Synthesis and Characterization of Nanostructured Vacuum Evaporated Bi Doped CdSe Thin Films

V. T. Patil[1], R. R. Attarde[2], Y. R. Toda[3], D. N. Gujarathi[3], D. J. Garole[4]

[1]Department of Physics, Arts, Science and Commerce College Chopda (M. S.), India
[2]Department of Physics, M. J. College, Jalgaon-425001, India
[3]Thin Film Research Laboratory, Department of Physics, Pratap College, Amalner (M.S.) India
[4]Directorate of Geology and Mining, Government of Maharashtra, Nagpur-440010, India

***Abstract:** Nano structured thin films having different thickness of bismuth CdSe were deposited by thermal evaporation techniques, onto precleaned amorphous glass substrate at room temperature. The structural properties of films were evaluated by XRD, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The quantitative analysis was done by Energy Dispersive Analysis for X – Ray to determine atomic % of the material used. The optical band gaps of the films were measured by using optical absorption spectra. The X-ray diffraction analysis confirms that films are polycrystalline in nature having hexagonal structure with a preferential orientation along the (002 and 101) plane. The degree of such a preferred orientation was found to increase with increase in concentration of bismuth. The lattice parameters (a = 4.3777 &c = 6.8648 Å) and crystallite size (D) were calculated and found to be 82.1 nm. Unit cell volume is found to be 113.929.SEM investigation confirms that films were uniformly deposited over the surface and particles were granular in nature. The particle size was determined by using SEM and found to be 10.1 – 13.2 nm. It is found that bismuth doped CdSe is direct band gap material having value of 1.7 – 2.2eV. The PL spectrum shows peaks in the infra red region, the bands at 825 and 970 nm are due to a defect complex incorporating V_{Cd}^{2-} and Bi_{Cd}^{+}. Such a complex was revealed in studies of photo electric properties of CdSe (Bi).*

***Keywords:** Optical band gap, thermal evaporation, XRD, SEM, AFM, EDAX, PL.*

I. Introduction

CdSe, a direct band gap material II-VI semiconductor with band gap energy of 1.74 eV, has long been found as promising material for optoelectronic devices such as solar cells, high efficiency thin-film transistors, electron-beam pumped lasers, LED, electroluminescent devices, etc [1-5]. In addition, CdSe has large absorption coefficient to visible light. This property is useful for good theoretical conversion efficiency and has led to the investigations for obtaining efficient solar cells. The electrical and optical properties of CdSe crystals doped with antimony or bismuth were studied earlier [6 – 9]. Group V elements were found to substitute for Cd, acting as donors. However these properties have not yet been studied in sufficient details. For instance, no data have been reported on the luminescent behavior of bismuth doped CdSe thin films.

In this work we focus on the effect of bismuth concentration on the structural, optical and luminescent properties of thermally evaporated Bi doped CdSe thin films. Structural parameters such as grain size measured from XRD spectra are found to depend on the film thickness. The details have been reported in this paper.

II. Experimental

Polycrystalline Bi doped CdSe films have been deposited by thermal evaporation technique under vacuum of about 10^{-5}torr onto precleaned amorphous glass substrate. The substrate to source distance was kept 15 cm. The samples of different thicknesses and concentrations 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. Further confirmation of thickness was estimated by Tolansky's method using multiple beam Fizeau fringes [10]. The deposition rate was maintained 5-10 Å/sec throughout sample preparation. Before evaporation, the glass substrates were cleaned thoroughly using concentrated chromic acid, detergent, isopropyl alcohol and distilled water.

X – Ray diffractograms (Bruker, Germany) were obtained 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 (CuK$_\alpha$ line). Surface morphological studies of the thermally deposited Bi doped CdSe thin films were done using the Scanning Electron Microscope (Zeiss EVO 50) operating with an accelerating voltage 10 KV and Atomic Force Microscopy (AFM). The quantitative compositional analysis of the Bi doped CdSe films were carried out by EDAX (Energy dispersive X-ray Analyzer) technique attached with the SEM. Optical absorption

was measured by UV-VIS spectrophotometer model no. Shimadzu-2450.The Photoluminescence spectra were recorded at RT using a set up Perkin Elmer FL – 50.

