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## Properties of Al-doped ZnS Films Grown by Chemical Bath Deposition

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### Abstract

Zinc sulphide (ZnS) buffer layers are a cadmium free, wider energy band gap, alternative to the cadmium sulphide (CdS) buffer layers commonly used in copper indium gallium diselenide (CuInGaSe<sub>2</sub>)-based solar cells. However extrinsic doping of the ZnS is important to lower the resistivity of the layers and to improve flexibility of device design. In this work, Al-doped ZnS nanocrystalline films have been produced on glass substrates using a chemical bath deposition (CBD) method. The Al- concentration was varied from 0 at. % to 10 at. %, keeping other deposition parameters constant. The elemental composition of a typical sample with 6 at. % 'Al' in ZnS was Zn=44.9 at. %, S=49.8 at. % and Al=5.3 at.%. The X-ray diffraction data taken on these samples showed a broad peak corresponding to the (111) plane of ZnS while the crystallite size varied in the range, 8 – 15 nm, depending on the concentration of Al in the layers. The films with a Al-doping content of 6 at. % had an optical transmittance of 75 % in the visible range and the energy band gap evaluated from the data was 3.66 eV. The films n-type electrical conductivities and the electrical resistivity varied in the range, 10<sup>7</sup>-10<sup>3</sup> Ωcm, it decreasing with an increase of the Al-concentration in the solution.

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*Keywords: ZnS films, Al-doping, Chemical bath deposition, Composition, Structure, Optical properties, Electrical properties.*

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### Introduction

Recently thin films of ZnS have been successfully used as buffer layers to replace the CdS used in CuInGaSe<sub>2</sub>-based solar cells and conversion efficiencies higher than 15 % have been achieved [1]. The main advantages of using ZnS are (i) ZnS is less toxic than CdS and (ii) its wider energy band gap (3.7eV) allows more of the blue end of the spectrum to reach the junction than CdS (energy bandgap,

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2.42eV) increasing the current generated. However, in order to achieve its full potential, the electrical resistivity needs to be reduced since un-doped ZnS films have electrical very high electrical resistivities (typically  $10^7 \Omega\text{cm}$ ). This is possible by doping these layers with suitable impurity atoms without affecting the optical properties of the layers too adversely [2, 3]. Efforts have been made by several research groups to dope ZnS films with elements such as In, Al, Cu and Cl. In this study, Al-doped ZnS films have been deposited by a simple chemical bath deposition (CBD) method. This method has been successfully used to deposit a variety of metal chalcogenides and oxides as this method is expected to dope the films uniformly [4-6]. This paper reports on the synthesis of Al-doped ZnS layers using different dopant concentrations and studies of the physical and chemical properties of the grown films.

## 2. Experimental details

Analar grade zinc acetate, sodium sulfide, and aluminum sulfate were used as the precursors for Zn, S and Al. The zinc acetate was dissolved in methanol to make a 0.1M solution, whereas the sodium sulphide and aluminium sulphate were dissolved in distilled water to make 0.4 M and 0.1 M solutions respectively. Appropriate amounts of the solutions were mixed to prepare the reaction bath. Since ZnS precipitation is reported to occur even for very low zinc and sulphur ion concentrations in solution, a suitable complexing agent was used to control the release of the ions in the solution [7]. In the present study, ammonia and hydrazine hydrate were used as complexing agents to control the free ion concentration. The pH of the solution was maintained as 5.8 during the deposition (measured using an INSAT Instruments pH meter). Ultrasonically cleaned glass were used as substrates. These were placed vertically inside the beaker containing the reaction bath. Stirring of the solution continued during the deposition using magnetic stirrer. The thin films were deposited at a bath temperature of 75 °C for a duration of 60 min. Finally the films were taken out of the reaction bath, washed with de-ionized water and dried in a hot air oven for 15 min. The surface topology was observed and the composition of the films was determined using a Zeiss scanning electron microscope (SEM) attached with Linc exL energy analyzer. The crystal structure, preferred orientation and other structural properties were carried out using Siefert X-ray diffractometer (XRD) using  $\text{Cu } k_{\alpha}$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) in the  $2\theta$  range,  $20^{\circ} - 70^{\circ}$ . The various functional groups present in the layers were identified using Thermo Nicolet Fourier Transform Infra Red spectrophotometer. The electrical resistivity of the layers was measured using two probe method using silver contacts while the conductivity type was determined by hot probe method.

