JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

A Study of Synthesis and Characterization of CdZnS Nanostructure Films Using CBD Method

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Abstract:

In this paper, synthesis and characterization of nanostructured CdZnS films were investigated to explore their potential applications in optoelectronic devices. Using a chemical bath deposition (CBD) method, high-quality CdZnS films with varying zinc molar concentrations of 0.25, 0.5 and 0.75 were successfully prepared in a polyvinyl alcohol (PVA) matrix at room temperature. This study aimed to optimize the synthesis parameters and characterize the structural, compositional, and morphological properties of the resulting films. Optimal conditions for the synthesis were determined to be a stirring rate of 200 rpm, a temperature of 72°C, and a stirring duration of 3.5 hours. These conditions ensured the proper mixing and reaction of precursor materials, resulting in uniform film deposition. X-ray diffraction (XRD) analysis revealed three broad peaks in all samples, corresponding to the (111), (220), and (311) lattice planes of the cubic phase structure of CdZnS. An observed shift in peak positions towards higher diffraction angles with increasing zinc content indicated the presence of residual stress and changes in lattice parameters due to the incorporation of zinc.

Energy dispersive X-ray (EDAX) analysis confirmed that the synthesized films comprised cadmium (Cd), zinc (Zn), and sulfur (S) without any detectable impurities, ensuring their purity for optoelectronic applications. The scanning electron microscopy (SEM) images showed nearly spherical nanoparticles uniformly distributed across the films, highlighting the uniformity and absence of significant agglomeration in most samples. The research findings demonstrated that the CBD method is highly effective in producing high-quality nanostructured CdZnS films. The films exhibit good crystallinity and uniformity, essential for their performance in various applications. The ability to control the zinc concentration allowed for the tuning of structural properties, which is crucial for optimizing the films for specific optoelectronic devices.

In conclusion, the synthesized CdZnS nanostructured films possess the desirable qualities for optoelectronic applications, including high crystallinity, uniformity, and controllable compositional properties. The study highlights the potential of the CBD method for producing advanced materials tailored for specific technological uses. Future research could further optimize the synthesis parameters and explore the integration of these films into various optoelectronic devices, enhancing their performance and expanding their applicability in fields such as photovoltaics, sensors, and light-emitting diodes.

Keywords: Optoelectronic, Morphological, Precursor, Diffraction, Photovoltaics, Crystallinity.

1. Introduction

Nanostructured inorganic semiconductor materials have garnered significant attention in recent years due to their unique properties, which open up new possibilities in science and technology. These materials exhibit distinct luminescence and optical characteristics, quantum size effects, and other physical and chemical properties that differ markedly from their bulk counterparts. Group IIVI nanostructured semiconductors, in particular, are pivotal in applications ranging from gas sensors and solar cells to biological detection and various luminescence devices. Among these, the cadmium zinc sulphide (CdZnS) ternary alloy stands out as a highly promising wide band gap material.

CdZnS offers a tunable band gap ranging from 2.42 eV (CdS) to 3.68 eV (ZnS), making it an excellent candidate for enhancing the performance of thinfilm photovoltaic cells such as CdTe and CIS types. The increased band gap with higher Zn content results in greater transparency to shorter wavelength light and a reduced electron affinity, thus enhancing conduction band alignment. These attributes facilitate the development of blue and UV diode lasers, highdensity optical recording, and heterojunction devices with improved opencircuit voltage and shortcircuit current. The material's broad green emission peaks, which shift towards shorter wavelengths with increasing Zn content, further underscore its versatility for shortwavelength diode laser applications.

Recent innovations in the synthesis of CdZnS nanomaterials have involved various techniques, including spray pyrolysis, dip coating, electrodeposition, metalorganic chemical vapor deposition (MOCVD), successive ionic layer absorption and reaction (SILAR), vacuum evaporation, and chemical bath deposition (CBD). By adjusting the Zn molar concentration and employing capping agents like polyvinyl alcohol, researchers have achieved highquality, uniformly distributed CdZnS films. These advancements hold significant potential for the development of optoelectronic devices, including photoluminescent, photoconductor, and electroluminescent applications, thus demonstrating the vast scope of CdZnS nanocompounds in modern technology.

