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Optical spectroscopic analysis of annealed $Cd_{1-x}Zn_xSe$ thin films deposited by close space sublimation technique

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$Cd_{1-x}Zn_xSe$ (x = 0, 0.40 and 1) thin films were deposited on a glass substrate at room temperature by closed space sublimation method. Optical investigation has been performed using spectrophotometry and ellipsometry. It has been found that for as deposited films the optical band gap increased and the optical constants decreased with increasing Zn content. To improve the optical properties of $Cd_{1-x}Zn_xSe$ thin films annealing effect at 400 °C was taken into consideration for various Zn contents. It was observed that the optical transmittance and band gap decreased while optical constants increased with increasing Zn content after annealing. The effects of composition and annealing on the optical dispersion parameters E_o and E_d were investigated using a single effective oscillator model. The calculated value of the average excitation energy E_o obeys the empirical relation ($E_o = E_g/2$) obtained from the single oscillator model.

Keywords: *thin films; optical constants; ellipsometry; $Cd_{1-x}Zn_xSe$; optical band gap*

1. Introduction

Over the last two decades, II–VI semiconductor thin films have attracted a considerable attention from the research community because of their wide use in the fabrication of solar cells and other optoelectronic devices [1, 2]. The group II-VI ternary compound semiconductor has a lot of applications in optoelectronics devices ranging from blue to near ultraviolet region [3]. Among them CdSe and ZnSe, which belong to the group II-VI semiconductors are technologically important due to their direct and wide band gap. Choosing semiconductor materials of various band gaps make it possible to control the band gap energy of a given semiconductor by reducing the particle size [4]. Alloying of semiconductors is another means that can be applied to achieve semiconductor materials with various band gap energies. Coupling of cadmium selenide and zinc selenide would produce a material with various band gap energies depending upon the composition, which may be suitable for increased absorption of solar spectrum and enhanced resistance towards photo corrosion [5]. Cadmium zinc-selenide [(CdZn)Se] is one of the important ternary compound semiconducting materials that due to its excellent optical properties and fast response times has a wide range of potential applications in the photo luminescent, electroluminescent, photoconductive and photovoltaic device applications [1, 6]. A number of thin film deposition methods, such as molecular beam epitaxy, electron beam pumping, chemical bath deposition (CBD) etc. have been used for preparing cadmium zinc-selenide thin films [7–9]. We have prepared $Cd_{1-x}Zn_xSe$ films by the resistive thermal evaporation technique with various zinc content. $Cd_{1-x}Zn_xSe$ thin films have been studied by many researchers [1, 10–12], but the effect of annealing temperature on the optical properties of $Cd_{1-x}Zn_xSe$ thin films is rarely presented in the literature. Therefore, it is worthwhile to study the effect of annealing on optical properties of $Cd_{1-x}Zn_xSe$ thin films. Optical constants

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of optical materials have considerable importance for applications in integrated optical devices, such as switches, filters, modulators etc. where the refractive index is the key parameter in the design of device. The aim of this study is to investigate the effect of Zn content and annealing temperature on the optical constants of $Cd_{1-x}Zn_xSe$ thin films such as refractive index n, extinction coefficient k, optical band gap E_g and optical dispersion parameters E_o, E_d.

2. Experimental work

$Cd_{1-x}Zn_xSe$ (x = 0, 0.40, and 1) thin films were deposited on a glass substrate at room temperature using resistive thermal evaporation technique. After deposition the films were allowed to cool at room temperature. The as deposited films were then annealed at 400 °C in air for one hour. The preparation parameters of $Cd_{1-x}Zn_xSe$ films obtained by resistive thermal evaporation method were described in detail in [13]. The optical transmittance measurements were carried out using UV-NIR spectrophotometer (Hitachi U-4001) in the spectral range from 300 to 2500 nm. Film thickness and optical constants (e.g. refractive index, extinction coefficient) were found using Jawoolam 200 VI ellipsometer. The details on SE can be found in the literature, only a brief description is given here. In ellipsometry, the objective is to measure the ratio of a complex Fresnel reflection coefficients, ρ:

$$\rho = r_p/r_s = \tan\psi \exp(i\Delta) \tag{1}$$

where the quantities r_p, and r_s are the Fresnel reflection coefficients for light polarized parallel/perpendicular to the plane of incidence, and ψ and Δ are the traditional ellipsometric angles. Note that both r_p and r_s contain information on the optical and structural properties of the sample. The ellipsometry measurements were carried out at room temperature in the 370–900 nm spectral range at an angle of incidence of 70°.

