

Preparation and study of thickness dependent electrical characteristics of zinc sulfide thin films

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Abstract. Zinc sulfide thin films have been deposited onto glass substrates by chemical bath deposition. The various deposition parameters such as volume of sulfide ion source, pH of bath, deposition time, temperature etc are optimized. Thin films of ZnS with different thicknesses of 76–332 nm were prepared by changing the deposition time from 6–20 h at 30°C temperature. The effect of film thickness on structural and electrical properties was studied. The electrical resistivity was decreased from $1.83 \times 10^5 \Omega\text{-cm}$ to $0.363 \times 10^5 \Omega\text{-cm}$ as film thickness decreased from 332 nm to 76 nm. The structural and activation energy studies support this decrease in the resistivity due to improvement in crystallinity of the films which would increase the charge carrier mobility and decrease in defect levels with increase in the thickness.

Keywords. Zinc sulfide; electrical properties; nanostructures.

1. Introduction

Recent investigations have evoked considerable interest in ZnS thin films due to their vast potential for use in thin film devices such as photoluminescent and electroluminescent devices and more recently as *n*-type window-layer heterojunction solar cells (Ortega Borges *et al* 1992). Zinc sulfide has found wide use as a thin film coating in the optical and microelectronic industries. It has high refractive index (2.25 at 632 nm), high effective dielectric constant (9 at 1 MHz) and wide wavelength pass-band (0.4–13 μm) (Orient Tom 1994). It is commonly used as filter, reflector and planar waveguide. It is also the most commonly used host material in thin film electroluminescence devices (Mach and Muller 1982). Chemical deposition of ZnS films has been carried out by a number of workers. Biswas and his co-workers reported a chemical method for the deposition of ZnS thin films at 30°C on glass substrate (Biswas *et al* 1986). In this paper, we report the preparation of ZnS films in alkaline medium.

2. Experimental

A very attractive method for producing ZnS thin films due to possibility of large area deposition of some sulphides and selenides is the so called chemical bath deposition (CBD) method (Kitaev *et al* 1965; Kitaev and Sokolova 1970; Kaur *et al* 1980; Dona and Herrero 1992). But, there are only a few reports on ZnS by CBD where the

main objective is the study of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films (Padam *et al* 1988; Lokhande 1991). Chemical deposition of ZnS thin films has been reported earlier using different zinc ion releasing sources such as zinc sulphate, zinc chloride etc. In the present case, ZnS films have been deposited chemically using thiourea as a sulfide ion source and zinc acetate as zinc ion source.

ZnS thin films are prepared by decomposition of thiourea in an alkaline solution containing a zinc salt and a suitable complexing agent. The deposition process is based on the slow release of Zn^{2+} and S^{2-} ions in solution which then condense on the substrate. The deposition of ZnS occurs when the ionic product of Zn^{2+} and S^{2-} exceeds the solubility product of ZnS.

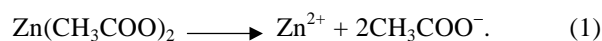
For preparation of ZnS films, 0.2 M zinc acetate solution was taken in a beaker and equal volume of 0.2 M thiourea solution was added. Ammonia solution was added slowly to form the complex and pH was raised between 9 and 10. The solution was stirred for 5–6 s and then transferred to another beaker containing cleaned glass substrate. The mixture was kept at 30°C temperature. After about 18 h the slide covered with a white deposit was taken out, washed with distilled water and dried in a desiccator.

3. Results and discussion

3.1 Reaction mechanism

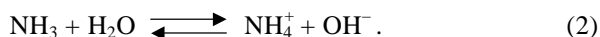
The formation of ZnS involves following steps.

Zinc acetate dissociates as

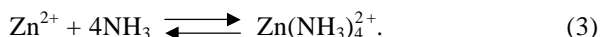


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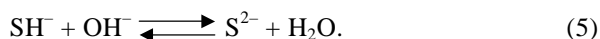
In the present case, ammonia hydrolyses in water to give OH^- according to



We can expect that the Zn^{2+} ions have to be in the form of $\text{Zn}(\text{OH})_2$ precipitate, however, it is not true due to the presence of NH_3 which forms with Zn^{2+} and the complex, $\text{Zn}(\text{NH}_3)_2^{2+}$, which is soluble in this medium.



In case of thiourea as the S^{2-} source, in an alkaline medium, the sulphide ions are released as follows



From (3) and (5), assuming a complex Zn^{2+} ion in the form of $\text{Zn}(\text{NH}_3)_4^{2+}$, the global reaction for the process is

