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INFLUENCE OF TEA (COMPLEXING AGENT) ON THE STRUCTURAL PROPERTIES OF CBD ZnS THIN FILMS

M. DHANAM, B. KAVITHA*
PG & Research Department of Physics, Kongunadu Arts and Science College, Coimbatore, Tamilnadu, India-641029.

This paper presents the preparation of ZnS thin films from different chemical baths having TEA as complexing agent with various pH values. XRD, EDAX, SEM, FTIR analysis of the prepared ZnS thin films have been carried out and the results are discussed in detail.

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1. Introduction

Materials containing zinc are interesting because of their applications in many areas of modern technology. Zinc sulfide thin films with wide direct band gap and n-type conductivity are promising for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. ZnS is an important semiconductor material with large bandgap (>3.7eV) [1]. It has found wide use as a thin film coating in the optical and microelectronic industries. It has high refractive index (2.25), high effective dielectric constant (9) and wide wavelength pass band (0.4 - 13μm). It is commonly used as a filter, reflector and planar waveguide. Various techniques such as molecular beam epitaxy [2], pulsed electrochemical deposition [3], sputtering [4], metal organic vapour phase epitaxy [5], successive ionic layer adsorption and reaction [6,7], spray pyrolysis [8], atomic layer deposition [9], dip technique [10] and chemical bath deposition [11] have been employed to prepare ZnS thin films.

In the past 10 years, extensive attention has been paid to the preparation and characterization of semiconductor sulfides as a consequence of their interesting properties and potential applications. In earlier works NH_3 has been used as a complexing agent whereas in the present work triethylamine has been used as complexing agent. This paper presents structural studies on CBD ZnS thin films using TEA as complexing agent [1-3].

2. Experimental details

Using CBD technique zinc sulfide thin films is prepared by varying different deposition parameters such as pH, deposition temperature, deposition time, volume and concentration of the solution. Aqueous solution of 10ml, 0.2M of zinc acetate $Zn(CH_3COO)_2$, 10ml of 0.6M thiourea $SC(NH_2)_2$, 10ml trisodium citrate and 1ml triethanolamine (TEA) were used to prepare ZnS thin films and the solution is stirred well [12]. A digital pH meter (model 101E-Electronic India) has been used to adjust the pH of the reaction mixture. pH meter was standardized using buffer solutions of pH 4 ± 0.05 and 9.2 ± 0.05.

The deposition of ZnS thin films is based on the reaction of Zn^{2+} and S^{2-} ions in deionized water solutions. The volume and concentration of the solutions used in the reaction mixture have been varied for a wide range and then they are optimized to obtain uniform and adherent films.

*Corresponding author: kavitha_48@yahoo.co.in

The optimized volume and concentration are employed to prepare the reaction mixture. A constant and very slow stirring is provided while adding the different solutions of the reaction mixture. The solution is continuously stirred for several minutes and it becomes clear and homogeneous. Deionized water was added to make the solution up to 50ml. The deposition temperature was varied from 60-85 ^{o}C and the optimized temperature is found to be 80°C. Similarly the deposition time was also varied from 50-120min and it has been found that the uniform films were obtained for the deposition times of 65-75 minutes. The pH of the solution was varied from 8-11 and the optimized values are from 8.2-8.6. Having pH values of 8.2, 8.5 and 8.6 three different chemical baths are prepared. The pretreated glass substrates were vertically immersed into the prepared chemical bath to get uniform ZnS thin films. The substrates used for the deposition of films were suspended closer to the inner wall of the deposition beaker for better uniformity and adherence of the film on substrate and to avoid shaking of substrates while deposition [13].

