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Structural and optical properties of ZnS thin films prepared by chemical bath deposition method

T. E. Manjulavalli*, A. G. Kannan

Department of Physics, NGM College, Pollachi- 642 001, Tamilnadu, India

Abstract: ZnS, a wide band gap semiconductor belonging to II-VI compounds are receiving ever increasing attention owing to its potential uses in science and technology. Zinc sulfide thin films were prepared using different molar concentration (0.5 M, 1 M and 2 M) onto the glass substrates by chemical bath deposition technique at a deposition temperature of 333 K. After the deposition, thicknesses of the samples were determined using microbalance technique. Structural, morphological and optical characterizations of the films were made using XRD, SEM, UV-visible and photoluminescence spectroscopy. Microstructural parameters deduced from the XRD profile exhibits increase in grain size with increase of molar concentration (10 nm to 14 nm). Optical analysis shows, that the band gap energy decreased from 3.96 eV to 3.84 eV with increase of molar concentration. The photoluminescence studies showed that the prominent peak is shifted towards longer wavelength region indicating loss of sulfur at higher concentration.
Keywords: ZnS thin film, Chemical bath deposition, Optical properties, Photoluminescence.

Introduction

The nano and polycrystalline ZnS thin films have attracted the attention of scientists and researchers as it plays a very crucial role in the optoelectronic and photovoltaic devices. ZnS is an important II-VI semiconductor with wide band gap (3.7 eV), high refractive index (2.35) and dielectric constant [1-4]. In recent years ZnS is used as a window layer in heterojunction solar cells due to its wide band gap which decreases the window absorption loses and improves the short circuit current of the cell [5-7]. In several types of thin film solar cells, such as $CuInS_2$ (CIS), $CuInSe_2$ (CISe), $Cu(In,Ga)S_2$ (CIGS), $Cu(In,Ga)Se_2$ (CIGSe) and $Cu(In,Ga)(SeS)_2$ (CIGSeS) ZnS is used as a buffer layer as the toxic hazards of CdS limits its use in these type of cells [8-10]. ZnS transmits more high-energy photons to the junction and enhance the blue region and provides better lattice matching with absorbers having energy band gaps in the range of 1.3 - 1.5 eV [11]. Also in the area of optics, ZnS can be used as a reflector and dielectric filter because of its high refractive index and high transmittance in the visible range, respectively [12]. In optoelectronics, it can be used as a light emitting diode in the blue to ultraviolet spectral region. Several techniques have been used to produce zinc sulfide thin films such as sputtering [13], molecular beam epitaxy [14], spray pyrolysis [15,16], successive ionic layer adsorption and reaction technique [17], electrodeposition [18], pulsed-laser deposition [19], metal–organic chemical vapour deposition [20] and chemical bath deposition [21-24]. Among them, the chemical bath deposition method is highly attractive since the technique possesses a number of advantages over conventional thin films deposition methods. The main advantages of this method are low cost, low deposition temperature and easy coating of large surfaces. The method is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. In the present work, the preparation of ZnS thin films by

chemical bath deposition using different molar concentration (0.5 M, 1 M and 2 M) at the deposition temperature of 333 K.

Experimental

All the reagents obtained from Merck are of analytical grade and used without any further purification. Thin films of ZnS are obtained by chemical bath deposition technique. The initial aqueous solution is prepared from zinc acetate at 0.5 M (and 1 M, 2 M) concentration in 25 ml of de-ionized water. Ammonia solution is added slowly to zinc solution and stirred for about two minutes using magnetic stirrer until a clear solution is obtained.

$$Zn(CH_3COO)_2 \rightarrow Zn^{2+} + 2CH_3COO^- \quad (1)$$

$$OH \rightarrow NH_4^+ + OH^- \quad (2)$$

Initially $Zn(OH)_2$ precipitates, but this re-dissolves in excess ammonia to give the zinc ammine complex.

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \quad (3)$$

$$SC(NH_12)_{\perp}2 + OH^{\dagger} - (SH^{\dagger} - + CH_12\,N_12 + H_12\,0 \quad (4)$$

The solution is heated to 333 K and equal volume of 0.5 M (and 1 M, 2 M) thiourea solution is added as a S^{2-} source and the solution is stirred for 5-6 minutes.

$$SH^{\dagger} - + OH^{\dagger} - (\text{[S]}^{\uparrow}(2-) + H_12\,0 \quad (5)$$

The pH of the final solution is raised to 9. The mixed solution is kept at 333 K temperature. And finally zinc sulfide films were formed according to the relation,

$$Zn^{2+} + S^{2-} \rightarrow ZnS \quad (6)$$

After about 45 minutes the slides were covered with white deposit. The substrate is removed and rinsed with de-ionized water. The thickness of the deposited film was determined using weight difference method. The structural studies of the chemical deposited zinc sulfide thin film samples were done by using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation (λ=1.5406 Å). The morphological analysis of the film was carried out using JEOL mode JSM 6390 SEM and optical studies of the samples were done using spectrophotometer Jasco corp. V-570 in the spectral range 300-2500 nm with 1 nm resolution. The photoluminescence studies have been carried out using Cary Eclipse WinFLR photoluminescence device.

