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Band gap energy determination by Absorption Spectrum Fitting (ASF) procedure and Lattice parameter for different composition of $Cd_xZn_{1-x}S$ thin films

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Abstract

Cadmium zinc sulphide ($Cd_xZ_{1-x}S$) thin films have been chemically prepared unto glass substrates from CdS/ZnS bilayer and its post thermal annealing. Structural and Optical properties of the deposited $Cd_xZ_{1-x}S$ thin films were studied using X-ray diffraction (XRD) and UV-Vis spectroscopy. The X-ray diffraction revealed a cubic structure with (111) preferential orientation. The lattice constants was determined using the Nelson-Riley plot analysis and the result obtained showed that the lattice parameters increase with increase in Cd composition. Starting with the Tauc model, the absorption spectrum fitting technique (ASF) was used in obtaining the optical band gap energy. The values of the direct band gap energy were seen to be in the range of 3.67 and 3.77 eV and depend on $Cd_xZn_{1-x}S$ composition. The reported optical properties of $Cd_xZn_{1-x}S$ ternary compound prepared under this present condition make the thin films useful as a buffer layer in thin film solar cells.
Keywords: Band gap energy, Williamson-Hall, Crystallite size.

1. Introduction

$Cd_xZn_{1-x}S$ is a ternary compound belonging to the II–VI semiconductor group and have attracted numerous attention in many applications. Its properties and parameters can be chosen in a wide range depending on x values (i.e the ratio of Cd^{2+} and Zn^{2+} ions) according to device requirements. It have been previously used as buffer layer in CdTe [1] and $Cu_2ZnSn(Se,S)_4$ [2] based solar cells. The relatively high band gap energy due to zinc-containing solution and the conduction band edge adjustment through the combination of cadmium and zinc has made $Cd_xZn_{1-x}S$ perform better as buffer layer in solar cell application [3]. $Cd_xZn_{1-x}S$ thin film has been prepared by different techniques such as; spray pyrolysis [4], simple ultrasonic radiation method [5], solution growth method [6], vacuum evaporation [7] and chemical bath deposition (CBD) [8]. In this study, CdZnS thin film has been prepared by post-thermal annealing induced inter-diffusion of CdS/ZnS bilayers deposited by chemical bath technique. Here, CdS layer deposition time has been varied leading to the fabrication of $Cd_xZn_{1-x}S$ ternary compound with different compositions. This approach has been formerly used for preparation of semiconducting compounds and alloys thin films including CdZnTe ternary systems [9]. Attention of researchers has recently being attracted to the deposition of semiconductor thin films by chemical method [10] as a result of its advantage of being simple and cost effective when compared to other deposition techniques for large-area solar cell fabrication [11].

It has been observed that the value of the lattice constant determined for different XRD lines of a particular thin film sample slightly differ from each other. Hence, Nelson–-Riley extrapolation method is commonly used to accurately determine the values of the lattice constants. Nelson Riley plot has been employed by many research groups to determine the lattice constant of a cubic system [12]

The study of optical materials involves deeper understanding of their optical band gap energy and hence the optical susceptibility. The most commonly employed procedure for estimating band gap energy of materials involves evaluating the optical absorption coefficient and applying the Tauc method. This method has been widely used for different binary and ternary semiconducting materials [8]. In determining the absorption coefficient,

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measurement of the film's absorbance, the reflectance and film thickness are necessary [13]. Another technique for estimating the band gap energy known as absorption spectrum fitting (ASF) has been proposed. In this procedure, band gap energy can be estimated with the measurement of film's absorbance only, and without information about the film's thickness and reflectance.

In this paper, the authors has employed Nelson-Riley plot analysis to study the effect of Cd contents on the lattice constant of $Cd_xZn_{1-x}S$ ternary thin film. In addition, absorption spectrum fitting (ASF) procedure was used to determine the band gap energy.