3. Results and discussion

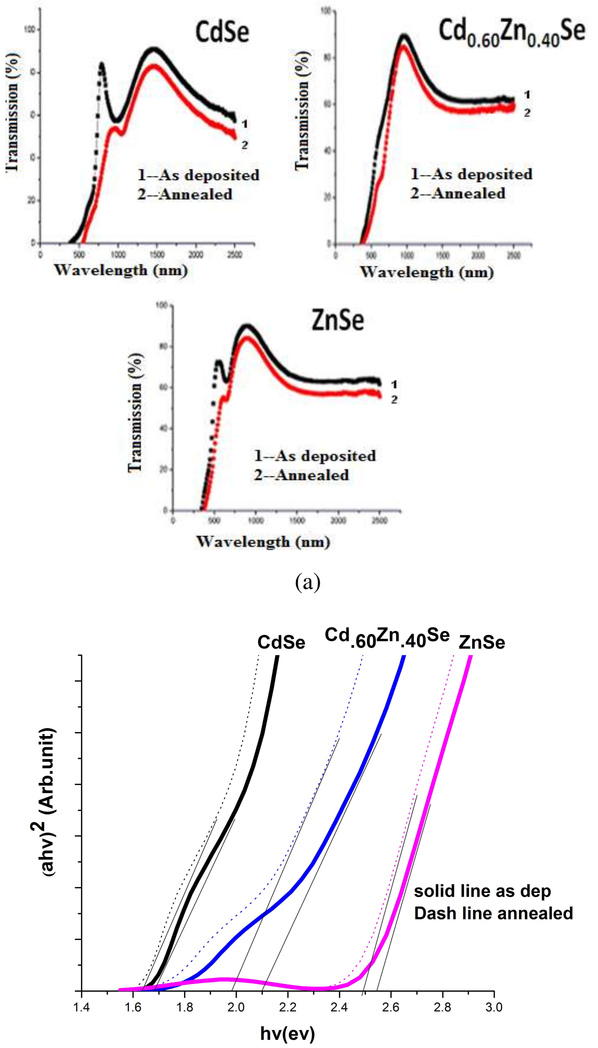
3.1. Spectrophotometry analysis

Fig. 1 shows the transmittance spectra in the wavelength range between 300 and 2500 nm for the as-grown $Cd_{1-x}Zn_xSe$ films on the glass substrates and for those samples after annealing. The spectra show two regions, one in higher wavelength with practically higher transmission and the other in lower wavelength in which transmission decreases steeply. The spectrum shows the interference pattern with a sharp fall at the band edge which is a confirmative evidence of the formation of uniform and good crystalline films [14]. As the x parameter increases, transmission shows an increasing trend with the wavelength, and the fundamental edge is shifted towards shorter wavelength (or higher energy) region indicating an increase in band gap energy. Optical transmission decreases after annealing, which is probably due to the increase in crystallite size and decrease in intercrystalline boundaries [15]. The absorption edge of the films was observed to shift towards longer wavelengths after annealing. In order to show the effect of annealing temperature, the absorption edge was investigated for the films annealed at 400 °C. The optical absorption edge was determined from the transmission spectra, which is a simple method that explains the features concerning the band structure of a film.

