

The role of Cu doping in properties of CdZnS thin films

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CdZnS thin films created via chemical bath deposition were examined to see how Cu doping affected their characteristics. Cu ions were added to the films in order to change their optical, structural, and morphological characteristics. These findings suggest that Cu doping can be used to modify the optical characteristics of CdZnS thin films. By using X-ray diffraction (XRD) and the energy dispersive analysis of X-ray method (EDAX), we were able to investigate the compositional ratio as well as the structural features of the films. The field emission scanning electron microscopy (FESEM) technique was utilized in order to investigate the surface morphology of the produced films. The morphology of prepared films was fiber-like and in nanoscale. In addition, the UV-vis spectroscopy technique was utilized in order to characterize the optical properties of thin films. The prepared Cu-CdZnS film was found to have direct band gap equal to 2.64 eV and indirect gap equal to 2.4 eV.

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1. Introduction

Chalcogenide semiconductors provide notable tuning capabilities, rendering them suitable for many applications such as laser, solar cell, transistor, sensor material, and diode [1]. Cadmium zinc sulfide (CdZnS) nanofilms have been widely utilized as a window materials with a wide bandgap in heterojunction solar cell and photo conductive devices. In the context of solar cell systems, it has been observed that the utilization of CdS films has shown to be efficient. However, the substitution of CdS with the ternary compound CdZnS, which possesses a greater band gap, has yielded a reduction in window absorption losses. Consequently, this substitution has led to an augmentation in the short-circuit current within the solar cell [2].

The fabrication of CdZnS thin films has involved many thin-film deposition procedures, such as vacuum evaporations, spray pyrolysis, dipping coater technique, electro deposition,

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chemical bath deposition, and successive ionic layer adsorption and reaction (SILAR) [3].

The CBD approach is chosen because of its cost-effectiveness and the absence of a need for vacuum conditions. In the meanwhile, the process can be characterized as straightforward, with deposition parameters that are comparatively more manageable [4,5].

The process of doping semiconductors enables investigators to effectively utilize the inherent features of the host material. The modulation of semiconductor conductivity can be achieved by increasing the concentration of charge carriers [6]. Many researchers worked on preparing of CdZnS thin films and alteration of their properties by doping process.

Dzhafarov et al. (2006), examined the properties of (CdZnS) films made by reactive diffusion of Zn in CdS. CdZnS ternary compounds with band gaps ranging from 2.64 eV near the surface to 2.43 eV [7]. Singhal et al. (2009), studied Zn_{0.6}Cd_{0.4}S thin films and found enhancement in structure superiority with growing flux density of laser within a certain range [8]. Chemical bath deposition was used by Akhtar et al. (2015), to deposit Fe-doped ZnS nanocrystalline thin films on glass and they found Iron incorporated into ZnS lattice changed the lattice parameters [9]. Jadhav and Betkar (2015), deposited Cd_{1-x}Zn_xS thin films on silicon glass substrates with Chemical Bath Deposition. Absorption data were used to determine energy band gap from UV-VIS spectroscopy. With increasing Zn content, the band gap energy increased from 2.7 to 3.9 eV. [10].

By chemical bath deposition at 2 and 4 mol% Sn concentrations, and synthesized Sn-doped CdZnS nanoparticles XRD confirmed the cubic and hexagonal structure of CdZnS, and Sn did not alter the structure [11]. A chemical bath deposition method was used by the researchers in (2015), to synthesize Cerium-doped CdZnS:Ce nanoparticles. X-ray diffraction found cubic and hexagonal structures in CdZnS. 470 and 455 nm were absorption bands. Energy band gap was 3.45-3.15 eV. [12]. Narasimman et al. (2016), prepared CdZnS thin films by spray pyrolysis with various levels of Zn doping. The films exhibited hexagonal structure (0 0 2). An SEM revealed needle-shaped grains with Zn doping. Transparency increased with Zn doping, showing 90% transmittance at 6 wt.% Zn. Zn doping shifts the optical band gap blue [13].

Mosavi and Kafashan (2019), synthesized un- and Cd-doped ZnS nanostructures using an electrodeposition method. Cd doping decreased crystallite size and increased lattice strain, lattice stress, dislocation density, and stacking fault energy. The Cd-doped samples had a smaller band gap energy and dielectric constant compared to undoped ZnS [14].

CBD technique had been conducted by the researchers in (2019) to synthesize CdZnS:CeSn nanoparticles from fixed Ce (3.84 mol%) as well as 3 concentrations of Sn. A peak in (CdZnS:Ce)Sn and (CdZnS:Ce)Sn films was observed at 540 nm, 560 nm, and 570 nm, respectively. Micrographs taken using a scanning electron microscope revealed leafy and ball-like structures. EDS analysis confirms Sn and Ce presence [15].

