STRUCTURAL AND OPTICAL INVESTIGATIONS OF CHALCOGENIDE CdSe_{1-x}S_x THIN FILMS FOR OPTOELECTRONIC APPLICATIONS

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Different compositions of $CdSe_{1-x}S_x$ thin film have been evaporated using thermal evaporation method. X-ray diffraction pattern has been used to determine the phase and microstructural parameters. The optical constants of $CdSe_{1-x}S_x$ thin film have been studied as a function of photon energy in the wavelength range 400 - 2500 nm. Both refractive index and film thickness have been determined using envelop method that suggested by Swanepoel. The refractive index found to be decrease with increasing the S content. Analysis of the optical absorption data shows that the rule of direct transitions predominates for all films. The energy gap, E_g^{opt} values of $CdSe_{1-x}S_x$ thin films were found to be increased with increasing the S content as expense of Se. The main importance of $CdSe_{1-x}S_x$ thin film is the change of band gap when incorporating S into the CdSe. This change in both refractive index and energy gap recommend $CdSe_{1-x}S_x$ thin film for optoelectronics devices and photovoltaic solar cells. The increasing in E_g^{opt} values was explained in term the change in microstructure parameters.

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1. Introduction

Semiconductors of II-VI films (CdSe, CdS, ZnTe, etc.) are characterized by their wide band gap [1], thus they have many applications in optoelectronics devices and photovoltaic solar cells. CdSe n-type semiconductor thin films with direct band gap ($E_g = 1.7-1.8 \text{ eV}$) can be grown in cubic or hexagonal forms with high absorption coefficient and transmittance in the visible region. Only CdSe films are widely used for optoelectronic devices fabrication [2] such as solar cells [3, 4], light emitting devices [5], lasers [6], photo detectors [7] and thin film transistors [8]. CdS thin films has wide band gap ($E_g = 2.42 \text{ eV}$) [9] used extensively for heterojunction solar cells as for window material in connection with other semiconductors such as CdTe [10]. The formation of ternary $CdSe_{1-x}S_x$ thin films improves the physical characteristics of the binary CdSe thin films. Electrical and optical properties of semiconducting thin films are vital requirements for appropriate applications in several optoelectronic devices [11, 12]. Modifying the composition of $CdSe_{1-x}S_x$ permits improvement of their structural, optical and electrical properties therefore; widening of their scientific and technological applications [13]. Nano-sized $CdSe_{1-x}S_x$ thin films can be prepared by several chemical and physical methods such as chemical bath deposition (CBD), chemical vapor deposition (CVD), RF-sputtering, spray pyrolysis, laser ablation and thermal evaporation techniques [13-16]. In the present work, $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) was prepared by a conventional solid-state reaction method, as a mixture of the two systems CdS and CdSe by a chemical reaction method.

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The thermal evaporation method has been used to get thin films in order to study the structural and optical properties. The X-ray diffraction has been used to investigate the microstructure of these films. Optical constants and energy gap have been deduced and their changes can be interpreted in terms of micro structural parameters.

2. Experimental procedures

Different compositions of $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) were prepared by a conventional solid-state reaction method. Using ball milling technique, stoichiometric amounts of high–purity (99.999%) analytical grade CdS and CdSe powders purchased form Aldrich were mixed in a ball mortar for about 30 min according to the following reaction:

$$xCdS+(1-x)CdSe \to CdSe_{1-x}S_x \tag{1}$$

The mixed powders were then pressed into a disk-shape pellet. Such pellets were used as the starting materials from which the thin film will be prepared, the same technique was proposed for different compound in our previous studies [17-20]. The compositions of $CdSe_{1-x}S_x$ (with $0 \ge x$ ≥ 1) thin films were deposited by thermal evaporating the powdered samples from a resistance heating quartz glass crucible onto dried pre-cleaned glass substrates at a pressure of about 10^{-6} Pa, using a conventional coating unit (Denton Vacuum DV 502 A). During evaporation process, the thickness of the produced films was monitored using FTM6 thickness monitor. The thicknesses of the as-deposited films were studied at different compositions, in order to avoid the effect of film thickness. During the deposition process, the substrates were kept at temperature 400 K and the deposition rate was adjusted at 2 nm/sec. Such a low deposition rate produces a film composition, which is very close to that of the bulk starting material [21, 22]. The substrates were rotated at slow speed of 5 rpm, to obtain a homogenous and smooth film. X-ray powder diffraction (XRD) Philips diffractometry (model: 1710), with Cu–K_{α} radiation ($\lambda = 1.54056$ Å) has been used to examine the phase purity and crystal structure of $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$). 20 ranged between 5° and 70° with step-size of 0.02° and step time of 0.6 seconds. The compositional analysis was carried out using energy dispersive X-ray spectroscopy (EDAX). The relative error of determining the indicated elements does not exceed 2.3 %. The absorbance optical spectra of the deposited films were performed at room temperature using UV-Vis-NIR JASCO-670 double beam spectrophotometer.