2. Experimental details

In this study, commercially available glass slide of dimension 25.4 mm x 76.2 mm x 1.2 mm was used as substrate, and since substrate cleaning plays a significant role in thin films deposition, the substrates were subjected to detailed cleaning before thin films deposition. The cleaning was done successively in an ultrasonic bath using methanol, acetone and distilled water, each taking a period of 45 min. CdS and ZnS thin films were prepared using the chemical bath deposition technique. The Cadmium sulphide bath contains an aqueous solution of 50 ml Cd $(CH_3COO)_2$. $2H_2O$ (0.2 M) and 50 ml $CS(NH_2)_2$ (0.5 M). Zinc Sulphide bath, on its part was prepared using a mixture of 50 ml $ZnSO_4$ (0.2 M) and 50 ml $CS(NH_2)_2$ (0.5 M). In both cases ammonia (NH_3) was used as the complexing agent, and the solution baths were prepared at pH of 10.5 and temperature of 343 K. The pre-cleaned glass substrates were inserted vertically in the CdS solution and removed after different times of 10, 15 and 20 mins in order to prepare the glass/CdS thin films. After, the previously prepare glass/CdS were each inserted into the ZnS bath for 45 mins, in such a manner as to vary the CdS layer thickness while keeping the thickness of ZnS layer constant. Panalytical multipurpose (X' Pert-Pro) operated at 40 kV and 30mA was used for structural characterization of the prepared thin film samples. The x-ray source utilized was of Cu-kα radiation with wavelength equal to 0.15406 nm. The elemental composition were studied using energy dispersive X-ray (EDX) spectrometer. The optical transmittance was carried out using Avantes-SAI-07086751 model UV-Vis spectrophotometer in the range 300 nm to 1000 nm.

3.0. Results and Discussion

3.1. EDS and XRD Analysis

The result of the EDS analysis performed on the prepared samples (spectra not shown) confirmed the presence of the three major elements: Cd, Zn and S. Moreover, an increase in the atomic percent of cadmium as CdS deposition time increases was observed, with Cd/Zn ratio of 0.20, 0.30 and 0.44 for 10-CdS/ZnS, 15-CdS/ZnS, and 20-CdS/ZnS samples recorded respectively. Moreover, $Cd_xZn_{1-x}S$ alloy compounds with varying compositions of $Cd_{0.16}Zn_{0.84}S$, $Cd_{0.20}Zn_{0.80}S$ and $Cd_{0.30}Zn_{0.70}S$ were determined.

Figure 1 shows the XRD spectra of the prepared thin film samples with different CdS layer deposition times and annealed at 400°C. The observed peaks are typical of (111), (220) and (311) planes of a cubic CdZnS ternary compound [14] without any phase transition with increasing CdS layer deposition times. The figure reveals a continuous shift in peaks position toward the lower angles as the Cd contents increase. The preferential orientation was observed for all the samples at the (111) plane and with its intensity increasing with the increase in CdS layer deposition times.