The optical absorption edge was analyzed by the following relationship [16]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{2}$$

where α is the absorption coefficient, h is the Planck's constant, A is a constant and E_g is the optical band gap energy. The band gaps estimated from the plots of $(\alpha h\nu)^2$ versus hν are shown in Fig. 1 for the as-deposited and annealed $Cd_{1-x}Zn_xSe$ thin films. The linear nature of the plots at the absorption edge confirms that $Cd_{1-x}Zn_xSe$ is a semiconductor with a direct band gap. The E_g values for our films vary from 1.69 to 2.57 eV for the as deposited and from 1.65 to 2.50 eV for the annealed films when zinc content varies from 0 to 1. The optical band gaps determined from these curves are listed in Table 1. It can be seen that the optical band gap decreases with annealing temperature. The decrease in optical band gap energy is generally observed in the annealed direct-transition type semiconductor films [17]. The shifts in optical band



(b)

Fig. 1. Transmission spectra (a) and optical band energy (b) of as deposited and annealed $Cd_{1-x}Zn_xSe$ thin films.

gap may be attributed to the improved crystallite size and morphology of thin films. Moreover, it is understood that the amorphous phase is reduced with annealing temperature, since more energy is supplied for crystallite growth, thus resulting in an improvement in crystallinity of $Cd_{1-x}Zn_xSe$ thin films.

3.2. Spectroscopic ellipsometry (SE) analysis

The SE spectra for $Cd_{1-x}Zn_xSe$ thin films annealed at 400 °C are shown in Fig. 2. From the figure it can be seen that the spectra exhibit oscillations, which is only due to interference effect of light. The oscillating frequency depends on the thickness of the film. Generally, the thicker the film, the higher is the frequency of oscillations. The optical constants derived from the ellipsometric parameters psi (ψ) and delta (Δ) have been analyzed by an effective medium approximation (EMA) model (air/CdSe+ZnSe/substrate). With the help of simulated optimization, the fitting parameters as well as the film thickness were determined by fitting the ellipsometric spectra. Clearly, the fit shown in Fig. 2 is a good fit.

The calculated values of refractive index n and extinction coefficient k were plotted as a function of wavelength, as shown in Fig. 3. It is observed that the refractive index n as well as extinction coefficient k decrease as the zinc concentration increases both before and after annealing. The decrease in refractive index n of the ternary alloy may also be due to the fact that the zinc ionic radius is smaller than that of cadmium; therefore the grain size as well as lattice constant are reduced [18]. Due to the reduction in grain size, crystallinity decreases which results in lowering the density of the alloy. From Fig. 3 it is evident that there is a sharp rise in the refractive index of the films at the absorption edge towards lower wavelength of the spectrum. This sharp rise in refractive index is assigned to Van Hove singularity in the joint density of state in the excitation of transition between two bands [19]. There is a slight increase in optical constants of $Cd_{1-x}Zn_xSe$ thin films after annealing which is a direct consequence of density and band gap of the material. Higher annealing temperature enhances the formation of larger and more closely packed crystals. The increase of the refractive index with annealing temperature can be partly attributed to the improvement in the film quality with the reduction in porosity of the $Cd_{1-x}Zn_xSe$ films. Since the refractive index is strongly correlated to the band gap energy, it can be concluded that the smaller band gap energy material has a larger value of refractive index in $Cd_{1-x}Zn_xSe$. This behavior is generally found for most common II-VI and III-V semiconductor alloys [20, 21].