Results and Discussion

XRD characterization

Fig. 1 (a, b and c) shows the XRD pattern of ZnS films on glass substrate prepared using different molar concentration (0.5 M, 1 M and 2 M) at the deposition temperature of 333 K. The XRD pattern shows preferential orientation at 2θ equal to 28.3^0 indicating nano crystalline nature. The diffraction peaks become slightly sharper and their intensity is relatively enhanced on increasing the molar concentration, while their location did not change significantly. The observed and standard 'd' values and their corresponding (h k l) planes are shown in table 1. The lattice parameters deduced using these 'd' values is found to be in good agreement with the standard JCPDS data (File No. 36-1450), conforming that the film prepared using chemical bath deposition is hexagonal in structure. From the h k l values, the lattice constants are evaluated using most prominent orientation along (0 0 2) direction. The slight deviation in the lattice parameters may be due to the concentration of imperfections and in the present case there may be the possibility of oxygen impurities in the film prepared by CBD method. The hexagonal structures of ZnS thin films using CBD method has been reported by H.K.Sadekar et al [25], Rangang Zhang et al [26], F.Gode et al [9]. A gradual increase in the

intensity of the peak is noticed with increase in molar concentration. The structural parameters such as lattice constant, grain size (D), dislocation density (δ), and number of crystallites per unit area (N) were determined using appropriate equation and are given in table 2.

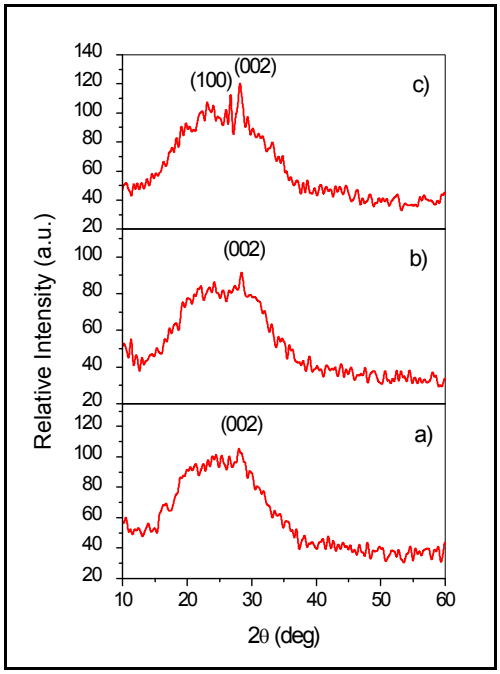

Fig. 1. XRD Spectrum of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Table 1. XRD data of ZnS thin films

Molar Concentration	Thickness (nm)	Observed values		Standard JCPDS values		h k l planes
		2θ (Degree)	d-spacing	2θ (Degree)	d-spacing	
0.5	308	28.08	3.1491	28.491	3.1303	0 0 2
1	320	28.49	3.1972	28.491	3.1303	0 0 2
2	397	26.68 28.13	3.3533 3.1509	26.915 28.491	3.3099 3.1303	1 0 0 0 0 2

XRD pattern clearly shows increase in grain size with increase of molar concentration from 0.5 - 2 M. Thus, the films at highest concentration have a better crystallinity, as indicated in the XRD pattern. The grain sizes of the film vary from 10 – 14 nm and similar results were obtained by several authors [18-20]. The calculated strain values support the results for these samples, because they decrease with increase of molar concentration. The number of crystallites per unit area decreases, which is evident from the increase of grain size with concentration.

Table 2. Structural parameters of ZnS thin films

Molar Concentration	Lattice parameters		Crystalline Size D (nm)	Dislocation density δ (10^{16} lines/m^2)	Strain ε (10^{-3})	Number of crystallites/ unit area (10^{17} m^{-2})
	Observed	JCPDS				
0.5	a=3.893 c=6.298		10	0.9992	3.852	3.0763
1	a=3.872 c=6.302	a=3.820 c=6.257	11	0.6401	3.0830	2.0332
2	a=3.887 c=6.299		14	0.6394	3.0812	1.6360

