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Effect of Bi doping on the properties of CdSe thin films for optoelectronic device applications

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A B S T R A C T

CdSe and Bi (1%, 2%, 3%) doped CdSe thin films were deposited on the glass substrates using thermal evaporation technique. Effect of Bi doping on the structural, optical, electrical and photo response properties of CdSe thin films were investigated. The X-ray diffraction studies reveals that undoped and Bi doped CdSe films are polycrystalline in nature with hexagonal crystal structure along (002) direction. No significant changes are observed in the lattice parameters or the grain size indicating minimum lattice distortion. The optical band gap of undoped CdSe film was estimated to be 1.67 eV. Replacement of cadmium by bismuth results in an increase in the electrical conductivity of doped films. Doping with bismuth is found to improve the photo sensitivity of CdSe thin films.

1. Introduction

CdSe is one of the binary compounds in IIA-VIB group of semiconductors. CdSe is a very interesting photovoltaic material because of its direct band gap of 1.74 eV [1] and for having a high absorption coefficient. It finds many applications in both microelectronics and optoelectronic devices. During recent years semiconductors in thin film form have attained special attention due to their physical properties such as high surface to volume ratio and quantum effects which lead to innovate many applications such as photo-detectors, transistors, solar cells, light emitting diodes and other optoelectronic devices [2–8] found that CdSe thin films prepared by electron beam evaporation technique show good photoconductive response and having high signal to noise ratio. In the recent years various researchers used Bi, Pr, Nd and Sm to dope CdSe, these are the potential candidates for various applications [9–13]. V.T Patil et al. studied the Bi doped CdSe thin films prepared by thermal evaporation. [12]. K. Heo. et al. reported the structural control on Bi doped CdSe nanostructures for practical applications [13]. The electrical properties of these films depends mainly on impurity concentration. A number of researchers attempted to enhance the electrical properties of CdSe thin film by adding impurity for different applications. However, the study of doping effect on the properties of CdSe thin films is still insufficient to evaluate the mechanism and its relation to the properties. CdSe thin films have band gap suitable for solar energy conversion that makes it suitable for next generation solar cells [14]. In the present study undoped and Bi doped CdSe thin films were synthesized using thermal evaporation technique and effect of Bi doping on the properties have been studied.

2. Experimental procedure

Undoped and Bi doped CdSe thin films were deposited on glass slides using thermal evaporation technique at residual pressure less than 5×10^{-6} Torr. CdSe fine powder of purity 99.995% and Bi lumps of 99.95% (SRL) were used to prepare undoped and Bi doped CdSe thin films. The glass substrates dipped in highly concentrated chromic acid for 24hrs to remove the additives on the surface and also it helps to increase the adhesion of deposited thin films. Then glass slides were cleaned with soap solution (labolin) further cleaned with lab grade acetone and gently rubbed with tissue paper. Molybdenum boat was used to evaporate. Deposition rate was maintained nearly 37 nm/min. CdSe powder and Bi lumps was co-evaporated form the single boat. During deposition the substrate temperature was maintained at 453 K and post deposition annealing was carried out at 453 K for 1hr. The thickness of the vacuum deposited films was evaluated from gravimetric method and it was found to be in the range of 450–500 nm. Structural characterization has been carried out using Rigaku Miniflex X-Ray diffractometer with CuKα radiation of wavelength (λ) = 1.5406 Å. FESEM images of films were obtained by Carl Zeiss scanning electron microscope, elemental analysis has been carried out using energy dispersive X-ray spectroscopy (EDAX). Absorption spectra of CdSe and Bi doped CdSe thin films were recorded using Shimadzu make

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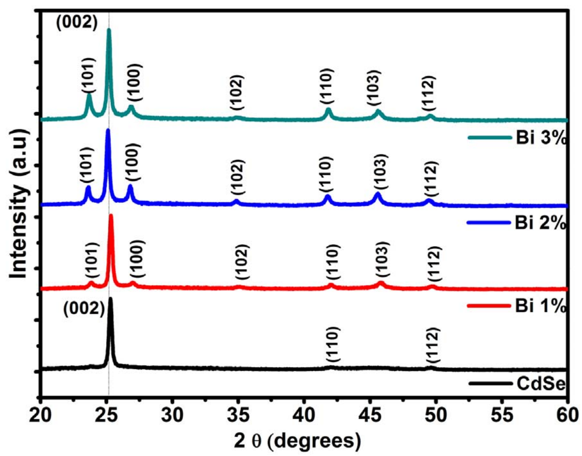

Fig. 1. XRD spectra of CdSe and Bi doped CdSe thin films.

UV–Vis–NIR 3600 spectrophotometer in the wavelength range of 300–1200 nm. For electrical studies silver contacts have been used prepared thin films. The variation of film resistance as a function of ambient temperature was determined. Photocurrent measurements were carried out using Xenon arc lamp (Newport, model 66902) for both undoped and Bi doped CdSe thin films.