## 3. Results and discussion

All the as-grown Al-doped ZnS films were yellowish in appearance, uniform and pinhole free. The colour of the films changed from yellowish to pale yellow depending on the dopant concentration in the solution. Clear film formation was observed on the substrate surface for dopant concentrations  $\leq 6$  at. % while the film surface became powdery for doping concentration  $> 6$  at. %. Visual observations revealed that the grown layers were highly transparent and the scratch tape test showed that films are highly adherent to the substrate surface. Energy dispersive X-ray analysis (EDAX) of the films revealed that the elemental composition of the layers was in agreement with that of the composition maintained in the starting solution, within the detection limit of the instrument ( $\pm 0.5$  eV). Figure 1 shows a typical EDAX spectrum of a ZnS:Al film formed with an Al-content of 8 at. %. As expected the data showed the presence of Zn, S and Al in the layers. Although, SnS and  $\text{ZnIn}_2\text{Se}_4$  films grown by the same process in our laboratory showed the presence of Cl, O in the films, such impurity elements were not observed in this study. The elemental composition was evaluated using the area under each peak along with other

instrumental parameters and was found to be Zn= 44.9 at. %, S=49.8 at. % and Al=7.4 at. % for the ZnS films doped with an Al-content of 8 at. % in the starting solution.

The X-ray diffraction spectra of ZnS films doped with different ‘Al’ concentrations are shown in Fig. 2. The broad peaks were as expected as the synthesized layers are nanocrystalline in nature. All the spectra showed peaks related to (111), (220) and (311) orientations corresponding to zinc blende structure ZnS [8] with the (111) plane as the dominant orientation. No other peaks related to secondary phases were found in the XRD spectra. However a shift in the peak positions was noticed with the increase of doping concentration. This is mainly due to the smaller atomic radius of  $\text{Al}^{3+}$  ion (0.54 Å) compared to  $\text{Zn}^{2+}$  ion (0.74 Å), resulting in the development of strain in the films.

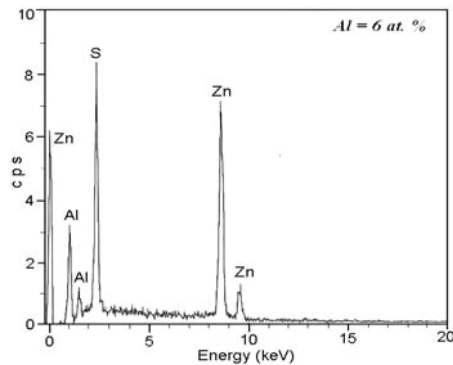


Figure 1. EDAX spectrum of the Al-doped ZnS layer formed by chemical bath deposition.

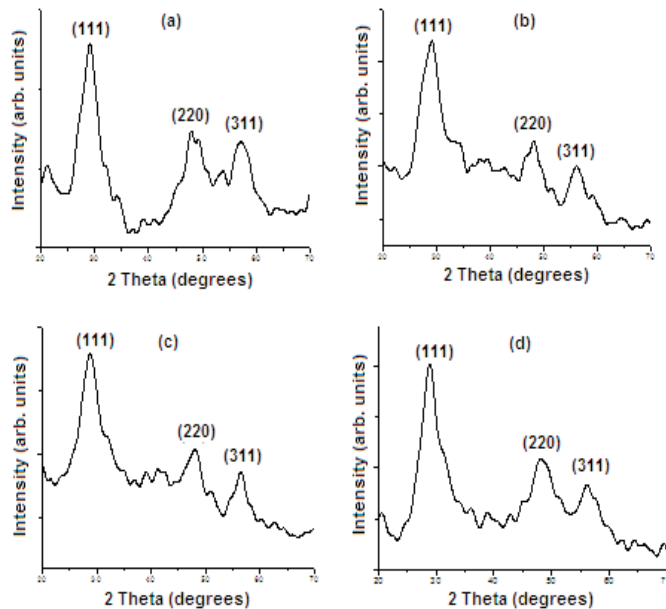


Figure 2. X-ray diffraction spectra ZnS:Al-doped thin films (a. 2 at. %; b. 4 at. %; c. 6 at. % and d. 8 at. %).

