# SYNTHESIS AND CHARACTERIZATION OF n-CdSe THIN FILMS DEPOSITED AT DIFFERENT SUBSTRATE TEMPERATURES

S. R. VISHWAKARMA<sup>\*</sup>, ANIL KUMAR, SANT PRASAD<sup>a</sup>, R. S. N. TRIPATHI Department of Physics & Electronics, Dr. R. M. L. Avadh University, Faizabad -224001, India

<sup>a</sup>Department of Applied Science, Institute of Technology & Management, GIDA, Gorakhpur- 273209, India

The n-CdSe thin films of thickness 1000 nm were fabricated on glass substrate at different temperatures by electron beam evaporation technique using optimized source material of composition  $Cd_{0.60}Se_{0.40}$ . The substrate temperature was in the range of 298K to 423K. These thin films were characterized by electrical, optical and structural measurements. The temperature dependent electrical, optical and structural properties are discussed. The X-ray diffraction (XRD) study reveals that for all the films preferred orientation plane was (002). The lattice constant, grain size, strain and dislocation density of the films were calculated and studied their variation with substrate temperature. The scanning electron microscope (SEM) study indicates that grain size increases with increase of substrate temperature. The direct band gap was calculated using absorption coefficient which is measured in the wavelength range 400nm to 700nm and found that the direct band gap varies between 1.48 eV to 1.38 eV with substrate temperature.

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## **1. Introduction**

CdSe is II-VI binary compound semiconductor. The electronic band gap of CdSe is most important parameter which determines the photosensitivity in visible range of electromagnetic spectrum .The high photosensitivity i.e. high absorption coefficient makes them suitable material for thin film photovoltaic device [1]. CdSe is also used in photo conducting, gamma ray detector, optoelectronics,thin film transistor and laser devices [2] due to their excellent electrical, optical and structural properties. The thin film of CdSe exhibits both types of semiconductivity depending upon the type of vacancies created during deposition of thin films.

The electronic behavior of CdSe thin films strongly depends upon method of deposition and source material used for film fabrication by physical evaporation technique in vacuum because of the non-stiochiometry created in film during deposition. The various vacuum and non-vacuum deposition methods have been used to deposit CdSe thin films. In the area of chemical deposition, the spray pyrolysis [3], electrochemical deposition [4], chemical bath deposition [5] and SILAR method [6, 7] have been used to deposit CdSe thin films. The thermal evaporation [8], laser ablation method [9] and electron beam evaporation technique [10] in the area of physical deposition in vacuum have been used to deposit CdSe thin films. The fabrication and characterization of CdSe thin films by different techniques have been studied extensively. Among these, electron beam evaporation technique is one of powerful technique to deposit CdSe thin film, on which very few literatures are available [11-14]. N. J. Suthan Kissijer et. al. [11] have fabricated CdSe thin films on glass substrate at room temperature using CdSe stoichiomertic powder and studied their structural and optical properties only. S. M.Hus et.al. [12] have also

<sup>\*</sup>Corresponding uthor: srvfzb@rediffmail.com

fabricated CdSe thin films on glass substrate at 150°C temperature using CdSe stoichiomertic powder. They studied their electrical, photo-electrical, structural, optical properties and reported ntype semiconductivity of these thin films due to Selenium vacancies or excess of Cadmium. They have reported high resistivity  $(5.9 \times 10^{\circ} \text{ohm.cm})$  of these films. H. M. Ali et. al. [13] have grown undoped and Indium doped CdSe thin films on glass substrate at room temperature using tablets of CdSe and indium doped CdSe and studied the influence of indium doping on structural, optical and electrical transport properties. Due to indium doping in CdSe thin film exhibited n-type semi conductivity. N. J. Suthan Kissijer et. al. [14] have also grown undoped CdSe thin films on glass substrate at different temperatures using CdSe stoichiomertic powder and studied the effect of substrate temperature on the structural and optical properties only. It is observed from the above that only few work have been reported on non-stiochiometry and controlled non-stiochiometry in CdSe thin films, particularly electrical property of CdSe thin films. Therefore, we planned to create controlled amount of non-stiochiometry in CdSe thin films i.e. selenium vacancies or Cadmium rich which is responsible for their n-type semiconductivity. To create controlled amount of non-stiochiometry in n-type CdSe thin film, we have prepared non-stiochiometry source materials and optimized their composition [15-16]. The thickness of n-CdSe thin film has also been optimized [17] and found1000 nm.

