Chalcogenide Letters Vol. 8, No. 3, March 2011, p. 223 - 229

SYNTHESIS OF CdSe FILMS BY ANNEALING OF Cd/Se BILAYER

MADHAVI THAKURDESAI[a*], NILESH KULKARNI[b], BHAGYASHRI CHALKE[b], AJIT MAHADKAR[b]

[a]*Department of Physics, Birla College , Kalyan - 421 304, India*

[b]*Tata Institute of Fundamental, Research Homi Bhabha Road, Colaba, Mumbai - 400 005*

CdSe thin films are synthesized by depositing Cd/Se bilayer on glass substrates using vacuum evaporation technique. These bilayer films are subsequently annealed in tube furnace at various temperatures in argon atmosphere. Surface modification due to annealing at elevated temperatures is investigated by Scanning Electron Microscopy (SEM). X-ray Diffraction (XRD) studies are carried out for structural analysis of the as-deposited Cd/Se bilayer films and annealed films. In the present investigation, effect of annealing temperature on CdSe phase formation is studied. Effect of annealing on band gap of the bilayer films is studied by UV- VIS absorption spectroscopy.

(Received March 16, 2011; Accepted March 30, 2011)

Keywords: Cadmium Selenide, Vacuum evaporation, SEM,
UV – VIS absorption spectroscopy.

1. Introduction

CdSe is a binary group II-VI semiconductor studied extensively for its wide application in the field of optoelectronic devices, γ ray detector, gas sensors etc. CdSe is used extensively for the development of solid state devices such as high efficiency thin film transistors, Light Emitting Diodes (LED), light amplifier, Liquid Crystal Displays (LCD) etc. CdSe is also a promising photovoltaic material and is popularly used in Photo Electro Chemical (PEC) solar cells. It has been reported that CdSe thin films having large crystallites preferably in hexagonal crystalline phase exhibit high conversion efficiency [1 - 3].

In case of CdSe, preparation conditions strongly influence the material properties thus many techniques such as hot wall deposition technique, molecular beam epitaxy, laser ablation, sputtering, electro deposition, electron beam evaporation, chemical bath deposition etc. are currently employed for the preparation of CdSe thin films [1,4 -7].

In the present investigation, CdSe films are synthesized by depositing Cd/Se bilayer with Cd: Se ratio of 1:1.8 by sequential deposition of 'Se' and 'Cd' on glass substrate at room temperature by vacuum evaporation method. The post deposition heat treatment of the bilayer results in the inter diffusion and reaction between the elements accomplished by the consequent nucleation and growth [8]. The post deposition annealing is expected to affect the grain size and morphology of the film as they are often defined during the film growth period [2,8]. Thus investigation of surface morphology, evolution of film microstructure is important as these parameters affect performance of active devices such as solar cells made from these layers. Therefore in the present investigation, effect of annealing temperature on CdSe phase formation, surface morphology, crystallite size, bandgap etc. are studied.

*Corresponding author: madhavithakurdesai@gmail.com

2. Experimental

a) CdSe film preparation: In the present investigation, Cd/Se bilayer films are prepared by evaporating Se (99.99%) and Cd (99.99%) powder onto glass substrates. Prior to the deposition the glass substrates were cleaned with isopropyl alcohol. The films having total thickness of 280 nm were prepared by depositing 180 nm thick layer of 'Se' followed by 100 nm thick 'Cd' layer. The deposition rate and thickness of the film were controlled and monitored using conventional *in situ* quartz crystal monitor. The post deposition furnace annealing was carried out at 250^{o}C, 300˚C and 350^{o}C in argon atmosphere for two hours at each temperature.

b) CdSe film characterization: The structural characterization of as-deposited and annealed films is carried out by X-ray diffractometer (XRD) using Cu-Kα radiation with λ= 1.5418 A^{0} on a Philips PAN analytical Expert Pro MPD spectrometer. The surface of the films is investigated by Scanning Electron Microscopy (SEM) using JSM 840 Scanning Electron Microscope. Optical characterization is carried out by absorption measurements using UV-VIS double beam spectrophotometer CARY 5000.

