ORIGINAL RESEARCH

Tunability of physical properties of (Cd:Zn)S thin film by Close Space Sublimation Process (CSSP)

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Abstract The present paper reports on a systematic study of the influence of Zn alloying on the structural and optical properties of Cd1−xZnxS thin films. X-ray diffraction study for structural analysis reveals that the two binary compounds have been completely transformed into ternary compound with hexagonal (wurtzite) structure with preferred orientation along c-direction with (002) planes. The optical properties such as optical constants and band gap energy of the films were examined by using spectroscopic ellipsometer and Photospectrometery. It was found that the optical constants (n and k) decrease with the addition of Zn content in the alloy. It was also confirmed that the band gap increases with increasing Zn amount in the alloy and is attributed to quantum size effect in the grain size. Raman spectroscopy analysis shows one dominant phonon band at 326 cm−1, the so-called longitudinal optical (LO) mode for all the alloy composition (x). The appearance of a single phonon band in the Raman spectra established the formation of single phase hexagonal structured Cd1−xZnxS thin film. The LO band is asymmetrically broaden and high frequency shifted due to potential fluctuation caused by the dopant material. The AFM results showed that the surface roughness was decreased with increasing Zn content.

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1. Introduction

The group II–VI compound semiconductors have attracted considerable attention in both fundamental research and technological applications because of their wide use in the fabrication of solar cells and other optoelectronic devices [1,2]. Cd1−xZnxS is a prominent ternary alloy among II–VI compound semiconductors for the fabrication of multilayer p-n...
junction’s device without mismatch of lattice parameter and electron affinities. CdS is an n-type direct band gap semiconductor material and is extensively used as a window layer for the fabrication of solar cells [3]. However, due to its low band gap, CdS window layer absorbs the blue portion of the solar spectrum which causes a decrease in the current density of solar cells. For the high performance of a solar cell device, it is necessary to use an appropriate window material. Since Cd_{1-x}Zn_xS has a larger band gap than CdS, therefore the replacement of CdS with Cd_{1-x}Zn_xS film can lead to a decrease in window absorption losses, and has resulted in an increase in short-circuit current [4–8]. The techniques which have been adapted for the preparation of Cd_{1-x}Zn_xS thin film of uniform composition are vacuum thermal evaporation [9], Chemical bath deposition [10], solution growth technique (SGT) [11], diffusion of Zn into CdS layer [12], screen printing and sintering [13] and vacuum thermal evaporation [14] etc.

The optimization of parameters of the existing solar cells and fabrication of new-optoelectronic devices frequently demand Cd_{1-x}Zn_xS layers with controllable distribution of Zn content. The dependency of optical and structural properties on composition was studied with the hope that such knowledge will enable us to prepare efficient materials for the solar cells and other optoelectronic devices. The tunability of physical properties of Cd_{1-x}Zn_xS films such as band gap and lattice parameters was observed with Zn content prepared by close space sublimation process. The advantages of Close Space Sublimation Process (CSSP) is stability, reproducibility, high deposition rate and economically viable as compared to other techniques for large area deposition. In this work, we have concentrated on the optical analysis of Cd_{1-x}Zn_xS thin films using spectroscopic Ellipsometer. Moreover, Raman spectroscopy was carried out to investigate different phonon modes and crystalline phases in the Cd_{1-x}Zn_xS samples.

2. Experimental work

Cd_{1-x}Zn_xS thin films with different Zn composition (x=0, 0.2, 0.4, 0.6, 0.8, 1.0) were deposited on glass substrate by Close Space Sublimation Process using a vacuum coating unit. For the evaporation of Cd_{1-x}Zn_xS solid solutions, CdS and ZnS binary compounds of high purity were mixed by method of solid state mechanical mixing with pestle and mortar for 60 min to get uniformly mixed powders. The different compounds have been taken as follows:

wt.(grams) of ZnS = MW × (1−X)

wt.(grams) of CdS = MW × X with MW = 144.48(CdS) 97.40(ZnS) and X = 0.0 to 1.0.