Morphological analysis

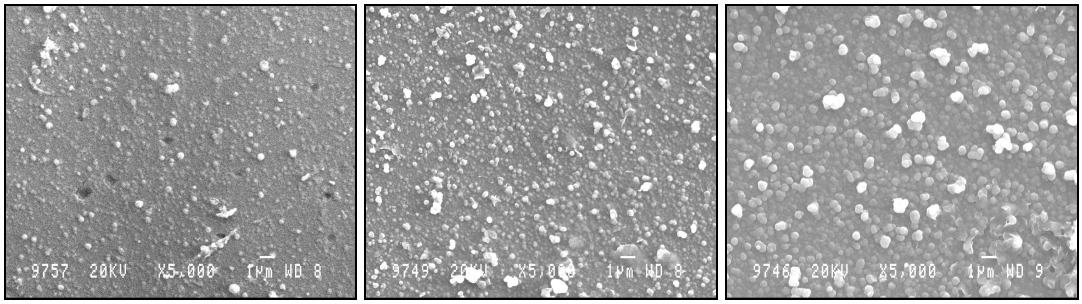

Fig. 2. SEM images of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Scanning Electron Microscopy is a convenient method to analyse the surface structure and roughness of the film. Fig. 2 shows the SEM micrographs of ZnS thin film prepared at bath temperature of 333 K by varying the molar concentrations (0.5 M, 1 M and 2 M). From all the micrograph it is observed that the film is homogeneous, continuous and dense microstructures. The films compactness are high, the grain size generally small and the grains size distribution is uniform. The presences of over grown ZnS particles are also observed.

Optical analysis

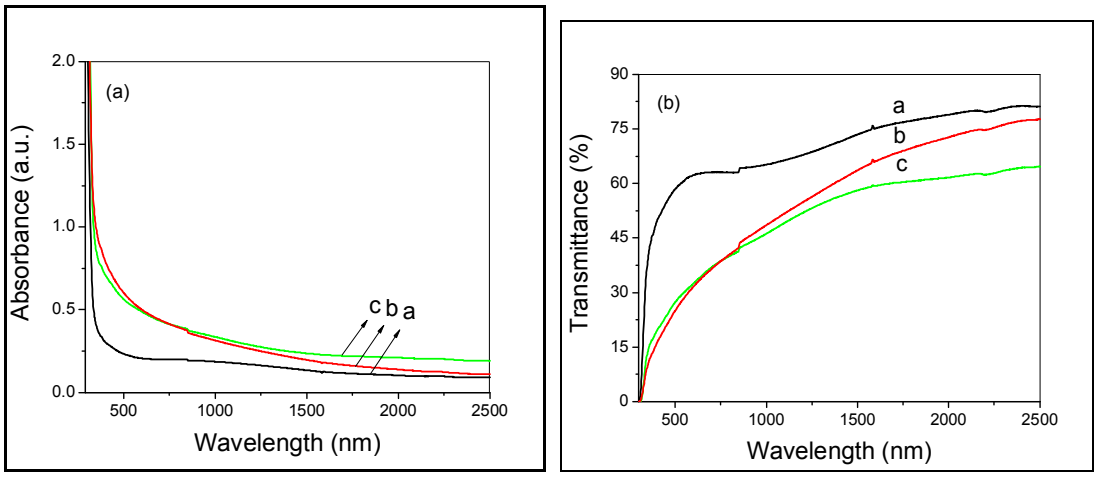

Fig. 3. (a) Absorbance and (b) Transmittance Spectra of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Fig. 3 (a and b) shows the optical absorption and transmittance spectra recorded in the spectral range of 300-2500 nm for ZnS films of different molar concentrations prepared at 333 K. It is observed that the absorption onset slightly shifts towards the high energy region indicating the improvement in crystallinity. From the transmittance spectra, the maximum transmissions observed are 80%, 77% and 65% for 0.5M, 1M and 2M respectively. F.Gode et al [9] also observed the transmission value in the range 66 - 82% for annealed films. The band gap energy was estimated on the basis of the recorded optical spectra. The best fit to the experimental data was obtained for n=1/2. This is in agreement with the literature data according to which ZnS is a semi-conducting material with a direct band gap [25, 30, 31]. In Fig. 4, the dependence of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for zinc sulfide thin film is presented. The ZnS films are characterized by band gap energy of 3.96 eV, 3.91 eV and 3.84 eV. The literature reported values for band gap energy of bulk ZnS are 3.6 eV. The higher calculated values of the band gap are presumably due to the quantum size effect [32-34]. In particular, it is well known that the optical band gap of thin film materials, which are characterized by a length scale less than 10 nm, is higher than that of bulk material. As the molar concentration increases, the absorption edge shifts gradually towards longer wavelength and shifts the band gap. This absorption edge shifts are associated with decrease in band gap with increase in molar concentration. All the films demonstrate the basic optical properties of ZnS films ie., the transmittance increases rapidly at 350 nm. The transmittance of ZnS films deposited at the temperature of 333 K is 50-80% when the wavelength is higher than 1000 nm. The ZnS films show high optical transmittance and can be used as buffer layer for CIGS solar cells [30].

