bias voltage. The number of free to trap charge density increases exponentially after threshold bias. Shallow traps play important role before threshold voltage but deep traps become responsible for photoconduction at high voltage. High bias voltage release trapped carriers from deep trapping centres by ionizing. The observed trap depths are not single valued and there is a quasi-continues distribution of various traps.

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Dhaneswar Kalita
Department of Instrumentation & USIC, Gauhati University- 781014, India.
E-mail: dhaneswarkalita2011@gmail.com