Size dependent optical characteristics of chemically deposited nanostructured ZnS thin films

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Abstract. **ZnS thin films of different thicknesses were prepared by chemical bath deposition using thiourea and zinc acetate as S^{2-} and Zn^{2+} source. The effect of film thickness on the optical and structural properties was studied. The optical absorption studies in the wavelength range 250–750 nm show that band gap energy of ZnS increases from 3·68–4·10 eV as thickness varied from 332–76 nm. The structural estimation shows variation in grain size from 6·9–17·8 nm with thickness. The thermoemf measurement indicates that films prepared by this method are of *n*-type.**

Keywords. **Thin film; ZnS; CBD method; optical properties.**

1. Introduction

Chemical bath deposition is a well known deposition process for some chalcogenides such as Zn, Co, Cd, Hg, Pb, sulphides and selenides (Mane and Lokhande 2000). Zinc sulfide is an important semiconductor material with large band gap (~3·5 eV), high refractive index (2·35 at 632 nm), high effective dielectric constant (9 at 1 MHz) and wide wavelength passband (0·4–13 μm). Its optical properties make it useful as a filter, reflector and planar wave guide (Mach and Muller 1982). It has a vast potential for use in optoelectronics and in electroluminescent devices (Mika *et al* 1988). Several methods have been applied to grow ZnS thin films by different workers such as sputtering (Cattell and Cullis 1982), molecular beam epitaxy (Tong *et al* 1996), layerwise chemisorption (Klechkovskaya *et al* 1989), chemical deposition (Fukarova *et al* 1997), chemical vapour deposition (Nicolau and Menand 1988; Kashani 1996) and liquid phase atomic layer expitaxy (Lindroos *et al* 1994). Every thin film deposition technique has its own advantages and disadvantages. In the present case chemical bath deposition technique (CBD) is studied for deposition of ZnS thin films since it is simple, relatively less expensive and convenient for large area deposition. The effect of preparative parameters like pH and temperature on deposition process has also been reported in this paper.

In recent years, interest in the physical properties of thin films has considerably increased. New effects can appear in the film states that are not observed in the bulk samples (Lokhande *et al* 1997). When the dimensions of the film are comparable with some characteristic length such as the electron mean free path or the de Broglie wavelength of the electron, the physical properties start to become functions of the film size. In particular, when the thickness of the film is of the order of the de Broglie wavelength of the electron, quantization of the electron levels due to size of the film introduces new size effects. In the present investigation, to study such size dependent properties, the thickness of ZnS film was varied by changing the deposition time period and its effect on bandgap energy, thermoemf and grain size, studied.

2. Experimental

A simple chemical bath deposition (CBD) method was employed to deposit ZnS thin films onto glass substrates using thiourea as sulfide ion source and zinc acetate as zinc ion source in alkaline bath. For the preparation of ZnS thin films, 0·2 M zinc acetate solution was taken in a beaker and an equal volume of 0·2 M thiourea solution was added. Ammonia solution was added slowly to form the complex and pH was adjusted between 9 and 10. The solution was stirred for a few seconds and transferred to another beaker containing glass substrates. The solution was kept at 303 K. Substrate cleaning plays an important role in the deposition of thin films. Commercially available glass microslides of dimensions $26 \times 76 \times 2$ mm were boiled in chromic acid for 2 h and kept in it for 12 h washed with detergent, and finally rinsed in acetone before use. The films with different thicknesses were obtained by varying the deposition time period. Amongst

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the different methods for measuring thickness, two methods viz. weight difference method and Fizzau's method, were used to measure the thickness. The grain size calculations were carried out by using XRD studies on Philips PW-1710 Diffractometer. The optical absorption studies were carried out using Hitachi-330, Japan, to calculate optical band gap.