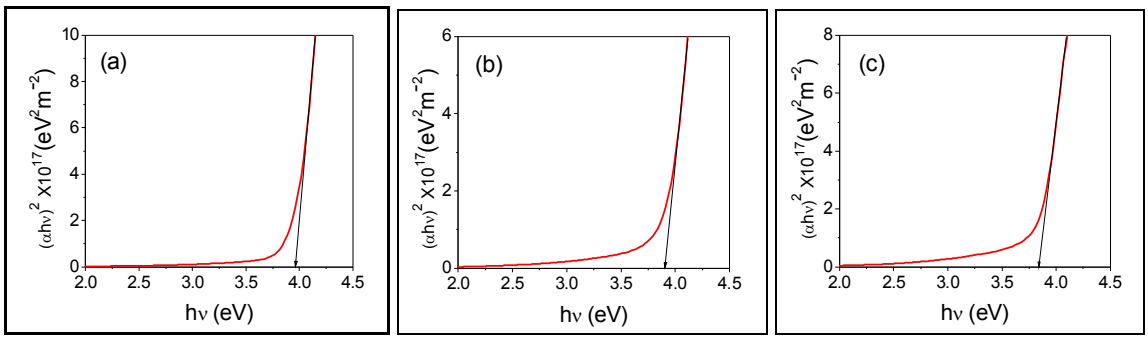

Fig. 4. Plot of $(\alpha h\nu)^2$ versus (hν) of ZnS thin films of molar concentration a) 0.5 M b)1 M c) 2 M.

Photoluminescence studies

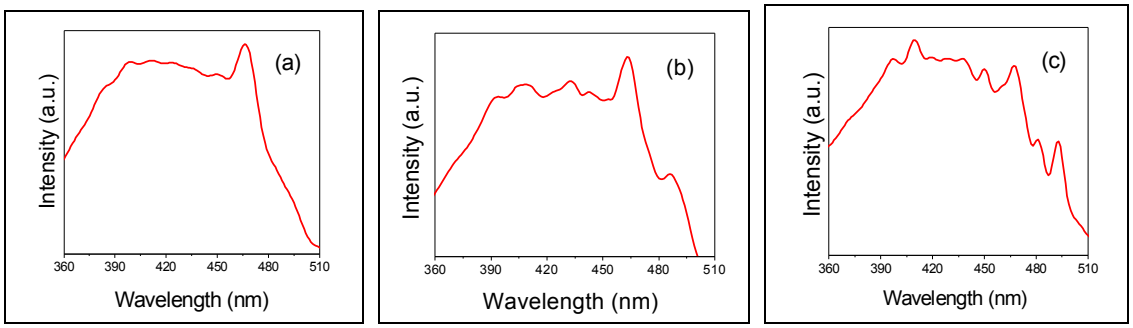

Fig. 5 PL Spectra of ZnS thin films of molar concentration a) 0.5M b) 1M c) 2M.

Fig. 5 shows the PL spectra of ZnS thin film prepared at bath temperature of 333 K by varying the molar concentration (0.5 M, 1 M and 2 M). It is inferred from the spectra that maximum intensity of the emission peak is around 466 nm for 0.5 M and 463 nm for 1 M. This is attributed to Zn^{2+} ion vacancy levels as reported by Baibaswata Bhattacharjee et al [35]. On increase of concentration to 2 M, the intensity of the peak centered around 466 nm as observed in 0.5 M and 1 M decreases and two more peaks at 409 nm and 492 nm are observed. The decrease in intensity of the peak at 466 nm may be due to loss of sulfur atoms and an increase of Zn atoms. The lower energy emission peak at 409 nm can be attributed to donor-acceptor band transition or may be due to excess of Zn atoms present in the film [36]. The relative higher wavelength peak at 492 nm may be due to the atmospheric oxygen impurity present in the surface of the film or may be assigned to the emission from the impurity either of the precursor of zinc or sulfur, which incorporate during the deposition process [37]. This shows that there is a gradual shift from blue to green region at higher concentration and this may be due to the transition from the conduction band to an acceptor level or due to interstitial sulfur.

Conclusions

ZnS thin films of different molar concentration (0.5 M, 1 M and 2 M) are prepared using zinc acetate and thiourea at a bath temperature of 333 K by chemical bath deposition method. The XRD analysis shows that all the grown films are nanocrystalline. The lattice parameters calculated are in good agreement with the standard data confirming that the ZnS films are hexagonal in structure. Morphological analysis shows increased grain size with increasing molar concentration. From the optical studies, band gap energy decreased from 3.96 eV to 3.84 eV with increase of molar concentration. Shifting of prominent peak to longer wavelength region indicates the loss of sulfur at higher concentration as is evident from PL studies.

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