A comprehensive study on the structural, morphological, compositional and optical properties of Zn\(_x\)Cd\(_{1-x}\)S thin films

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Abstract

The absorption loss in cadmium sulfide (CdS) thin films which are widely used as a window layer in a photovoltaic cell limits the efficiency of the device. This issue can be addressed by Zn\(_x\)Cd\(_{1-x}\)S thin films due to its tunable band gap nature. Herein, the various composition of Zn\(_x\)Cd\(_{1-x}\)S (x = 0, 0.15, 0.30, 0.45, 0.70, 0.85, 1) thin films were grown by a vacuum thermal evaporation technique and the characteristics of the films were investigated by varying the composition ‘x’. The x-ray diffraction (XRD) studies displayed that the as-deposited films consist of diffraction peaks from both CdS and ZnS lattice. The formation of ternary Zn\(_x\)Cd\(_{1-x}\)S films was verified when the deposited films were subjected to an annealing treatment. The morphology of the films was analyzed using a scanning electron microscope (SEM) and it was observed that the films are uniform, homogeneous and free from any pin-holes and cracks. The presence of Zn, Cd and S elements were quantized using an energy dispersive spectroscopy. Optical studies showed a successful non-linear band gap engineering (2.42–3.49 eV) for the deposited Zn\(_x\)Cd\(_{1-x}\)S thin films. All films showed a very high optical transmittance of above 70% in the visible wavelength region.

1. Introduction

In the present decade, there has been substantial research attention in the II–VI compound semiconductors for the use in opto-electronic devices [1–3]. Among these II–VI semiconductors, cadmium and zinc compounds are extensively studied due to their suitability for solar cells applications since they are direct band gap semiconductors and have high absorption coefficients [4]. CdS is a wide band gap material and used extensively as a window material in non-linear optical devices and photovoltaic cells. But the absorption loss of CdS thin films in the blue region limits the efficiency of the photovoltaic cells [5] which can be overcome by using a relatively wider band gap material than CdS. ZnS, on the other hand, is having a relatively wider band gap than that of CdS and crystals in with a cubic or hexagonal structure. It is an n-type semiconductor, has a very high transmittance (>85%) in the visible wavelength range and is chemically stable [6]. Zn\(_x\)Cd\(_{1-x}\)S films can be formed by diffusion of Zn in CdS. The semiconducting behavior of the Zn\(_x\)Cd\(_{1-x}\)S compound can be tuned between the values corresponding to its pure binaries depending on the device requirements. This makes Zn\(_x\)Cd\(_{1-x}\)S thin films more interesting for solar cell development [7]. Zn\(_x\)Cd\(_{1-x}\)S thin film can be utilized as a window layer for p–n junction devices without lattice mismatch based on quaternary materials such as CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) [8].

A handful of methods are available to grow Zn\(_x\)Cd\(_{1-x}\)S films viz., chemical bath deposition [9–14], spray pyrolysis [15–18], closed spaced sublimation [19], microwave irradiation [20], vacuum evaporation [4, 21–25], and solution growth technique [26]. Among these, the vacuum thermal evaporation process is a well-known simple technique that can be used to deposit thin films with uniform thickness and noble crystallinity. Therefore, in the present report, an effort has been made to deposit high quality Zn\(_x\)Cd\(_{1-x}\)S (x = 0, 0.15, 0.30, 0.45, 0.70, 0.85, 1) thin films using a thermal evaporation system. By altering the composition of the Zn\(_x\)Cd\(_{1-x}\)S
thin films, the structural, morphological, compositional, and optical properties of the films have been investigated in detail.