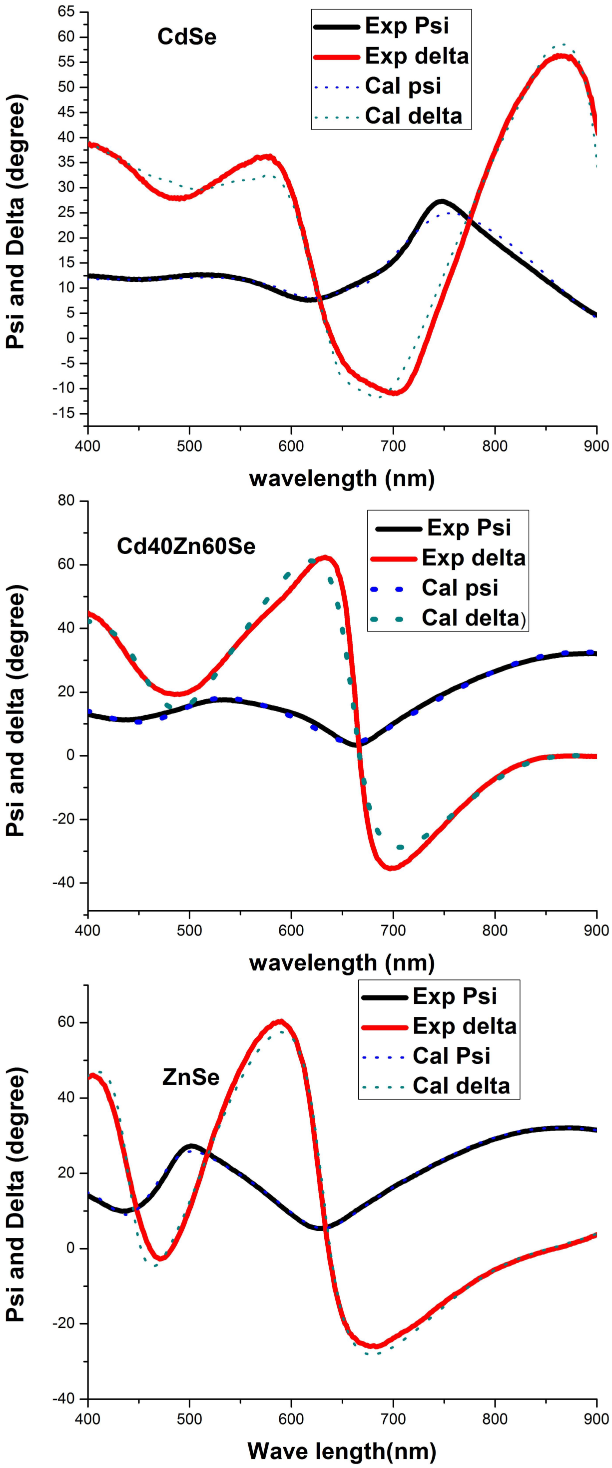


Fig. 2. Experimental and modeled values of ψ and Δ for $Cd_{1-x}Zn_xSe$ thin films annealed at 400 °C.

The dispersion of refractive index according to the single effective oscillator model proposed by

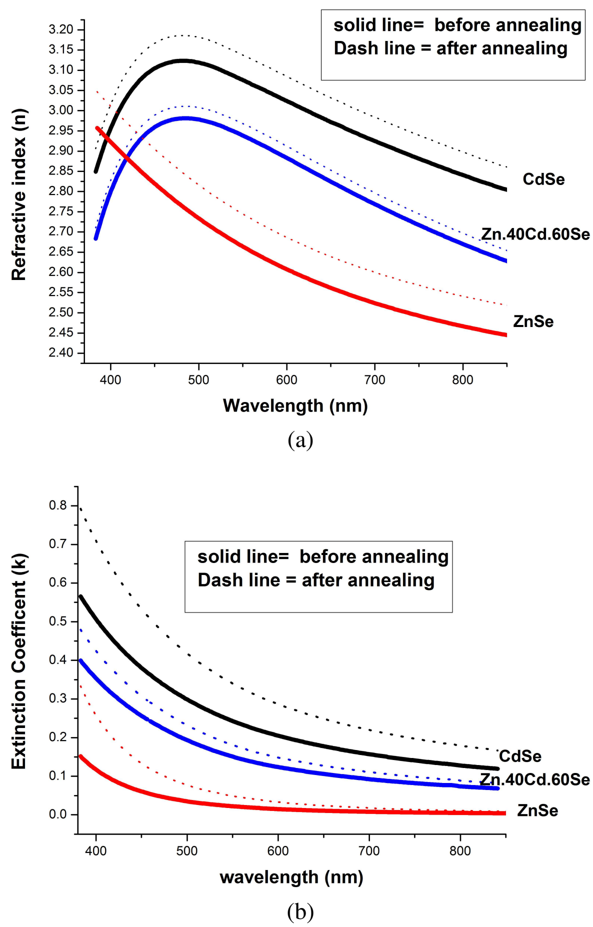


Fig. 3. Variation of optical constants (a) refractive index and (b) extinction coefficient in $Cd_{1-x}Zn_xSe$ thin films.

