

Structural, optical, and electrical properties of electron beam evaporated CdSe thin films

M. G. Syed Basheer Ahamed¹, A. R. Balu², V. S. Nagarethinam², A. Thayumanavan², K. R. Murali³, C. Sanjeeviraja⁴, and M. Jayachandran^{*3}

¹ MIET Arts and Science College, Trichy – 620 007, India

² Department of Physics, A.V.V.M Sri Pushpam College, Poondi, India

³ Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi – 630 006, (Council of Scientific and Industrial Research, New Delhi), India

⁴ Department of Physics, Alagappa University, Karaikudi-630 003, India

Received 4 January 2010, revised 8 January 2010, accepted 11 January 2010

Published online 29 January 2010

Key words CdSe, thin films, II-VI, semiconductors.

CdSe films have been deposited on glass substrates at different substrate temperatures between room temperature and 300 °C. The films exhibited hexagonal structure with preferential orientation in the (002) direction. The crystallinity improved and the grain size increased with temperature. Band gap values are found decreasing from about 1.92 eV to 1.77 eV with increase of the substrate temperature. It is observed that the resistivity decreases continuously with temperature. Laser Raman studies show the presence of 2 LO and 3 LO peaks at 416 cm⁻¹ and 625 cm⁻¹ respectively.

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1 Introduction

The II–VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe), are considered to be very important materials for photovoltaic applications [1–3]. CdSe is a promising photovoltaic material because of its high absorption coefficient and nearly optimum band gap energy for the efficient absorption of light and conversion into electrical power [4]. Thin films of CdSe have been also prepared and characterized for their structural, optical and electrical properties [5].

CdSe thin films can be deposited by various techniques such as vacuum evaporation [6], electro-deposition [7], spray pyrolysis [8], thermal evaporation [9], successive ionic layer adsorption and reaction (SILAR) [10] and chemical bath deposition (CBD) [11–13]. Among these methods chemical bath deposition (CBD) has been extensively employed for the deposition of CdSe thin films.

In this work, CdSe films were deposited by the Electron Beam Evaporation (EBE) technique on glass substrates maintained at different temperatures and their structural, optical, electrical, photoluminescence and morphological properties are presented and discussed.

2 Experimental

CdSe films were deposited using Hind Hivac electron beam evaporation unit on glass substrates at different substrate temperatures in the range RT – 300 °C. Substrate temperature was fixed on the basis of the TGA data of the CdSe powder. The films were deposited with 5 kV and 10 mA under a vacuum of 10⁻⁶ Torr. Film thickness was measured by the stylus Profilometer (Mitutoyo). The films were characterized by X-ray diffraction (XRD) studies using CuK α radiation from an X'pert Pro PANalytical XRD unit. Optical studies were made at room temperature using a Hitachi-330 UV-Vis-NIR spectrophotometer. Surface morphology of

* Corresponding author: e-mail: mjayam54@yahoo.com

the films was studied by Nanoscope E-3138j AFM/STM Molecular Imaging system atomic force microscope. The elemental composition was found using an energy-dispersive X-ray (EDX) spectrometer attached with the HITACHI Model S-3000H SEM instrument. Raman studies were made using Renishaw Invia Laser Raman microscope using a 18 mW 633 nm He-Ne laser. PL studies were made using Varian Cary Eclipse Fluorescence Spectrophotometer. Electrical resistivity was evaluated by providing Al contact.

