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Fabrication of Nanostructured Cadmium Selenide Thin Films and Study of its Electrical Properties

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Abstract

Cadmium selenide (CdSe) thin films having different thicknesses were prepared by thermal vacuum evaporation method onto precleaned amorphous glass substrate. The surface morphological properties of as prepared CdSe films have been characterized by various techniques, such as, X-ray diffraction (XRD), EDAX, field emission scanning electron microscopy (FESEM). XRD studies identify that the as-deposited CdSe films are highly oriented to [100] direction and they belong to nanocrystalline hexagonal phase. The lattice parameters (a = 4.292 and c = 7.012) and crystallite size (D) were calculated and found to be 156 nm. FESEM investigation confirms that films were uniformly deposited over the surface and particles in irregular morphologies in the form of fibrous texture. The electrical properties of the films have been evaluated such as resistivity (5.115 x 10^{-3} ohm-cm), carrier concentration (4.79 x 10^{12} /cm^3), mobility (2020.2 cm^2/Volt-Sec), activation energy (0.295 – 0.305 eV). TEP measurement confirms the deposited films are of P type semiconducting in nature.

Keyword: XRD, FESEM, Four probe, TEP, Fermi energy.

1. Introduction

In modern days, there has been a swift expansion in the field of II-VI group (CdSe, CdS, ZnSe, CdTe) semiconductor thin films owing to their broad range of applications. As an significant member of this cluster of binary compounds cadmium selenide (CdSe) is of concern for its applications as high efficiency thin film transistors [1, 2], solar cells [3], photoconductors [4], gas sensors [5, 6], acoustic optical devices [7], electrical and electrophotographic [8]. Chief awareness have been given in recent years to explore the electrical properties of CdSe thin films in organize to develop the performance of the devices and also for pronouncement novel applications [9].

Polycrystalline semiconductor materials have come under enlarged inspection because of their probable use in cost reduction for device applications.

Different techniques such as chemical vapour deposition [10], thermal evaporation technique [11], electrodeposition [12], physical vapour deposition [13], dip coating [14], chemical bath deposition [15], and spray-pyrolysis [16] have been employed for depositing cadmium selenide thin films.

In present work, the effect of film thickness of thin CdSe films over the thickness range of thickness 1000 – 3000 Å has been investigated. An attempt has been made to evaluate the electrical parameters such as Fermi energy, bulk resistivity, and mean free path of charge carriers as a function of thickness. Using bulk resistivity and mean free path, carrier concentration has also been evaluated. Also the variations in optical band gap as a function of thickness, structural, surface morphological properties were studied. The details have been reported in paper.

2. Experimental

2.1 Material Preparation

The compound ingots of CdSe were acquired by taking suitable amount of 99.999% pure Cd and Se in an evacuated quartz ampoule. The ampoule with the charge was then sealed under a pressure of 10^{-5} torr and was placed in rotating furnace. The temperature of the furnace was elevated gradually to 950 K and left at this temperature for about 12 h. Well mixed charges were then quenched in an ice bath. The CdSe ingot was taken out from the ampoule and made into fine powder and used for thin film preparation.

2.2 Synthesis and Characterization of sample

CdSe films have been deposited by thermal vacuum evaporation technique under vacuum of about 10^{-4} torr. The source to substrate distance was kept 9 cm. The samples of a variety of thicknesses were deposited under similar conditions. The thickness of the films was controlled by quartz crystal thickness monitor model No. DTM-101 provided by Hind-Hi Vac. The deposition rate was upholding to 8-10 Å/sec during sample preparation. Preceding to evaporation, the glass substrates were cleaned carefully using concentrated chromic acid, detergent, isopropyl alcohol and distilled water.

X – Ray diffractogram (Bruker, Germany) were get hold of these samples to find out structural information and to identify the film structure qualitatively. The scanning angle (2θ) range was from 20^0 - 80^0 (CuKα line). Surface morphological studies of the thermally deposited

CdSe thin films were done using the Field Emission Scanning Electron Microscope (Zeiss) operating with an accelerating voltage 15 kV. The quantitative compositional analysis of the CdSe films were carried out by EDAX technique attached with the FESEM. The thermo electric power of samples was measured by TEP set up using model no. DMV-001, "Pushpa Scientific, Haiderabad" as a function of thickness and temperature. Resistivity of the samples was measured by four probe technique using model No. DEP-02 "Scientific Equipment Roorkee", as function of thickness and temperature. A small oven has been provided to facilitate measurements at various temperatures ranging from room temperature 303 K to 473K. A highly regulated constant current generator specifically designed to provide the required varying current. (0 to 20 mA with resolution 10 μA) has been provided for the purpose.