In present investigation we have used electron evaporation technique and optimized nonstiochiometry source material ( $Cd_{0.60}Se_{0.40}$ ) for deposition of n-CdSe thin films. Due to high power density and wide range of controlled evaporation, the electron beam evaporation technique is more suitable for the deposition n-CdSe thin films. The evaporent material is directly converted from solid to vapor [13]. During deposition of film, evaporent material is placed in water cooled graphite crucible, so that only its upper surface gets high temperature. Thus, metallurgical reaction between evaporent material and crucible is eliminated. This technique provides economical and efficient use of evaporent material enabling constant rate of deposition.

In present work, n-CdSe thin film of thickness 1000nm has been fabricated by electron beam evaporation technique using optimized non-stiochiometry composition  $(Cd_{0.60}Se_{0.40})$  of source material at different substrate temperatures. Then study the variation of structural, optical and electrical properties with substrate temperature. The deposition temperature is optimized on the basis of the variation of these properties with temperature.

## 2. Experimental technique.

The n-CdSe thin films of thickness 1000 nm were deposited at different substrate temperatures on ultrasonically cleaned glass substrate by electron beam evaporation technique using source material of optimized composition ( $Cd_{0.60}Se_{0.40}$ ). The pressure in vacuum coating unit (H. H. Vacuum Coating Unit-12A4) was kept below 10<sup>-5</sup> torr and films were cooled in same vacuum. The source material was targeted by electron beam emitted from heated tungsten filament. Before strikes, the electron beam is deflected 180° and accelerated at voltage of 2.1kV. The evaporated particles of source materials from the graphite crucible were deposited on glass substrate as thin film. The power of electron beam gun was about 150 watts during deposition of thin films. The substrate was placed at distance of 12.5 cm from the crucible. During deposition of thin film, substrate was placed normal to the line of sight from the evaporation surface at different polar angles to obtain uniform deposition. The source material about 85 mg was used for deposition of each thin film. In each cycle of deposition fresh source material was kept in crucible. The deposition rate and thickness of the film was measured using digital thickness monitor (VICO, DTM-10). During the deposition of the film, the sensor of DTM was attached parallel to substrate. The sensor of DTM is a quartz crystal and vibrating at frequency is of of 6 MHz. The rate of deposition (40-45 Å/s) was kept constant during deposition of films and it is controlled by current and voltage of gun power supply. The substrate temperature was measured using digital temperature meter (PTS-9601: GELCO) attached with thermocouple sensor. The tip of the thermocouple sensor was in contact with the surface of substrate. The different substrate temperatures were obtained by changing the current of substrate heater. The n-CdSe thin films were electrically characterized by measuring resistivity, activation energy and Hall coefficient. The electrical resistivity of the samples was measurement using standard four point probes set up

and the Hall coefficient was measured by Hall set up. These setups are designed by Scientific Equipment and Services, Roorkee, India. The galvanometric measurement has been also used to confirm the type of semi conductivity of the thin films. The optical absorption coefficient of the n-CdSe films was recorded by using double beam UV-VIS spectrophotometer (Model:  $\lambda$ -25, Perkin Elmer) in the wave length range 400-900 nm at ACBR, University of Delhi, Delhi, India. The spectral resolution of the spectrophotometer was 2nm throughout the experiments. The direct and indirect band gaps have been calculated using this absorption coefficient. The structural property of thin films was studied with the help of X-ray diffraction patterns recorded by D-8, Discover XRD-diffractometer (Bruker) using Cu<sub>Ka1</sub> radiation ( $\lambda$ =1.540598Å) with Ni-filter at University of Delhi, Delhi, India. The surface morphology was studied using SEM images observed by scanning electron microscope operated at 20 kV (ZEISS EVO-18) at Department of Physics, I.I.T. New Delhi, India.