In current paper, we have deposited nanofilms of Cu-CdZnS via the chemical bath deposition (CBD) approach. In this experimental procedure, the precursors employed for the fabrication of CdZnS films consisted of cadmium chloride, zinc nitride, and thiourea. The concentration of copper in the resulting films was controlled by introducing a precise quantity of cupric chloride, which was adjusted to achieve a specific weight percentage relative to cadmium chloride. A comprehensive investigation was conducted to examine the impact of copper doping on the structure, optical, morphology, and composition characteristics of nanofilms.

2. Experimental procedure

The deposition of a nanocrystalline Cu-CdZnS thin film onto glass substrates is achieved using the chemical bath deposition (CBD). In the synthesis of copper (1%) doped cadmium zinc sulfide nanoparticles, a 0.05 M of copper chloride (CuCl₂) was introduced into a solution containing 0.5 M cadmium chloride (CdCl₂), both with a volume of 10 ml. The aforementioned solution was combined with 0.5 M of Zinc nitride [Zn(NO)₃] in a volume of 10 ml. An ammonia solution was introduced to modify the pH of the solution to a value of 11. Subsequently, a gradual addition of 10 ml of a 0.5 M thiourea solution was made to the aforementioned mixture, resulting in a final volume of 100 ml achieved by supplementing the mixture with deionized water. The

mixture was agitated using a magnetic stirrer for a duration of five minutes. The substrates were vertically immersed in the beaker and thereafter positioned on the hot plate at a temperature of 70 oC for a duration of 60 minutes. Subsequently, the specimens are extracted from the solution and subjected to a rinsing process utilizing distilled water in order to eliminate any impurities, after which they are allowed to air-dry. The structure possessions of CdZnS nanofilms are examined using (XRD) using Cu-K radiation having a wavelength of 1.5418. The surface morphology analysis was conducted using (FESEM). The absorption coefficient (α) and band gap (E_g) are determined through the measurements of absorption using a UV-VIS Spectrophotometer across a wavelength range spanning from 350nm to 1000nm, followed by subsequent calculation of the obtained data.

3. Results and discussion

3.1. Results of X-ray Diffraction (XRD)

The XRD method is used to analyze materials' crystal structure and phase composition. Cu-doped CdZnS thin films can be investigated using XRD to interpret how copper dopants affect their structural properties. XRD analysis of Cu-doped CdZnS thin films can reveal the following:

i-The XRD peaks of CdZnS with Cu doping changed. CdZnS may change its lattice parameters and crystal structure due to copper ions. A Cu dopant may broaden the peak. The crystallite size or microstructure could change.

ii-New XRD peaks may appear depending on the level of Cu doping and processing conditions. Cu can change the intensity of XRD peaks by reacting with CdZnS to form CuS. Peak appearances and intensities can indicate changes in crystallinity and phase content. Cu doping could influence the preferred crystallographic orientation of the thin films, leads to variations in the comparative intensities of certain peaks. This could be an indicator of texture development in the films. Copper ions can induce lattice strain in the CdZnS lattice due to differences in ionic radii. XRD can reveal strain-induced shifts in peak positions and peak shape changes. Structure and crystallinity can be determined quantitatively from XRD data. Copper doping influences XRD peak profiles and reveals crystalline growth mechanisms. It depends on factors such as the concentration, the method, the annealing conditions, and the overall processing procedure. A comprehensive understanding of how Cu doping affects CdZnS films should include XRD, FESEM, and EDS.

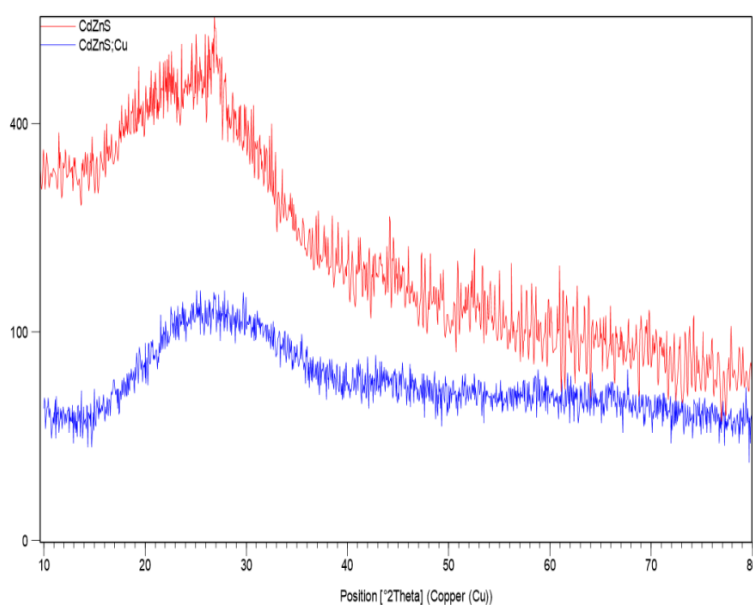


Fig. 1. XRD spectra of Cu-doped and undoped CdZnS.