As these weights were being very large, we reduced them in the same proportion. Prior to growth, the substrates were cleaned ultrasonically in a bath of acetone for about 30 min followed by isopropanol for about 15 min and finally dried using an air gun. The vacuum was 2 × 10⁻³ Torr during deposition of the films. All the films of Cd_{1-x}Zn_xS system were deposited under the same experimental conditions.

Ellipsometric analyses of the films were carried out by spectroscopic ellipsometry; model SE-830 of Sentech. The optical spectra were recorded in the wavelength range 300–850 nm, using UV–vis–NIR Photospectrometry, model U-4001f Hitachi. The structural properties of the films were studied by the Bruker D-8 X-ray diffractometer (XRD) using Cu Kα radiation (λ=1.5405 Å). To investigate different phonon modes and crystalline phases in the Cd_{1-x}Zn_xS samples, Vibrational spectroscopy was carried out using Raman spectroscopy system model, MST-4000A (DONGWOO OPTRON Co., Ltd.). To focus the sample, it was illuminated by ordinary flash light through objective lens (100 × 0.70, f = 200). After focusing in image mode, the sample was shined by intense He–Cd laser source of wavelength (λ) 442 nm/80.0 mW and beam diameter 2.00 mm. The signals were collected and detected in scan mode by the same objective lens and air cooled at −50 °C CCD detector. The Raleigh peak at 442 nm was eliminated by using 442 nm cutoff filter. The spectrum was taken in the range from 200 cm⁻¹ to 800 cm⁻¹ using DM320 monochromator and ANDOR DV 401A-BV CCD software. Surface morphology was examined by using Atomic Force microscopy AFM (QScope™ 350) in tapping mode.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The XRD study was carried out and the results so obtained were analyzed to get an insight of various crystallographic aspects of the samples. Fig. 1 shows the XRD patterns of Cd_{1-x}Zn_xS films with (x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0).

The presence of sharp and well defined peaks in the XRD patterns confirmed polycrystalline nature of the films. The strongest peak corresponds to (002) plan is that of Cd_{1-x}Zn_xS thin film [15], while the reflection corresponds to (111) plan is that of pure ZnS [16]. These results indicate that Cd_{1-x}Zn_xS thin films have hexagonal crystallographic structure except the ZnS film which exhibited fcc (cubic) structure [17]. Furthermore, the diffraction angle 2θ is found to be shift towards higher angle side with the addition of zinc content in the Cd_{1-x}Zn_xS, which is an evidence of the complete transformation of binary compounds into ternary compound and single phase formation of the film. The shift in the diffraction angles due to the incorporation of Zn at the sub-lattice sites of Cd. Moreover, the lattice constant decreases with increasing Zn concentration in the film [4] which is

![Fig. 1 XRD pattern of Cd_{1-x}Zn_xS thin films.](image-url)
an effect of the Zn substitute Cd in the CdS. The reduction in grain size leads to two effects; first all the states at the bottom of valance band and top of conduction band become discrete; secondly blue shift of the optical transition. The inter-planar distance ($d$) for different composition of Cd$_{1-x}$Zn$_x$S is calculated from Bragg’s relation.

$$d = \frac{\lambda}{2\sin \theta}$$  

The lattice parameters are calculated for hexagonal structure by using the following relation;

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

Whereas, for cubic structure, the following expression is used to calculate the lattice parameter '$a$'

$$a = d\sqrt{h^2 + k^2 + l^2}$$

where $h$, $k$, $l$ are the Miller indices of the lattice plane;

The grain size ($D$) was calculated from the full width at half maximum (FWHM) ($\beta$) by using the Scherrer’s formula [18].

$$D = \frac{0.942}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of X-ray (1.5405 Å) and $\theta$ is the Bragg’s angle. The variation in lattice parameters and grain size with different Zn concentration is shown in Fig. 2. From the figure it is quite evident that the lattice parameters and grain size ($D$) decrease with the increase in Zn content.

