

## Research Article

# Studying the Effect of Metallic Precursor Concentration on the Structural, Optical, and Morphological Properties of Zinc Sulfide Thin Films in Photovoltaic Cell Applications

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Thin films of zinc sulfide (ZnS) with different concentrations of zinc acetate have been made by chemical bath deposition technique in acidic medium (pH = 5) on glass substrate using zinc acetate and sodium sulfide as sources of  $Zn^{+2}$  ion and  $S^{-2}$  ion, respectively, and ethylenediaminetetraacetate as complexing agents and sulfuric acid to adjust pH value at a constant deposition temperature of 85°C, and the deposition time of 90 minutes was used. The effect of the concentration of metallic precursor on the structural, morphological, and optical properties of chemical bath deposited zinc sulfide thin films was investigated in this study. The XRD result confirmed mixed phases of crystalline and amorphous structure dominating other phases, which is witnessed by larger crystallite size than other phases. It reveals that the thin films had hexagonal structure at the medium concentration with preferred orientation along (111) plane, and at lower and higher concentration, it showed that film has an amorphous structure in nature. The crystallinity of all the phases significantly enlarged with increasing the zinc precursor concentration. The SEM micrographs showed high-pitched edged irregular-shaped grains covering the substrate with pinholes and bangs. The optical properties investigated by the UV-VIS spectrometer specified a decrease in the optical bandgap of the films between 3.5 eV and 2.6 eV as the zinc acetate concentration in the solution increased from 0.1 to 0.2 M. It showed that the zinc sulfide had high absorption in the UV radiation. The main finding of this paper is that metallic precursor concentration has a significant role in the optical, morphological, and microstructural properties of the cobalt sulfide thin films, which are most suitable for photovoltaic applications.

## 1. Introduction

In today's world, most of the energy comes from fossil fuel, coal, oil, and gas, besides electricity and nuclear power. However, if they are not sustainable, the emissions from the combustion of fossil fuel increase the concentration of  $CO_2$  in the atmosphere that enhances the greenhouse effect. This,

in turn, leads to global warming which could have adverse consequences on the food production and water supply [1]. Solar energy, on the other hand, is a clean energy option that is significantly cleaner, providing a solution to many of the environmental and social issues linked to fossil and nuclear fuels. As a result, solar energy technologies have clear environmental advantages over traditional energy sources,

leading to the long-term sustainability of human activities. Their primary benefit is reduced carbon dioxide (CO<sub>2</sub>) pollution and, in most cases, the absence of any air pollution or harmful chemicals during their service. Furthermore, due to their critical position in photovoltaic technology, optical switches, and solar cell processing, metal sulfide semiconducting thin films have gained a lot of attention in recent years. Hence, ZnS thin films can be substitute chalcogenides. Since it has direct bandgaps in the absorption area, they are ideal for high photosensitivity in the infrared range, solar panels, large coefficients of optical absorption, and excellent semiconductor characteristics stability. However, the limited reports on the chemical bath deposition in the acid medium of ZnS show that most of the depositions are carried out in alkaline baths and have not been given yet to the chemical bath deposition of ZnS thin films [2]. Therefore, it is anticipated that novel chemical bath deposition routes for ZnS can be established if sufficient attention is given. The researchers, therefore, inspire the use of acidic zinc (Zn(Ace)<sub>2</sub>·2H<sub>2</sub>O) and sodium sulfide (Na<sub>2</sub>S) as important complexing agents to compare the advanced thin films of the ZnS semiconductor material to synthesize and characterize zinc sulfide thin films utilizing chemical bath process deposition of acidic medium [3]. There are many deposition methods to synthesize ZnS thin films. However, it is widely accepted that the high quality of thin films deposited by CBD can be deposited in vast areas [1]. ZnS thin films were deposited using chemical bath deposition. The high resistivity and low optical transmittance of such materials' films restrict their use as optical materials for thermoelectric materials, necessitating the need to develop their optical and electrical properties [4]. Furthermore, there is a scarcity of knowledge on the structural, morphological, and optical properties of ZnS thin films in an acidic medium (pH = 5). Thin films deposited in a simple (alkaline) environment usually produce oxides or hydroxides, which can degrade the film's consistency [5]. It will be hard to manufacture high-quality ZnS thin films inside of an alkaline chemical soak environment unless the challenge of ZnS deposition is overcome [6–10]. The impact of hydroxide is minimized when ZnS is deposited in an acidic chemical bath. For most metal ions widely used in CBD, it is fair to conclude that no hydroxide is available under such conditions and also that deposition occurs through an ion-by-ion process [11–14]. The aim of this research was to look at ZnS thin films deposited under different defined temperatures for photovoltaic cell applications.