III. Results And Discussions

XRD characterization

Fig. 1 shows the XRD pattern of Bi doped CdSe thin film prepared at substrate temperature of 303K. The 2θ peak observed at 24.25^0, 26.5^0, 41^0, 42^0, 46.25^0, $50.40^0$and 51.50^0exhibit the formation of the hexagonal phase of Bi doped CdSe which correspond to the (100), (002, 101), (110), (110), (103), (201) and (201) planes of reflections. The presence of large number of peaks indicates that the films are polycrystalline in nature. It can be seen that the Bi concentration strongly affects the XRD pattern. It is observed that Bi peak intensity increases with increasing Bi concentration and decreases CdSe peak intensity. As the Bi concentration increases, the (002) diffraction peak becomes more and more dominant.

The average grain size is evaluated by well known Scherrer's formula and found to be 82.1nm well agrees with already reported [12] and JCPDS data for CdS (47 – 1179).

$$d = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where, λ the wavelength of X-ray used ($\lambda = 1.54060$Å), β is full width at half maxima (29.807^0).

The lattice parameters a and c in the prepared thin films have been determined as 4.3777 and 6.8648 Å respectively and are in good agreement with the values listed by the American society for testing materials (ASTM).
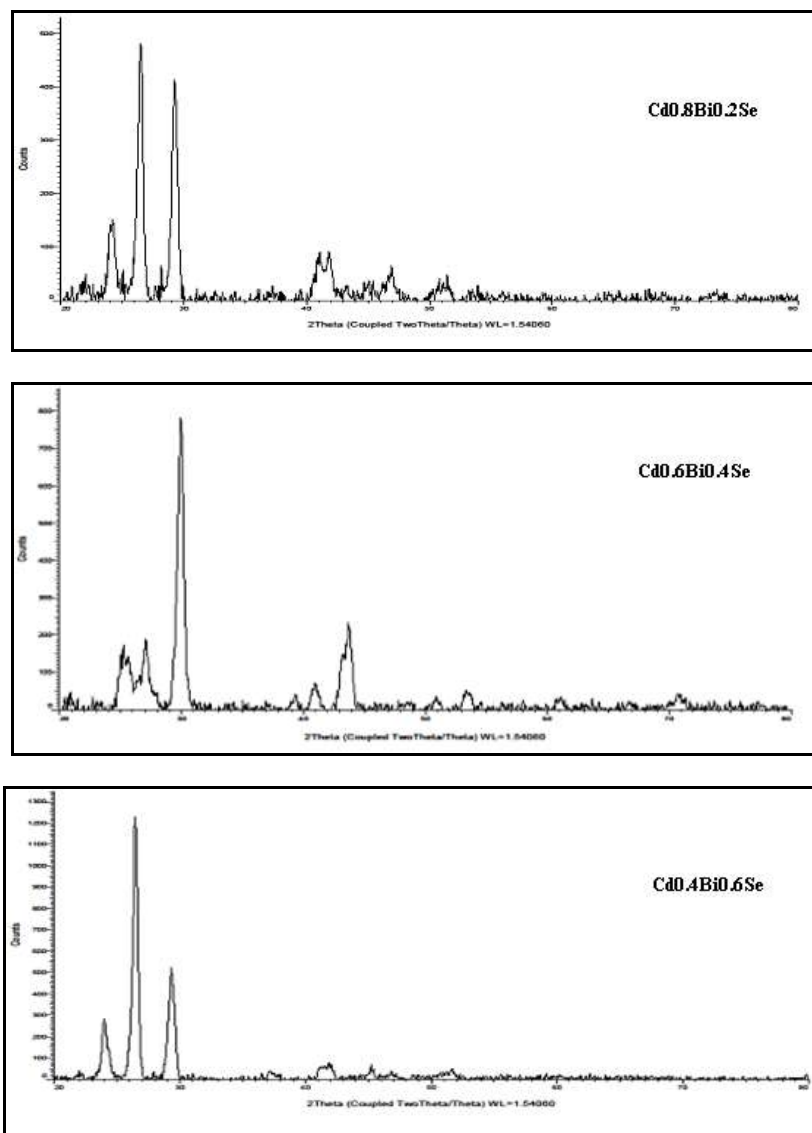