# 3. Results and discussion

The n-CdSe thin films fabricated at different substrate temperatures (298K to423K) were characterized by analysis of X-ray diffraction (XRD) patterns. The measured XRD) patterns at diffraction angle (20) from  $20^{\circ}$  to  $70^{\circ}$  for these films are shown in Fig. 1. The (h k l) miller indices for each diffraction peak was calculated from corresponding observed & standard d-values and compared with Joint Committee on Powder Diffraction Standard (JCPDS-00-008-0459) data. The XRD patterns reveal that films were polycrystalline because these have more than one peak. The high intense (002) peak, low intense (100) peak and lower intense (110) peak were identified for CdSe. The peaks of Cd and Se were not observed. The peaks (002) and (100) are corresponding to hexagonal structure. The intensity of (002) peak was increased while intensity of (100) and (110) peak were decreased with increase of the substrate temperature up to 348K. The single high intense (002) peak was observed for n-CdSe thin films deposited at 373K. The intense (002) peak was observed in all films which indicates that (002) plane is preferred orientation. Similar structure and preferred orientation have also been reported by other investigators [11, 12,14] for CdSe thin films fabricated by e-beam technique using stoichiometric CdSe powder. The intensity of (002) peaks was increased with the increase of substrate temperature due to improvement in crystallinity of the films.



Fig. 1. XRD patterns of n-CdSe thin films of different substrate temperature.

The lattice constant (c) of n-CdSe films was calculated using equation (1) [14] and given in table I.

$$c = d\sqrt{h^2 + k^2 + l^2}$$
(1)

where d is inter planar spacing and ( h k l ) is Miller indices.

Table 1.	Substrate tem	perature dep	pendent structura	l parameters d	of n-CdSe thin	films
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Deposition	Plane	Lattice	Grain	$R_c/R_b$	Strain	Dislocation	Lattices
Temperature	(h k l)	spacing	size	Ratio	(ε)X10 <sup>-4</sup>	density	constant
(K)		'd'(nm)	'D'(nm)		(line <sup>-2</sup> m <sup>-</sup>	$(\delta)X10^{15}$	'c'(nm)
		· · · ·	· · · ·		<sup>4</sup> )	$(line m^{-2})$	· · ·
298	002	3.89	138.5	12.37	10.68	5.21	0.773
323	002	3.86	142.3	12.70	10.38	5.92	0.772
348	002	3.87	149.7	13.37	9.39	4.46	0.772
373	002	3.86	153.6	13.71	9.58	4.24	0.772
398	002	3.86	153.6	13.71	10.18	4.80	0.772
423	002	3.86	153.6	13.71	10.28	4.83	0.773

The full width half maxima (FWHM)  $\beta$ , dislocation density  $\delta$ , strain  $\epsilon$  and grain size D were evaluated from diffraction pattern of (002) plane for each film and given in table-I.

The grain size of thin films was calculated using diffractrogramme of n-CdSe thin films and Debye- Scherer's formula [18]

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{2}$$

Where  $\lambda$  is wavelength of X-ray (~1.540698) and  $\theta$  is diffraction angle.

The dislocation density ( $\delta$ ) of n-CdSe films was calculated using Williamson and Smallman's formula [18]

$$\delta = \frac{n}{D^2} \tag{3}$$

Where n is a factor, which equals unity giving minimum dislocation density.

The line strain ( $\epsilon$ ) of the film was calculated by using equation (4) [18]

$$\varepsilon = \beta \cos \frac{\theta}{4} \tag{4}$$

It was observed from XRD patterns that  $\beta$  corresponding to (002) plane was decreased slowly with increase of substrate temperature from 298K to 373K due to improvement of crystallinity in thin films. The XRD patterns also show that crystallites grow for (100) plane was decreased with increase of substrate temperature and diminishes at substrate temperature of 373K.