The value of $c$ was decreased from 1.341 to 1.265 nm while $a$ decreased from 0.774 to 0.731 nm with increasing Zn content confirming the solid solution formation between CdS and ZnS binary compounds for the selected compositions to make various ternary alloys. Further, the lattice parameters of these films follow the Vegard’s law which means that the lattice parameters of Cd$_{1-x}$Zn$_x$S ternary alloys, with zinc content $x$ can be linearly varied from the leading binary alloy CdS.

3.2. Raman spectroscopy analysis

Raman spectroscopy provides complementary information to understand the vibrational phonon bands in the materials. Raman analysis was made with 442 nm excitation wavelength far below the band gap of the material. Fig. 3 shows the Raman spectra of Cd$_{1-x}$Zn$_x$S thin films for different compositions.

Form the spectra we can see that all the compositions have one dominant Raman phonon band called the longitudinal optical (LO) phonon mode assigned to the hexagonal structured Cd$_{1-x}$Zn$_x$S thin film. Interestingly, the peak position changes smoothly with the alloy composition ($x$) like 313, 319, 321 and 325 cm$^{-1}$ for $x=0.2, 0.4, 0.6$ and 0.8 respectively. The observed blue shift and the corresponding increase in the line width (asymmetrical broadening) with Zn concentration is expected may be due to the enhance structural fluctuation, phonon confinement and substitutional disorder [19]. The most important effect, the blue-shift, can be explained by the gradually increased incorporation of Zn atoms into the Cd sites, which results in more Cd–Zn bonds with a higher LO phonon frequency. Genzal et al. have also obtained theoretically like phonon behavior in bulk Cd$_{1-x}$Zn$_x$S crystals [20]. Moreover, dopants induce potential fluctuation in the material account for the blue shift and asymmetrical broadening in the LO phonon band.

3.3. Atomic force microscopy (AFM) analysis

Atomic Force Microscope was used to examine the surface morphology of the films. Fig. 4 shows the surface morphology of Cd$_{1-x}$Zn$_x$S thin films deposited on glass substrate at room temperature (a) Cd$_{0.8}$Zn$_{0.2}$ S (b) Cd$_{0.6}$Zn$_{0.4}$S. Fig. 4 shows that surface morphology was changed as the amount of Zn composition increases. The values of RMS roughness of the films obtained from the analysis were 4.864 and 3.497 nm respectively, which is due to the decrease of grain size effect.

![Fig. 2](image-url) Variation of lattice parameters $a$, $c$ and grain size with zinc concentration.
It also showed that surface of the samples was approximately smooth and uniform.

3.4. Photospectrometry analysis

The optical spectra were recorded in the wavelength range 300–800 nm, using UV–vis–NIR Photospectrometry. Fig. 5 shows the optical transmission spectra of Cd$_{1-x}$Zn$_x$S thin films various compositions ($x$=0.0, 0.2, 0.4, 0.6, 0.8, 1.0). The spectrum shows the interference pattern with sharp fall at the band edge which is a confirmative evidence of the formation of uniform and good crystalline films [21]. The valleys in the spectra reveal the interference taking place in the films. Moreover, the band edge shifts towards lower wavelength side with the increase in Zn content indicating the increase in band gap energy.

The energy band gap of these thin films was determined from transmission spectra using Tauc’s relation [22].

$$ (zhv)^2 = A(hv-E_g) $$

where $A$, is a constant which is different for different transitions, $E_g$ is the band gap energy of the material and $h$ is the planks
constant. The value of the absorption co-efficient ‘\(a\)’ has been calculated using the relation.

\[
a = \frac{-\ln T}{t} \text{nm}^{-1}
\]

where ‘\(T\)’ is the value of normalized transmittance at a particular wavelength and ‘\(t\)’ is the thickness of the film measured by ellipsometry. Then a plot of \((ah)\) vs \(h\) was obtained for each composition as shown in Fig. 6.

