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STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF THERMALLY EVAPORATED CdSe AND In-DOPED CdSe THIN FILMS

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In this study, semiconducting thin films of undoped and In doped CdSe have been deposited by conventional thermal evaporation technique on cold glass substrates. The structural and electrical properties of the films have been investigated by means of XRD, SEM, temperature dependent electrical conductivity and Hall Effect measurements. X-ray diffraction (XRD) analysis indicated preferential orientation in the (002) direction. XRD and SEM measurements presented an increase of grain size from 26 to 29 nm with In doping. Conductivity measurements showed that In doping causes an increase in conductivity around four orders of magnitude. Information about the band gap of these films has been investigated by means of spectral distribution of photocurrent and absorption measurements. The band gap energies calculated from photoconductivity measurements and compared with results deduced from absorption spectra.

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Keywords: CdSe; Thin films; Thermal evaporation; Doping; Electrical properties

1. Introduction

The II-VI binary semiconducting compounds belonging to the cadmium chalcogenide family (CdS, CdSe and CdTe) are considered to be very important materials for different optoelectronic devices [1,2]. CdSe is a promising photovoltaic material because of its near optimum direct energy gap and high absorption coefficient for the efficient absorption of light and conversion into electrical power. Its interesting properties make the material suitable for many potential applications in a variety of solid state devices such as solar cells, high efficiency thin film transistors, light-emitting diodes, gamma ray detectors, photo anode in photo electrochemical (PEC) cells and electroluminescent devices, etc. [3-5]. The electronic and optical properties of semiconductors are strongly influenced by the doping process. The increase of the doping density causes the broadening of the intra gap, the formation of band tails and band gap renormalization [6-9].

For the preparation of CdSe thin films, different methods have been used such as thermal evaporation technique [1], chemical bath deposition [10], pulsed laser deposition technique [7], electrodeposition [9], molecular beam epitaxy (MBE) [11], spray deposition [12], successive ionic layer adsorption and reaction method (SILAR) [13]. The structural parameters such as lattice constant, grain size, etc. are dependent on the deposition conditions. Structural and transport properties of CdSe thin films is dependent on the rate of deposition, substrate temperature, vacuum conditions, film thickness, preparation technique etc. [1, 14]. Semiconductor devices based on CdSe thin films strongly depend on the structural and optical properties of the films obtained from various experimental conditions [10].

By using different elements, the effects of doping on CdSe films prepared by different methods have been studied extensively. However, doping effect studies on CdSe by thermal evaporation are very limited. In this paper, the structural, morphological, transport and optical

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properties of both In doped and undoped CdSe films prepared by thermal evaporation method have been reported.

2. Material and methods

Thin films of CdSe and CdSe:In having thicknesses around 0.5μm were deposited on chemically and ultrasonically cleaned cold glass substrates with the help of a Vaksis PVD-Handy vacuum coating unit. Sintered CdSe and 1 % In doped CdSe powder were used as the source. Stoichiometric quantities of Cadmium, Selenium and Indium of 4Ns purity were used for synthesis of evaporation source. These elements were loaded to a cleaned crucible, evacuated and sealed. The constituent elements were reacted to synthesize in the constant temperature zone furnace. In order to complete the reaction and homogeneity, the charge was slowly heated up to 1473 K while shaking the crucible and kept at this temperature for 48 h. Evaporation source was obtained by crushing the resulting ingot into powder. Stoichiometric powder was kept in a molybdenum boat. The thickness of the deposited films and the rate of evaporation were controlled by a thickness monitor. A vacuum of 10^{-6} Torr was maintained during the time of deposition with a 20 A^{o}/s deposition rate.

Structural characterization of the films was made by using a Rigaku (SmartLab) X-ray diffractometer. The surface morphology of the films was investigated by means of JEOL (JSM-7600F) scanning electron microscopy (SEM). The temperature-dependent conductivity and Hall Effect measurements were carried out in between 80-360 K by using a Keithley 2400 programmable source-measure unit and Keithley 2700 electrometer equipped with a Keithley 7709 matrix card. The temperature was accurately monitored with a Lake-Shore 320 temperature controller. As the current flows along the layer a magnetic field of 1.2 T was applied perpendicular to the layers for the Hall Effect measurements by using a GMW magnet. Optical absorption measurements were made employing a UNICO SQ 2802 UV/VIS spectrophotometer. Furthermore, for the spectral analysis, an Acton SP2300 monochromator was used and the photocurrent was measured while varying the wavelength from 450 to 800 nm in steps of 5 nm.