3. Results and Discussions

3.1 XRD Analysis

In order to get information about crystal structure, crystalline size, purity of sample etc. of synthesized CdSe thin films, X-ray diffraction was carried out. X-ray diffraction pattern of synthesized samples was obtained at room temperature. The scanning angle 2θ was varied from 20^0 - 80^0 in steps of 0.5^0 /min using CuK_α radiation. The X-ray diffraction (XRD) pattern of the obtained samples was recorded by D8Advance, Brucker, Germany. Fig. 1 shows the XRD pattern of CdSe thin films having thickness of 2000 Å. The 2θ peak observed at 22.9^0, 24.10^0 and 28.80^0 which correspond to the (100), (002) and (101) planes of reflections. The XRD spectrum reveals that the films are polycrystalline in nature and hexagonal (wurtzite) in structure (JCPDS card No. 08 - 0456) [17, 18]. For 2000 Å film thickness, the (100) diffraction peak becomes more and more dominant. This suggests that, at the preliminary stage of film formation i.e., for the period of the atomistic condensation of the film formation, the deposited atoms are at arbitrary orientation. Since the thickness of the film increases the polycrystalline grains initiate to orient mostly along (100) direction which is marked from the Fig. 1 The assessment of the lattice parameters achieve from the analysis of x-ray diffraction pattern were a = 4.292 and c = 7.012 [19]. Unit cell volume was established to be 92.5. The average grain size was established to be 156 nm calculated by using the Scherrer formula:

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \qquad \ldots (1)$$

The average dislocation density was found to be 0.197 $X10^{14}$ lines/m^2 calculated by:

$$\delta = \frac{1}{D^2} \quad \ldots (2)$$

The number of crystallites per unit area (N) and the strain (ε) of the films were determined by following relations:

$$N = \frac{t}{D^3} \quad \ldots (3)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad \ldots (4)$$

Where, t is the thickness of the film. The evaluated structural parameters are N = 0.866 X 10^{15}, ε = 0.09164 lines^{-2}m^{-4} [20, 21]. The small values of δ obtained in the current study authenticate the good crystalline of thin films fabricated by the thermal vacuum evaporation method.