The curves in Fig.1 represent the XRD arrangements of CdZnS and Cu doped CdZnS films, respectively. The pure CdZnS thin film diffraction peaks are recorded for angles 13.351, 28.729, 34.131, 38.907, 44.696, 48.615, 61.690, 63.883, 65.735, 71.742, 74.317, 77.351, 78.339, and 79.880 corresponding to the lattice planes are (001), (002),(010), (011), (003), (012), (004), (100), (101), (102), (020), (014), (021), and (103) respectively. The Cu doped CdZnS showed the diffraction peaks of angles 13.323, 25.606, 28.97675, 37.44958, 40.772, 45.15631, 53.32695, 56.662, 60.07161, 62.4625, 68.65444, 74.13161, 76.866, 78.23499, and 79.91643. The corresponding lattice planes are (001), (100), (011), (012), (003), (110), (112), (004), (022), (113), (023), (114), (105), (122), and (204) respectively [16].

Table 1. CdZnS and Cu doped CdZnS films XRD results.

Sample	Pos. 2theta (degree)	FWHM	d-spacing [Angstrom]	Rel. Int. [%]
CdZnS	13.351	3.162278	6.62647	26.85
	28.729	3.162278	3.1049	100
	34.131	3.162278	2.62485	30.61
	38.907	3.162278	2.31293	17.4
	44.696	3.162278	2.02586	1.62
	48.615	3.162278	1.87133	4.85
	61.690	3.162278	1.50237	4.42
	63.883	3.162278	1.456	4.43
	65.735	3.162278	1.41939	4.31
	71.742	3.162278	1.31458	2.98
	74.317	3.162278	1.27529	2.77
	77.351	3.162278	1.23266	1.14
	78.339	3.162278	1.21957	2.49
	79.880	3.162278	1.19987	6.64
Cu doped CdZnS	13.323	0.1	6.64022	25.06
	25.606	0.1	3.47611	55.51
	28.97675	0.1	3.07894	31.35
	37.44958	0.1	2.39952	8.54
	40.772	0.1	2.2113	1.71
	45.15631	0.1	2.00628	38.58
	53.32695	0.1	1.71655	13.09
	56.662	0.1	1.62318	0
	60.07161	0.1	1.53893	4.08
	62.4625	0.1	1.48565	0.46
	68.65444	0.1	1.36598	5.81
	74.13161	0.1	1.27801	1.83
	76.866	0.1	1.23922	3.01
	78.23499	0.1	1.22093	0.82
79.91643	0.1	1.19942	0.79	

3.2. Results of field emission scanning electron microscopy (FESEM)

The morphologies of surfaces observe using (FESEM), which used to examine the surfaces morphologies and microstructure of materials at high magnifications. FESEM can reveal

differences in their surface features, particle sizes, and overall structural characteristics. The surface in Fig. 4 a,b, of CdZnS and figure 4 c,d of Cu-doped CdZnS, both doped and pure films exhibit fiber-like in morphology [17-19].

Doping with copper influence in particles and their distribution. The dopants affect nucleation and growth processes, leading to changes in particle size and distribution. Aggregation of particles observed, depending on the synthesis conditions. Aggregation could result from coalescence during growth or agglomeration during deposition.