3. Results and discussion

Stoichiometries of the CdSe and CdSe:In thin films evaporated on cold substrates were examined with Scanning electron microscope equipped with EDAX unit which are shown in Fig. 1 (a) and (b). It has been found that atomic weight ratios of Cd and Se in the undoped films were around 47.35 % and 52.65 %, respectively, while doped samples had a composition of 47.78 % Cd, 51.32 % Se and 0.90 % In. Composition analysis showed that the samples were slightly selenium rich. From the EDAX spectrum, no impurities were observed in the structure.

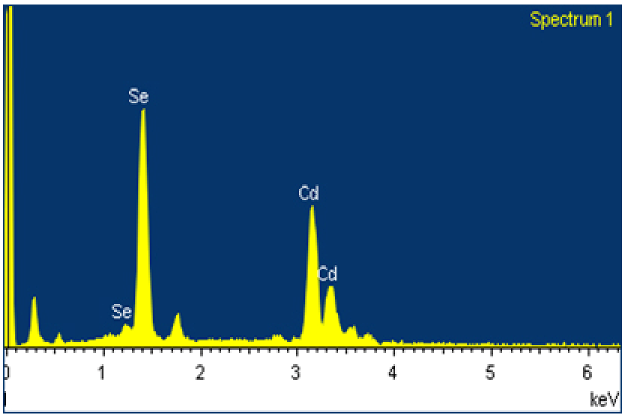

Fig. 1 (a) Typical EDAX pattern of 'as-deposited' CdSe films.

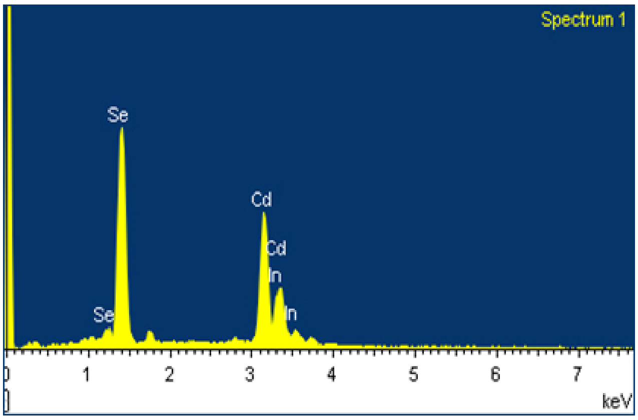

Fig. 1(b) Typical EDAX pattern of 1.0 % In doped CdSe films.

The surface morphology of the films was analyzed using a scanning electron microscope (SEM), which is a convenient technique to study the microstructure of thin films. The surface morphology of undoped and In doped CdSe thin films is shown in Fig. 2 (a) and (b) of magnification 50,000 x. By comparing the micrograph of CdSe and CdSe:In; it is seen that the surfaces are found to be quite similar for both thin films. From the micrograph, it is observed that both undoped and In doped CdSe films are homogeneous, without cracks or holes and covered with uniform spherically shaped grains. The nanosized grains are distributed uniformly over the entire surface of the film which led to the formation of relatively big islands with nearly the same size. The sizes of the grains are found to be in the range between 26 and 29 nm which are in good agreement with the reports Borah et al. [15].

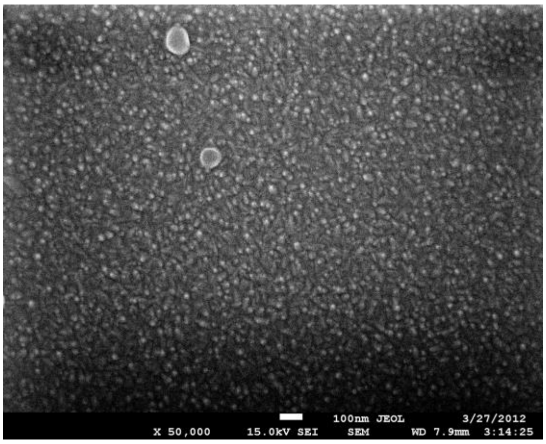

Fig. 2 (a) SEM of 'as-deposited' CdSe film of magnification 50,000 x.