Extrapolation of the linear portion to the \((ah)\) axis gives the value of band gap energy. The band gap energy varies from 2.40 eV to 3.42 eV as shown in Fig. 7. Interestingly, the optical band gap was finely tuned for applications in band gap engineering.

The decrease in the optical constants is attributed to the mixing of higher band gap material (ZnS) with smaller band gap material (CdS). The decrease in extinction coefficient indicates that the films become transparent with the addition of Zn content in the alloy. This is due to the fact that as Zn content increases in Cd\(_{1-x}\)Zn\(_x\)S film, the band gap energy of the films increases as manifested in the Photospectrometry data. The calculated various parameters so obtained for the deposited thin films are summarized in Table 1.

4. Conclusions

The structural and optical analyses of Cd\(_{1-x}\)Zn\(_x\)S thin films prepared by Close Space Sublimation Process were investigated. The tunability of optical constants, band gap, grain size, \(d\)-spacing
and lattice parameter with Zn addition in Cd$_{1-x}$Zn$_x$S film was observed. XRD analysis suggested that all films of Cd$_{1-x}$Zn$_x$S are polycrystalline in nature and have hexagonal structure over the entire composition range (0.0–0.8). The optical band gap was finely tuned from 2.40 to 3.42 eV as Zn content varies from 0.0 to 1.0. The increase in band gap in the solid solution of Cd$_{1-x}$Zn$_x$S for higher Zn content is a bulk property. On the other hand, as x increases, particle size decreases, resulting in higher band gap due to the increasing contribution of quantum size effect. The ellipsometry analysis reveals that the optical constants ($n$ and $k$) decrease with the increase of Zn content in the alloy. In Raman spectra, the shifting of peak position to higher wave number and broadening of optical phonon spectra with increasing Zn content is due to phonon confinement and substitutional disorder. RMS roughness decreases with the increase of Zn concentration in the alloy. The tuning of all optical and structural properties with the addition of Zn into Cd$_{1-x}$Zn$_x$S alloy reveals the transformation of binary compound CdS into ternary compound.

References


Table 1 Variation of peak position, band gap, grain size, d-spacing and lattice parameter due to Zn addition in Cd$_{1-x}$Zn$_x$S film.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Peak angle (2θ)</th>
<th>Film thickness (nm)</th>
<th>Optical band gap (eV)</th>
<th>Grain size (nm)</th>
<th>Lattice parameter C (nm)</th>
<th>Plane (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>26.52</td>
<td>304.088</td>
<td>2.40</td>
<td>15.87</td>
<td>1.341</td>
<td>H(002)</td>
</tr>
<tr>
<td>Cd$<em>{0.8}$Zn$</em>{0.2}$S</td>
<td>26.96</td>
<td>345.368</td>
<td>2.51</td>
<td>14.33</td>
<td>1.317</td>
<td>H(002)</td>
</tr>
<tr>
<td>Cd$<em>{0.6}$Zn$</em>{0.4}$S</td>
<td>27.36</td>
<td>300.799</td>
<td>2.69</td>
<td>14.05</td>
<td>1.301</td>
<td>H(002)</td>
</tr>
<tr>
<td>Cd$<em>{0.4}$Zn$</em>{0.6}$S</td>
<td>27.68</td>
<td>326.130</td>
<td>2.74</td>
<td>13.88</td>
<td>1.285</td>
<td>H(002)</td>
</tr>
<tr>
<td>Cd$<em>{0.2}$Zn$</em>{0.8}$S</td>
<td>28.12</td>
<td>352.233</td>
<td>3.10</td>
<td>13.65</td>
<td>1.265</td>
<td>H(002)</td>
</tr>
<tr>
<td>ZnS</td>
<td>28.56</td>
<td>318.401</td>
<td>3.42</td>
<td>12.42</td>
<td>0.696</td>
<td>C(111)</td>
</tr>
</tbody>
</table>

Fig. 9 Variation of optical constants (a) refractive index with wavelength and (b) extinction coefficient value with wavelength.