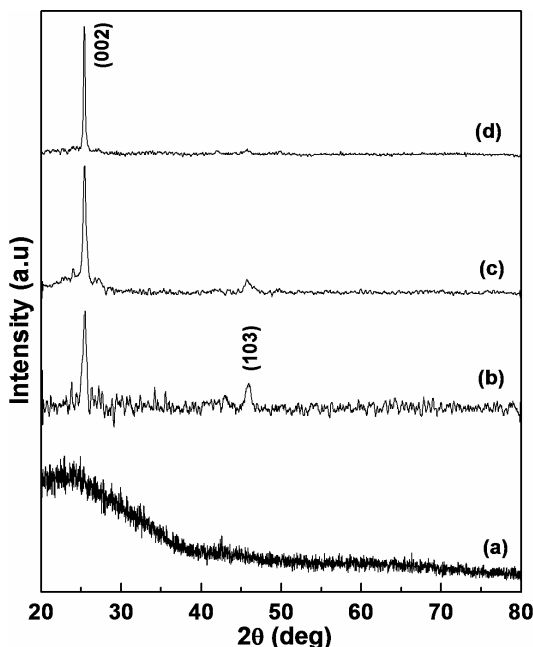


Fig. 1 XRD patterns of CdSe films deposited at different temperatures on glass substrates (a) RT, (b) 100 °C (c) 200 °C and (d) 300 °C.

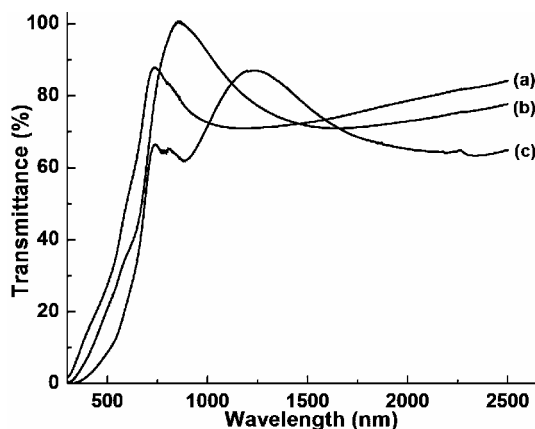


Fig. 2 Transmittance spectra of CdSe films deposited at different substrate temperatures (a) RT, (b) 100 °C and (c) 300 °C.

3 Results and discussion

Figure 1 shows the XRD patterns of CdSe thin films deposited at different temperatures. The spectra revealed mostly single peak corresponding to highly oriented CdSe layers formed by Electron Beam Evaporation (EBE) technique. They also confirm the polycrystalline nature. The CdSe films deposited at various substrate temperatures ranging from room temperature to 300 °C showed only hexagonal structure in the present study. All the films have thickness in the range of 300 nm. A sharp peak is observed mostly in all films close to $2\theta = 25.3^\circ$ corresponding to (002) plane of the hexagonal phase. Another peak commonly observed is at about $2\theta = 45.9^\circ$ with broad and of low intensity corresponding to (103) plane of hexagonal structure (JCPDS 8 – 0459). When the substrate temperature is increased, the films became highly orientated along (002) direction and the other peaks are greatly suppressed. Such results have been observed for the CdSe films deposited by molecular beam epitaxy technique [14].

Table 1 Microstructural parameters of CdSe films deposited at various temperatures.

Temp. (°C)	Lattice spacing d (Å)	Grain size D (nm)	δ ($\times 10^{14}$ lines/m ²)	Strain $\epsilon \times 10^{-3}$	Lattice parameters (nm)	
					a	c
RT	3.491	28	24.6	1.90	0.434	0.699
100	3.493	45	21.2	1.82	0.437	0.699
200	3.497	67	16.4	1.72	0.434	0.698
300	3.499	74	9.2	1.23	0.435	0.697

The effect of substrate temperature on the microstructure of CdSe films are summarized in table 1. The grain size of CdSe can be tuned between 74 nm to 28 nm by varying the substrate temperature. Grain size was

calculated using Scherrer's equation $D = 0.9\lambda / \beta \cos\theta$, where, D is the grain size, λ is the wavelength of x-rays (Cu K α radiation – 1.5443 Å), β is the full width at half maximum and θ is the Bragg Angle.

It is generally observed that strain and dislocation density in the film decreases as the particle size increases which is a well-known phenomenon [15]. Strains are inherent and natural components of nano grained materials. Due to the large number of grain boundaries and the concomitant short distance between them, the intrinsic strains associated with such interfaces are always present in nanophase films. Moreover, the increasing surface energy contributes to the varying magnitude of strain. Similar results have been observed with increase of substrate temperature for vacuum evaporated CdSe films.