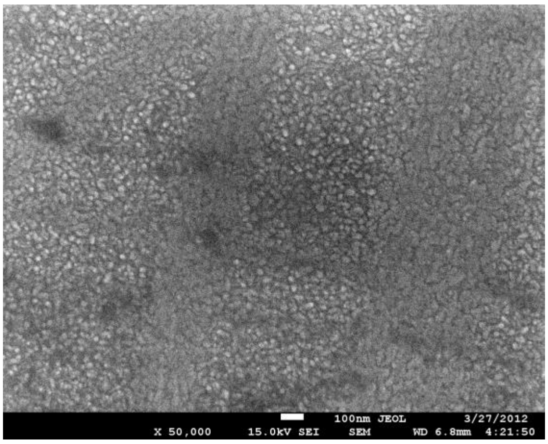

Fig. 2 (b) SEM of 1.0 % In doped CdSe film of magnification 50,000 x.

Fig. 3a and Fig. 3b shows X-ray diffraction pattern of undoped and In doped CdSe thin films, respectively. It is seen that the peak at about 25.4^o is observed for both undoped and doped samples and no major difference is observed in the peak position of the In doped CdSe. This can be attributed to very small percentage of In doping concentration. The orientation corresponding to this value is (002) which is possible only in the hexagonal structure of CdSe. This confirms that the CdSe thin films deposited on glass substrate using thermal evaporation method possess hexagonal structure. Similar results are also reported by other researchers [16, 17].

The crystallite size (*D*) of the films was calculated from the Debye-Scherrer's formula from the full-width at half-maximum (FWHM) β of the peaks expressed in radians [18].

$$D = \frac{k\lambda}{\beta Cos\theta} \tag{1}$$

where, the constant *k* is the shape factor, taken as 0.94, λ is the wavelength of X-rays (1.5406 A^o for CuK$_\alpha$) and θ is the Bragg's angle. The average grain sizes of the deposited films, estimated according to the Debye–Scherrer's relationship are D=26 and 29 nm for the undoped CdSe and CdSe:In samples, respectively. These values calculated from XRD measurements are compatible with SEM pictures. By comparing the XRD spectra Fig. 3a and Fig. 3b, it can be deduced that the peak positions of the In doped sample agree with the undoped one but the sharpness of the (002) CdSe peak increases for the In doped sample results in an increase for the value of crystallinity of CdSe:In thin films. Similar behavior has been reported for the Fe doped CdSe thin films [9]. It is reported that the grain size shows decreasing trend with increasing In percentage due to the increased lattice dislocation leading to an increase of donor sites developed at the nano-grain boundaries. The grain size of In doped CdSe films with In = 25 %, 50 % and 75% has been reported as 29, 24, 20 nm, respectively. [5]. The effects of different doping concentration of In to the CdSe have been reported for CdSe thin films deposited by laser ablation technique. It is reported that while $CdIn_2Se_4$ and InSe compounds are deposited at higher In concentration, at low In density, only the CdSe lattice is present in the deposited film. [8].

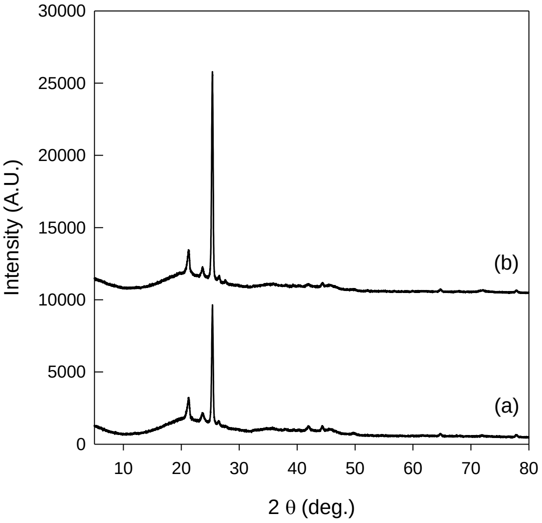

Fig. 3. XRD patterns of: (a) CdSe thin film and (b) 0.1 % In doped CdSe thin film.

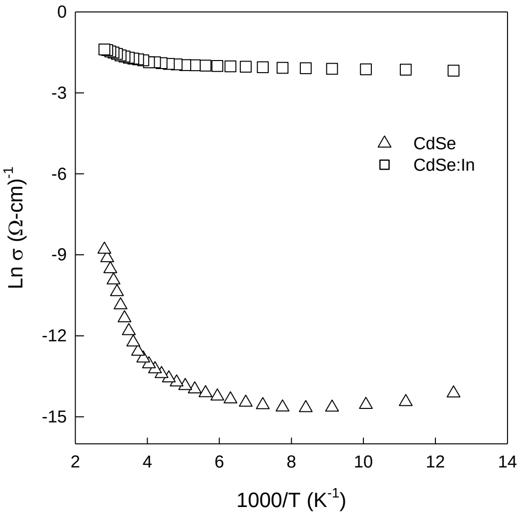

Fig. 4. Temperature dependence of electrical conductivity for undoped and In doped CdSe thin film.