3. Results and discussion

3.1 XRD Study: XRD was employed to identify the formation of CdSe phase from elemental layers of Cd and Se. Fig 1 shows XRD spectra of as-deposited Cd/Se bilayer film and annealed films. The XRD pattern of as deposited film shows all the peaks corresponding to Cd. No peak corresponding to Se is seen indicating amorphous nature of Se in the as-deposited Cd/Se bilayer [Fig 1(a)]. The film annealed at 250^{o}C exhibits three peaks at 2θ equal to B_1 (25.43^{0}), B_3 (42.05^{0}) and B_4 (49.71^{0}) corresponding to (002), (110), (112) orientation indicating CdSe phase formation [Fig 1(b)]. However, a peak at 2θ equal to B_2 (31.05˚) indicates presence of Cd in the film along with CdSe phase. This indicates that Cd and Se layer mixing begins at 250^{0}C but can not be completed. Further, the bilayer films are annealed at 300˚C and 350^{o}C temperature. The peak position in the XRD spectra of the film annealed at 300˚C exhibit three peaks at 2θ equal to C_1 (25.43^{0}), C_2 (42.05^{0}), C_3 (49.71^{0}). Similarly the peak position in the XRD spectra of the film annealed at 350˚C exhibit three peaks at 2θ equal to D_1 (25.43^{0}), D_2 (42.05^{0}), D_3 (49.71^{0}). The peak positions in both the films annealed at 300˚C and 350^{o}C indicate polycrystalline nature of the films with pure CdSe hexagonal phase (Wurtzite type) [Fig 1(c), (d)]. The observed peak positions are found to be in good agreement with the standard JCPDS data [9]. Table 1 summarizes the XRD results for all the films.

During thermal annealing, diffusion of one component in a bilayer thin film across the interface increases thereby resulting in intermixing of layers [8] leading to formation of CdSe phase. The peak at 25.43^{0} (002) plane indicates the preferred orientation of crystalline grains along c axis. The increase in peak height in XRD spectra of film annealed at 350˚ C indicate that annealing at elevated temperature improves film crystallinity.

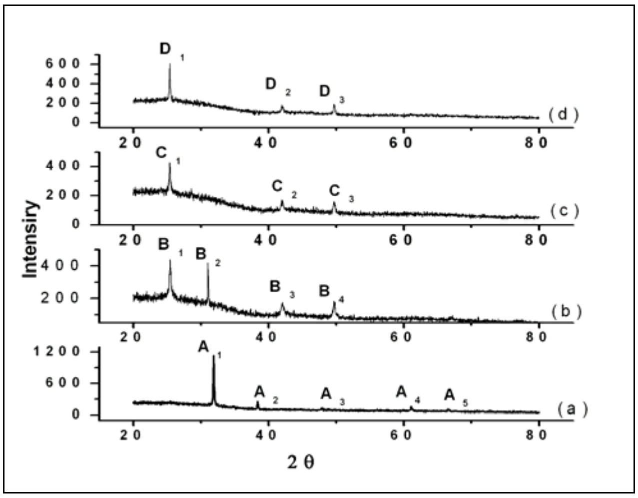


Fig.1. XRD spectrum of Cd/Se bilayer (A) as-deposited (B) annealed at 250°C (C) annealed at 300°C (D) annealed at 350°C

The lattice parameters `a' and `c' for hexagonal structure formed in bilayer films annealed at 300°C and 350°C are determined by the formula [10]

$$1/d^2 = 4/3\ (h^2 + hk + k^2)/\ a^2 + l^2/c^2 \tag{1}$$

The calculated value of lattice parameters
a = 4.256 A° and c = 7.02 A° are in good agreement with the standard values as well as the values reported in literature [11-13]. The'd' values are calculated using Bragg's formula

$$2d \sin\theta = n\lambda \tag{2}$$

Table 1. XRD peaks and corresponding angle of as deposited and annealed CdSe bilayer films

Peak labels	**Peaks**	**angle 2θ^O**
As deposited		
A_1	(002) Cd (H)	31.86
A_2	(101) Cd (H)	38.37
A_3	(102) Cd (H)	47.86
A_4	(103) Cd (H)	61.12
A_5	(004) Cd (H)	66.59
Annealed at 250°C		
B_1	(002) CdSe (H)	25.43
B_2	(002) Cd (H)	31.05
B_3	(110) CdSe (H)	42.05
B_4	(112) CdSe (H)	49.71
Annealed at 300°C		
C_1	(002) CdSe (H)	25.43
C_2	(110) CdSe (H)	42.05
C_3	(112) CdSe (H)	49.71
Annealed at 350° C		
D_1	(002) CdSe (H)	25.37
D_2	(110) CdSe (H)	42.05
D_3	(112) CdSe (H)	49.71

Table 2: Observed and standard values of `d' spacing for all the peaks for annealed CdSe films.