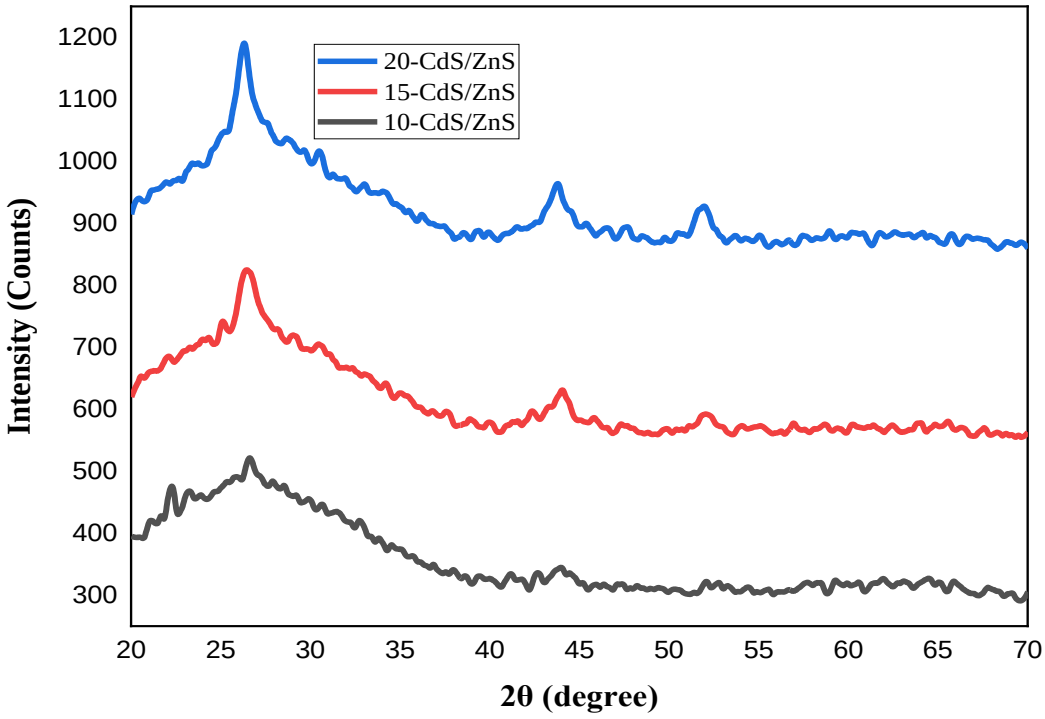

Figure 1: X-ray diffraction (XRD) Analysis of CdZnS thin films

3.1. Nelson-Riley plot analysis

The Nelson-Riley plot was applied in other to estimate the values of the lattice parameters for the film samples. The Nelson-Riley plot involves the graph between the calculated lattice parameters (a) for the different planes (as against employing only the preferential plane), and their error functions [15, 16]. The same method has been used to determine the lattice parameter of CuO_2 thin film prepared by spray pyrolysis technique [12]. Analyzing lattice constants with Nelson-Riley plot correction is vital for accurately assessing a crystalline material's parameters. These refined constants are crucial for understanding its crystallographic properties, predicting its behavior, and making precise calculations for various applications. The lattice constants and error functions for each plane were determined using equations 1 and 2 respectively [17];

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \quad (1)$$

and

$$f(\theta) = \frac{1}{2}\left(\frac{cos^2\theta}{sin\theta} + \frac{cos^2\theta}{\theta}\right) \quad (2)$$

A typical Nelson–Riley plots for $Cd_xZn_{1-x}S$ alloy thin film samples are shown in Fig. 2 and the value of the corrected lattice constants presented in table 1.