The lattice parameters values of the hexagonal structure (planes) are calculated from the following equation $1/d^2 = 4/3a^2(h^2 + hk + k^2) + l^2/c^2$. The values of lattice constants for CdSe films are listed in table 1. It is observed that the lattice parameter values show very close agreement with the standard values. The 'c' values are nearly the same but may be relatively less than the standard value of 0.701 nm for the bulk. The 'a' values are found to be higher than the bulk value of 0.429 nm. The values of dislocation density and lattice strain were calculated using the following relations (Also shown in table 1), Dislocation density (δ) = $15\beta \cos\theta / 4aD$, lattice strain (ϵ) = $\beta \cos\theta / 4$.

The variations in lattice constants with nano grained materials can be attributed to an increased lattice strain. Such strains create local deviation of lattice constants from its bulk value which is size dependent [16]. In the present study, all the deposited CdSe films show reduced 'c' values which indicate that the nano crystallites are experiencing compression in the a-direction. These EB evaporated CdSe films have larger 'a' values indicating the action of tensile strength along c-direction.

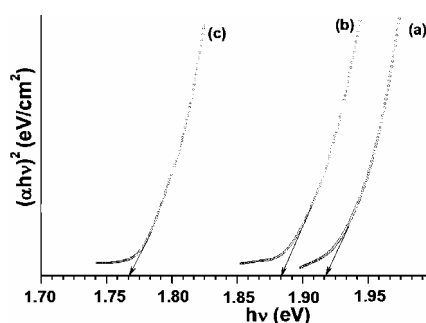


Fig. 3 $(\alpha hv)^2$ vs $h\nu$ plot for the CdSe films deposited at different substrate temperatures (a) RT, (b) 100 °C and (c) 300 °C.

The transmission spectra of the films deposited at different substrate temperatures was studied in the wavelength range 450 to 2500 nm. Figure 2 shows the transmission spectra of the CdSe films. The spectra exhibit interference fringes. The absorption co-efficient (α) was estimated from the transmission spectra. In order to find out the nature of the band gap of the CdSe films, i.e. direct or in-direct band gap, α and $h\nu$ values were used to fit-in with the following equation, $(\alpha hv) = A (h\nu - E_g)^{1/2}$ for direct band gap, where E_g is the band gap of the CdSe films, α is the absorption coefficient, A is the constant and $h\nu$ is the photon energy. The $(\alpha hv)^2$ versus $(h\nu)$ plots (Fig. 3), for all the films deposited on glass substrates, show straight line portions which cut the $h\nu$ axis (x-axis) on extrapolation giving the band gap values. It is observed that all graphs for the films deposited at different substrate temperatures have straight line portions in the high energy region which confirms the direct band gap nature for all the CdSe films prepared by EB evaporation technique here. The value of E_g values are 1.92, 1.88 and 1.77 eV for the CdSe films deposited on glass substrates at RT, 200 and 300 °C respectively. It is observed that the E_g value decreases with increasing substrate temperature. Which, in turn, depend on the increase of grain /particle size of the CdSe films with increasing substrate temperature, such observations have been reported for vacuum evaporated films [17]. A band gap variation in the range of 1.79 – 1.62 eV was observed for the vacuum evaporated CdSe films [18] when the substrate temperature was increased from RT to 200 °C. A decrease of band gap from 2.30 to 1.90 eV was observed when the substrate temperature was increased from 0 °C to 85 °C for chemically deposited CdSe thin films [19]. Band gap decrease from 2.2 to 1.82 eV for deposition temperature of 27 to 47 °C for electrodeposited CdSe films has also been reported [20].