Peaks	2θ	d expt	d std
Annealed at 300° C			
(002) CdSe (H)	25.38	3.5	3.5
(110) CdSe (H)	42.03	2.14	2.15
(112) CdSe (H)	49.71	1.83	1.83
Annealed at 350 °C			
(002) CdSe (H)	25.37	3.5	3.5
(110) CdSe (H)	42.02	2.14	2.14
(112) CdSe (H)	49.71	1.83	1.83

The calculated 'd' values for the films annealed at 300°C and 350°C listed in Table 2 are found to be in good agreement with the standard JCPDS data [9].

The strain and particle size of the film annealed at 300°C and 350°C are calculated from Williamson Hall (W-H) plot [14]. The Williamson Hall equation for the Gaussian fit is given by

$$(\beta^2_{obs} - \beta^2_{inst}) \cos^2\Theta = \varepsilon \, 16 \sin^2 \Theta + \lambda^2 / D^2 \tag{3}$$

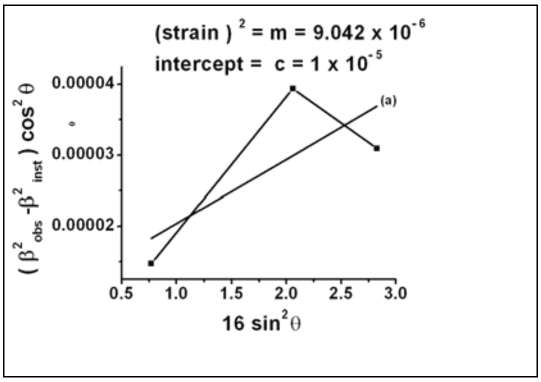
Where 'ε' is strain, 'β' is Full Width Half Maximum (FWHM), 'D' is particle size. The W-H plot is plotted between $(\beta^2_{obs} - \beta^2_{inst}) \cos^2\Theta$ on Y axis and $16 \sin^2 \Theta$ on X axis, where β_{obs} is observed FWHM and β_{inst} is instrumental error taken as 0.05. The line marked as 'a' in the Fig 3(I) and (II) shows straight line fit. The slope of the straight line gives the value of strain and the intercept which is equal to λ^2 / D^2 gives the value of particle size [9].

The dislocation density is calculated from Williamson Smallman relation [15] and are listed in Table3,

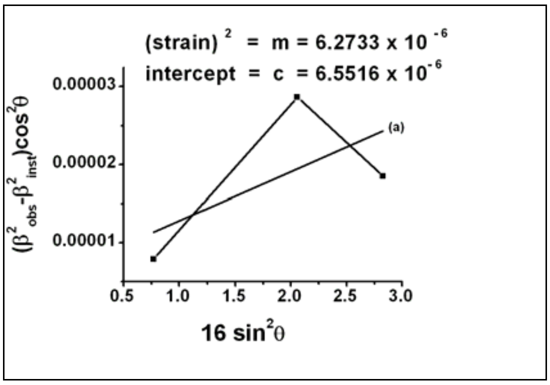
$$\text{Dislocation density } \delta = 1/ D^2 , \tag{4}$$

where 'D' is particle size.

In the present investigation, CdSe phase is formed after annealing of bilayer at 300°C and 350° C. It is observed that the particle size increases with annealing may be due to the aggregation or coalescence of smaller particles at the expense of bigger ones. Increase in particle size after the formation of CdSe phase also suggests the improved crystallinity of the film. In polycrystalline samples, dislocated atoms occupy the regions near the grain boundary. Due to large number of grain boundaries and the short distance between them, the intrinsic strains are always associated with such interface. Annealing allows atoms to diffuse more easily to find their proper location. When inter layer mixing takes place as a result of annealing, surface energy increases and a state of equilibrium may be achieved causing reduction in strain after annealing at elevated temperature [11] as observed from the values listed in table 3.



(I)



(II)

Fig. 2. W-H plot for CdSe bilayer film (I) annealed at 300 ˚C (II) annealed at 350 ˚C

Table 3. : Structural parameters of as- deposited and annealed CdSe bilayer films

Film description	**Particle size (nm)**	**Strain x 10^{-3} lines^{-2} m^{-4}**	**Dislocation density x 10^{14} lines/m^2**
Annealed at 300 ˚C	48	3.0	4.3
Annealed at 350 ˚C	60	2.5	2.77

3.2 SEM study: Fig 4 shows the SEM micrographs of as-deposited and annealed films at 5µm magnification. The surface of as-deposited film shows granules of irregular shape (Fig 3a). The surface morphology slightly changes after annealing at 300˚C and granules merge into each other (Fig 3b). Further annealing at 350˚C does not cause any change in surface morphology (Fig 3c) indicating surface features once formed does not respond to change in temperature.