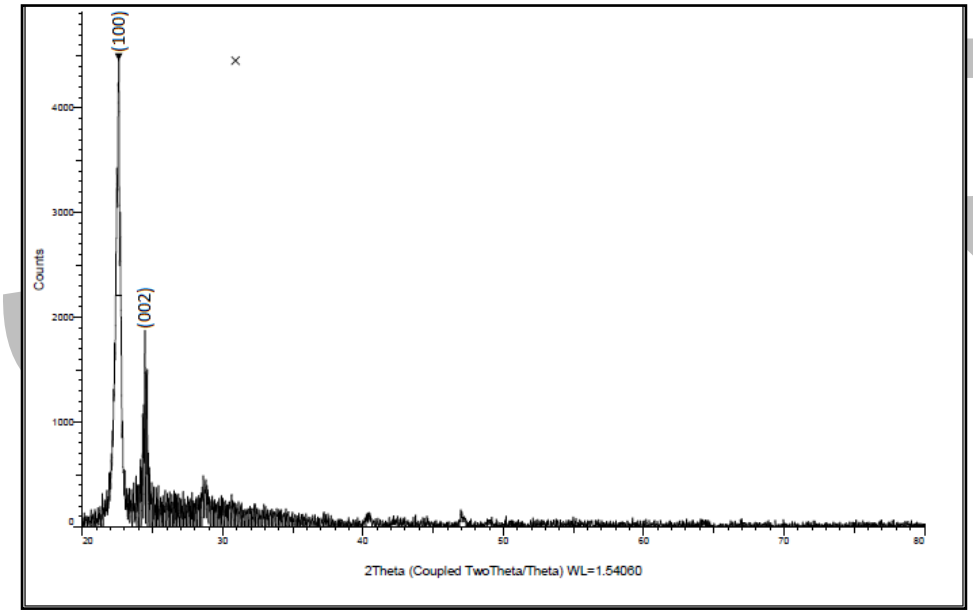


Fig. 1: XRD pattern of CdSe of thickness 2000 Å

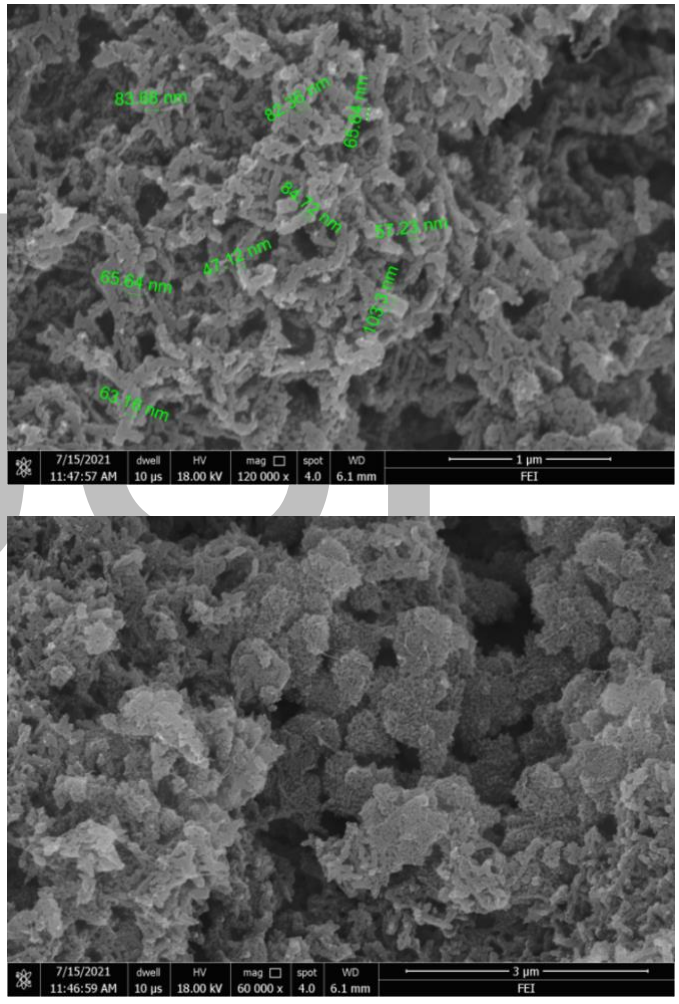
Table 1: Crystalline Parameters of the CdSe Thin Films

Parameter	
Crystal Size (D) (nm)	156
Dislocation Density (δ) (lines/m^2)	0.197 X10^{14}
Number of Crystals Per Unit (N)	0.866 X 10^{15}
Micro Strain (E) (lines^{-2}m^{-4})	0.09164

3.2 Field Emission Scanning Electron microscope (FE-SEM)

Field Emission Scanning Electron Microscopy (SEM) was applied to study the surface morphology and particle distribution of the prepared sample. The SEM analysis was done with help of FESEM (Zeiss EVO50).

Fig. 2 (a, b, c) shows SEM images of CdSe thin film of thickness 2000Å with various magnifications 120K, 60K and 30K.At low resolution the surface morphology is look like fibrous texture but as resolution increases the small grains are found. In higher resolution the grains are clearly seen. The particle sizes were found to be 57 - 103 nm.