2. Experimental information

The Zn₀.₄₅Cd₀.₅₅S (x = 0, 0.15, 0.30, 0.45, 0.70, 0.85, 1) thin films were deposited onto pre-cleaned glass at a substrate temperature of 373 K by vacuum thermal evaporation method. The thickness of the films was maintained at ∼500 nm for all the compositions. Commercially available ZnS (purity 99.995%, Sigma Aldrich) and CdS (purity 99.999%, Alfa Aesar) powder were mixed proportionally for various compositions and was used as the source material. Gravimetric analysis was employed to determine the thickness of the films. Cross-sectional SEM was also used to cross-verify with the gravimetric analysis data. The deposited films were subjected to annealing at 373 K in vacuum for a duration of 2 h in order to get pure ZnₓCd₁₋ₓS phase. XRD (Rigaku MiniFlex 600 with CuKα source having λ = 1.5418 Å) analysis was used to examine the structural properties of the deposited films. The surface morphological analysis was characterized using a scanning electron microscope (FE-SEM, Carl Zeiss) and the elemental information of the films was obtained by an energy-dispersive x-ray spectroscopy (EDS) method. A UV–vis spectrometer (SpectraPro 2300i) was utilized to record the optical spectra versus wavelength of the deposited films in the range of 325–750 nm at room temperature.

3. Results

3.1. X-ray studies

X-ray diffraction analysis was carried out to obtain information about the various crystallographic aspects of the ZnₓCd₁₋ₓS films. Figure 1 displays the XRD spectra of the Zn₀.₄₅Cd₀.₅₅S thin film deposited at a substrate temperature of 373 K prior to the annealing treatment. The two distinct peaks at 2θ = 26.46° and 28.52° in figure 1, indicate the improper formation of ternary ZnₓCd₁₋ₓS alloy. Therefore, all the compositions of the deposited films were subjected to an annealing treatment at 373 K in vacuum for a duration of 2 h in order to get pure ZnₓCd₁₋ₓS phase. XRD analysis was used to examine the structural properties of the deposited films. The surface morphological analysis was characterized using a scanning electron microscope (FE-SEM, Carl Zeiss) and the elemental information of the films was obtained by an energy-dispersive x-ray spectroscopy (EDS) method. A UV–vis spectrometer (SpectraPro 2300i) was utilized to record the optical spectra versus wavelength of the deposited films in the range of 325–750 nm at room temperature.
Bragg’s relation was used to calculate interplanar spacing values ‘d’ for the diffraction peaks.

\[ n\lambda = 2d_{hkl} \sin \theta \]  

(1)

Using Scherrer’s formula, the crystallite size was calculated.

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]  

(2)

where, ‘\( \beta \)’ is ‘full width at half maximum of the diffraction peak’, ‘\( \lambda \)’ is ‘wavelength of the x-ray used’ and ‘\( \theta \)’ is the ‘Bragg diffraction angle’.

Figure 2. XRD diffractograms of Zn\(_x\)Cd\(_{1-x}\)S thin films with x = a) 0, b) 0.15, c) 0.30, d) 0.45, e) 0.70, f) 0.85, and g) 1.

Figure 3. Shift in the (002) and (111) peak position of Zn\(_x\)Cd\(_{1-x}\)S thin films with x = a) 0, b) 0.15, c) 0.30, d) 0.45, e) 0.70, f) 0.85, and g) 1.
For the cubic phase, the lattice parameter ‘$a$’ was calculated using:

$$a = \frac{d}{\sqrt{h^2 + k^2 + l^2}}$$  \hspace{1cm} (3)

whereas for the hexagonal crystal system, the lattice parameters ‘$a$’ and ‘$c$’ were determined using:

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

From table 1, it can be noticed that the crystallite size of the (002) predominant peak reduces as Zn content in the Zn$_{x}$Cd$_{1-x}$S thin films increases up to 0.45 in the hexagonal phase which may be due to the stress produced prior to phase change from hexagonal to cubic crystal structure. The lattice parameter, as well as the interplanar spacing of the hexagonal and cubic crystal system, decreases with increasing Zn concentration in the films. A similar decrease in the lattice parameter and interplanar spacing was also observed for Zn$_{x}$Cd$_{1-x}$S films deposited using co-evaporation technique as reported by W Li et al [23]. This is attributed to higher ionic radii of Cd$^{2+}$ (0.95 Å) compared to that of Zn$^{2+}$ (0.74 Å) in the crystal lattice. The decrease in the lattice parameter and interplanar distance thereby concludes the successful substitution of Cd$^{2+}$ by Zn$^{2+}$ and hence verifies the development of the Zn$_{x}$Cd$_{1-x}$S films.