## 2. Experiment

Before the experiment, the chemicals used to make the chemical soak were of experimental chemical agent grade (AR) from Aldrich, which had a purity of 99.9%. Zinc acetate (Zn(Ace)<sub>2</sub>·2H<sub>2</sub>O) and sodium sulfide (Na<sub>2</sub>S) were used as precursors for Zn<sup>2+</sup> and S<sup>2-</sup> sources, respectively. For the main chemical process, TEA has been used as a complexing agent, and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) has been used to change the pH to 5. Substrates were cleaned with detergent and H<sub>2</sub>O until being ultrasonically cleaned with acetone, alcohol, and

deionized (DI) water and then dried in the air before deposition. Chemical concentrations were calculated as follows: 0.1, 0.2, and 0.3 M of (Zn(Ace)<sub>2</sub>·2H<sub>2</sub>O) and 0.1 M of (Na<sub>2</sub>S) in equal volume quantitative relation, and TEA was taken as complexing agent. Initially, the solution was prepared by separately solubilizing chemicals in filtered water using magnetic stirring.

After preparing all of the solutions, they were mixed together, and the maximum hydrogen ion concentration was regulated by adding caustic soda to the solution. The mixture was heated to 85°C, and clean SLG substrates were submerged in it. Figure 1 depicts a graphical representation of chemical bath deposition. For deposition of ZnS thin films, 0.1, 0.2, and 0.4 M of Zn(Ace)<sub>2</sub>·2H<sub>2</sub>O and 0.1 M of Na<sub>2</sub>S were drawn in equivalent volume quantitative relation. The same technique was used to deposit ZnS film on a substrate at various concentrations of zinc sulfate over a 90-minute period. The accumulated films were separated from the solution, washed in DI water to eliminate the ions, dried in the air, and stored for characterization.

Once making ready all the solutions, they were mixed, and the final hydrogen ion concentration was controlled by adding a caustic soda. Clean SLG substrate was immersed within the solution and heated to 85°C. A schematic diagram of the deposition by chemical bath is shown in Figure 1. For deposition of ZnS thin films, 0.1, 0.2, and 0.4 M of Zn(Ace)<sub>2</sub>·2H<sub>2</sub>O and 0.1 M of Na<sub>2</sub>S were taken in equal volume quantitative relation. The same procedure was followed for deposition of film at different concentrations of zinc sulfate for 90 minutes. ZnS film was deposited on the substrate. Deposited films were removed from the solution, rinsed in DI water to remove the ions from the film, dried in air, and preserved for characterization.

## 3. Results and Discussion

**3.1. Characterization.** The physical properties of deposited ZnS thin films were investigated using a PANalytical X'Pert specialist X-ray diffraction device with copper (Cu), which has K radiation with an X-ray emission wavelength of 1.5418 in the range of 0.1 to 0.3 M. Using the Scherer relationship, mean crystallite sizes were estimated to be compatible with the increase of peaks. A scanning electron microscope was used to investigate the morphology of the surface (SEM). The LAMBDA 950 UV/Vis/NIR Spectrophotometer was used to investigate the UV characteristic [14–16].

**3.2. X-Ray Diffraction.** The activity structural analysis of as-deposited, processed thin films on glass substrate was performed using the X-ray diffraction (XRD) technique [17]. The spectra of the as-deposited ZnS film are shown in Figure 2. At 0.1, 0.2, and 0.3 M, Figure 2(a) reveals optical phenomena with sharp peaks at 25.23°, 18.99°, and 38.51°, suggesting the amorphous existence of the as-deposited film. The area units (111), (110), and (100) will be calculated by evaluating measured “*d*” values with experimental “*d*” values of normal crystal-shaped ZnS crystal corresponding phases [18].

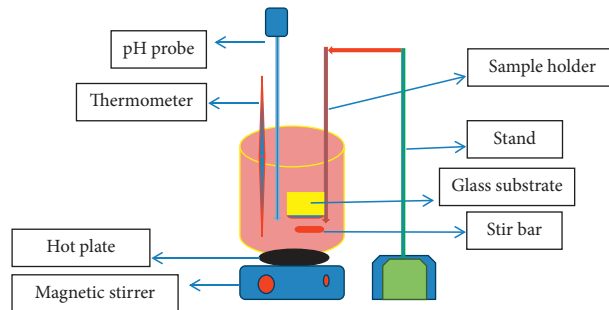


FIGURE 1: Setup of chemical bath deposition technique.