Formation of ZnS thin films is due to the following reactions

With the addition of TEA to zinc acetate Zn^{2+} can be complexed as

$$Zn\ (CH3COOO)_3 + TEA \rightarrow [Zn(TEA)]^{2+} + 3CH_3COO^- \quad (1)$$

From thiourea, in an alkaline medium, the sulphide ions are released as follows

$$SC(NH_2)_2 + OH^- \rightarrow SH^- + CH_2N_2 + H_2O_2 \quad (2)$$

$$SH^- + OH^- \leftrightarrows S^{2-} + H_2O \quad (3)$$

Then the overall reaction of formation of ZnS can be written as

$$[Zn(TEA)]^{2+} + SC(NH_2)_2 + 2OH \rightarrow ZnS + TEA + CH_2N_2 + 2H_2O \quad (4)$$

TEA has been complexed with zinc acetate to release Zn^{2+} ions slowly. Trisodium citrate was used in the reaction mixture to adjust the pH value of the reaction mixture. Trisodium citrate plays an important role in the crystallization of CBD ZnS as reported earlier [14].

A Shimadzu XRD-6000 X-ray diffractometer with vertical goniometer fitted with vanadium filter and copper radiation (λ = 1.5406 Å) was used for the structural analysis of thin films of different thicknesses. The surface morphology of ZnS thin films was studied using a scanning electron microscope (JEOL-JSM-100). A JASCO (V570: UV-VIS-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400-2500 nm. Energy dispersive x-ray analyzer (LEICA.S44Oi) confirmed the composition of the constituents in CIAS thin films. The FTIR analysis of CBD ZnS was studied by FTIR spectrophotometer (FTIR-8400S) on a Michelson interferometer with 30° incident angle. The data sampling is done by He-Ne laser having a compartment of 200(W) x 230(L) x 170(H) mm.

3. Results and discussion

3.1. XRD analysis

The x-ray diffraction patterns of CBD ZnS thin films of thickness 2230Å, 5700 Å and 9700 Å prepared from three chemical baths of different pH values (Table 1) are shown in Fig. 1(a, b & c). The predicted peaks (012) (010) and (107) are reported as the identifying peaks for ZnS thin films as reported by JCPDF (12-688) and earlier reports [15-17]. The presence of these prominent peaks confirm the hexagonal wurtzite phase of the as-grown ZnS films. Many researches reported the structure of ZnS thin films as cubic [18- 34] which may be due to the

different preparation techniques or the precursors employed. The observed 'd' (lattice spacing) and I (intensity) values of prepared thin film from three different chemicals baths are presented in Table 2.

Table 1. Preparatory conditions of the thin films of chemical baths

Chemical baths	Thickness (Å)	Temperature (°C)	Time (mins)	pH
Bath 1	2230	80	70	8.5
Bath2	5700	80	70	8.2
Bath3	12970	80	70	8.6

The prepared films have the preferential orientation along (012) plane whereas the preferential orientation planes were reported as (010) and (107) by earlier workers [15,17]. The change in the preferential orientation may be due to complexing agent TEA. A method that evaluates the magnitude of the preferred orientation factor 'f' for a given plane (peak) relative to other planes (peaks) in a material was employed. According to this method, the preferred orientation factor f (012) of the 012 plane for the ZnS thin film has been calculated by evaluating the fraction of (012) plane intensity over the sum of intensities of all peaks with in a given measuring 2θ range [20º – 60º]. Similarly the orientation factor of the other peaks has been evaluated for all the films and their values are presented in Table 3.

Table 2 XRD data of CBD ZnS thin films.

Bath	Film Thickness (Å)	2θ (degree)	d spacing		h k l
			Observed	JCPDS	
1	2230	27.261	3.26	3.12	0 1 0
		34.186	2.62	2.66	1 0 7
		41.236	2.18	2.08	0 1 2
2	5700	27.243	3.27	3.12	0 1 0
		34.158	2.62	2.66	1 0 7
		41.221	2.18	2.08	0 1 2
3	9700	27.202	3.27	3.12	0 1 0
		34.153	2.62	2.66	1 0 7
		41.210	2.18	2.08	0 1 2

Table 3 Structural parameters of CBD ZnS thin films

Film Thickness (Å)	Lattice Constants (Å)				c/a axial ratio	Volume of the unit cell (Å^3)		Crystalline size D_c (nm)	Dislocation Density (10^{14} lines/m^2)	Number of Crystallites Per unit area (10^{15}m^{-2})	Strain (10^{-4})
	a		c								
	Observed	JCPDS	Observed	JCPDS		Observed	JCPDS				
2230	3.82		5.91		1.55	217		96	10.9	252	3.63
5700	3.80	3.82	5.93	6.21	1.56	217	235	144	7.69	384	3.22
9700	3.78		5.96		1.57	217		147	4.62	408	2.38

Table 4 Confirmation of preferential orientation.