2 Synthesis of CdZnS Nanofilms using Chemical Bath Deposition (CBD) Technique:

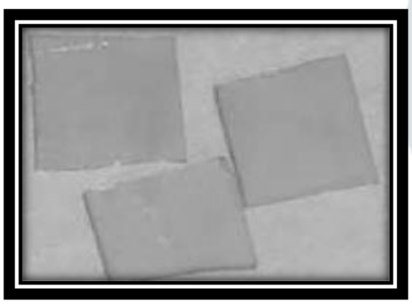
2.1 Material Used:

The following materials were used for synthesizing CdZnS nanostructured films on glass substrates via the chemical bath deposition method:

Material	**Purity**	**Molecular Weight**
Polyvinyl alcohol (PVA)	Pure	125,000
Monohydrate cadmium chloride ($CdCl_2 \cdot H_2O$)	Pure	201.32 g/mol
Zinc chloride ($ZnCl_2$)	Dry Purified	136.28 g/mol
Nonahydrate sodium sulphide ($Na_2S \cdot 9H_2O$)	Pure	78.05 g/mol

2.2 Details of Synthesis using CBD method:

CdZnS nanostructured films were synthesized using the chemical bath deposition (CBD) method on meticulously cleaned glass substrates with zinc molar concentrations of 0.25, 0.5 and 0.75. $CdCl_2$, $ZnCl_2$, and Na_2S served as the sources of Cd^{2+}, Zn^{2+}, and S^{2-} ions, respectively, while polyvinyl alcohol (PVA) was utilized as a capping agent. The procedure for preparing the CdZnS1 film involved adding 0.5 M $CdCl_2$ solution and 0.25 M $ZnCl_2$ solution to an aqueous PVA solution under vigorous stirring at 200 rpm. All solutions were equal in quantity. The stirring was conducted at a constant temperature of 72°C for 3.5 hours.



The mixture was then allowed to stand for 13 hours to ensure complete dissolution. Subsequently, a 0.25 M Na_2S solution was introduced into the mixture, stirred for 20 minutes, and left undisturbed for 35 minutes. The resulting CdZnS solution, containing PVA, was cast onto the glass substrates and left to dry in a closed chamber at ambient temperature to form the CdZnS1 film. **Fig. 1 Sample of CdZnS** The film was further dried for 5-6 days at room temperature. For the preparation of CdZnS2 and CdZnS3 films, the molarity ratios of $CdCl_2$ to $ZnCl_2$ solutions were adjusted to 0.5:0.5 and 0.5:0.75, respectively, while maintaining the Na_2S molarity at 0.25 M. The same preparation process was followed for each film. All deposited CdZnS films exhibited a golden yellow color, were uniform, and showed high adherence to the substrates.

2.3 Result and Discussion

2.3.1 X-ray Diffraction Analysis of CdZnS Nanostructured Films

The X-ray diffraction (XRD) patterns of CdZnS nanostructured films synthesized in a PVA matrix at room temperature were obtained using Pro XRD systems with CuKα radiation (λ=1.54046 Å) in Bragg-Brentano mode. The data were collected at a scan rate of 0.02°/s with a 0.6 s per step increment. Figures 2 given below illustrate the XRD patterns for CdZnS1, CdZnS2 and CdZnS3 films, respectively.