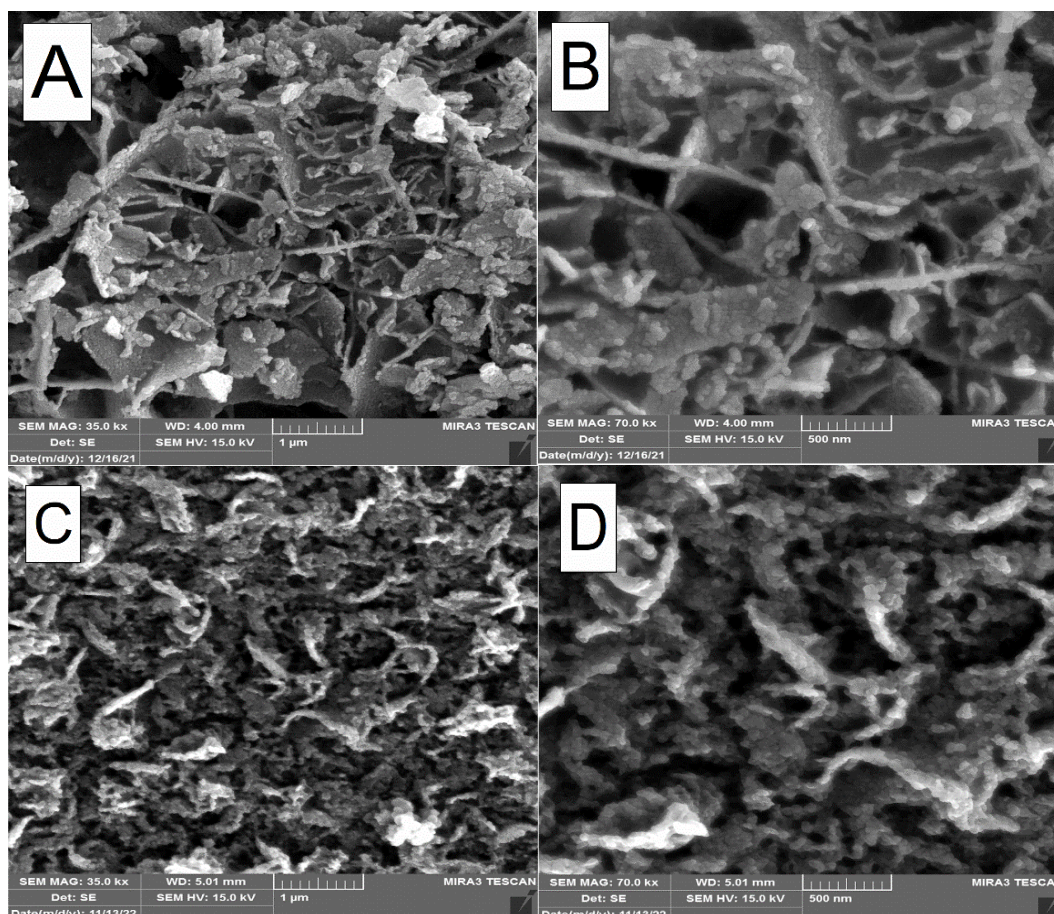


Fig. 2. Different magnification of SEM images of Cu-CdZnS thin film.

3.3 Results of Energy Dispersive X-Ray Spectroscopy (EDS)

The EDS spectra of Cu-CdZnS, as depicted in Figure 3, indicate the detection of significant chemical components, specifically cadmium, sulphur, zinc, and copper. A prominent peak corresponding to copper (Cu) was observed in the spectra, which can be attributed to its comparatively higher concentration when compared to Cd and Zn. Table 2 presents the element structure examination of Cu-doped CdZnS, thereby confirming that the majority of Cu ions are really doped within the CdZnS substrate. No further peaks were observed in the spectrum, hence validating the great purity of the produced films.

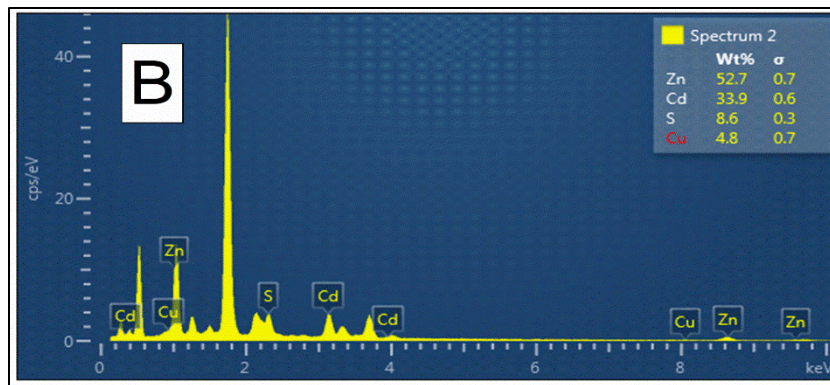


Fig. 3. EDX spectrum for Cu-CdZnS.

Table 2. EDS elemental analysis for Cu doped CdZnS.