3. Results and discussion

3.1. Structural and Morphological studies

Fig. 1 shows the XRD pattern of CdSe and Bi (1%, 2% and 3%) doped CdSe thin film prepared at 453 K substrate temperature. The average grain size was calculated by well-known Scherrer's formula [15].

$$D = \frac{0.9\lambda}{\beta.\cos(\theta)} \tag{1}$$

where, 'λ' the wavelength of X-ray used (λ = 1.54060 Å), 'β' is full width at half maxima of predominant peak (002). The lattice parameters '*a*' and '*c*' were calculated from the following relation [16].

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

Variation of crystallite size and lattice parameters of undoped and Bi doped CdSe thin films were tabulated in Table 1. The presence of large number of peaks indicates that the films are polycrystalline in nature. The obtained diffraction patterns of undoped and Bi doped CdSe thin films exhibits hexagonal crystal structure and agrees well with JCPDS data (008-0459). As the Bi concentration increases, the (002) and (101) diffraction peak becomes more dominant and shifts towards the lower diffraction angle. The marginal increase in grain size was observed with increase in Bi dopant concentration. The increase in Bi content from 1 to 3 wt% leads to increase in the crystallinity of the doped CdSe thin films as compared to undoped CdSe thin films. This kind of doping effect on the crystallinity of the CdSe thin films was observed by [17–19] for Cu doped CdSe and In doped CdSe thin films.

Fig. 2 indicates SEM micrographs of Bi (1%, 2% and 3%) doped CdSe thin film. It is observed that the prepared thin films contain nano size grains which are uniformly distributed over smooth homogeneous background and free from microscopy defect like cracks or peeling.

Table 1
XRD data of undoped and Bi doped CdSe thin films.

Sample	2θ	Plane	*d* (Å)	*D* (nm)	*a* (Å)	*c* (Å)	Cd%	Se%	Bi%
CdSe	25.30	(002)	3.516	32.68	4.295	7.03	50.36	49.63	
Bi 1%	25.30	(002)	3.514	32.35	4.299	7.03	49.47	49.42	1.11
Bi 2%	25.17	(002)	3.532	33.34	4.318	7.06	48.36	49.56	2.08
Bi 3%	25.10	(002)	3.540	33.87	4.323	7.08	46.76	49.83	3.41

3.2. Optical properties

The optical absorption and transmittance spectra were recorded in the 300–1200 nm wavelength range, using a Shimadzu 3600 UV–Visible model of the spectrophotometer. The optical band gap of these films has been calculated using the Tauc's relation [17].

$$(\alpha h\nu) = B(h\nu - E_g)^n \tag{3}$$

where 'hυ' is the photon energy, 'α' is the absorption coefficient, '*Eg*' is the band gap, '*B*' is constant and, $n = 1/2$ for direct band gap semiconductor material.

The plot of $(\alpha h\upsilon)^2$ (vs) hυ for CdSe and Bi doped CdSe thin films was shown in Fig. 3. The band gap values were estimated form the '$(\alpha h\upsilon)^2$', verses photon energy (hυ) plot. The best fit to the experimental data was obtained for $n = 1/2$. The straight line portion is extrapolated to cut the x-axis, which gives the energy gap. Linear portion in undoped and Bi doped CdSe films supporting the interpretation of direct band gap semiconductors. The obtained band gap values for CdSe and Bi doped CdSe thin films were tabulated in the Table 2. The obtained band gap of pure CdSe thin film is estimated to be 1.67 eV which is close to previously reported data [8]. There is no significant change in the optical band gap for the doped CdSe films compared to undoped CdSe thin films. The optical transmittance of doped CdSe films decreases as the Bi dopant concentration increases (Fig. 4). This decrease in the transmittance may be due to scattering losses at the film surface [20] with increased Bi dopant concentration.

3.3. Electrical properties

The electrical measurements were carried for undoped and Bi doped CdSe thin films. Fig. 5 shows the variation of ln *R* versus invers temperature of Bi doped CdSe thin films. The activation energies of the undoped and Bi doped CdSe thin films was studied.

It is observed that the resistance decreases with increasing temperature indicating the semiconducting nature of the undoped and Bi doped CdSe thin films. The resistance variation with temperature exhibits an Arrhenius behavior.

$$R = R_0 \exp\left(\frac{E_a}{k_B T}\right) \tag{4}$$

Where '*R*' is the resistance of the film at temperature '*T*', 'R_0' is a constant, 'k_B' is Boltzmann's constant and 'E_a.' is the activation energy for conduction. Activation energy was evaluated from the ln *R* versus $1000/T(K^{-1})$, using slope of linear portion in the plot. Activation energy decreases with increasing Bi dopant concentration. This may due to the increase in the charge carrier concentration. Bi doped CdSe films shows single linear region having single slope represents the deep donor levels which contribute to conduction mechanism [21]. In literature, this is interpreted to be due to the energy brought by thermal agitation. Due to the thermal energy, ionization of the impurities takes place and these ionized charge carries move from deep donor levels in the band gap to conduction band of the semiconductor sample. Electrical conductivity (σ) increases with increasing Bi dopant concentration. This increased electrical conductivity with Bi concentration can be interpreted by the increase in the number of free charge carriers from the Bi dopant atoms incorporated by substituting cadmium atoms. Similar observation has been made by [22] for Bi doped ZnO thin films deposited by spray pyrolysis.

3.4. Photocurrent response

Photocurrent (I_{Ph}) was measured a function of wavelength for CdSe