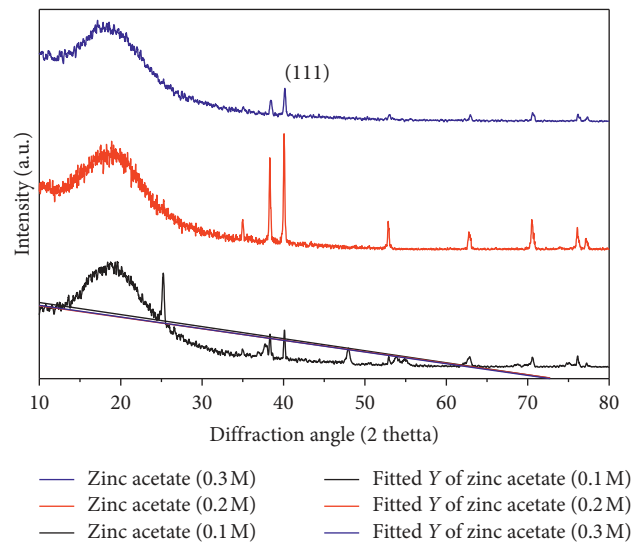


FIGURE 2: XRD patterns of deposited ZnS thin film at different zinc acetate concentrations.

Figure 2 shows the surface morphologies of ZnS thin films of different concentrations of metallic precursor. The microstructure of thin films is significantly influenced by changes in zinc acetate concentration. All the films are free from cracks and cover the substrate completely. For 0.1 M acetate, the SEM micrographs consisted of nearest to hexagonal grains at topmost with compact background grains. The scanning electron microscope micrographs of ZnS film deposited by 0.2 M zinc acetate consist of a chain of sharp irregular-shaped grains over a flat background morphology. The formation of collars between jots indicates the porousness of grains. In the case of ZnS thin films deposited by 0.3 M zinc acetate, the background morphology is similar to that deposited by 0.1 M zinc acetate; however, the large top surface grains become polygonal in shape. The two main thin film deposition mechanisms in chemical bath deposition are named ion-by-ion and cluster-by-cluster deposition mechanisms. The cations and anions bind to the substrate first and then engage in chemical reactions to form the film in the ion-by-ion process, while in the cluster-by-cluster mechanism, the ions react and form a deposit within the solution before adhering to the substrate [18].

Table 1 shows the film's FWHM of diffraction peaks and size distribution. The synthesis of a crystal isometric formed ZnS thin film is adjusted using this analysis. As a result, the

findings are in accordance with those obtained previously [19, 20]. The intensity of the peak corresponding to part (111) is found to be significantly higher than that of other peaks, indicating that this is the most common alignment for treated film in this region. When the concentration of zinc acetate increased from 0.1 M to 0.2 M, the peaks are increasingly formed, and when it is increased to 0.3 M, it becomes less peak; this shows that, at higher concentration, the ZnS thin films changed from crystalline to amorphous structure. This result agrees with the previous report [21].

**3.3. Scanning Electron Microscope.** As shown in Figure 3, the smooth background layer for ZnS thin films deposited by 0.1, 0.2, and 0.3 M of zinc acetate could be formed by an ion-by-ion deposition mechanism [19]. However, the top layers with large grains signify the clusters of grains initially grown within the solution and adsorbed to the substrate at the final phase of the deposition. As the idea of reporters, it showed that high concentration, temperature, and deposition time lead to cluster-by-cluster deposition [22].

Fine elongated particles of various sizes are evenly distributed around the substrate. The surface is also covered with small agglomerates of varying sizes. It is difficult to get an accurate estimate of particle size. It is also possible to see

TABLE 1: Parameters of XRD spectra for ZnS thin films at different zinc acetate concentrations.

2 theta (degree)	$d$ (Å)	Concentration (M)	hkl	FWHM (Rad)	Grain size (nm)
25.23	3.36	0.1	(111)	1.19	22.3
18.99	2.69	0.2	(110)	8.41	24.5
38.51	1.91	0.3	(100)	0.87	30.2