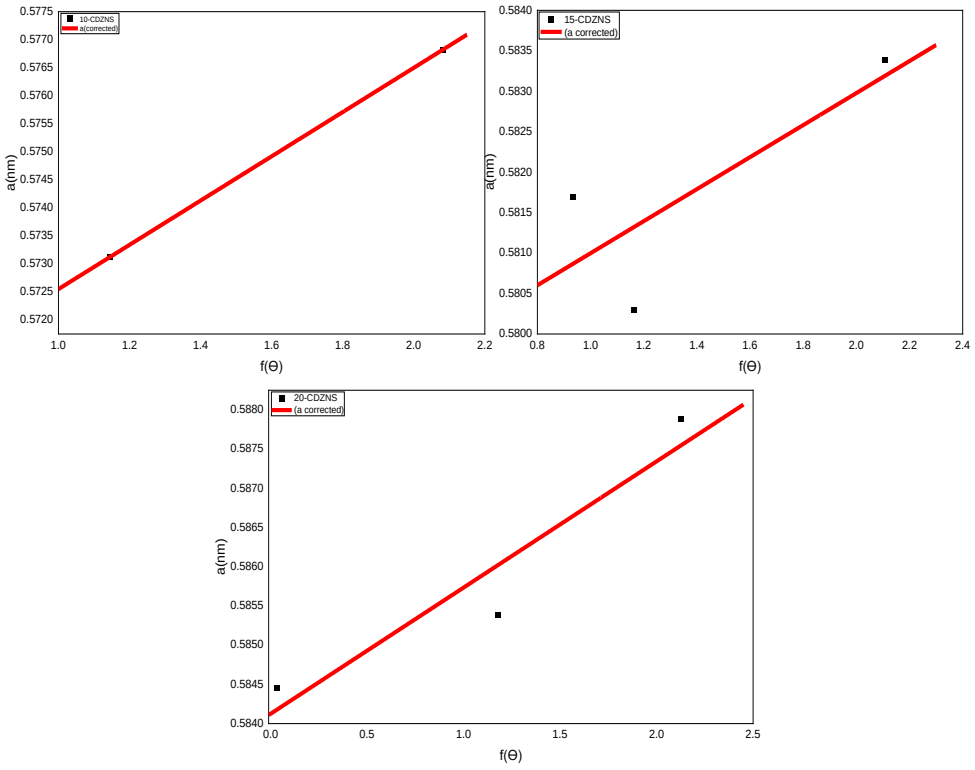

Figure 2: **Nelson-Riley plots of the prepared thin film samples**

It can be observed that the corrected lattice constant increases with increasing cadmium composition and this may be attributed to the greater ionic radius of Cd^{2+} (0.97 Å) as compared to Zn^{2+} (0.74 Å). More cadmium ion is assumed to be introduced into the CdZnS structure as CdS deposition time increases which leads to increase in lattice constant.

Table 1: Structural parameters of the 10-CdS/ZnS, 15-CdS/ZnS and 20-CdS/ZnS thin films showing corrected lattice constant

Samples	hkl	2θ (degree)	β (degree)	d (nm)	a (nm)	a corrected (nm)	f(θ)
10-CdS/ZnS	111	26.7645	0.8187	0.33303	0.57682	0.56886	2.0815
	220	44.1060	0.9444	0.20263	0.57312		1.1442
15-CdS/ZnS	111	26.4480	0.8187	0.33682	0.58339	0.57902	2.1078
	220	44.1060	0.8187	0.20517	0.58030		1.1633
	311	52.1040	0.7128	0.17539	0.58169		0.9343
20-CdS/ZnS	111	26.2334	0.3070	0.33941	0.58789	0.58412	2.1259
	220	43.6987	0.8187	0.20699	0.58539		1.1771
	311	51.8142	0.8186	0.17621	0.58446		0.0312

3.3. Absorption Spectrum Fitting (ASF)

Absorption spectrum fitting (ASF) involves only the measurement of film's absorbance without the need for additional parameters like thickness and reflectance. In this procedure, the relation $\nu = \frac{c}{\lambda}$ is used to transform the Tauc's equation (Eq. 3) into a similar equation with function of wavelength (Eg. 4). Bhogi *et al* (2022) previously used the method to determine the band gap energy of Li_2O–SrO–B_2O_3–MnO quaternary glass system [18].

$$\alpha h\nu = \boldsymbol{A}\left(h\nu - E_g\right)^m. \quad (3)$$

$$\frac{\alpha hc}{\lambda} = \mathbf{A}\left(\frac{hc}{\lambda} - \frac{hc}{\lambda_{gap}}\right)^m. \quad (4)$$

where, α, h, c and λ_{gap} are the absorption coefficient, planks constant, velocity of light and the wavelength corresponding to optical gap value respectively, p is the power factor and **A** is the proportionality coefficient.

The Beer-Lambert's law, $\alpha(\lambda) = \frac{2.303\ \text{Abs}\ (\lambda)}{t}$ was further employed to transform equation 4 as indicated below:

$$\frac{\text{Abs}\ (\lambda)}{\lambda} = K_1 \times \left(\frac{1}{\lambda} - \frac{1}{\lambda_{gap}}\right)^m + K_2. \quad (5)$$

where $K_1 = \frac{\mathbf{A}t(hc)^{m-1}}{2.303}$ and K_2 is a constant that takes into account the reflection.

For allowed direct transition, m = ½. Thus, a plot of $\left(\frac{\text{Abs}\ (\lambda)}{\lambda}\right)^2$ against $\frac{1}{\lambda}$ is presented in Figure 3.

The wavelength that corresponds to the band gap energy (λ_{gap}), is deduced by extrapolating the linear portion of the curves to $\frac{1}{\lambda} = 0$. Thus, the band gap energy (in electron volt) for the prepared thin film samples can be computed using $E_g = \frac{1239.83}{\lambda_{gap}}$ [19]. The values of the estimated direct band gap energy are; 3.77, 3.73 and 3.69 eV, for 10-CdS/ZnS. 15-CdS/ZnS and 20-CdS/ZnS respectively, signifying reduction in the band gap energy of the ternary thin film compound with increasing Cd composition. Continuous reduction in the band gap of $Cd_xZn_{1-x}S$ thin film with increasing Cd composition can be attributed to the introduction of more CdS compound with lower band gap energy into the structure as its deposition time increase. This assertion confirms that the band gap energy

of CdZnS ternary compound thin films can be tuned to a desired value with the adjustment of the CdS layer deposition times.