3. Results and discussion

3.1 *Reaction mechanism*

ZnS thin films were prepared by decomposition of thiourea in an alkaline solution containing a zinc salt. The reaction mechanism for deposition of ZnS films has been reported earlier by Ubale and Kulkarni (2005). In aqueous solution zinc acetate dissociates to give Zn^{2+} ions. Hydrolysis of ammonia in water gives OH^- ions, which forms complex $Zn(NH_3)_4^{2+}$. Thiourea in alkaline medium acts as an S^{2-} ion source. In short, the reaction for the process is

$$Zn(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow$$
$$ZnS \downarrow + 4NH_3 + CH_2N_2 + 2H_2O. \quad (1)$$
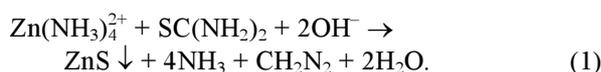
3.2 *Effect of preparative parameters*

The effect of preparative parameters such as pH of the reaction mixture and deposition temperature was studied. Figure 1 shows variation of film thickness with deposition time at 303 and 318 K temperatures. The deposition process clearly shows two different growth phases: quasi-linear phase and saturation phase. Many researchers have observed similar growth rate dependence on temperature for CdS and Sb_2S_3 film by CBD (Lincot and Vedel 1991; Dona and Herrero 1992; Savadogo and Mandal 1992). It can be seen from this figure that in the initial stage of the process, the film thickness increases at a fast rate and then growth rate decreases resulting in a terminal thickness. The average growth rate at 303 K is slow (18·6 nm/h) and terminal thickness of ~330 nm is attained after ~20 h. However, the average growth rate at 318 K is higher (20·20 nm/h) and terminal thickness of ~310 nm is reached after ~17 h.

Figure 2 shows variation of ZnS film thickness with deposition time for different NH_3 concentrations i.e. for different pH values. NH_3 acts as a complexing agent as well as pH enhancer to the Zn salt solution. It was found that, for low NH_3 concentration, i.e. when the OH^- concentration is low, the Zn^{2+} ion concentration in the solution is more due to less complexation of Zn^{2+} ions, and the homogeneous process takes place at slow rate resulting in a lower terminal thickness. At high NH_3 concentration, availability of Zn^{2+} ions is low due to higher complexation, but S^{2-} ion concentration is more that gives higher deposition rate.

3.3 *Grain size studies*

The XRD pattern of ZnS thin film of thickness, 332 nm (figure 3) shows that films are polycrystalline in nature. Comparison with ASTM data for ZnS shows that the material is ZnS with hexagonal structure (ASTM data file).
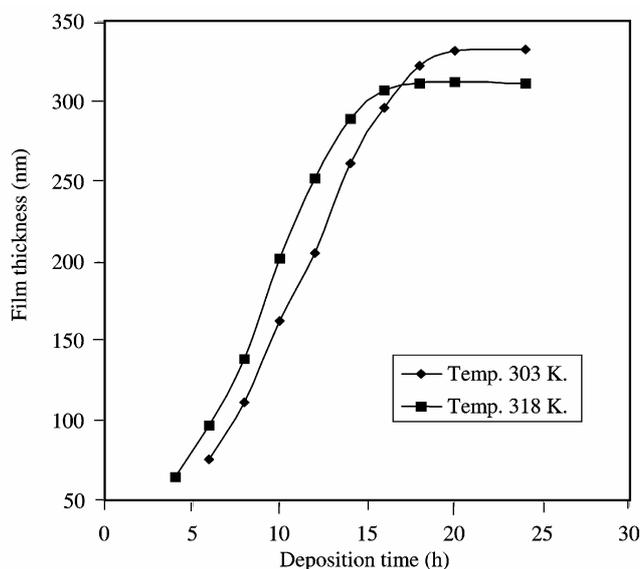