Chemical bath	**Film thickness (Å)**	**Plane**	**Preferential Orientation factor**	**Preferential orientation**
Bath 1	2230	(0 1 0) (1 0 7) (0 1 2)	1.085 0.351 0.280	0 1 2
Bath2	5700	(0 1 0) (1 0 7) (0 1 2)	1.454 0.285 0.227	0 1 2
Bath3	9700	(0 1 0) (1 0 7) (0 1 2)	6410 0.488 0.391	0 1 2

From the observed d-spacing the lattice constants and hence the axial ratio, volume of the unit cell, crystallite size, dislocation density and strain are evaluated using the methods reported earlier [13, 35] and are presented in Table 4. The calculated crystallite size values ranges from 96-147 nm, indicating that the as-prepared ZnS films are made up of nanocrystals. It is interesting to note that irrespective of the chemical bath, the grain size improves and the defects like dislocation density and strain in the films decrease with film thickness. This is due to the improvement in crystallinity in the films with film thickness. Preferred orientation (012) and lattice constants were

same for the films from three chemical baths it can be concluded that chemical bath having pH value 8.2 – 8.6 may be used to prepare the films with the similar properties. Hence a film of any of the three baths has been used for other analysis.

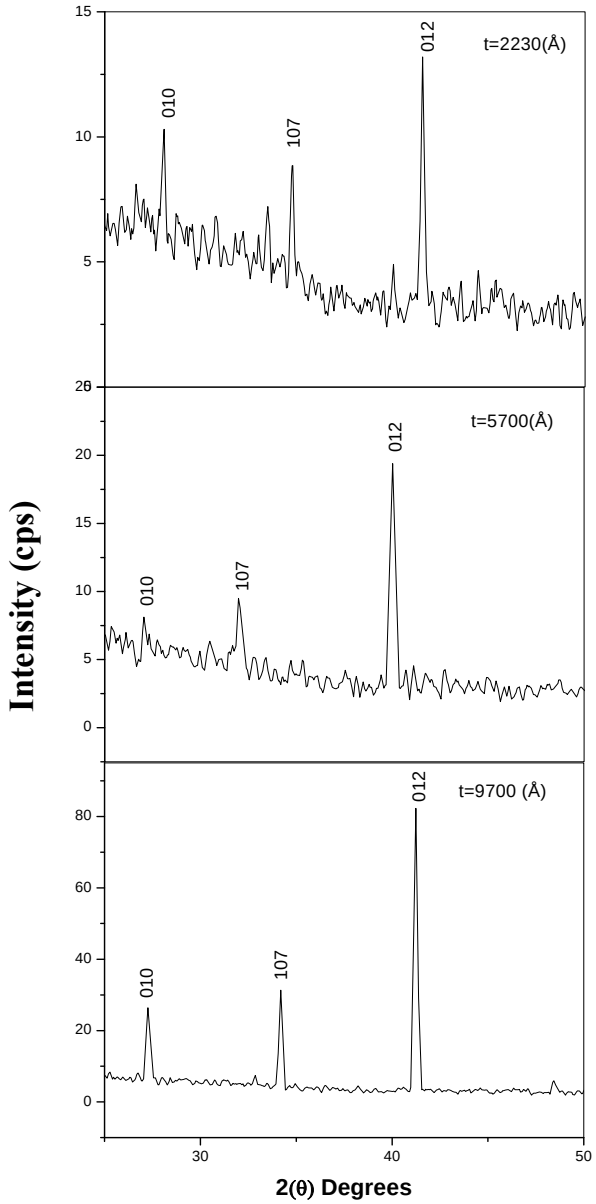

Fig 1 XRD spectra of CBD ZnS thin films of different thicknesses

3.2. EDAX Analysis

Fig 2 shows the EDAX result of ZnS thin films of thickness 7860Å prepared from chemical bath1. EDAX analysis confirms the presence of zinc and sulfur in ZnS thin film with the composition $Zn_{1.03}S_{0.97}$. The proportion of the constituent elements measured was Zn=51.79% and S=48.21%. The compositions show that near stoichiometric films can be obtained from the single and economic CBD technique. EDAX spectrum also shows that prepared films are free from impurities. The presence of silicon (Si) and oxygen (O) are due to glass substrates [14,30].