From the XRD spectra the crystallite size was determined using the (111) peak from the Scherrer's formula [9],

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \dots (1)$$

where  $D$  is the crystallite size,  $k$  is a constant (0.94),  $\lambda$  is the wavelength of X-rays used,  $\beta$  is the full width at half maximum (FWHM) of the (111) peak and ' $\theta$ ' is the corresponding diffraction angle. The evaluated crystallite size varied in the range, 8 - 15 nm with the change of Al-doping content in the films. It was found that the crystallite size increased with the increase of Al-doping concentration, reached a maximum at Al = 6 at. % and then decreased at higher doping levels (> 8 at. %). Figure 3 shows the scanning electron micrograph of a typical 6 at. % Al-doped ZnS film. The micrograph showed circular grains of different sizes that were uniformly distributed over the substrate surface.

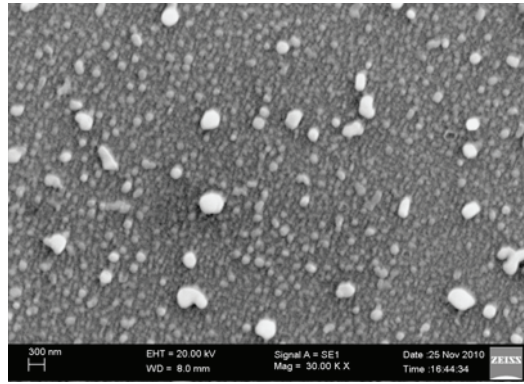


Figure 3. SEM picture of 6 at. % al-doped ZnS layer deposited by CBD.

In this work, the FTIR studies were conducted in order to verify the formation of ZnS and also to find the other functional groups present on the surface of the films. Figure 4 shows the typical Fourier transform

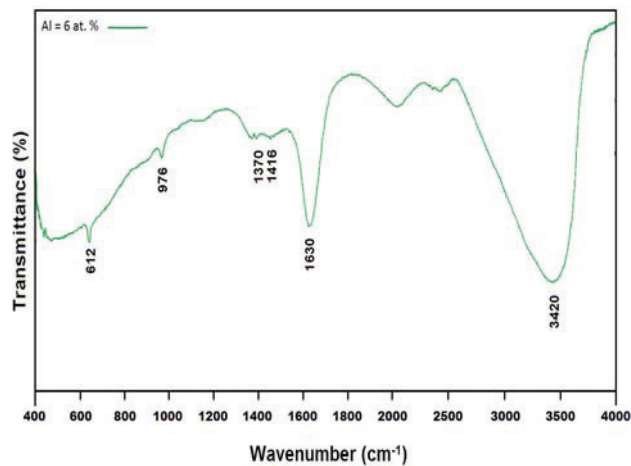


Figure 4. FTIR spectrum of chemical bath deposited ZnS: Al film.

infra red (FTIR) spectrum of Al-doped ZnS film prepared with 6 at. % Al-dopant concentration. The spectrum indicated two strong absorption peaks at  $1630\text{ cm}^{-1}$  and  $3420\text{ cm}^{-1}$ . These are attributed to the stretching modes of C=O group in acetates and –OH group in water respectively. The peak at  $612\text{ cm}^{-1}$  is characteristic of ZnS and revealed its presence in the layers. The spectrum also showed a weak band in the region,  $900 - 1475\text{ cm}^{-1}$ . These are due to the stretching modes of C-O and bending modes of C-H respectively. ZnS layers doped with other dopant concentrations showed all these peaks while the intensity of the characteristic ZnS peak at  $612\text{ cm}^{-1}$  is maximum for 6 at. % Al-doping.

Figure 5 shows the optical transmittance spectra of as-deposited ZnS:Al films with different Al-dopant concentrations. It can be seen the films are highly transparent in the visible region and have steep optical absorption edges. The transmittance was high for a Al-doping concentration of 6 at. %. This is probably due to roughening of the layers for doping concentrations  $> 6$  at. % [10]. The steep optical absorption shows a homogeneous distribution of the grains and low defect density near the band edge. A slight blue shift was observed in the absorption edge with the increase of doping content in the films. This can be attributed to the effective incorporation of dopant atoms into the ZnS lattice [11].