Figure 1. Variation of ZnS film thickness with deposition time at temperatures 303 and 318 K.
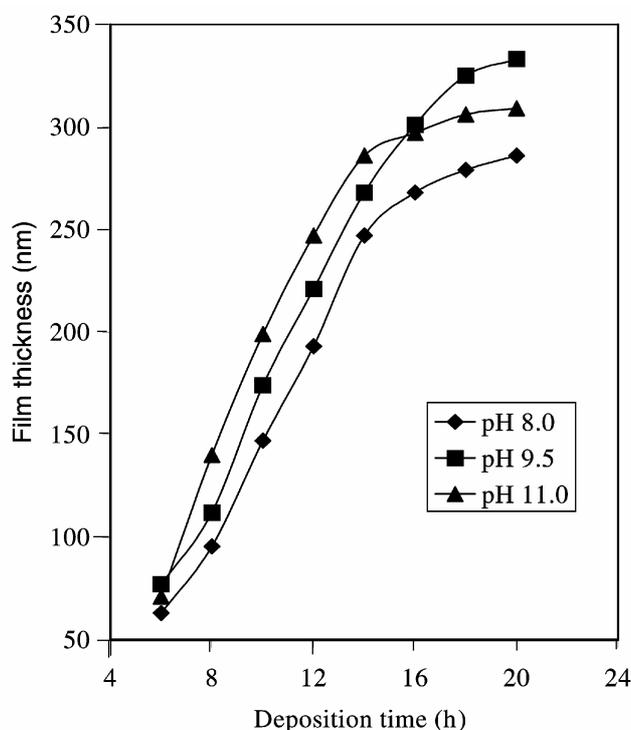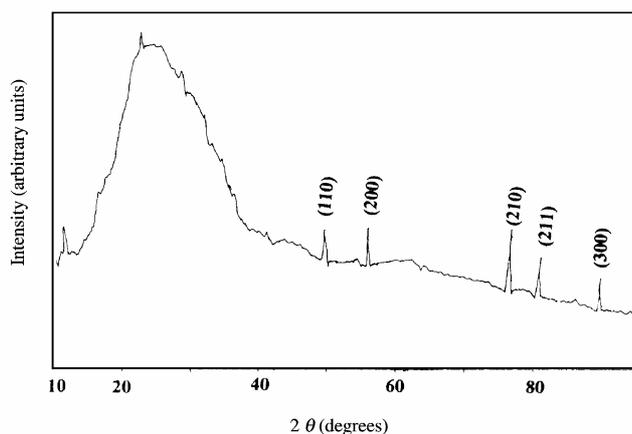

Figure 2. Variation of ZnS film thickness with deposition time for different pH values.

In order to determine grain size of ZnS particles by considering a common plane (210), slow scan between angle 75° and 80° was carried out with a step of 0·02°/10 s for the films with different thicknesses as shown in figure 4.
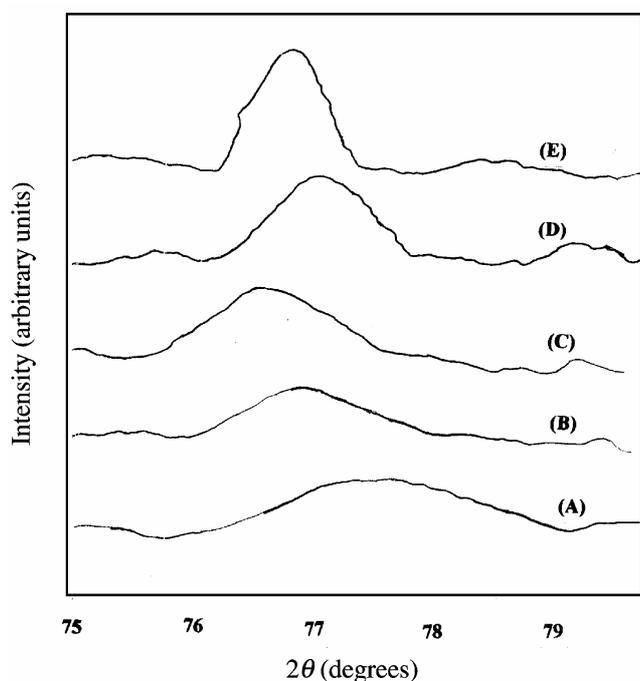
The crystallite size is calculated using Scherrer's formula

$$d = \lambda/\beta \cos \theta, \tag{2}$$

where λ is the wavelength used (1·54 Å), β the angular line width at half maximum intensity in radians and θ the Bragg's angle.