**Figure 1:** X-ray diffractograms of Bi doped CdSe thin films

SEM Studies

The SEM image of CdSe (Fig. 2 a) thin film shows that the film is uniform, polycrystalline, well cover on glass slide and free from microscopy defect like cracks or peeling. Nano size grains were uniformly distributed over smooth homogeneous background. The particle sizes were found to be 12-20 nm.SEM images of Bi doped CdSe for various concentrations (0.2, 0.4, and 0.6) (Fig. 2 b - d) thin film of thickness 2000Å with magnifications 100K. The SEM images shows that the film is uniform that is grains are uniformly distributed, polycrystalline and well cover on glass slide and free from microscopic defect like cracks or peeling. Nano size grains were uniformly distributed over smooth homogeneous background although there is some difference in grain size. The particle sizes were found to be 20.7–26.4nm. The size of clusters was found approximately 12.6nm to 19.9 nm
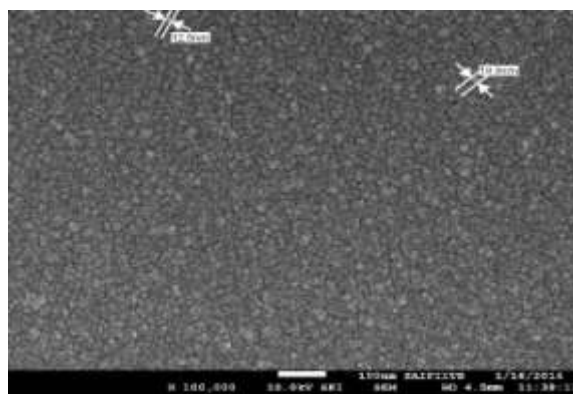
SEM images of Bi_2Se_3 thin film of thickness 2000Å with magnification 120K (Fig. 3). At low resolution the surface morphology is look like texture but as resolution increases the small grains are found. In higher resolution the nano rod are clearly seen. The small gains in Figure are the tips of nano rod seen in Fig. It is clear that these nano rods are uniformly distributed over smooth substrate. The particle size was fund to be in the range of 6.88 nm to 10.86 nm. The grain size calculated by SEM is slightly greater than the values of grain calculated by XRD. These values are in close agreement with other.
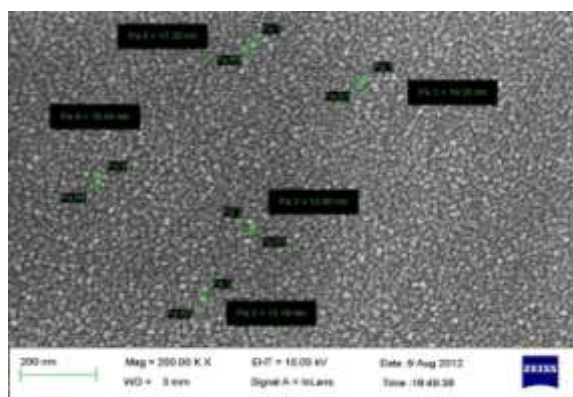
Figure 2 a: SEM image of CdSe thin film
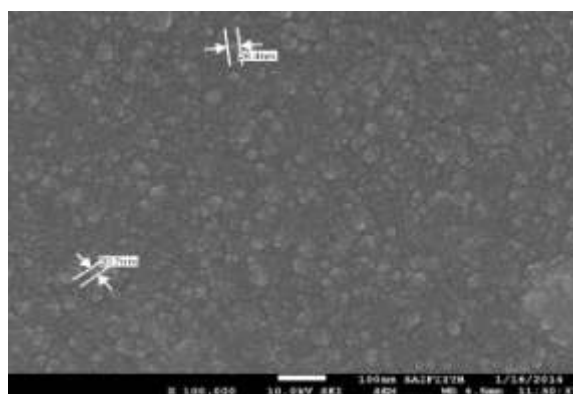
Figure 2 b: SEM image of Bi doped CdSe thin film (0.2)