### 3.2. Surface morphological/compositional studies

The FE-SEM images of the thermally deposited Zn$_{x}$Cd$_{1-x}$S thin films are displayed in figure 4. The SEM images indicate the presence of homogeneously distributed large grains throughout the surface of the films without the presence of any pinholes or cracks. Figure 4(h) illustrates the cross-sectional micrograph of Zn$_{0.15}$Cd$_{0.85}$S thin film. The thickness of the film computed from figure 4(h) was found to be in good agreement with the one calculated from the gravimetric analysis. The average grain size values estimated from SEM images are tabulated in table 2. The various elemental compositions of Zn$_{x}$Cd$_{1-x}$S films were verified using EDAX analysis.

| Sample | Composition | 2$\theta$ (°) | Plane | Crystallite Size, D (nm) | Interplanar spacing, $d$ (Å) | $a$ (Å) | $c$ (Å) |
|--------|-------------|---------------|-------|-------------------------|-----------------------------|---------|---------|
| a      | CdS         | 24.77         | 1 0 0 | 22.96                   | 3.592                       | 4.147   | —       |
| b      | Zn$_{0.15}$Cd$_{0.85}$S | 24.79         | 1 0 0 | 19.55                   | 3.589                       | 4.144   | —       |
| c      | Zn$_{0.30}$Cd$_{0.70}$S | 24.89         | 1 0 0 | 17.09                   | 3.574                       | 4.128   | —       |
| d      | Zn$_{0.45}$Cd$_{0.55}$S | 25.16         | 1 0 0 | 14.46                   | 3.523                       | 4.076   | —       |
| e      | Zn$_{0.70}$Cd$_{0.30}$S | 28.24         | 1 1 1 | 11.12                   | 3.158                       | 5.469   | —       |
| f      | Zn$_{0.85}$Cd$_{0.15}$S | 28.42         | 1 1 1 | 21.96                   | 3.138                       | 5.435   | —       |
| g      | ZnS         | 28.52         | 1 1 1 | 25.27                   | 3.127                       | 5.417   | —       |

Figure 4. FE-SEM images of Zn$_{x}$Cd$_{1-x}$S thin films (a) CdS, (b) Zn$_{0.15}$Cd$_{0.85}$S, (c) Zn$_{0.30}$Cd$_{0.70}$S, (d) Zn$_{0.45}$Cd$_{0.55}$S, (e) Zn$_{0.70}$Cd$_{0.30}$S, (f) Zn$_{0.85}$Cd$_{0.15}$S, (g) ZnS and (h) cross-sectional view of Zn$_{0.15}$Cd$_{0.85}$S films.
EDAX spectra of Zn$_{0.15}$Cd$_{0.85}$S thin film is shown in figure 5 (a) whereas the elemental mapping shown in figures 5 (b)–(d) revealed that Zn, Cd, and S are equally dispersed through the surface of the sample. The composition of the films listed in table 2 was found to be in good agreement with the expected values.

3.3. Optical studies

The Zn$_x$Cd$_{1-x}$S thin films were subjected to a UV–Vis spectrometer at room temperature to study its optical properties. The transmittance spectra obtained for the Zn$_x$Cd$_{1-x}$S films are presented in figure 6. It can be seen that all the films are having a transmittance of above 70% and the transmittance of the films rises as the Zn content in the film increases. The presence of the interference pattern in the transmittance spectra at a higher wavelength region indicates the uniform thickness of the films. It can also be observed that as the Zn concentration in the films increases, the absorption edge moves to lower wavelength values, as reported in other investigations [20]. This further confirms the formation of Zn$_x$Cd$_{1-x}$S ternary compound as suggested by the XRD analysis.