The presence of Cd and Se elements in the evaporated films deposited at different substrate temperatures of RT, 100, 200 and 300 °C were studied by EDAX analysis attached to SEM instrument. The atomic percent (at%) was calculated from the EDAX spectra given in figure 4. All the films are found to be nearly

stoichiometric. A slight excess of Cd in all the CdSe films has been observed. They may act as donor sites in the crystal lattice which provides the n-type conductivity in the EB evaporated CdSe films. The Cd excess may be due to the higher sticking coefficient of Cd compared to that of Selenium.

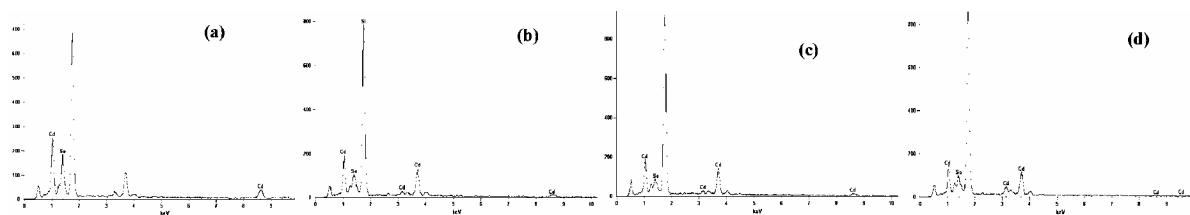


Fig. 4 EDAX spectrum for the CdSe films deposited at different substrate temperatures (a) RT, (b) 100 °C, (c) 200 °C and (d) 300 °C.

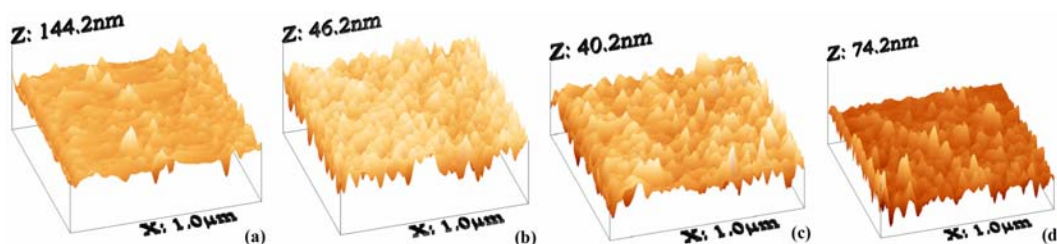


Fig. 5 Three dimensional (3D) topographic AFM images of CdSe films EB evaporated on to glass substrates at (a) RT, (b) 100 °C (c) 200 °C and (d) 300 °C. (Online color at www.crt-journal.org)

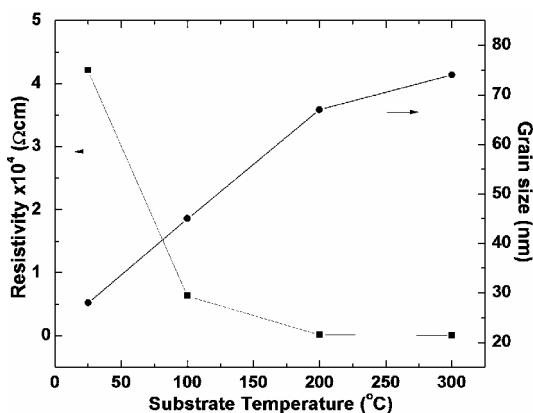


Fig. 6 Variation of resistivity and grain size with substrate temperature.

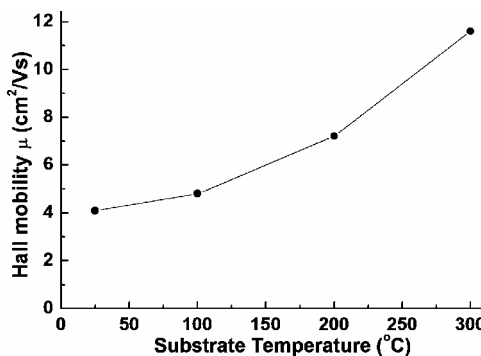


Fig. 7 Hall mobility (μ_H) with different substrate temperature for CdSe films.