Figure 3. X-ray diffraction pattern of ZnS thin film of thickness, 332 nm.


Figure 4. XRD patterns (slow scan between 75 and 80°) of ZnS thin films of different thicknesses: (A) 76 nm, (B) 141 nm, (C) 207 nm, (D) 272 nm and (E) 332 nm.

The variation of grain size with film thickness is shown in figure 5. The grain size was changed from 6·9–17·8 nm as film thickness was changed from 76–332 nm. This change supports the size effects observed in semiconductors.

3.4 *Thermoemf measurements*

The dependence of thermoemf on temperature and thickness is shown in figure 6. The temperature difference
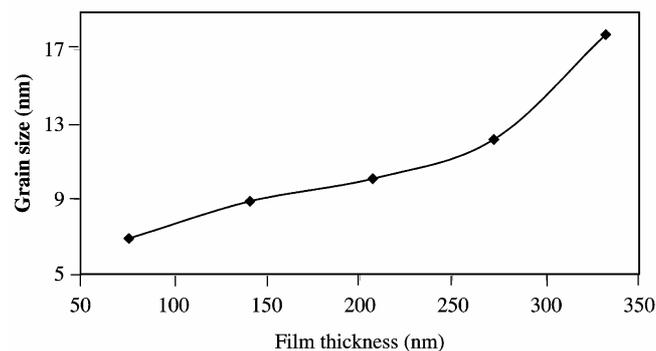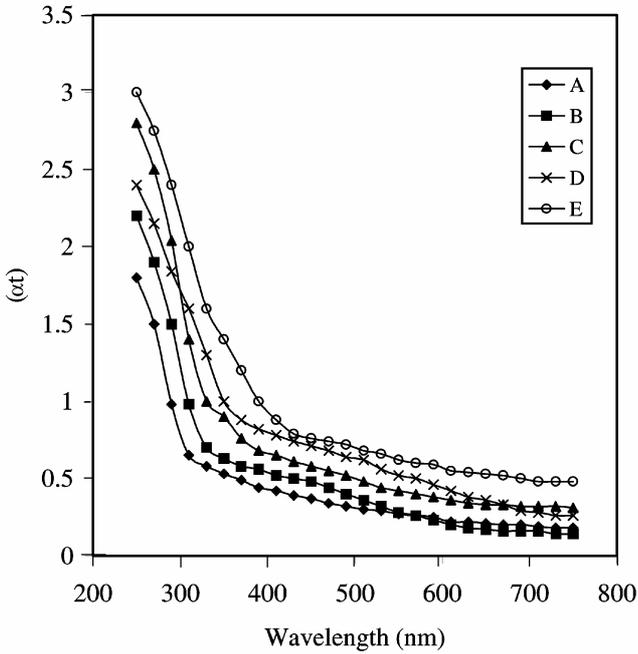