3. Results and discussions

3.1. X-Ray diffraction analysis for CdSe_{1-x}S_x thin films

The X-ray diffraction patterns of the $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) powder with their characteristic peaks of reference code corresponding to each composition are shown in Fig. 1, which exhibit polycrystalline nature. The XRD pattern for $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) thin films onto glass substrate are shown on Fig. 2. The figure shows that the films have good crystallinity with the wurtzite structure for all compositions between CdSe and CdS according to reference JCPDS code mentioned at the inset of Fig. 1. Fig. 2 exhibits the sharp diffraction line of the preferred crystalline orientation (002) that indicating a good crystallinity of the prepared thin films. There are significant shifts to higher angles of the (002) peaks for the films with incorporating S at expense of Se in $CdSe_{1-x}S_x$ thin films (clearly shown in Fig. 3). This shift may be attributed to the atomic radius of S atom (1.09 Å) is smaller than the atomic radius of Se atom (1.22 Å) [23, 24].



Fig. 1. XRD pattern of $CdSe_{(1-x)}S_x$ powder.



Fig. 2. XRD pattern of $CdSe_{(1-x)}S_x$ thin films.



Fig. 3. XRD data related the variation of (002) with composition for $CdSe_{(1-x)}S_x$ thin films.

The hexagonal crystals are characterized by two lattice parameters, a and c, and the interplanar is given by [25]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$
(2)

where *hkl* are Miller indices of the plane. The interplanar spacings d_{hkl} for these thins films were calculated from Bragg's law [25]

$$\lambda = 2d_{hkl}\sin\theta \tag{3}$$

where θ is the diffraction angle. The lattice parameters (*a* and *c*) were determined and the variation in lattice parameters (*a* and c) with composition from x = 0 to x = 1 are shown in Figs. 4 and 5. The lattice parameters (*a* and c) decrease linearly with S content in CdSe_{1-x}S_x films. The variation in lattice parameters with the composition as shown in Fig. 4 and 5 would appear to obey Vegard's [26].



Fig. 4. Lattice parameter (a) as a function of composition.



Fig. 5. Lattice parameter (c) as a function of composition.

Fig. 6 also shows the axial ratio c/a decreases with increasing x concentration of the CdSe_{1-x}S_x thin films.



Fig. 6. Axial ratio (c/a) as a function of composition.

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Microstructural parameters, crystallites size (D_v) and lattice strain (*e*) of CdSe_{1-x}S_x films were calculated by analyzing the XRD data using the Scherrer's formula, [25, 27]

$$D_{v} = \frac{k \lambda}{\beta \cos(\theta)}$$

and Wilson formula [25, 27]

$$e = \frac{\beta}{4\tan(\theta)}$$

where β is the structural broadening, which is the difference in integral X-ray peak profile width between the thin film and a standard (silicon) and is given by $\beta = \sqrt{\beta_{obs}^2 - \beta_{std}^2}$ [21, 22]. Fig. 7 and Fig. 8 show a comparative look of microstructure parameters (D_v and e) of the CdSe_{1-x}S_x films. It is observed that the crystallite size decreases sigmoidally with increasing of S at expense of Se as shown in Fig. 7 as a sigmoidal curve, but the lattice strain ascends up sigmoidally as shown in Fig. 8. The decreasing in crystallite size with S content may be attributed to the reduction in both lattice parameters a and c but the increasing in lattice strain maybe awing to the increasing in lattice defects among the grain boundary, which might be attributed to the increase of breadth with increasing S content.



Fig. 7. Crystallize size as a function of composition.



Fig. 8. Lattice strain as a function of composition.

3.2. Optical properties CdSe_{1-x}S_x thin films

The double beam spectrophotometer was adopted to measure the transmittance, *T* and reflectance, *R* in wavelength range extended from 400 to 2500 nm for different composition of $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) films as shown in Fig. 9. This figure shows that the absorption edge shifted towards lower wavelength with increasing the S at expense of Se.



Fig. 9. Optical transmission and reflection spectra for $CdSe_{(1-x)}S_x$ *thin films.*



Fig. 10. Optical transmission spectrum of $CdSe_{0.50}S_{0.50}$ thin film. The top and bottom transmittance envelope T_{Max} and T_{min} shown as filled blue circle and red circle, respectively.

The refractive index (*n*) is an important parameter, which is an essential property for the practical applications. It is associated with the electronic polarizability of ions as well as electric field within the material. The refractive index of the investigated films is calculated utilizing the experimentally measured transmission data by the envelope method which has been suggested by Swanepoel [26, 27]. Fig. 10 shows application of the envelope method on the optical transmittance T_{λ} of CdSe_{0.50}S_{0.50} thin films as an example. The same procedures were used for the data measured at other different composition of CdSe_{1-x}S_x (with $0 \ge x \ge 1$) films. Based on the Swanepoel method, the refractive index (*n*) can be deduced at any wavelength from the following formula [28, 29]:

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}$$
(4)

where

$$N = 2s \frac{T_{Min} - T_{min}}{T_{Min} T_{min}} + \frac{s^2 + 1}{2} , \qquad s = \frac{1}{T_s} + (\frac{1}{T_s^2})^{1/2}$$
(5)

where, T_{Max} and T_{min} are the interference fringes maxima and minima, respectively; s is the refractive index of the substrate. The variation of refractive index (*n*) of CdSe_{1-x}S_x (with $0 \ge x \ge 1$) thin films with the wavelength of the incident photon are shown in Fig. 11.