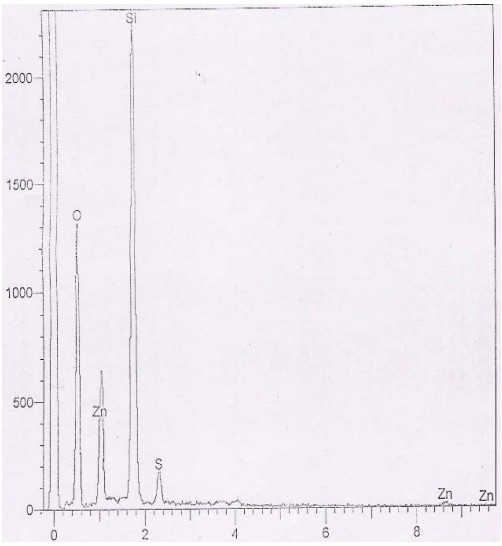

Fig 2 EDAX spectra of CBD ZnS.

3.3. SEM Studies

The scanning electron micrographs of the deposited ZnS thin films of thickness 9700 Å are shown in Fig.3 of magnification x 500, x1000 and x 4000 respectively. SEM pictures prove that the films have highly oriented microstructure composed of slanted columns. The pores in between the columns will inevitably influence the optical properties of thin films. The similar image has observed in ZnS thin films prepared from the chemical bath having NH_3 as a complexing agent [20].

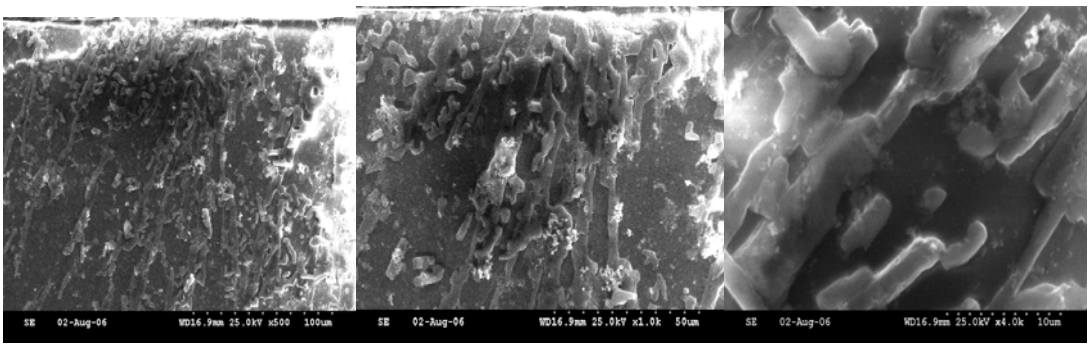

Fig 3 SEM image of CBD ZnS thin film of thickness 9700 Å
for different magnifications

3.4. FTIR analysis

Fig 4 shows the FTIR spectra of ZnS thin film of thickness 7600(Å). The spectrum has been recorded in the region 400-4000 cm^{-1}. The vibrational frequencies of the various chemical bonds in the films can be assigned from FTIR spectra interms of the peak positions. By the assignments of stretching and bonding modes of vibrations to the observed frequencies confirmational preference of the molecule can be identified. The ZnS stretching vibration is at 290cm. Since the FTIR spectrum has been taken in the range 400-4000cm^{-1}, the presence of chemical constituents cannot be identified using the FTIR spectrum. If the range has been widened FTIR spectrum is applicable to confirm the presence of constituents qualitatively or quantitatively, because metal sulphide stretching bonds occur within 200-400 cm^{-1}.