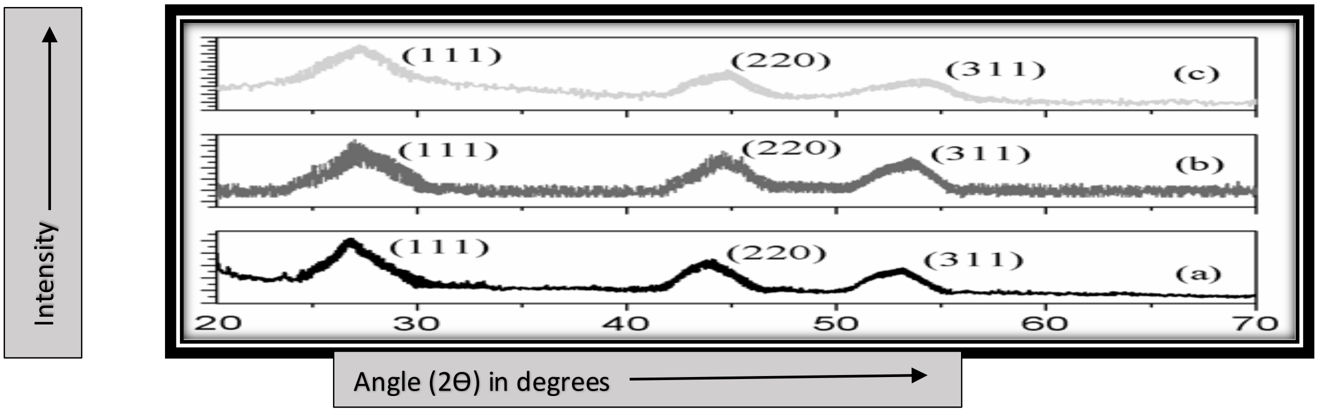


Fig. 2: Diffraction pattern obtained for 3 different samples of CdZnS nano-films

Each pattern exhibits three distinct and broad peaks, indicating the good crystallinity and nanostructured nature of the films. The diffraction peak positions for all samples are listed in Table 1 given below.

Type of Sample	**2*θ* (in degrees)**	**Calculated value of *d* (A)**	***d* (A) from JCPDS**	**Position of Plane (*hkl*)**
CdZnS1 (0.25 M conc. of Zn)	26.897	3.311	3.137	(111)
	44.005	2.102	1.922	(220)
	52.88	1.761	1.638	(311)
CdZnS2 (0.5 M conc. of Zn)	26.996	3.398	3.137	(111)
	44.657	2.027	1.922	(220)
	53.408	1.751	1.638	(311)
CdZnS3 (0.75 M conc. of Zn)	27.263	3.281	3.137	(111)
	44.726	2.068	1.922	(220)
	53.932	1.764	1.638	(311)

Table 1: Showing diffraction peaks and their corresponding planes for CdZnS

For sample of CdZnS1, the peaks are centered at 2θ = 26.897°, 44.005°, and 52.88°. In the cases of sample film for CdZnS2 and CdZnS3 the peak positions are centered at 2θ = 26.996°, 44.657°, 53.408° and 27.263°, 44.726°, 53.932° respectively. These well-defined peaks correspond to the (111), (220), and (311) planes, which is the characteristic of a face-centered cubic (fcc) structure of CdZnS films. The broad nature of the XRD peaks across all samples indicates the presence of strain within the films. Additionally, a slight shift in the diffraction angles towards higher values with increasing Zn molar concentration suggests residual stress induced during the deposition process and variations in the lattice parameters due to the incorporation of Zn in CdZnS.

2.3.2 Composition Analysis of Chemically Synthesized CdZnS Films

To analyze the composition of chemically synthesized CdZnS films, energy dispersive X-ray (EDAX) analysis was conducted using scanning electron microscopy (SEM). Figures 3 given below display the EDAX spectra for nanostructured CdZnS1 (0.25 M of Zn conc.), CdZnS2 (0.5 M of Zn conc.), and CdZnS3 (0.75 M of Zn conc.) films respectively, prepared in a PVA matrix at room temperature. Prominent peaks corresponding to Cd, S, and Zn are observed in all the spectra, although some additional weak peaks appear, likely due to residual reagents such as $CdCl_2$ and Na_2S. The elemental compositions of the films are summarized in Table 2.