The electrical conductivity of undoped and In doped CdSe thin films were measured under vacuum by the four-probe method of Van der Pauw technique in the temperature range of 80–360 K. Fig. 4 shows the variation of conductivity in logarithmic scale with inverse temperature. It is observed that the conductivity of undoped and In doped CdSe samples increases with increasing temperature, indicating semiconducting nature of the films. As it is seen from Fig. 4, In doping to CdSe causes a sharp increase in conductivity of the samples. It was found that the room temperature electrical resistivity of the undoped CdSe film is 8.44x 10^4 Ω.cm which then decreased to 5.22 Ω.cm after In doping. A similar decrease in resistivity with doping was reported for Ag doped CdSe [19]. The room temperature electrical resistivity was reported as 3.25x 10^5 Ω.cm [20] and 4.00x 10^4 Ω.cm for as-deposited CdSe thin films [21]. The decrease in electrical resistivity after doping may be due to the change in structural parameters, improvement in crystallinity and grain size.

The temperature dependence of the electrical conduction in the whole temperature range was analyzed by using the conductivity expression

$$\sigma = \sigma_o \exp(-E_a / kT) \tag{2}$$

where σ_o is the pre-exponential factor depending on the sample characteristics, E_a denotes the thermal activation energy of electrical conduction and k is the Boltzmann constant. Semiconductors usually show strong increase in conductivity with temperature due to the exponential increase in the number of carriers excited across the band gap, which overwhelms the weaker mobility variation. As seen in Fig. 4, the conductivity of samples is increasing exponentially with increasing temperature in the studied temperature range. Thus, a plot of $ln\ \sigma$ versus 1000/T will be a straight line of slope $-E_a/kT$ and one can find activation energy E_a from the slope. The variation of conductivity with temperature shows three distinct regions for undoped sample and two distinct regions for In doped sample. The activation energies obtained from the slopes are given in Table 1 for all samples. The different values of E_a in different temperature regions indicate the extrinsic nature of conduction. Especially due to the weak conductivity temperature dependence of CdSe:In film in the whole temperature range, Mott calculations for the hopping mechanism in conductivity was also carried out. We find out that calculated parameters does not satisfy the Mott requirements of αR >1, W>k_BT and T_o>10^3 K for the variable range hopping mechanism [22]. Furthermore, we observed that temperature dependence of carrier density is weak over the whole temperature range same as conductivity. This may be due to the degenerate structure of the semiconductor.

Table 1: Summary of the electrical parameters and activation energies of the samples.

Sample	$\rho_{300\ K}$ (Ω-cm)	E_{a1} (meV)	E_{a2} (meV	E_{a3} (meV	$\mu_{H\ 295\ K}$ (Cm^2 V^{-1} s^{-1})	n $_{295\ K}$ (cm^{-3})
CdSe	8.44x 10^4	368	74	11	-	-
CdSe:In	5.22	25	3	-	0.4	3.8x10^{18}

In order to determine the transport parameters, the temperature dependent Hall Effect measurements have been performed by using van der Pauw method. The temperature dependent mobility of undoped CdSe film could not be measured due to the high resistivity of the film. Therefore, Hall Effect measurements were carried out only on the CdSe:In samples whose conductivity is high enough to take reliable data. The sign of Hall-voltage showed that In doped sample is *n* type. The carrier density for CdSe:In film at 295 K symbolized with n is given in Table 1. Fig.5 shows Hall mobility-temperature dependency of the In doped CdSe film. In this figure, the mobility computed from the Hall effect and conductivity data, is plotted as a function of temperature on a Log-Log scale to deduce the dominant scattering mechanism assuming a relation $\mu \alpha T^{\pm\gamma}$, where γ (±3/2) is the temperature exponent. It is seen that in the measured temperature range, the Hall mobility is limited by ionized impurity scattering with γ=1.26. It is known that there are a lot of parameters affecting the transport and optical properties of the films such as deposition methods and growth parameters like rate of deposition and substrate temperature. The Hall mobility around 8 cm^2/V.s was reported at room temperature for vacuum evaporated CdSe films [21]. However, comparing with the reported results by other workers, we may conclude that In doping causes a decrease in mobility.