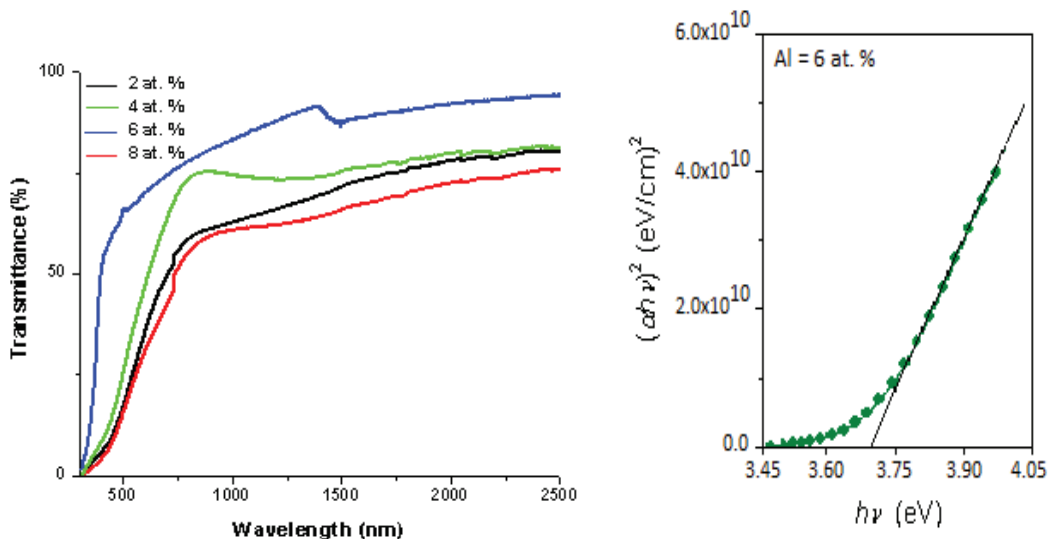


Figure 5 (a) Transmittance vs. wavelength spectra of Al-doped ZnS films; (b)  $(\alpha h\nu)^2$  versus  $h\nu$  plot.

For a direct energy band gap material [12]:

$$(\alpha h\nu)^2 = C (h\nu - E_g) \quad \text{---- (2)}$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $C$  is a constant and  $E_g$  is the energy band gap. Extrapolation of plots of  $(\alpha h\nu)^2$  versus  $h\nu$  onto the energy axis will give the energy band gap. Fig.6 shows such a plot for ZnS films doped with an 8 at.% Al-content. The energy band gap of the layers varied in the range,  $3.54 - 3.76\text{ eV}$ . The variation with Al-doping concentration is in agreement with the behaviour reported in the literature [13-15].

The hot probe test indicated that all the layers were n-conductivity type. The electrical resistivity of un-doped films was  $10^7 \Omega\text{cm}$ , which decreased to  $10^3 \Omega\text{cm}$  for an Al-dopant concentration of 6 at.%. The electrical resistivity increased again for doping concentrations  $> 6$  at. %. The initial decrease of resistivity with Al-doping was due to the increase of carrier density because of the difference in the valence between Al (3+) and Zn (2+). The increase of resistivity at higher dopant concentrations ( $> 6$  at. %), was most probably due the formation of additional phases which could not be detected in the X-diffraction spectra due to their amorphous structure. Alternatively interstitially incorporated Al atoms might have segregated at the grain boundaries to form an  $\text{Al}_2\text{S}_3$  phase. This would cause an increase in the grain boundary barrier height leading to higher resistivity films [16].

#### 4. Conclusions

Nanocrystalline ZnS layers doped with different 'Al' concentrations (0-10 at. %) have been grown by chemical bath method using a bath temperature of  $75^\circ\text{C}$ . The EDAX composition analysis revealed that the stoichiometry is approximately maintained in the deposited layers. The FTIR spectra confirmed the presence of ZnS phase in the layers. All the films exhibited a strong (111) peak as the preferred orientation with the grain size varying in the range, 8–15 nm. The layers showed an average optical transmittance of 75 % in the visible region.. A considerable decrease in the electrical resistivity from  $10^7 \Omega\text{cm}$  to  $10^3 \Omega\text{cm}$  was observed by doping the ZnS films with 6 at. % Al. The electrical resistivity value observed in this study is lower than that reported on Cu-doped ZnS layers grown by spray pyrolysis [17].

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