It was observed from table I that the grain size of crystallite in thin films increases with increase of substrate temperature 298K to 373K and being saturated for other higher temperatures. It was due to increase of growth of crystallite with increase of the substrate temperature. In present investigation, the grain size of n-CdSe film deposited at 373K has been found 153.6nm while other workers reported the grain size of 46 nm [11] and 42 nm [14]. The strain in thin film is defined as the miss arrangement of lattice created during the deposition and depends upon the deposition parameters. In present study, the strain was decreased (10.48 to 9.58)  $\times 10^{-4}$  line<sup>-2</sup> m<sup>-4</sup> with increase of substrate temperature. The lower strain 9.58  $\times 10^{-4}$  line<sup>-2</sup> m<sup>-4</sup> was observed for film deposited at substrate temperature 373K which indicates better lattice arrangement. The strain 12.4  $\times 10^{-4}$  line<sup>-2</sup>  $m^{-4}$  was reported by other worker [14. The dislocation is imperfection in the crystal which is created during growth of the thin film. It was observed in present study that the dislocation density decreases (5.21 to 4.24)  $x10^{13}$  line m<sup>-2</sup> with increase of substrate temperature of film. The minimum dislocation density 4.24  $\times 10^{13}$  line m<sup>-2</sup> has been observed for the film deposited at substrate temperature 373K which was lower than dislocation density reported by other investigators  $77.7 \times 10^{13}$  line m<sup>-2</sup> [11] and  $98.0 \times 10^{13}$  line m<sup>-2</sup> [14]. The lattice constant for each n-CdSe thin film deposited at substrate temperatures (298K to 423K) was found nearly equal i.e. 0.772 to 0.773 nm. The observed lattice constant, in present, study was in agreement with the result 0.703 nm as reported by other worker [11] and standard value of 0.701nm [JCPDS-00-008-0459 data].

SEM images of n-type CdSe thin films deposited at substrate temperatures (298K to 423K) are shown in Fig. 2. It has been found from Fig. 2, that the films were fully covered, homogeneous, well adherent and free from crystal defects such as pin hole and cracks. It was also observed from Fig.2 that the grain size of crystallite increases with increase of substrate temperatures (298K to 373K).



Fig. 2. SEM images of n-CdSe thin films of different substrate temperatures.

The electrical resistivity of n-CdSe thin films fabricated at substrate temperatures (298K to 373K) was measured. The Hall Effect measurement was also carried out for each film. The Hall measurement shows that the behavior of these films was n-type semiconducting. The galvanometric [TEP] measurement was performed for these films. The low temperature end of film shows negative potential with respect to hot end due to the transfer of electron from hot end to cold end, which confirms that films were n- type semiconducting. The variation of resistivity these films with deposition temperatures are shown in Fig. 3. It was observed from Fig. 3 that the resistivity decreases rapidly  $(5.51 - 0.86) \times 10^{-3}$  ohms-cm up to 373K and their after increases slowly for other temperatures. This decrease in resistivity with deposition temperatures (298K-373K) is due to small increase of carrier concentration and large increase of mobility of charge carrier i.e. increase of grain size. The resistivity of films was increased for deposition temperatures 398K to 423K due to decrease in non-stiochiometry in the films. The n-CdSe thin films exhibit ntype semi conductivity because of non-stiochiometry i.e. Se vacancies in thin films. The minimum resistivity of  $0.86 \times 10^{-3}$  ohms-cm has been observed in the present study while other workers have reported 5.85 x10<sup>5</sup> ohms-cm [12] and 0.41 x10<sup>-2</sup> ohms-cm [13]. Fig.4 shows the variation of activation energy with substrate temperatures. Fig. 4 clearly indicates that activation energy decreases (4.87- 4.70) x10<sup>-2</sup> eV slowly with increase of deposition temperatures up to 373K and saturated for other temperatures. The decrease in activation energy with films deposition temperature is due to shifting of donor level towards conduction band. The activation energy,  $4.70 \times 10^{-2}$  eV was observed in present study, while other investigators have reported (0.318eV) [12] and (0.68eV) [13]. The variation of Hall mobility with substrate temperatures is shown in Fig. 5. It was observed from Fig. 5 that the mobility increases with films deposition temperatures up to 373K and saturated for other temperatures. This increase in mobility is due to decrease in grain boundary-scattering of the charge carriers. The grain boundary scattering of charge carriers depends upon crystallite size of grain i.e. high grain boundary scattering occurs for small crystallite size while low grain boundary scattering occurs for large crystallite size. The maximum mobility 985cm<sup>2</sup>/volt-sec was observed for thin film deposited at 373K which corresponds to larger grain size 153.60 nm. The mobility of (80cm<sup>2</sup>/volt-sec) was reported in previous study [19] which may due to small grain size of crystallite. The dependence of carrier concentration in n-CdSe thin films on their deposition temperature is shown in Fig. 6. The carrier concentration increases (2.10-7.38)  $x10^{19}$  cm<sup>-3</sup> with increase of substrate temperatures up to 373K and their after