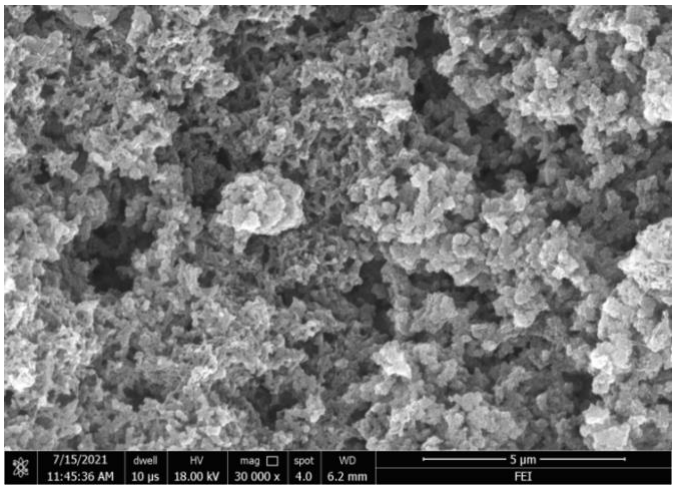


Fig. 2 (a, b, c): SEM images of CdSe thin film (2000Å)

3.3 Elemental Analysis of CdSe Thin Films

The as grown CdSe thin film was subjected to EDAX in order to ascertain the chemical composition or element present. The EDAX analysis was carried out by EDAX technique attached with the SEM. The EDAX spectrum of the CdSe thin film is shown in Fig. 3.