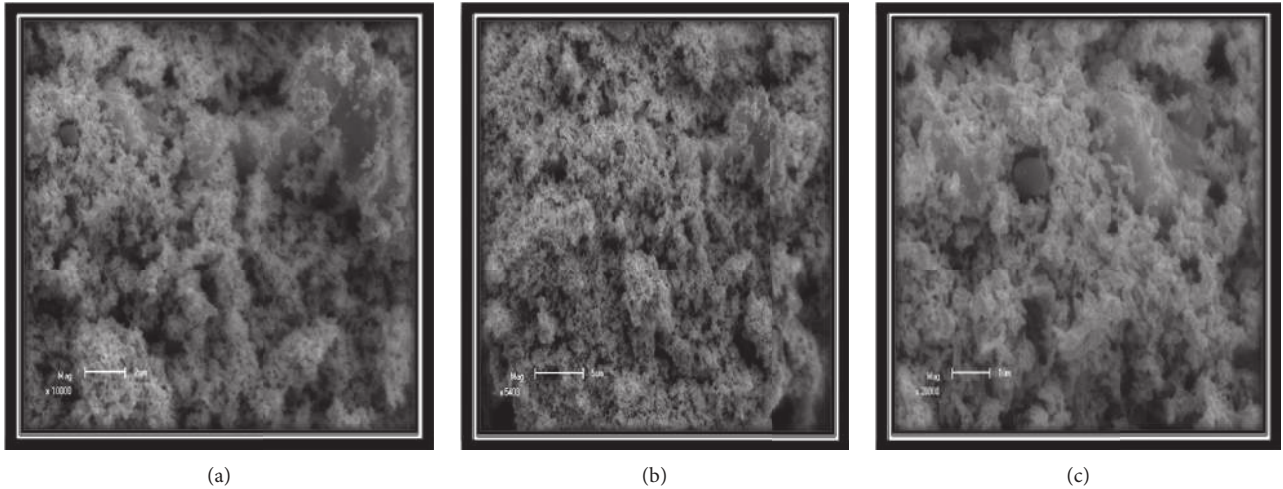
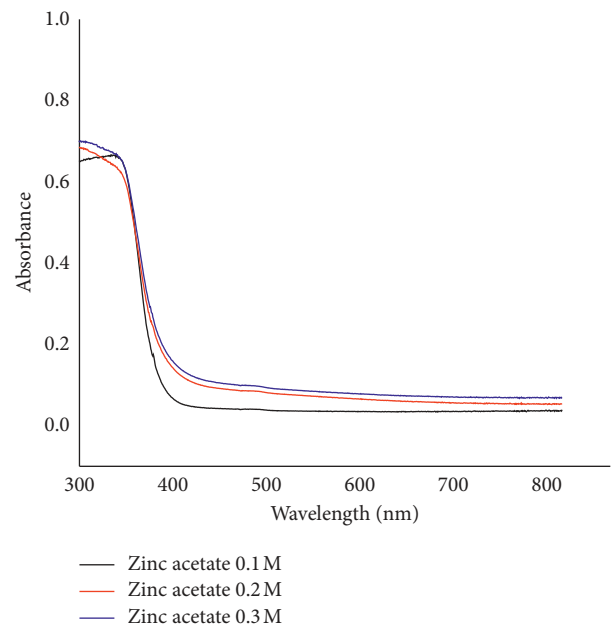


FIGURE 3: Scanning electron microscopic images of ZnS thin films at different zinc acetate concentrations: (a) 0.1 M, (b) 0.2 M, and (c) 0.3 M.

some microporous gap between the fine particles. The porous structure of films will help boost the redox balance [23, 24].

**3.4. Optical Absorption Study.** The optical absorption of zinc sulfide thin films formulated from various zinc acetate concentrations was calculated throughout the range of wavelength of 450 to 2250 nm. The absorbance of the films significantly increased with increasing the cobalt acetate concentration within the considered range of wavelength. The apparent wavelength spectrum is where the films' maximum absorption is observed.

As shown in Figure 4, the bandgap of the films is determined by extrapolating the linear portion of a  $(h\nu)^2$  versus  $(h\nu)$  curve. As the amount of zinc acetate solution increased from 0.1 M to 0.3 M, the bandgap of the films reduced from 3.5 eV to 2.6 eV. The decrease in bandgap may be due to an increase in crystallite size as the concentration of zinc acetate in the deposition bath is increased [25]. All ZnS thin films have high absorbance in the visible light area and bandgaps in the range of 3.5 eV to 2.6 eV, making them candidate materials for absorber layers in thin-film solar cells as well as effective visible light photocatalysts [26–31].

FIGURE 4: Plots of variation of optical absorption ( $\alpha t$ ) versus wavelength films using different zinc acetate concentrations (0.1, 0.2, and 0.3 M).

## 4. Conclusion

The chemical bath deposition (CBD) method was implemented by changing parameters and using an 80°C deposition temperature and a 90-minute deposition time for the synthesis of ZnS thin films. Different characterization techniques were used to classify thin films that were deposited. The surface morphology of a ZnS thin film indicates that as the amount of zinc acetate is increased, the grain size increases, and the optical bandgap energy decreases from 3.5 eV to 2.6 eV, which is ideal for a photoabsorber.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that there are no conflicts of interest.

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