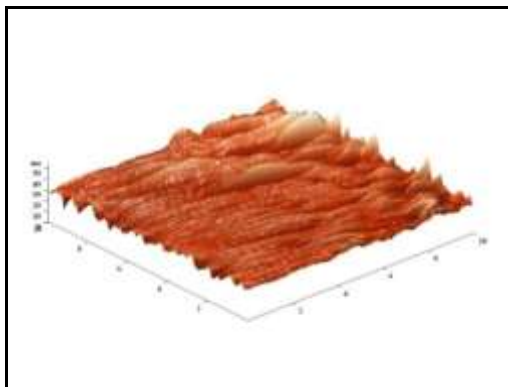**Figure 2 c:** SEM image of Bi doped CdSe thin film (0.4)

Figure 2 d: SEM image of Bi doped CdSe thin film (0.6)

Figure 3: SEM image of Bi_2Se_3 thin film

EDAX studies

The elemental analysis of Bi, Cd and Se has been carried out EDAX in the binding energy region between 0 to 9 KeV shown in Figure - 4. This spectra shows the excepted elements detected. The spectrum peak reveals presence of Bi, Cd and Se at 1.4 and 3.5KeV which confirms the presence of Bi, Cd and Se. Also there was no evidence for the appreciable amounts of impurities. The atomic percentage of Bi, Cd and Se were found to be 26.08%, 2.32 % and 71.60% respectively.

Figure 4: EDAX spectrums of CdSe (Bi)

Atomic Force Microscope studies (AFM)

Figure 5 and figure 6 show AFM 3D and 2D images respectively. The image shows well defined particle's somewhat elongated/granular morphology. Surface of the image is found to be homogeneous without any void and crack. In Bi doped CdSe films particles are agglomerated that led to the formation of islands of different sizes. The roughness of the film surface is small and found to be 12.5nm. The Bi doped CdSe films deposited at RT show the most uniform surface with minimum surface average roughness value. These observations show that CdSe (Bi) films deposited at RT have the device quality surface which will be suitable for developing solar cells.

Figure 5: AFM 3-D image of CdSe (Bi) film

Figure 6: AFM 2D view of CdSe (Bi) film

Optical Properties

The optical absorption spectra were obtained in the 200 nm – 900 nm wavelength ranges by employing a Shimadzu 2450 UV-Visible model of the spectrophotometer.

The optical band gap of these films has been calculated using the relation (Tauc 1974).

$$(\alpha\, h\, \upsilon)^2 = A \left(h\, \upsilon - E_g \right)^n$$

Where, $h\upsilon$ is the photon energy, α is the absorption coefficient, E_g the band gap, A is constant and, n = 0.5 for direct band gap material, n = 2 for indirect band gap material.

The plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for these CdSe films is presented in figure - 7 (a, b). This figure clearly shows the linear dependence for the value of P=1/2. This is attributed to an allowed and direct transition with direct band gap energies. The observed trend at absorption edge towards lower photon energies for the increasing film thickness could be attributed to the change in the grain size and the stoichiometric. The straight line portion is extrapolated to cut the x-axis, which gives the energy gap. All graphs show straight line portions supporting the interpretation of direct band gap for all the films.