Using Tauc’s relation, the optical band gap energy ‘E$_g$’ of the deposited films [29] was determined.

$$\alpha \nu = B(\nu - E_g)^n$$  \hspace{1cm} (5)

where ‘B’ is a constant and the value of ‘n’ is ½ for allowed direct transition type.

| Sample | Zn (at%) | Cd (at%) | S (at%) | Avg. Grain Size (nm) | Band Gap, E$_g$ (eV) |
|--------|----------|----------|---------|----------------------|----------------------|
| a      | 0        | 51.59    | 48.41   | 113                  | 2.42                 |
| b      | 7.87     | 44.77    | 47.36   | 137                  | 2.46                 |
| c      | 16.95    | 35.66    | 47.39   | 144                  | 2.50                 |
| d      | 23.17    | 28.22    | 48.61   | 140                  | 2.65                 |
| e      | 35.61    | 17.90    | 46.49   | 117                  | 2.89                 |
| f      | 48.11    | 7.61     | 44.28   | 127                  | 3.08                 |
| g      | 54.70    | 0        | 45.30   | 68                   | 3.49                 |
Figure 7 shows the Tauc’s plot of the Zn$_x$Cd$_{1-x}$S thin films. The band gap was estimated from the absorption spectra of the films. The band gap energy values calculated differs from 2.42–3.49 eV as the composition ‘$x$’ increases from 0.0 to 1.0. Therefore, it can be mentioned that a successful band gap engineering has been achieved for the thermally evaporated Zn$_x$Cd$_{1-x}$S thin films. The optical band gap for the corresponding binary elements i.e., ZnS and CdS was found to be 3.49 eV and 2.42 eV respectively, as reported in our previous studies [27, 28]. The obtained band gap values of the films are presented in table 2. Figure 8 shows the variation of band gap over the range of composition ‘$x$’. By fitting the obtained band gap values with the below quadratic relation, the degree of the non-linear variation of the films can be calculated [26]:

$$E_g(x) = a + bx + cx^2$$  \hspace{1cm} (6)

where ‘$c$’ is called ‘bowing parameter’, which is characteristic of a particular alloy system, and ‘$x$’ is the composition of the film. Equation (6) can be simplified to the following relation by polynomial fitting the present data to a quadratic equation:

$$E_g(x) = 2.43 + 0.19x + 0.93x^2$$  \hspace{1cm} (7)

The bowing parameter of 0.93 eV obtained here agrees well with the films obtained by Dzhafarov, T D et al [30] ($b = 0.91$ eV) and Borse et al [26] ($b = 0.85$ eV).
The distinct band gap values with exceptional film quality suggest the usage of these films as a window/buffer layer in photovoltaic cells. Generally, CdS is used as a buffer layer in CdTe based solar cells. However, due to its narrow band gap of $\sim 2.4$ eV, CdS absorbs light in the blue wavelength region and hence, the overall cell efficiency of the CdS/CdTe based solar cell gets affected. This issue can be overcome by using Zn$_x$Cd$_{1-x}$S films as it has a much wider band gap. Further, the band gap of the Zn$_x$Cd$_{1-x}$S films can be tuned accordingly to the device requirements. In addition, the films with Zn concentration $< 0.45$ can be utilized as a photosensor, which is being reported elsewhere (B. Barman et al [31]).

4. Conclusion

High quality polycrystalline ternary Zn$_x$Cd$_{1-x}$S thin films were grown using a thermal evaporation system onto glass substrates. XRD analysis revealed that post-annealing treatment plays an important role in the formation of polycrystalline Zn$_x$Cd$_{1-x}$S films. The Zn$_x$Cd$_{1-x}$S thin films were found to have a hexagonal crystal structure with a preferential orientation along (002) plane and as the Zn concentration increases beyond 0.45, the crystal system changes to a cubic structure along (111) plane. The optical energy band gap was found to be increasing non-linearly with increasing Zn concentration in the mixed Zn$_x$Cd$_{1-x}$S thin films. The optical transmittance of the films was found to be above 70% and a bowing parameter of 0.93 eV was determined. A successful band gap tailoring was achieved by a suitable variation in the composition of the films. The obtained properties of the Zn$_x$Cd$_{1-x}$S films suggest that the films can be utilized as a promising material for window layer in solar cells.

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