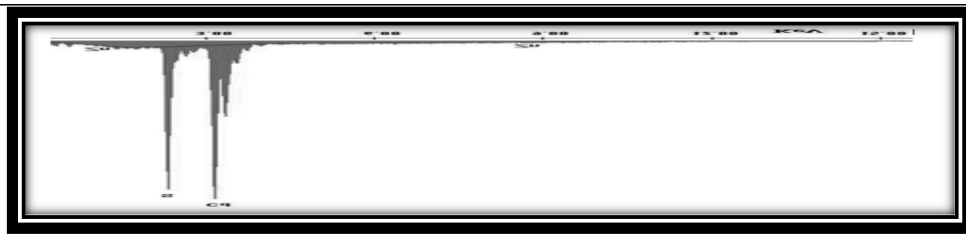
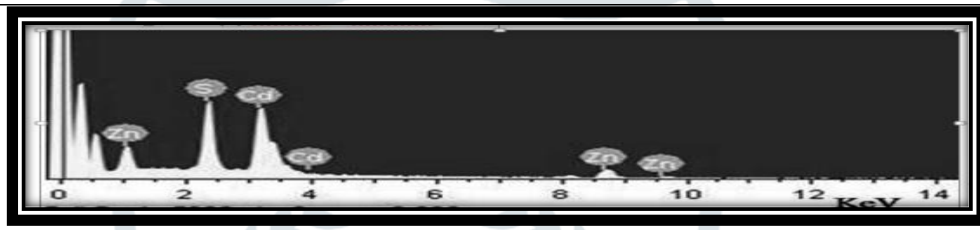
Type of Sample	Obtained Pattern of EDAX
CdZnS1	
CdZnS2	
CdZnS3	

Fig. 3: EDAX Spectra for various samples of CdZnS nanocompound

For the CdZnS films with 0.25 M and 0.5 M Zn concentrations (CdZnS1 and CdZnS2), the EDAX data reveal high weight and atomic percentages for Cd and S, but lower values for Zn, as illustrated in Figures 3 shown above.

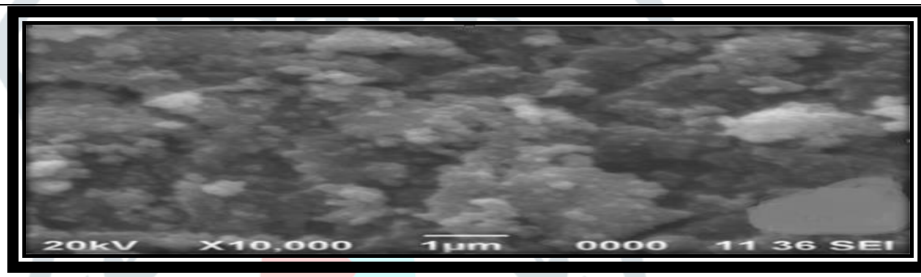
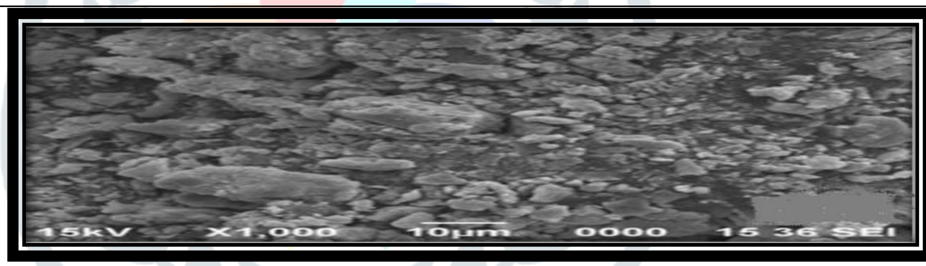
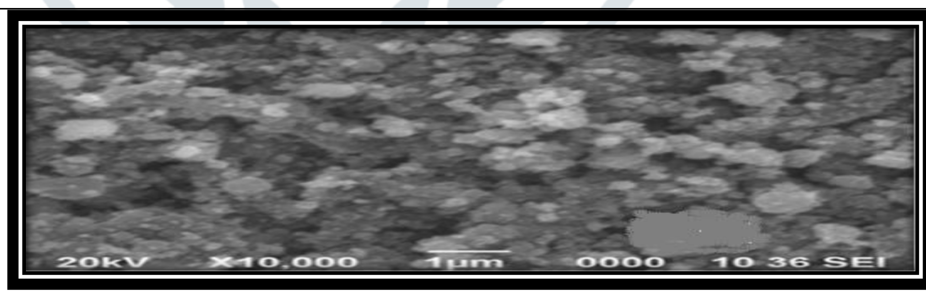
Type of Sample	Element	Weight (in % age)	Atomic % age wise
	CdL	77.02	50.82
CdZnS1	ZnK	00.87	00.96
	S K	22.12	48.22
	CdL	72.77	44.81
CdZnS2	ZnK	00.63	00.66
	S K	26.61	54.52
	CdL	38.88	29.79
CdZnS3	ZnK	17.73	07.37
	S K	43.39	62.84