The estimated band gap values were obtained as 1.7 – 2.2 eV for Bi doped CdSe as shown in figure 7c. Hence the Bi doped CdSe can be used in development of efficient photovoltaic application.
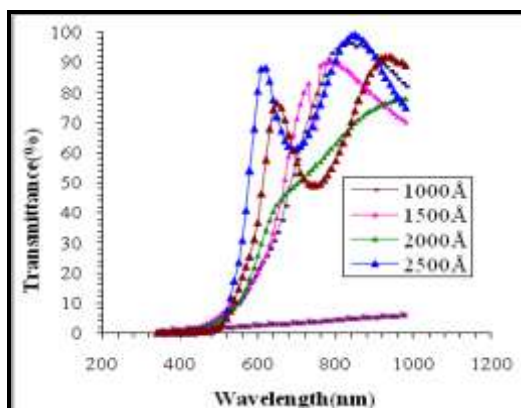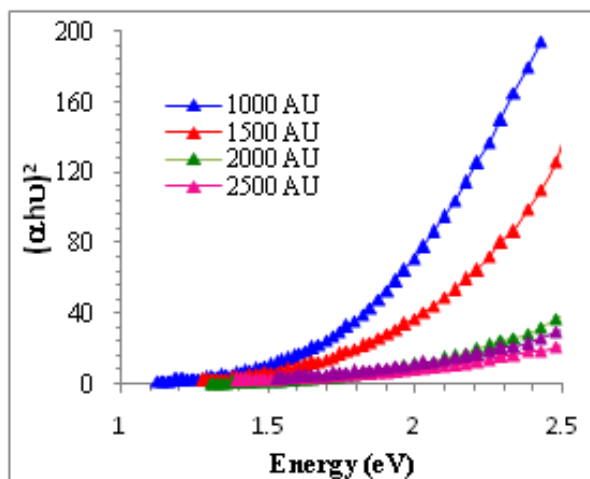

Fig.7 a: Transmittance Spectra of CdSe Thin Film
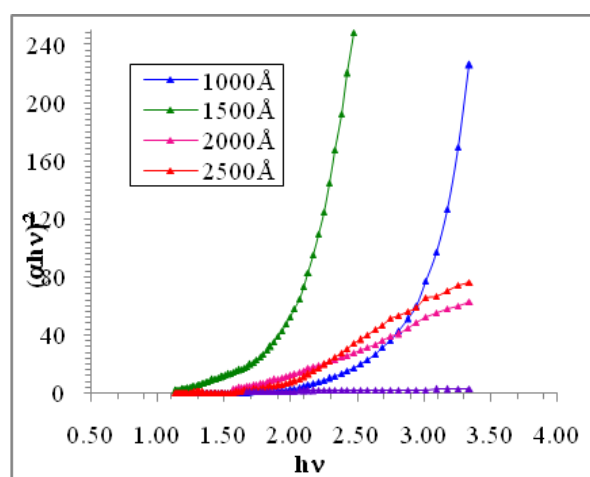
Figure 7 b: Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (CdSe)

Figure 7 c: Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (Bi doped CdSe)

Photoluminescence Properties

      To reveal emissions related to the dopants, we compared the luminescence spectra of undoped and doped CdSe. The spectra were interpreted based on earlier data [11 – 12]. The introduction of dopant (bismuth) into CdSe causes transformation in the PL spectrum, due to generation of shallow levels in the band gap. The PL spectrum shows peaks in the infra red region, at 825 and 970 nm. The intensity of these lines increases sharply with increasing Bi dopant in CdSe. We assume that the bands at 825 and 970nm are due to a defect complex incorporating V_{Cd}^{2-} and Bi_{Cd}^{+}. Such a complex was revealed in studies of photo electric properties of CdSe (Bi).
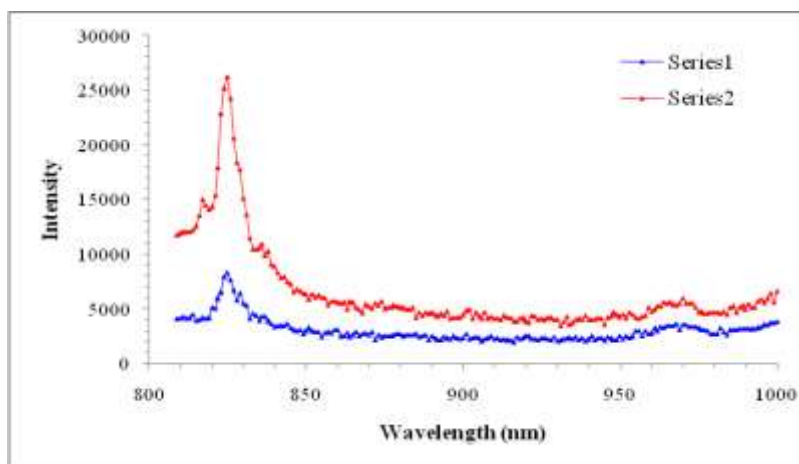