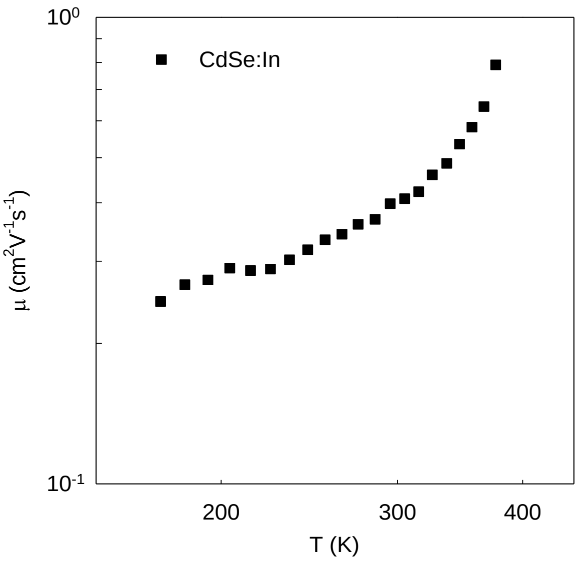

Fig. 5. Mobility-temperature dependence of the CdSe:In sample.

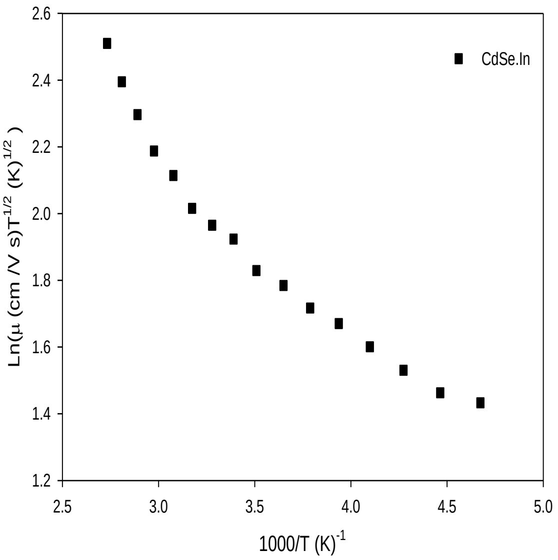

Fig. 6. The variation of ln($\mu T^{1/2}$) as a function of the inverse absolute temperature for In

The analysis of the temperature dependent mobility were performed according to the conduction mechanism of thermionic emission where the effective mobility as a function of potential barrier height at the grain boundary, ϕ_b, may be expressed as [23]

$$\mu = \mu_o T^{-1/2} \exp\left(\frac{-q\phi_b}{kT}\right) \tag{3}$$

The slope of $Ln(\mu T^{1/2})$-1000/T plot (Fig. 6) gives the barrier height. For the In doped CdSe sample, barrier height is calculated to be 45 meV at high temperature region (in 215-365 K).

The optical absorption measurements of thermally evaporated CdSe and CdSe:In thin films have been carried out in the wavelength range 190 nm to 1100 nm at room temperature. In general, the relation between α and the incident photon energy ($h\nu$) can be written as [24]

$$\alpha h\nu = A(h\nu - E_g)^r \tag{4}$$

Where A is a constant, E_g is the band gap of the material, ν is the photon frequency and r is equal to 1/2 for materials with a direct gap and 2 for materials with an indirect gap. The linear nature of the plot indicates the existence of the direct transition. Therefore, from a linear extrapolation to the energy axis of the $(\alpha h\nu)^2$ versus ($h\nu$), we obtain the optical gap values. The direct band gaps of as-deposited CdSe thin films on cold substrate have been determined as 1.91 eV. The direct band gap of bulk CdSe has been reported as 1.70 eV [25]. However, the band gap of CdSe films varies according to the deposition techniques. Depending on the deposition methods, band gap of the CdSe films have been reported in the range of 1.70-2.1 eV [2,26,27]. The band gap deduced from Fig. 7 which exceeds the reported value for bulk CdSe could be related with small grain size resulting quantum confinement of electronic states in the thin films and similar shift to higher energies of the optical band gap was reported for CdSe films [28]. However, our results are comparable with the results obtained earlier on electron beam evaporated [17] and chemical-bath deposited CdSe films [29]. It was observed from Fig. 7 that a slight decrease in the optical gap occurs with In doping and band gap energy was found to be around 1.83 eV. This decrease in the value of band gap may be attributed to the increase in the free carriers with doping and improvement of grain structure of the films which may be due to the segregation of impurity atoms along the grain boundaries and similar behavior has been reported for In and Fe doped CdSe thin films [6,8,9,16,30].