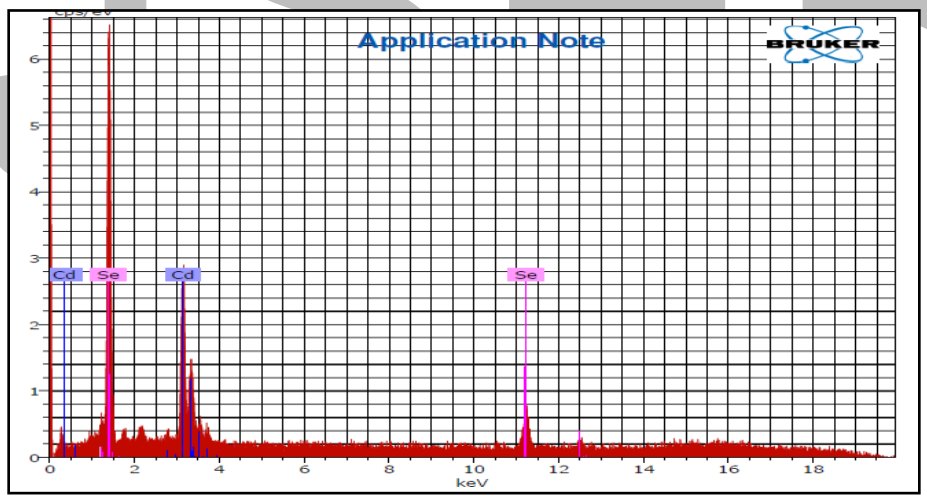


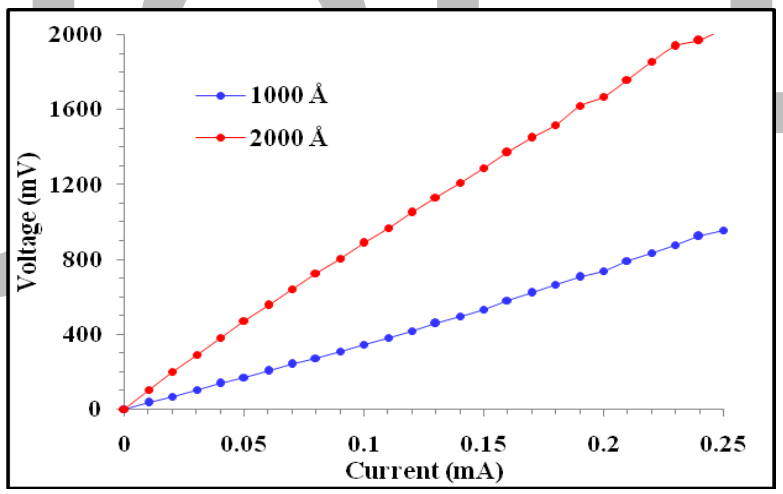
Fig. 3: EDAX Pattern of CdSe Thin Film

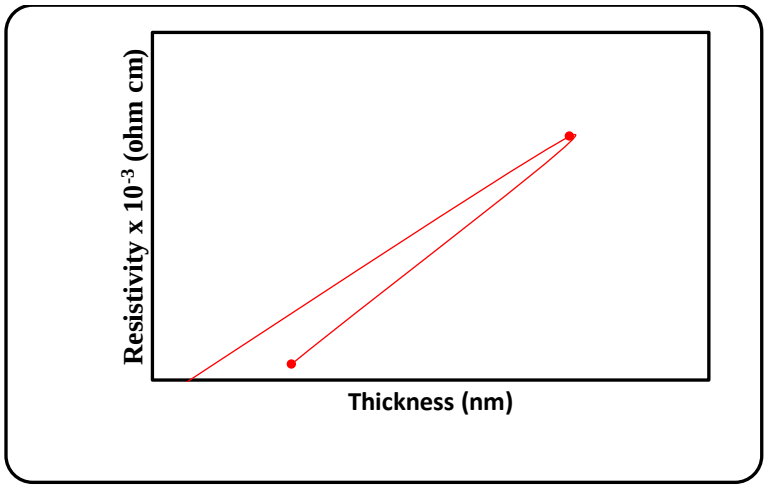
The spectrum peaks reveals presence of Cd and Se at 0.3KeV, 1.5KeV and 3.2KeV. The atomic percentage of Cd and Se were found to be 40.82% and 61.18% respectively. The obtained percentages of the constituent elements in all investigated films indicate that samples are non stoichiometric. The acquire outcome sustain for the eminence of the prepared CdSe films by

thermal vacuum evaporation technique. It was establish that the prepared films are selenium rich due to difference in vapor pressure of Se and Cd.

3.4 Four Probe Method

The resistivity of CdSe thin films of a range of thicknesses (1000 - 2000Å) were deliberate for all samples at room temperature. The graphical design of probe voltage versus probe current for a range of thicknesses is as shown in Fig. 4 (a). The plot of resistivity as a function of thickness identify that the resistivity of films rises as thickness increases, obeying Fuch Sondheimer size effect theory. The high resistivity of as deposited films may be credited to the imperfection and dislocation of the films. The raising in resistivity with thickness established the change in grain size and enlarges in grain boundaries as well as domains [22, 23]. This information is additionally confirmed from the slopes and intercepts of these plots (Fig. 4 (b), 4 (c) & 4 (d)) bulk resistivity (ρ_0) and the mean free path of the charge carrier in bulk material were evaluated and found to be $\rho_0 = 5.115 \text{ X } 10^{-3}$ ohm - cm, $\lambda_0 = 876.89$ Å.