**Figure 5.** Variation of grain size of ZnS material with film thickness.
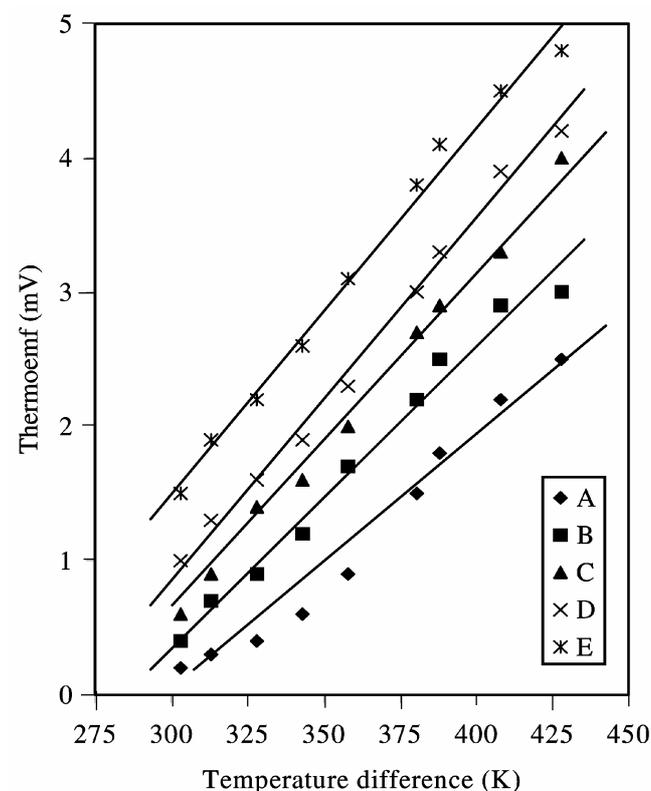
Figure 6. Plots of thermoemf vs temperature difference for different thicknesses of ZnS films: (A) 76 nm, (B) 141 nm, (C) 207 nm, (D) 272 nm and (E) 332 nm.
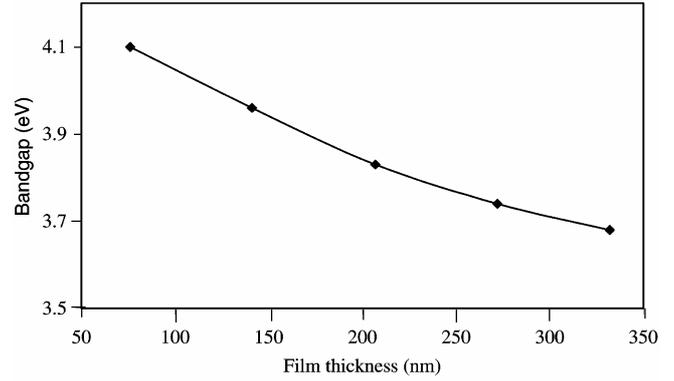
between the ends of sample causes transport of carriers from hot to cold end and thus creates electric field, which

Figure 7. Plots of optical absorption (αt) vs wavelength (nm) for different thicknesses of ZnS film: (A) 76 nm, (B) 141 nm, (C) 207 nm, (D) 272 nm and (E) 332 nm.
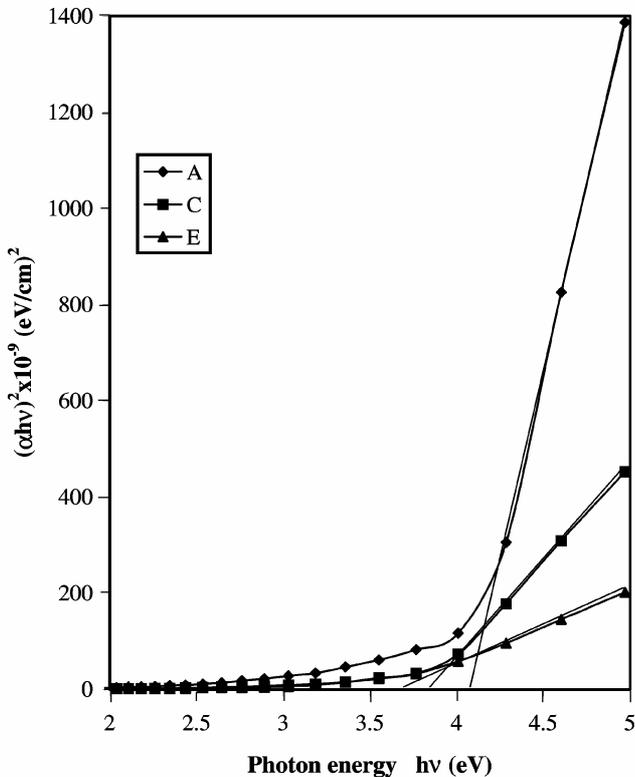
Figure 8. Plots of ($\alpha h\nu)^{-2}$ vs $h\nu$ for ZnS film with thicknesses: (A) 76 nm, (C) 207 nm and (E) 332 nm.