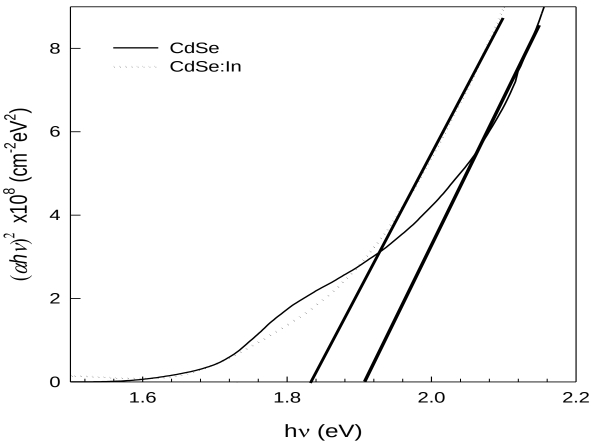

Fig. 7. Optical absorption spectra of undoped and In doped CdSe films.

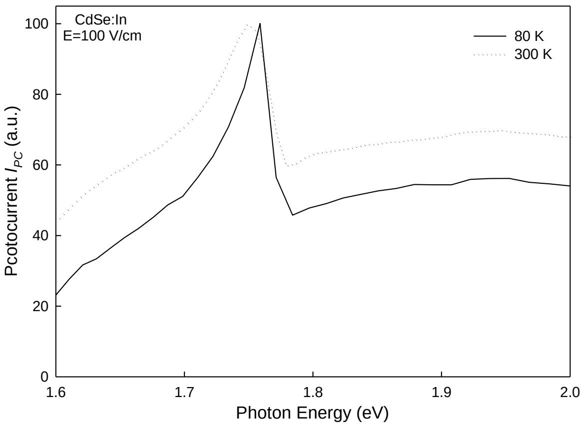

Fig. 8. Spectral distribution of photoconductivity of CdSe:In film.

CdSe films measured at 80 and 300 K, are presented. Similar photoconductivity behavior was observed for undoped samples. The maximum of the photoconductivity shifts towards the shorter photon energies with increasing temperature. The maximum response of PC spectra was obtained at about 1.76 eV at 80 K and 1.75 eV at 300 K. These high energy maxima probably correspond to a band to band transition. The values of energies corresponding to the maxima were smaller than those of deduced from the optical absorption measurements. Similar results have been reported for the CdSe thin films prepared by vacuum evaporation technique. Baban et al. found that the band gap energy (1.53–1.63 eV) calculated by using the Moss rule is smaller than those of determined from absorption spectra [31]. The broadening and asymmetrical band of PC spectrum can be ascribed by the presence of structural defects and impurities.

4. Conclusion

Using thermal evaporation technique, undoped and 1% In doped CdSe thin films were deposited on glass substrates at room temperature. The stoichiometric and homogeneous formations of crystalline grains were observed from SEM micrograph. The X-ray diffractogram showed that the film is polycrystalline in nature with hexagonal phase. The room temperature electrical resistivity decreased from 8.44x 10^4 Ω cm to 5.22 Ω cm after In doping. Hall Effect study showed that all samples were *n*-type semiconductors and the dominant scattering mechanism was mainly due to the ionized impurity scattering. The optical absorption measurements revealed the direct transition band gaps for as-deposited thin films which were found to be 1.91 for CdSe and 1.83 eV for In doped sample. The maximum response of PC spectra was obtained at about 1.75 eV at 300 K corresponding to a band to band transition.