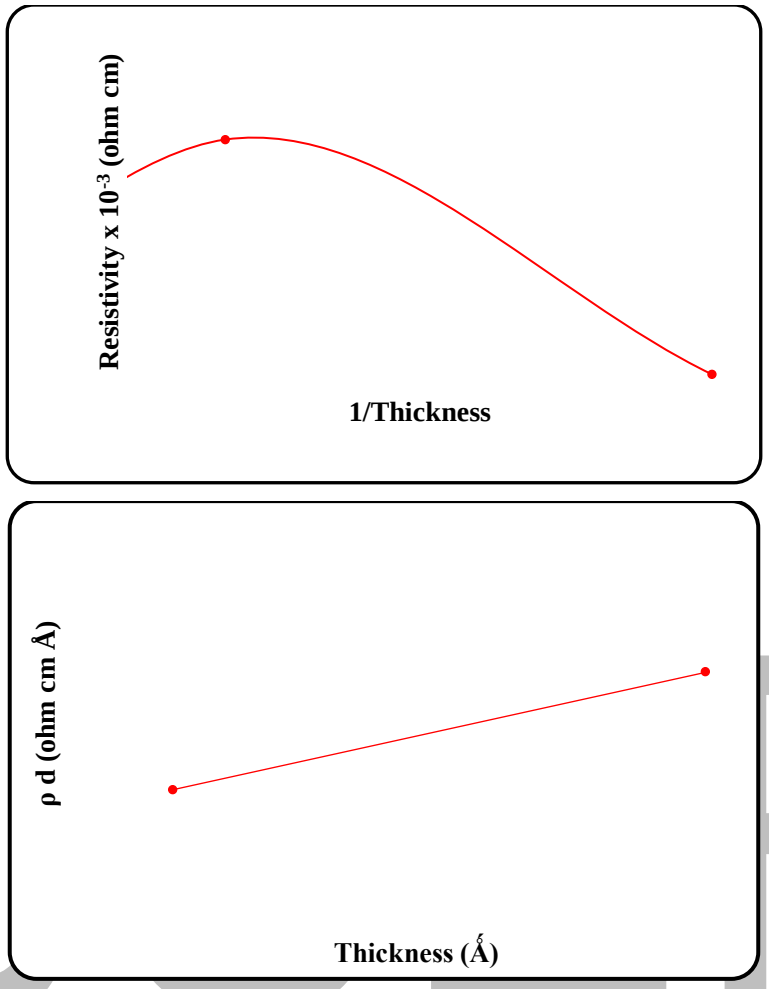


Fig. 4 : a) I-V characteristics of CdSe thin films, b) Plot of resistivity vs. thickness, c) Plot of resistivity vs. 1 / thickness, d) Plot of ρd vs. thickness

Using these values, charge carrier concentration was estimated as n = 4.79 x 10^{12}/cm^3 and mobility was found μ = 2020.2 cm^2/Volt-Sec

Table 2: Estimated parameters of CdSe thin films

Bulk Resistivity ρ_0 (ohm-cm)	5.115 X 10^{-3}
Mean free path λ_0 (Å)	876.89
Carrier Concentration n (/cm^3)	4.79 x 10^{12}
Mobility μ (cm^2/Volt-Sec)	2020.2

The measurement of temperature dependence of electrical resistivity showed that CdSe films always have positive temperature coefficients. The plots of log ρ as a function of reciprocal

of absolute temperature are represented in Fig. 5. The dependence is almost linear indicating the presence of only one type of thermally activated conduction mechanism in the film.

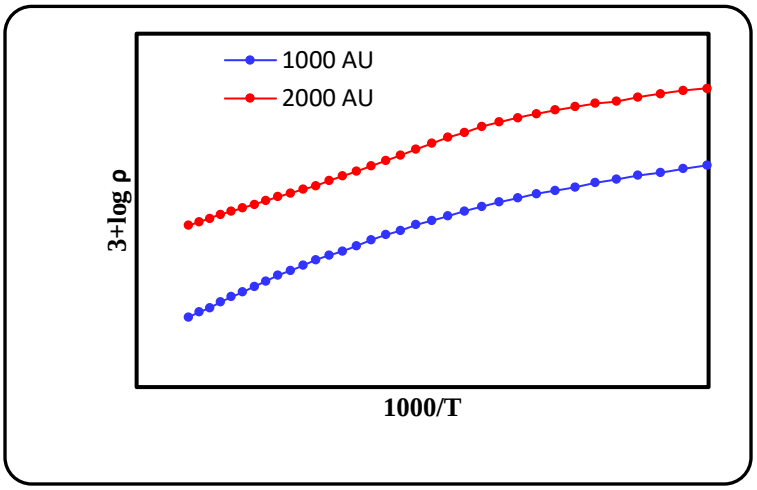


Fig. 5: Plot of log of resistivity vs. reciprocal of temperature

These plots are linear for each thickness. The activation energy is represented in Table 3. The plots follow the relation,

$$\rho = \rho_0 exp\left(\frac{\Delta E}{KT}\right) \quad \ldots\ldots\ldots (8)$$

Table 3: Experimental values of activation energy for CdSe thin films

Thickness(Å)	Activation Energy(eV)
1000	0.305
2000	0.295

Literature review point out that thermionic emission is one of the chief charge transfer mechanisms across grain boundary barriers in polycrystalline semiconductors [24] and if the resistivity of a material reveals Arrhenius activities subsequently thermionic emission is one of the key electrical transport mechanisms [25]. As mentioned to the grain boundary trapping theory, free carriers are trapped by trapping states at the boundary leading to an energy barrier between neighboring grains.

Lower activation energy is apparently due to slightly higher atomic percentage of selenium. Due to lofty reactivity larger atomic percentage of selenium ions would be integrated in composition, which direct to higher conductivity and lower activation energy.