Figure 9. Variation of optical band gap, E_g (eV), with ZnS film thickness (nm).

gives thermal voltage. The plots show that voltage developed across the junction increases with temperature difference, which is due to rise in concentration and mobility of the charge carriers (Lokhande *et al* 1998). This thermally generated voltage is directly proportional to the temperature difference created across the semiconductor. In the present work, it was found that films are of *n*-type.

3.5 *Optical absorption studies*

Study of materials by means of optical absorption provides a simple method for explaining some features concerning the band structure of materials. In the present investigation, optical absorption (figure 7) in ZnS films with different film thicknesses was studied in the wavelength range 250–750 nm. The nature of transition (direct or indirect) is determined by using the relation

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}, \tag{3}$$

where $h\nu$ is the photon energy, E_g the band gap energy, A and n are constants. For allowed direct transition, $n = 1/2$ and for allowed indirect transition, $n = 2$.

The plots of $(\alpha h\nu)^2$ vs $h\nu$ are shown in figure 8, for ZnS films. The linear nature of the plots indicates the existence of direct transitions. It is seen that band gap was increased from 3·68–4·10 eV as thickness was reduced from 332–76 nm. The value of E_g for bulk ZnS is 3·7 eV (Dube 1960). Figure 9 shows variation of E_g with film thickness (Lokhande *et al* 1997).

4. Conclusions

In this paper we have reported the thickness dependent optical properties of ZnS thin films deposited in alkaline medium by chemical bath deposition. The thermoelectric power measurement shows that the films were of *n*-type.

When film thickness is changed from 76–332 nm, the grain size was changed from 6·9–17·8 nm, with change in optical band gap from 4·10–3·68 eV (i.e. 0·42 eV shift).

Acknowledgement

References

ASTM Diffraction data file card, No. 12-688, 10-434, and 5-0492

Cattell A F and Cullis A G 1982 *Thin Solid Films* **92** 211

Dona J M and Herrero J 1992 *This Journal* **139** 2810

Dube R H 1960 *Photoconductivity of solids* (New York: Wiley) p. 233

Fukarova M, Juruskovska, Ristov M and Andonow A 1997 *Thin Solid Films* **299** 149

Kashani H 1996 *Thin Solid Films* **288** 50

Klechkovskaya V V, Maslov V N and Murad M B 1989 *Sov. Phys. Crystallogr.* **34** 105

Lincot D and Vedel J 1991 *Proceedings of 10th European photovoltaic solar energy conference, Lisbon* (Dordrecht, The Netherlands: Kluwer Academic Publishers) p. 931

Lindroos S, Kanniainen T and Leskela M 1994 *Appl. Surf. Sci.* **75** 70

Lokhande C D, Ubale A U and Patil P S 1997 *Thin Solid Films* **302** 1

Lokhande C D, Yermune V S and Pawar S H 1998 *J. Electrochem. Soc.* **135** 1852

Mach R and Muller G O 1982 *Phys. Status Solidi* **A69** 11

Mane R S and Lokhande C D 2000 *Thin Solid Films* **65** 1

Mika P V and Lindroos S 1988 *Appl. Surf. Sci.* **136** 131

Nicolau Y F and Menand J C 1988 *J. Cryst. Growth* **92** 128

Savadogo O and Mandal K C 1992 *Solar Energy Mater. Solar Cells* **26** 117

Tong W, Wagner B K, Tran T K and Ogle W 1996 *J. Cryst. Growth* **164** 202

Ubale A U and Kulkarni D K 2005 *Bull. Mater. Sci.* **28** 43