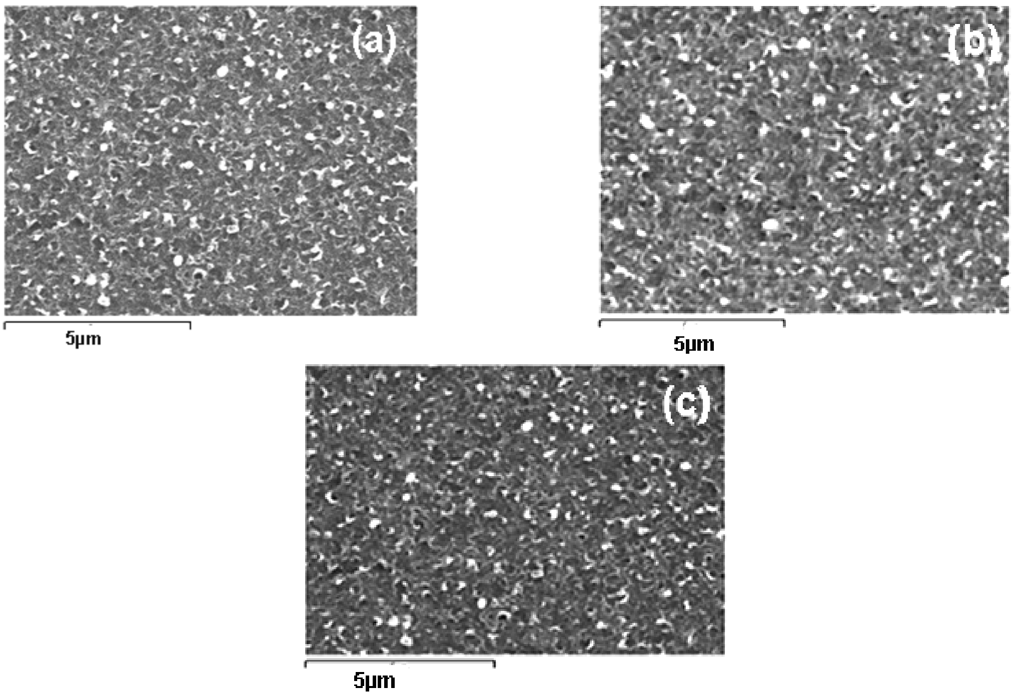
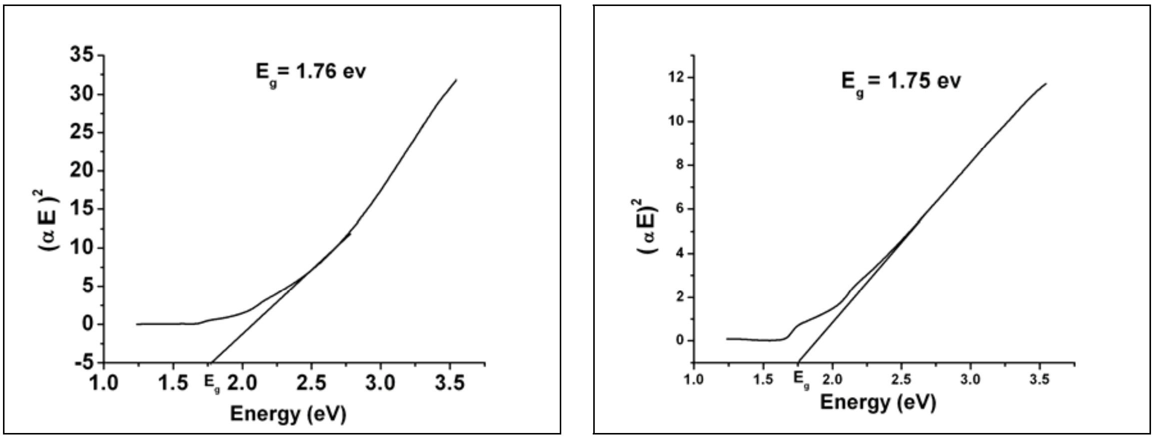