Figure 5 shows the three dimensional (3D) topography of these CdSe films which shows very clearly the ups and downs and the presence of pin holes or other defects. Presence of agglomerated crystallines are observed for the films deposited at RT and 300 °C and the films deposited at 100 and 200 °C have uniform dispersion of smaller sized particles throughout the surface with size distribution of 40 – 220 nm. These observations show that CdSe films deposited at 100 °C have the device quality surface which will be suitable for developing photo electrochemical (PEC) solar cells.

From the observation of the direction of current flow and using the hot probe method all the EB evaporation CdSe films, irrespective of the deposition temperature and thickness are found to be n-type. The electrical resistivity values of CdSe films deposited at RT, 100, 200 and 300 °C were measured at room temperature. The values are in the range of 10^4 ohm cm and are three orders lower than the published values of about $1\text{--}3 \times 10^7 \Omega\text{cm}$ [21] for chemical bath deposited CdSe films. Further, it is an obvious fact that the resistance of nanocrystalline thin films and materials is always higher compared to the corresponding larger grained polycrystalline films [22]. Figure 6 shows the variations of the resistivity values with substrate temperature of the CdSe films. The resistivity values decrease from 5.1×10^4 to $0.7 \times 10^4 \Omega\text{cm}$ with increase of

substrate temperature due to increase in particle to particle contact and larger grains at higher substrate temperature. Figure 6 shows the variations of the resistivity values and grain size with substrate temperature of the CdSe films. The resistivity values decrease from 5.1×10^4 to $0.7 \times 10^4 \Omega\text{cm}$ with increase of substrate temperature due to increase in particle to particle contact and larger grains at higher substrate temperatures. A decreasing trend in resistivity is also observed with increasing grain size. The high resistivity value for CdSe films at room temperature is attributed to the presence of fine grains of about (28 nm). The lower value of resistivity measures for the CdSe films deposited at 300 °C is due to the increase in grain size to about 74 nm. The behaviour of the Hall mobility (μ_H) with substrate temperature for CdSe films is shown in figure 7. Mobility values are found to increase with deposition temperature reflecting the influence of increased grain size. The calculated carrier concentration values are nearly constant about $3.6 - 4.5 \times 10^{18} \text{ cm}^{-3}$.

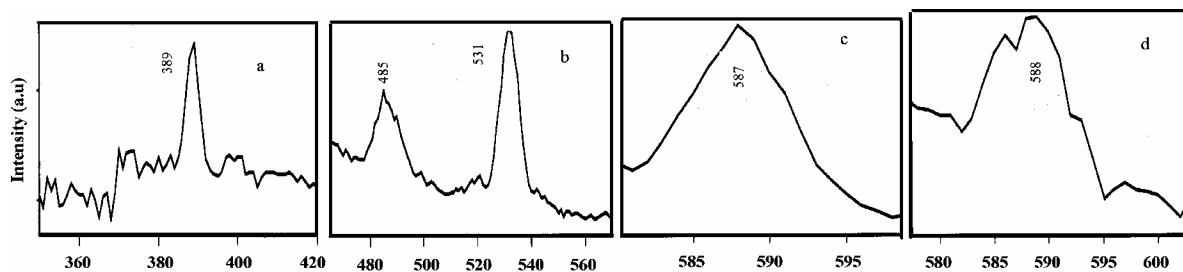


Fig. 8 Room temperature PL spectra of CdSe thin films deposited at different substrate temperatures (a) Excitation spectrum, (b) RT, (c) 100 °C and (d) 200 °C.