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References

[1] K. D. Patel, M. S. Jani, V. M. Pathak, R. Srivastava, Chalcogenide Letters **6**(6), 279 (2009).
[2] K. Girija. S. Thitumalairajan, S. M. Mohan and J. Chandrasekaran, Chalcogenide Letters **6(**8), 351 (2009).
[3] C. Baban, G.I. Rusu, Applied Surface Science **211**, 6 (2003).
[4] K.R. Murali, K. Srinivasan and D.C. Trivedi, Materials Letters **59**, 15 (2005).
[5] M. G. Syed Ahamed Basheer, K. S. Rajni, V. S. Vidhya, V. Swaminathan, A. Thayumanavan, K. R. Murali, M. Jayachandran, Cryst. Res. Technol. **46**(3), 261 (2011).
[6] T. Mahalingam, R. Mariappan, V.Dhanasekaran, S. M. Mohan, G. Ravi J.P.Chu, Chalcogenide Letters, **7**(12), 669 (2010).
[7] G. Perna, V. Capozzi, M. Ambrico, V. Augelli, T. Ligonzo, A. Minafra, L. Schiavulli M. Pallara, Applied Surface Science **233**, 366 (2004).
[8] G. Perna, V. Capozzi, A. Minafra, M. Pallara, M. Ambrico, Eur. Phys. J. B32, 339 (2003).
[9] S. Thanikaikarasana, K. Sundaram, T. Mahalingam, S. Velumani and Jin-Koo Rhee, Materials Science and Engineering **B174**, 242 (2010).
[10] R. B. Kale, and C. D. Lokhande, Semicond. Sci. Technol. **20**, 1 (2005).
[11] N. Samarth, H. Luo, J. K. Furdyna, S. B. Qadri, Y. R. Lee, A. K. Ramdas, N. Otsuka, Appl. Phys. Lett., **54**(26), 2680 (1989).
[12] A.A. Yadav, E.U. Masumdar, J. of Alloys and Compounds **505**, 787 (2010).
[13] B. Guzeldir, M. Saglam, A. Ates, J. Optoelectronics and advanced materials, **14**(3-4), 224 (2012).
[14] S. M. Hus, M. Parlak, J. of Phys. D-Appl. Phys. **41**(3), 035405 (2008).

[15] M. N. Borah, S. Chaliha, P. C. Sarmah, A. Rahman, Optoelectron. Adv. Materials, **2**(6), 342 (2008).

[16] S.M. Pawar, A.V. Moholkar, K.Y. Rajpure, C.H. Bhosale, Applied Surface Science **253**, 7313 (2007).

[17] N. J. S. Kissenger, M. Jayachandran, K. Perumal and C. Sanjeevi Raja, Bull. Mater. Sci., **30**(6), 547 (2007).

[18] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, MA, 1972.

[19] M. N. Borah, S. Chaliha, P. C. Sarmah and A. Rahman, Ind. J. of Pure&Appl. Phys. **45**, 687 (2007).

[20] R.B. Kale, C.D. Lokhande, Applied Surface Science **223**, 343 (2004).

[21] S.A. Mahmoud, A. Ashour and E.A. Badawi, Applied Surface Science **253**, 2969 (2006).

[22] N.F. Mott, E.A. Davis, Electronic Process in Non-Crystalline Materials, Clarendon Press, Oxford, 1979.

[23] J.Y.W. Seto, J. Appl. Phys. **46**(12), 5247 (1975).

[24] J.I. Pankove, Optical Processes in Semiconductor, Prentice-Hall Inc., London, 1971.

[25] T. Zeng, B. Zhao, S. Zhu, Z. He, B. Chen and Z. Tan, J. of Crys. Growth, **316**, 15 (2011).

[26] T.S. Shyju, S. Anandhi, R. Indirajith and R. Gopalakrishnan, J. of Alloys and Compounds **506**, 892 (2010).

[27] M. G. Syed Basheer Ahamed, A. R. Balu, V. S. Nagarethinam, A. Thayumanavan, K. R. Murali, C. Sanjeeviraja, M. Jayachandran, Cryst. Res. Technol. **45(**4), 387 (2010).

[28] V. M. Garcia, M. T. S. Nair, P. K. Nair and R. A. Zingaro, Semicond. Sci. Technol. **11**, 427 (1996).

[29] H.E. Esparza-Ponce, J. Hernandez-Borja, A. Reyes-Rojas, M. Cervantes-Sanchez, Y.V. Vorobiev, R. Ramirez-Bon, J.F. Perez-Robles and J. Gonzalez-Hernandez, Materials Chemistry and Physics **113**, 824 (2009).

[30] A. M. Perez Gonzalez and I. V. Arreola, Revista Mexicana De Fisica **55**(1), 51 (2009).

[31] C. Baban, M. Caraman, G.I. Rusu, J. Optoelectron. Adv. Mater., **8**, No. 3, 917 (2006).