Fig. 11. Dispersion of refractive index of $CdSe_{(1-x)}S_x$ thin films obtained from transmission spectra.

Moreover, if n_{e1} and n_{e2} are the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2 , it follows that the film thickness is given by the expression

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_{e_2} - \lambda_2 n_{e_1})} \tag{6}$$

The values of film thickness were about 700 nm for all thin films. Furthermore, the values of *n* can be fitted using the two term of Cauchy dispersion relationship, $n(\lambda) = a + b/\lambda^2$, which can be used for extrapolation the whole regions of wavelengths [30-32] as shown in Fig. 11. In terms of the least squares fit of the two sets of values of *n* for the different thickness thin films are $n = 2.45 + 1.82 \times 10^5/\lambda^2$ for CdSe sample, $n = 2.38 + 1.78 \times 10^5/\lambda^2$ for CdSe_{0.75}S_{0.25}, $n = 2.35 + 1.75 \times 10^5/\lambda^2$ for CdSe_{0.50}S_{0.50}, $n = 2.32 + 1.71 \times 10^5/\lambda^2$ for CdSe_{0.25}S_{0.75} and $n = 2.29 + 1.71 \times 10^5/\lambda^2$ for CdS, respectively. Fig. 11 shows that the refractive index increases with increasing S content, over the entire spectral range studied.

The absorption coefficient (α) can be obtained in the strong absorption region of the experimentally measured values of *R*, *T* and *d* according to the following expression [31-34]:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2 + \left[(1-R)^4 + 4R^2T^2 \right]^{1/2}}{2T} \right]$$
(7)

The nature of transition, direct or indirect, is given according to the relation [31-34]:

$$\alpha(h\nu) = \frac{K\left(h\nu - E_g^{opt}\right)^n}{h\nu} \tag{8}$$

where K is a constant, which depends on the transition probability and is E_g^{opt} the optical band gap. and the exponent 'n' depends upon the type of transition.



Fig. 12. The dependence of $(\alpha hv)^2$ on photon energy hv for the different composition of $CdSe_{(1-x)}S_x$ thin films, from which the optical band gap E_g^{opt} is estimated.



Fig. 13. Energy gap as a function of the S concentration of the $CdSe_{(1-x)}S_x$ films.

Fig. 12 shows a good fitting of $(ahv)^2$ versus photon energy (hv) for CdSe_{1-x}S_x (with $0 \ge x$ ≥ 1) films. The values of the optical band gap E_g^{opt} were taken as the intercept of $(\alpha hv)^2$ versus (hv)at $(\alpha h v)^2 = 0$ for the allowed direct transition. The optical band gap derived for each film is shown in Fig. 13. As shown in Fig. 13, the estimated optical band gap found to be increased sigmoidally with increasing the S content for $CdSe_{1-x}S_x$ thin film. The increasing in optical band gap may be attributed to the first is the decreasing of crystallize size with increasing the S content. Band gap energy increases with decreasing particle size due to quantum confinement effects. When photons are incident on the semiconductor material they will be absorbed only when the minimum energy of photons is enough to excite an electron from the valence band to the conduction band or when the photon energy equal to the energy gap of the material. The prepared nanoparticles are highly confined and the absorption spectrum of it becomes more structured because its electronic band structure changes to molecular level with non-vanishing energy spacing. So, the material needs more energy for electronic transition from valence band to conduction band. Hence the band gap energy of nanoparticles is more than that of the bulk. The second is as the particle size reaches the Nano scale, where every particle is made up only a very small number of atoms, the number of overlapping of orbitals or energy level decreases and the width of the band gets narrow. This will cause an increase in energy gap between the valance band and the conduction band.

4. Conclusions

Polycrystalline powder of $CdSe_{1-x}S_x$ (with $0 \ge x \ge 1$) have been prepared by ball milling technique by mixing ZnSe and ZnS. Thin films have been fabricated as thin films by evaporation technique. The $CdSe_{1-x}S_x$ thin films have a wurtzite structure for which the lattice constants vary linearly with composition over a wide range (0 < x < 1). Both crystallize size and lattice strain are calculated. It observed that the crystallize size decreases, but the lattice strain increases with increasing S at expense of Se in $CdSe_{1-x}S_x$ films. the refractive index has been calculated in terms of envelop method and found to be increased with increasing S content, over the entire spectral range studied.

The estimated band gap E_g^{opt} found to be allowed direct transition and increases sigmoidally with increasing S content. The increasing in energy gap was explained in terms of decreasing particle size on the basis of quantum confinement effects. This change in both refractive index and energy gap recommend $CdSe_{1-x}S_x$ thin film for optoelectronics devices and photovoltaic solar cells. The increasing in E_g^{opt} values was explained in term of the change in microstructure parameters.

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