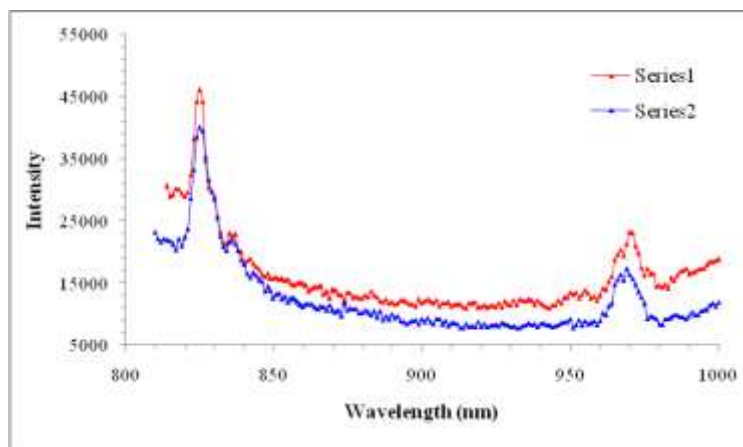**Figure 8:** PL spectrum of nanocrystalline Bi (0.2) doped CdSe

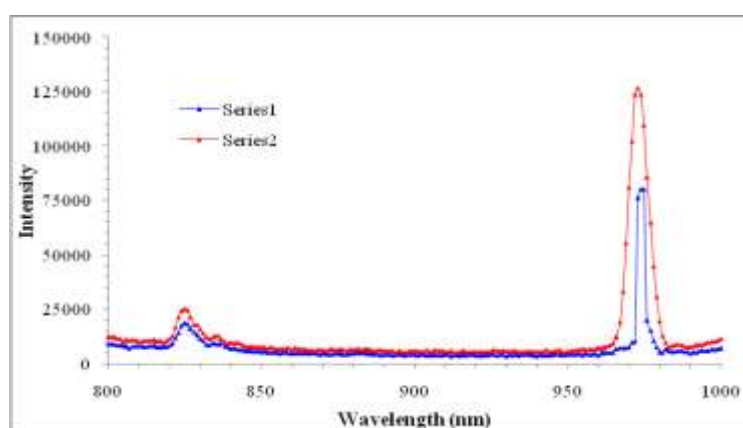**Figure 9:** PL spectrum of nanocrystalline Bi (0.4) doped CdSe

Figure 10: PL spectrum of nano crystalline Bi (0.6) doped CdSe

IV. Conclusion

Bi doped CdSe thin films of different thickness and concentrations have been deposited successfully on glass substrate with different thicknesses. XRD confirms that the structure of the film is polycrystalline in nature and having hexagonal structure. From SEM study it is observed that deposited CdSe (Bi) film were homogenous and granular structure with nano crystalline in nature. The particle size varies from 10 to 13 nm. From AFM study it is observed that surface image is homogeneous and well connected grains. Analysis of the transmission data for CdSe (Bi) thin films, deposited at RT, showed the absorption coefficient, $a = 10^{-4}$ cm^{-1}, and the energy band gap, E_g, in the range of, 1.7 - 2.2 eV, hence the CdSe (Bi) can be used in development of efficient photovoltaic application in the next phase of work. The PL spectrum shows peaks in the infra red region, the bands at 825 and 970nm are due to a defect complex incorporating V_{Cd}^{2-} and Bi_{Cd}^{+}. Such a complex was revealed in studies of photo electric properties of CdSe (Bi).

Acknowledgements

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