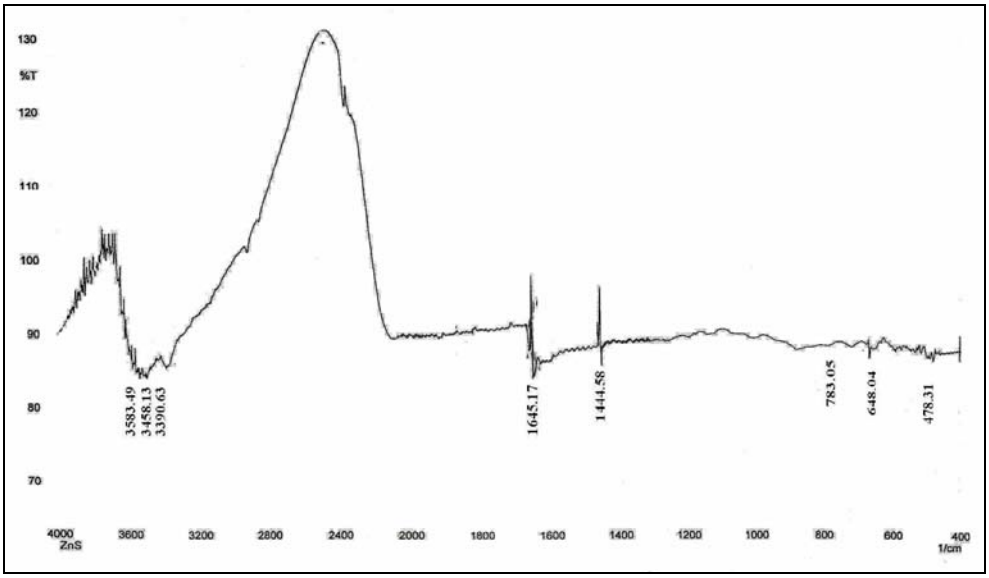

Fig 4 FTIR Spectrum of ZnS thin film of thickness 7600 Å.

The water (O-H) stretching vibration is at 3390cm^{-1} and bending vibration at 1645 cm^{-1} has been observed in ZnS thin films as reported earlier [32]. This confirms that oxygen appears as water in ZnS thin films. The two peaks at 3583 and 3458cm^{-1} are due to hydroxy groups [32, 35]. The absorption band at 648cm^{-1} is Zn-OH stretching peak [36, 37]. The absorption band at 1444cm^{-1} and 1384cm^{-1} are due to Zn-O (HCO_2) as reported [38,39]. The less intense peaks at 783cm^{-1} and 478cm^{-1} enable to conclude that a small amount of ZnO is also present in ZnS thin films. Thus FTIR spectrum has been employed to conclude the form of the occurrence of oxygen in CBD grown ZnS thin films as water, carbonate, zinc hydroxide or zinc oxide. FTIR spectra analysis of thin films prepared by chemical bath deposition technique has not been reported elsewhere.

4. Conclusion

X-ray analysis of thin films prepared from three chemical baths using TEA as complexing agent with different pH values [8.2-8.6] are found to have a preferential orientation (012). The chemical constituents and their compositions of the films have been estimated by the energy dispersive x-ray analysis. The deposited films are identified as $Zn_{1.03}S_{0.97.}$ The morphology of the deposited films has been found as highly oriented microstructure composed of slanted columns as in the case of films from chemical bath having TEA as complexing agent. FTIR spectra enabled to realize the form of occurrence of oxygen in the prepared ZnS thin films.

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