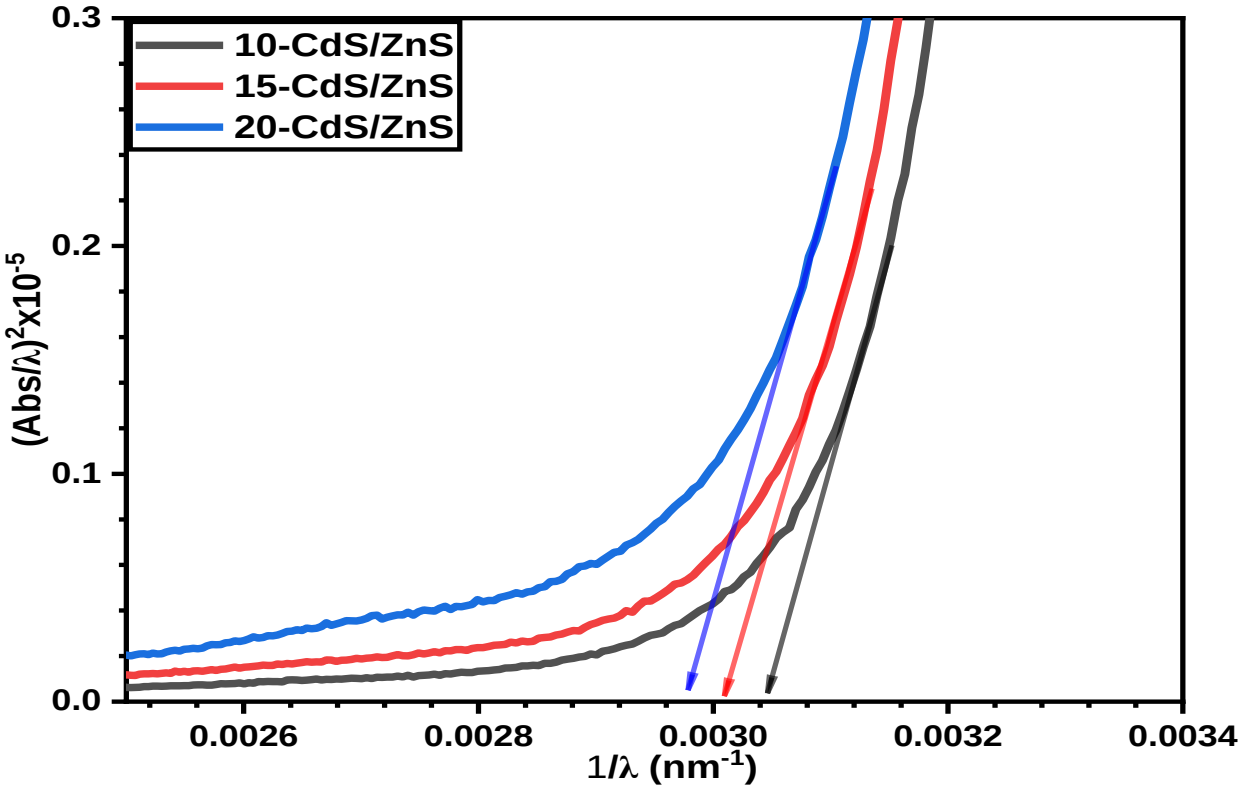

Figure 3: Absorption spectrum fitting plot for the prepared CdZnS thin film samples

4. Conclusion

In this study, $Cd_xZ_{1-x}S$) thin films was prepared unto glass substrates through chemical bath deposition route from CdS/ZnS bilayer and its post thermal annealing. The band gap energy of the prepared thin films have been determined by absorption spectrum fitting (ASF) technique and the values ranging between 3.67 and 3.77 eV. The bang gap energy was observed to decrease with increasing CdS layer deposition times. The XRD data was employed in determining the lattice constants using the Nelson-Riley plot analysis and the result obtained showed that the lattice parameters increase with increase in Cd composition. The reported optical properties of $Cd_xZn_{1-x}S$ ternary compound prepared under this present condition make the thin films useful as a buffer layer in thin film solar cells.

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