Table 3: Concentration profile for different samples of CdZnS

As the Zn molar concentration increases, the Zn content in the samples also increases, which is evident from Table 2 and Figure 3 given above, where the weight and atomic percentages of Zn are recorded as 17.73% and 07.37%, respectively. The EDAX analysis confirms that the synthesized nanostructured CdZnS films are composed of cadmium (Cd), zinc (Zn), and sulfur (S).

3 Characterization of Chemically Synthesized CdZnS Films through SEM Analysis

Scanning electron microscope (SEM) images of the chemically synthesized CdZnS films were obtained and in order to mitigate charging issues during scanning, the CdZnS films were coated with a thin layer of gold (Au) via sputtering. Figures 4 shown below displays the SEM micrographs of samples of CdZnS1 (0.25 M of Zn conc.), CdZnS2 (0.5 M of Zn conc.), and CdZnS3 (0.75 M of Zn conc.) films, respectively.

S.No.	Type of Sample	Obtained Pattern of SEM
1	CdZnS1 (0.25 M of Zn conc.)	
2	CdZnS2 (0.5 M of Zn conc.)	
3	CdZnS3 (0.75 M of Zn conc.)	

The micrographs reveal that the films are nearly homogeneous, consisting of a large number of particles without any visible cracks. In Figures 4 (1) and 4 (2), the particles appear well-defined, mostly spherical, and exhibit minimal grain agglomeration. However, in the SEM micrograph of CdZnS2, taken at an accelerating voltage of 15 kV, there is significant grain agglomeration, as shown in Figure 4 (2). This suggests that a higher accelerating voltage can provide more detailed SEM images. All SEM micrographs indicate that the particles tend to aggregate, forming clusters. The SEM observations also reveal that the particle sizes are larger compared to those measured by X-ray diffraction (XRD).

4 Conclusion:

In this study, high-quality nanostructured CdZnS films with zinc molar concentrations of 0.25, 0.5 and 0.75 were successfully synthesized using a polyvinyl alcohol (PVA) matrix at room temperature through the chemical bath deposition (CBD) method. The optimal conditions for preparing the CdZnS films were determined to be a stirring rate of 200 rpm, a constant temperature of 72°C, and a stirring duration of 3.5 hours. These parameters were found to be crucial in ensuring the proper mixing and reaction of the precursor materials, resulting in uniform film deposition.

X-ray diffraction (XRD) analysis of the films revealed three broad peaks for all samples, which corresponded to the (111), (220), and (311) lattice planes of the cubic phase structure of CdZnS. A notable observation was the shift of these peaks towards higher diffraction angles with increasing zinc content, indicating the presence of residual stress within the films and variations in lattice parameters due to the incorporation of zinc. Energy dispersive X-ray (EDAX) analysis confirmed the elemental composition of the films, showing that they consisted of cadmium (Cd), zinc (Zn), and sulfur (S), with no detectable impurities. This purity is essential for the performance of the films in optoelectronic applications. Furthermore, the scanning electron microscopy (SEM) images demonstrated the formation of nearly spherical nanoparticles that were uniformly distributed across the films. This uniformity and the absence of significant agglomeration in most samples suggest good control over the synthesis process.

The successful synthesis of these nanostructured CdZnS films highlights the effectiveness of the CBD method in producing high-quality materials with controlled properties. The films exhibit good crystallinity and uniformity, making them suitable for a range of optoelectronic applications, including photovoltaic cells, sensors, and light-emitting devices. This study provides a solid foundation for further exploration and optimization of CdZnS films for advanced technological applications.

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