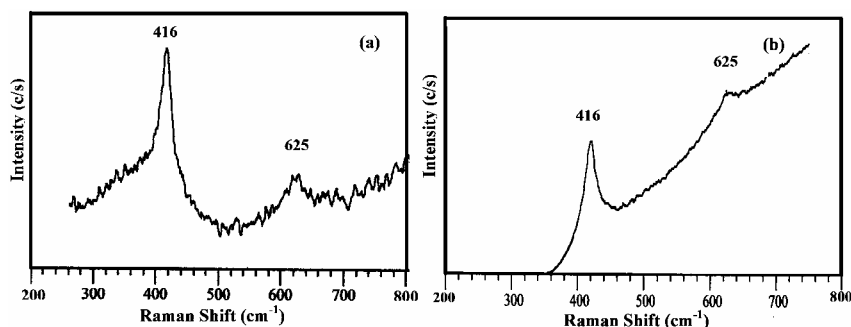


Fig. 9 Raman spectra for the CdSe films deposited on glass substrates at different substrate temperature (a) RT and (b) 300 °C.

The PL spectra of CdSe thin films deposited at RT, 100 and 200 °C are shown in figure 8 respectively which were recorded at room temperature. CdSe films deposited at RT have lower grain size whose PL spectrum (Fig. 8b) shows an intense band in the green region (531 nm) and a less intense in the blue region (485 nm). The CdSe films deposited at 100 and 200 °C have intense green bands at 588 and 589 nm respectively. These results shows that the EB evaporated CdSe films have strong PL in the green region. It can be noticed that a blue shift is observed in the green band as the deposition temperature is decreased from 300 °C to RT. This is associated with the decrease of particle size. The band gap of the RT deposited CdSe film is about 1.92 eV and the emission band values observed in PL studies are very much blue shifted. Such a large stokes shift between the optical absorption spectrum and PL emission band may be attributed to the presence of one deep trapping site and electron hole recombination via trap state or imperfection site (donor here) [23]. Such lattice phenomena are observed in nanomaterials and these results confirm the nano crystalline nature of the EB evaporated CdSe films in the present study. Deep states in nanocrystalline materials are mainly associated with stoichiometric defects, dangling bonds or external ad atoms such as oxygen [24].

Figure 9 shows the Raman spectra for the CdSe films deposited on glass substrates at RT and 300 °C. The Raman spectrum for bulk CdSe is characterized by two peaks, one at 209 cm^{-1} and its overtone at 410 cm^{-1} which are assigned to the longitudinal optical (LO) phonon mode [25,26]. The CdSe thin films, deposited in the present study, show the peak corresponding to the second order (2 LO) and third order LO (3 LO) phonon modes at 416 and 625 cm^{-1} respectively. The first order LO phonon mode at 209 cm^{-1} is not observed. It is reported that the first order LO is observed for CdSe nanoparticles with crystallite sizes below 18.3 nm prepared by chemical route [27]. Further, it is also mentioned that chemically prepared CdSe samples with

bigger nanocrystals show second - order 2 LO phonon band near 420 cm^{-1} followed by a weak peak near 620 cm^{-1} attributed to 3 LO phonon scattering. These results show that our CdSe films should have nanocrystallites in the range greater than 18.0 nm. This is supported by the observed grain size in the range of about 28 – 74 nm.

Further, the full width at half maximum (FWHM) of the CdSe LO phonon peaks are nearly the same for all the films deposited at RT and 300 °C. Except for the reduction in intensity of the peaks with increased substrate temperature, no change in FWHM and no shift in peak values confirm the uniform size distribution of the grains for the EB evaporated CdSe films in our study. Desmica-Frankovic et al. [28] have studied CdSe Quantum dots (QDs) prepared by ion beam synthesis in which films showed a LO peak at 255 cm^{-1} corresponding to Cd – deficiency and formation of selenium clustering in thin CdSe films. This also confirms that we are able to prepare stoichiometric CdSe films without any selenium clustering.

4 Conclusion

CdSe films prepared at various substrate temperatures exhibited electrical resistivities in the range of $10^4\text{ }\Omega\text{cm}$. The films have exhibited hexagonal structure with grain size in the range of 40-220 nm. The band gap value decreased from 1.92 to 1.77 eV with increase of substrate temperature.

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