3.5 Thermo Electric Power (TEP) Measurement

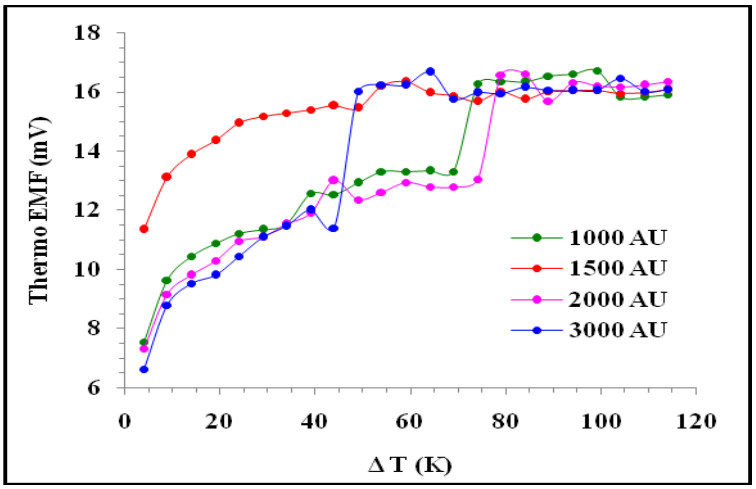
It is renowned that thermoelectric power offers an self-determining method for decisive the Fermi energy, carrier sign, scattering parameter. The thermoelectric effect suggests a typical advantage over other methods since the measured thermoelectric voltage is directly linked to the carrier concentration, which formulate the thermoelectric measurements reliable for low mobility materials.

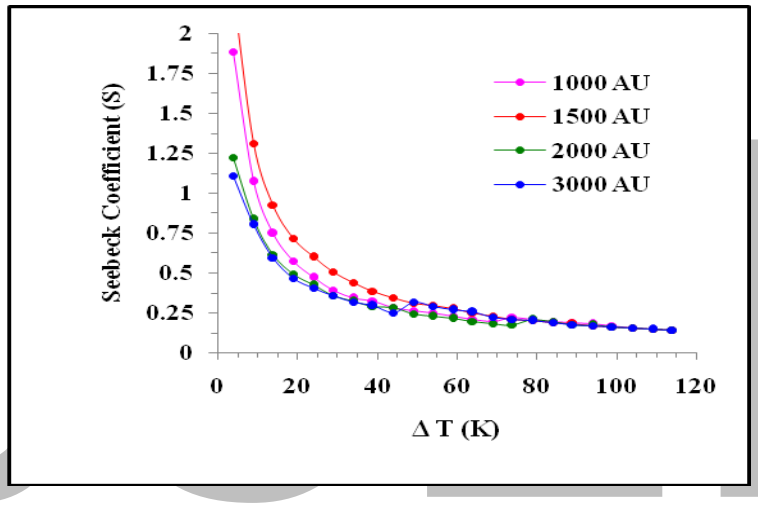
The thermo electric power is measure of magnitude of induced thermo electric voltage acknowledge to the temperature difference across the material as persuade by seebeck effect. The seebeck coefficient can be determined from thermo electric voltage (ΔV) against temperature difference (ΔT) between two terminals.

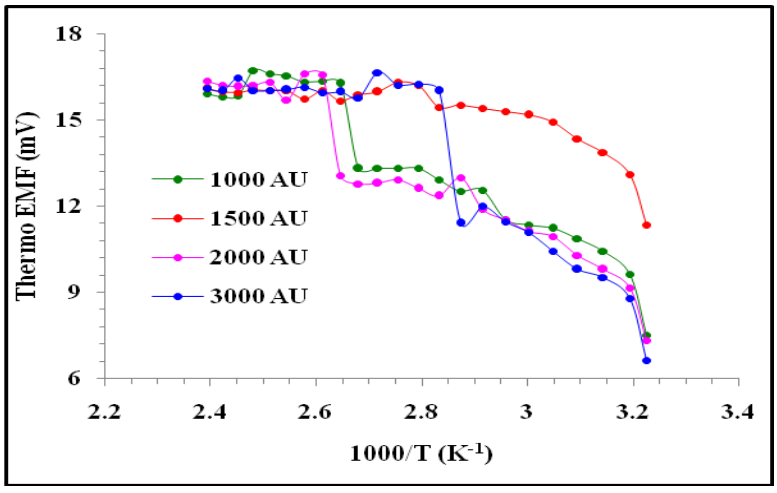
$$S = \frac{-\Delta V}{\Delta T} \quad \ldots (9)$$

Seebeck effect generally conquered by the giving charge carrier diffusion which tend to drive charge carrier towards the cold side of material awaiting the compensating voltage has build up. As result in P type semiconductor S is positive even as for N type semiconductor S is negative.