Element	Line Type	Apparent Concentration	Wt%	Wt% Sigma	Atomic %
S	K series	0.49	8.59	0.29	18.46
Cu	L series	0.16	4.84	0.70	5.25
Zn	L series	1.68	52.71	0.73	55.55
Cd	L series	1.61	33.85	0.64	20.75
Total:			100.00		100.00

Figure 4 illustrates the absorbance of the substance. As observed from the figures, the nanofilm has a great absorption at a wavelengths fewer than 400 nm; however, when the wavelength is larger than 400 nm, the absorbance rapidly declines, and by the time it reaches a very tiny value, it has reached an extremely low value [20,21]. The inset figure represent the absorption coefficient of Cu-CdZnS film which is shows good absorption range in the uv region.

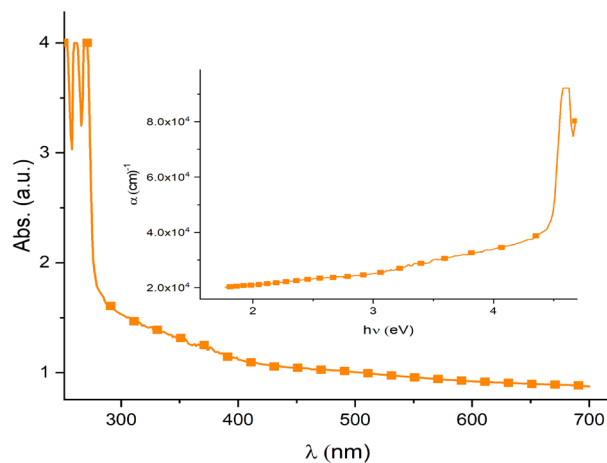


Fig. 4. The spectrum of absorbance for prepared film of Cu-CdZnS.

It was possible to regulate the energy bandgaps of prepared films by analyzing the absorption spectra. Figure 4 and 5 show the indirect and direct energy gaps. The indirect E_g value for the Cu-CdZnS film was found to be equal to 2.4 eV. The direct E_g value for the Cu-CdZnS film was found to be equal to 2.63 eV, and this values precisely coincides with the value that was published in [22].

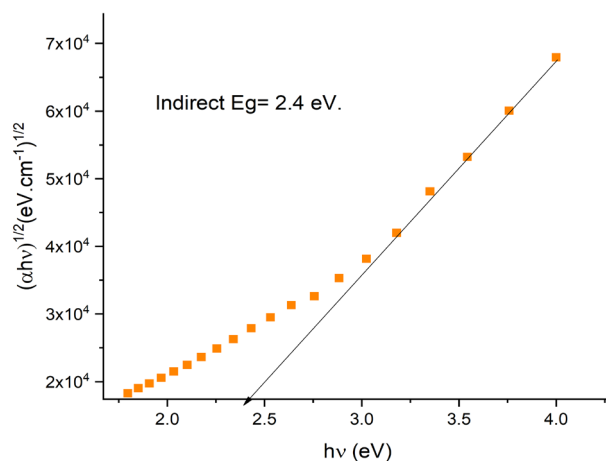


Fig. 4. Indirect band gap of Cu-CdZnS film.

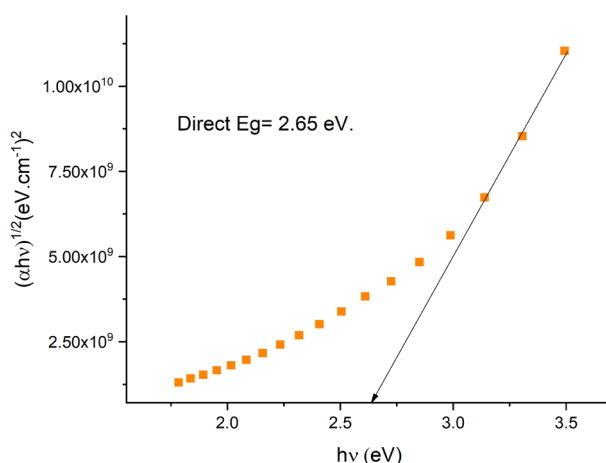


Fig. 5. Direct band gap of Cu-CdZnS film.

4. Conclusion

The presence of Cu dopants can influence the microstructural characteristics, resulting in changes to grain size, texture, and surface morphology. Cu-doped CdZnS can be tailored for specific applications by controlling the Cu dopant concentration. For instance, it might be optimized for enhanced photocatalytic activity, improved gas sensing, or modified light emission. The introduction of Cu dopants can lead to changes in the crystal structure and lattice parameters of CdZnS. The presence of Cu ions may induce lattice strain or alter the arrangement of atoms. The morphology of prepared films was fiber-like and in nanoscale. In addition, the UV-vis spectroscopy technique was utilized with the purpose of characterize the optical possessions of prepared films. The prepared Cu-CdZnS film was found to have direct band gap equal to 2.64 eV and indirect gap equal to 2.4 eV.

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