Wemple and Di Domenico [22], which describes the dielectric response for transitions below the interband absorption edge in the low absorption region, is given by expression:

$$n^2(h\upsilon) = 1 + \frac{E_o E_d}{E_o^2 - (h\upsilon)^2} \tag{3}$$

where h is Planck's constant, E_o is the average excitation energy for electronic transition which is empirically related to the optical band gap, while E_d is the dispersion energy which measures the average strength of optical transitions. By plotting the $(n^2-1)^{-1}$ versus $(h\nu)^2$ and fitting a line as shown in Fig. 4 the values of E_o and E_d can be obtained from the slope $(E_oE_d)^{-1}$ and intercept (E_o/E_d) on the vertical axis. The values of energy dispersion parameters for the as deposited and annealed

Table 1. Optical band gap and dispersion parameters for investigated thin films.

Composition	E_g (eV) as dep	E_g (eV) annealed	E_o (eV) as dep	E_o (eV) annealed	E_d (eV) annealed	E_d (eV) annealed	Thickness (nm) as dep	Thickness (nm) annealed
CdSe	1.69	1.65	3.42	3.19	19.37	18.78	180	177
$Cd_{.60}Zn_{.40}Se$	2.1	2	4.07	3.96	20.87	20.88	158	154
ZnSe	2.57	2.5	4.85	4.58	22.67	22.47	190	179

samples are listed in Table 1. The obtained values of E_o and E_d increase with increasing Zn content and decrease with annealing effect. If the bonds in our samples are supposed to be covalent, then the increase in E_d can be assigned to higher number of nearest neighbors in the alloy with respect to pure compound [23]. The variation in E_o with Zn content and annealing temperature may be due to the behavior of optical band gap. The values of band gap energy E_g which have been obtained by using the single oscillator model agree with those determined by the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ as in Table 1.

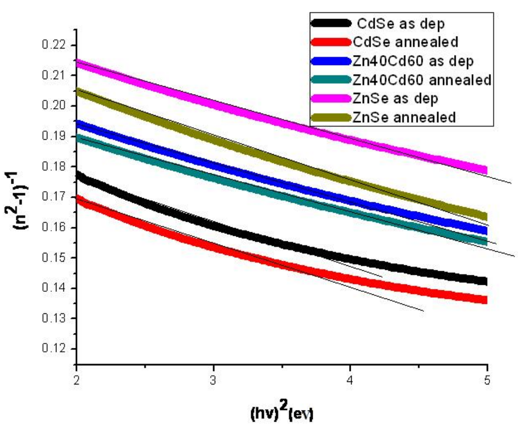


Fig. 4. The plot of $(n^2-1)^{-1}$ versus photon energy $(h\nu)^2$ for as deposited and annealed $Cd_{1-x}Zn_xSe$ thin films.

4. Conclusions

$Cd_{1-x}Zn_xSe$ ($x = 0$, 0.40 and 1) thin films have been prepared on glass substrate using thermal evaporation technique. The as deposited films were annealed at 400 °C in ambient air for one hour to improve the optical properties. Spectrophometer and ellipsometry were used to investigate the optical properties of the films. Transmission and optical band gap have been investigated using the spectrophotometry. Optical band gap varied from 1.69 to 2.57 eV for as deposited films and from 1.65 to 2.50 eV for annealed films as zinc content increased from 0 to 1. Optical constants of $Cd_{1-x}Zn_xSe$ thin films were investigated using ellipsometry. Optical constants were modified after annealing, which may be due to the improvement in crystalline structure of $Cd_{1-x}Zn_xSe$ thin films. Ellipsometry results were confirmed by calculating the optical band gap of $Cd_{1-x}Zn_xSe$ thin films using the single effective oscillator model.

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