Fig.3 : (a) 5µm SEM micrograph of Cd/Se bilayer as-deposited (b) 5µm SEM micrograph of Cd/Se bilayer annealed at 300^{o}C (c) 5µm SEM micrograph of Cd/Se bilayer annealed at 350^{o}C

3.3 UV-VIS absorption spectroscopy study: UV-VIS absorption spectroscopy is carried out to estimate the band gap of the bilayer films. As CdSe is a direct band gap semiconductor, the band gap is calculated by plotting $(\alpha E)^2$ (α is absorption coefficient) on Y axis and 'E' on X axis for all the films. The straight-line portion of the graph extrapolated to cut the x-axis, gives the energy gap [16]. The band gap of both the annealed film annealed at 300˚C and 350˚C is found to be 1.75 eV and 1.76 eV indicating formation of CdSe phase (Fig 4a and 4b). The observed band gap is in good agreement with the value of bulk CdSe band gap value reported in literature. It is observed that for the annealed films once the CdSe phase is formed at annealing temperature of 300˚ C further increase in temperature slightly changes the band gap.



(I) **(II)**

Fig. 4 Band gap plot of Cd/Se bilayer film (I) annealed at 300° C (II) annealed at 350° C

4. Conclusions

Present investigation shows that CdSe thin films can be prepared by sequential deposition of Se and Cd bilayer by thermal evaporation method followed by furnace annealing. The Cd/Se bilayer annealed at 300˚C results in formation of hexagonal CdSe phase with the preferential orientation in (002) direction along c axis. Further annealing at 350 ˚C does not cause any phase change. The Band gap of both the annealed CdSe bilayer film is found to be ~ 1.75eV and is independent of temperature change. SEM studies indicate that the surface features once formed as a result of annealing, does not respond to further change in temperature. The XRD, SEM and UV VIS absorption spectroscopy results indicate that once the CdSe phase is formed at 300˚C, further increase in temperature does not affect the structure, surface morphology and band gap of the film.

Acknowledgements

Authors are thankful to Mr. Meghan Patankar, TIFR, Mumbai for his help in carrying out UV-VIS absorption spectroscopy.

References

[1] N. Kissinger, M.Jayachandran, K. Perumal and C Sanjeevi Raja, Bull. Mater. Sci. **30,** 547 (2007)
[2] R. Kale and C. Lokhande, J. Phys. Chem., B **109,** 20288 (2005)

[3] K Girija, S. Thirumalairajan, S.M.Mohan, J.Chandrasekaran, Chalcogenides Letters, **6,** 351 (2009)
[4] S.Velumani, K.Narayandas, D.Mangalraj, J.Sebestian and X .Mathew, Sol. Energy Mater. And Sol. Cells, **81,** 328 (2004)
[5] H.Loo, N.samarth, C. Zang, A.Pareek, M. Dobrowolska and K.Furdyna, Appl. Phys. Lett , **58,** 1783 (1991)
[6] C.Baban, G.G.Rusu, I.Nicolaescu and G.I. Rusu , J. Phys.:Condens.Matter **12,** 7687 (2000)
[7] K.Murali, V.Subramanian, N.Rangarajan, A.Lakshmanan, S.Rangarajan, J. Electroanal. Chem. **95,** 368 (1995)
[8] K .Bhahada, B Tripathi, N.Acharya, P. Kulriya, Y.Vijay, Chalcogenides Letters , **5** 137 (2008)
[9] JCPDS X-ray powder file data
[10] A. Sakthivelu, V.Saravasan, M.Anusuya, J. Joseph Prince , J. of Ovonic Research, 7 **1 (**2011)
[11] P.Hankare, V.Bhuse, K.Garadkar, S.Delekar and I.Mulla, Semicond. Sci. Technol. **19** 70 (2004)
[12] K Sarmah, R.Sarma, H. Das, Chalcogenides Letters **5** 153 (2008)
[13] K.Sarmah, R.Sarma , H.L Das, J. of Non-Oxides Glasses **1,** 143 (2009)
[14] P. Karen & P.M. Woodward, J. Solid State Chem,. **141**, 78 (1998)
[15] G.B. Williamson, R.C. Smallman, Philos. Mag. **1,** 34 (1956)
[16] D. Patidar, K. Rathore, N. Saxena, Kananbala Sharma, T. P. Sharma Chalcogenide Letters, **5,** 21 (2008)