decreases for other higher deposition temperatures. This increase in carrier concentration is due to small increment in non-stiochiometry in the films created during their deposition. In present study, the carrier concentration of  $7.38 \times 10^{19} \text{ cm}^{-3}$  has been reported while other investigators have reported 1.43  $\times 10^{15} \text{ cm}^{-3}$  [5] 1.70  $\times 10^{18} \text{ cm}^{-3}$  [20] and 1.09  $\times 10^{19} \text{ cm}^{-3}$  [21] for CdSe films deposited by other techniques. But no data's for carrier concentration are available for films fabricated by e-beam.



Fig. 3. Variation of resistivity of n-type CdSe thin films with substrate temperature.



Fig. 4. Variation of activation energy of n-type CdSe thin films with substrate temperature.



*Fig. 5. Variation of carrier concentration of n-type CdSe thin films with substrate temperature.* 



Fig. 6. Variation of Hall mobility of n-type CdSe thin films with substrate temperature.



*Fig. 7. Photon energy vs. square of absorption coefficient of n-CdSe thin films of different substrate temperature.* 



Fig. 8. Photon energy Vs Square root of absorption coefficient of n-CdSe thin films of different substrate temperature.

The optical absorption behaviors of n-CdSe thin films deposited at different substrate temperatures (298K to 423K) are shown in Fig. 7-8. The variation of square of absorption coefficient with photon energy is shown in Fig. 7 and variation of square root of absorption coefficient with photon energy is shown in Fig. 8. From these figures, it was observed that all these films exhibit good optical absorption  $[\alpha_{hv} \approx 10^5]$  in visible range (400nm-900nm) and the absorption increases with increase of substrate temperature due to increase of crystallite size. The bigger size of crystallite reduces the reflectivity of incident photon on the film surface and correspondingly increases absorption due to multiple reflections. The direct energy band gap has obtained by extrapolating the straight portion of the curve of Fig. 7. The intercept portion of  $\alpha_{hv}^{2} = 0$  line gives the value of the direct band gap. It was found that the direct energy band gap of n-CdSe thin films decreases from 1.48 to 1.39eV with increase of substrate temperatures. The direct energy band gap 1.39 eV has been found for film deposited at 373K. This decrease in direct band gap with increase of substrate temperature is due to increase in grain size of film which can be explained on the basis of quantum size effect. The Bohr's diameter for CdSe film is 11.2 nm. It is clear from table I that crystallite diameter to Bohr diameter ratio  $(R_c/R_B)$  is greater than four for CdSe thin films. Hence, weak quantum size effect will be operative [22]. The low direct band gap of 1.39eV was observed in present study while band gap of 1.92eV, 1.71eV, 1.73eV and 1.77eV have been reported by other workers [11-14]. The straight portion of the curve of Fig. 8 was extrapolated and found indirect energy band gap. The indirect band gap also decreases (0.92eV to 0.85eV) with increase of substrate temperature (298K to 423K).