The pictorial depiction of thermo e. m. f. vs. change in temperature (Seebeck coefficient vs. change in temperature) for various thicknesses (1000-3000Å) of CdSe thin films were revealed in Fig. 6 (a) and Fig. 6 (b) respectively. The pictorial depiction of thermo e. m. f. vs. 1000 / T and Seebeck coefficient versus 1000/ΔT for different thicknesses of thin films were shown in Fig. 6 (c) and Fig. 6 (d) respectively. From these illustration the Fermi energy and absorption coefficient were calculated and signify in Table 4. The Fermi energy of CdSe thin films is thickness reliant. TEP measurement confirms the deposited films are of P type semiconducting in nature. The positive sign of TEP propose that conduction should occur primarily due to holes, which recognized the *p*-nature of the CdSe thin films.


Thermo EMF (mV)
18
16
14
12
10
8
6
0
20
40
60
80
100
120
Δ T (K)
1000 AU
1500 AU
2000 AU
3000 AU


Seebeck Coefficient (S)
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
0
20
40
60
80
100
120
Δ T (K)
1000 AU
1500 AU
2000 AU
3000 AU


Thermo EMF (mV)
18
15
12
9
6
2.2
2.4
2.6
2.8
3
3.2
3.4
1000/T (K-1)
1000 AU
1500 AU
2000 AU
3000 AU

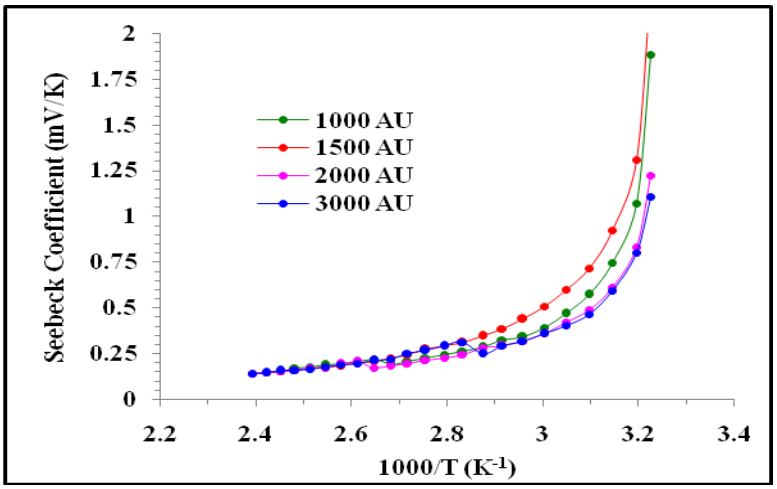


Fig. 6: a) Plot of Thermo e. m. f. vs. ΔT, (b) Plot of Seebeck Coefficient vs. ΔT, (c) Plot of Thermo e.m.f. vs. 1000/T, (d) Plot of Seebeck Coefficient vs. 1000/T

Table 4 : Estimated Parameters from TEP (CdSe thin films)

Thickness(Å)	Fermi Energy (eV)	Absorption Coefficient
1000	0.007	0.115
1500	0.0079	0.325
2000	0.023	0.740
3000	0.035	0. 9015

4. Conclusion

CdSe thin films of different thicknesses have been deposited successfully on glass substrate. XRD studies confirm that the films are highly oriented to [100] direction and they belong to nanocrystalline hexagonal phase. FESEM confirms that films were uniformly deposited over the surface and particles in irregular morphologies in the form of fibrous texture. The electrical properties of the films have been evaluated such as resistivity (5.115 x 10^{-3} ohm-cm), carrier concentration (4.79 x 10^{12} /cm^3), mobility (2020.2 cm^2/Volt-Sec), activation energy (0.295 – 0.305 eV). TEP measurement confirms the deposited films are of P type semiconducting in nature.

5. References

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