#### 4. Conclusion

From above, we concluded that the improved structural, optical and electrical properties are obtained by use of optimized nonstoichiometric source material for electron beam evaporation technique. The n-CdSe thin films of 1000 nm thickness were deposited by electron beam evaporation technique using optimized nonstoichiometric composition of source material ( $Cd_{0.60}Se_{0.40}$ ) at substrate temperature range (298- 423)K and characterized. The films are found to have preferred orientation along (002) plane. The n-CdSe thin film deposited at substrate temperature range

(298K to 423K) because of the larger grain size 153.6 nm, high carrier concentration  $7.38 \times 10^{19}$  per cm<sup>3</sup>, high mobility 985 cm<sup>2</sup>/volt sec, low strain 9.58 x10<sup>-4</sup> lin<sup>-2</sup>m<sup>-4</sup>, dislocation density 4.24x10<sup>13</sup> line m<sup>-2</sup>, low resistivity  $0.86 \times 10^{-3}$  ohms-cm, small direct band gap 1.39eV and indirect band gap 0.85eV have been obtained for this film.

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## References

- [1] H. Hakan Gurel, Ozden akinci and Ailmi Unlu, Thin solid films 516, 7098 (2008).
- [2] S. Erat, H. Metin and M. Ari, Material chemistry and Physics 111, 114 (2008).
- [3] A. A Yadav M.A. Barote and E.U. Masumdar, Solar Energy 84, 763 (2010).
- [4] A. V. Kotate, U. B. Suryavanshi and C.H. Bhosale, Solar Energy 80, 156 (2006).
- [5] M. Dhanan, Rajeev R. Prabhu and P. K. Manoj, Materials chemistry and Physics 107, 289 (2008).
- [6] Yunus Akathun, M. Ali Yildirim, Aytune Ates and Muhammet Yildirim, Optics communication 284, 2307 (2008).
- [7] H. M. Pathan, B. R. Sankapal, J. D Desai and C. D. Lokhande, Mat. Chem. & Phys. 78, 11 (2002).
- [8] M. A. M. Hasan, Optoelectronics and Advanced Materials-rapid communication 5, 634 (2011).
- [9] G. Parna, V. Capozzi, A. Minafra, M. Pallara and M. Ambica, Eur. Phys. J.B 32 339 (2003).
- [10] K. R. Murali K. Sivaramamoorthy, M. Kottaisamy and A. Asath Bahadur, Physics B 404, 2449 (2009).
- [11] N. J. Suthan Kissinger, M. Jayachandra, K. Perumal and C. Sanjeevi Raja, Bull. Mat. Sci., 30.547 (2007).
- [12] S. M. Hus and P. Parlak, J. Phys. D, Applied Phys. 41, 035405 (2008).
- [13] H. M. Ali and H. A. Abd EI-Ghanny, Phys. Condensed Matter 20, 155205 (2008).
- [14] N. J. Suthan Kissinger, J. Suthagar, B. Saravana Kumar, T. Balasubramaniam, K. Perumal, Acta Physica Polonica A, 118, 623, (2010).
- [15] S. R. Vishwakarma, A. K. Verma, R. S. N Tripathi and Rahul, J. Nano-electronics. Phys. 3, 558 (2011).
- [16] Ravishankar Nath Tripathi, A. K. Verma, Rahul and S. R. Vishwakarma, AIP Conference Proc. 1391, 761 (2011).
- [17] S. R. Vishwakarma, Anil Kumar, Sasmita Das, A. K. Verma R. S. N Tripathi, Chalcogenide Letters 7, 221 (2013).
- [18] K. Girija S. Thirumalairajan and S. M. Mohan, Chalcogenide Letters 6,351 (2009).
- [19] S. A. Mahmoud, A. Ashour and E. A. Badwi, Applied Surface Science 353,2969 (2006)
- [20] S. Velumani, X. Mathew and P. J. Sebastia, Journal of Materials Science Letters 22, 25 (2003).
- [21] K. D. Patel, R. K Shah, D. L. Makhija V. M. Pathak and R. Srivastava, Journal of Ovonic Research 4, 129 (2008).
- [22] Himani Sharma, Sailash N. Sharma, Gurumeet Singh and S. M. Shivaprasad, Physica E 31, 180 (2006).