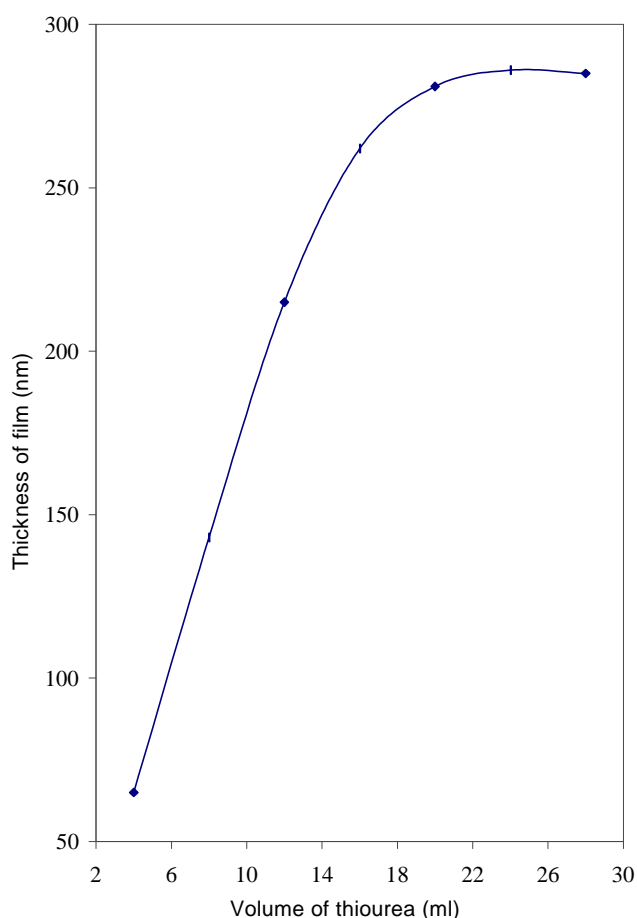
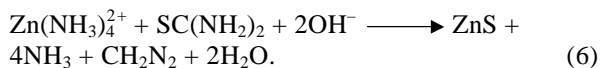


Figure 1. Optimization of volume of sulfide ion source (Deposition time, 16 h; temperature of bath, 30°C; pH of the bath, 9.0–10).

3.2 Optimization of preparative parameters

3.2a Volume of sulphide ion source: For optimization of volume of sulphide ion source, concentration of zinc acetate (0.2 M), pH (~9.5) of the bath, temperature (30°C) and deposition time (16 h) are kept constant. The variation of ZnS film thickness with thiourea volume for 20 ml zinc acetate with NH_3 , and 16 h deposition time is shown in figure 1. When ionic product (IP) of Zn^{2+} and S^{2-} exceeds the solubility product (SP) (i.e. $S > 1$) of ZnS, ZnS is formed. Ions form ZnS nuclei onto substrate and in solution which grow with time to give the film. Rate of deposition becomes zero when $S < 1$ and film attains terminal thickness.

The rate of deposition is high in the initial process of growth due to high concentrations of Zn^{2+} and S^{2-} . As more and more ZnS is formed, solution becomes deficient in ions giving lower rate of deposition. Rate of deposition becomes zero when $S \leq 1$, and film attains terminal thickness. After attaining terminal thickness further additional volume of thiourea does not increase thickness of film as appropriate volume of thiourea (~20 ml) is utilized.

3.2b Optimization of deposition time: Deposition time is optimized by taking a substrate out of bath at regular interval of 2 h. Figure 2 shows the variation of film thickness with deposition time. Film thickness increases up to 20 h deposition time and then remains nearly constant. The average rate of deposition is 18.6 nm/h. The maximum thickness obtained by this method is about 332 nm. The maximum rate of deposition is 28 nm/h at 14th h.

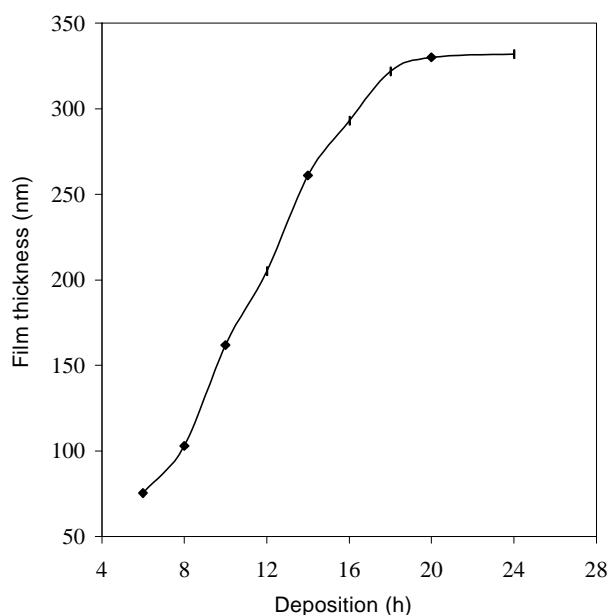


Figure 2. Variation of ZnS film thickness with deposition time (Bath composition: zinc acetate (0.2 M); NH_3 ; thiourea (0.2 M); temperature of bath, 30°C; pH of the bath, 9–10).

In order to study the thickness dependent properties, films having different thicknesses were prepared by varying the deposition time from 6–20 h. Table 1 shows variation of film thickness with deposition time.

3.3 Studies of X-ray diffractometry

Figure 3 shows the XRD patterns of ZnS films deposited at $30 \pm 2^\circ\text{C}$ bath temperature for deposition periods 6, 9, 12, 15 and 20 h.

The patterns indicate that films are polycrystalline or nanocrystalline in nature. The observed broad hump in XRD patterns of all samples is due to amorphous glass substrates. Comparison of d -values with ASTM data for ZnS (ASTM Data file) shows that the material is ZnS.

Table 1. Variation of film thickness with deposition time.

Sl. no.	Deposition time (h)	Film thickness (nm)
(A)	06	76
(B)	09	141
(C)	12	207
(D)	15	272
(E)	20	332

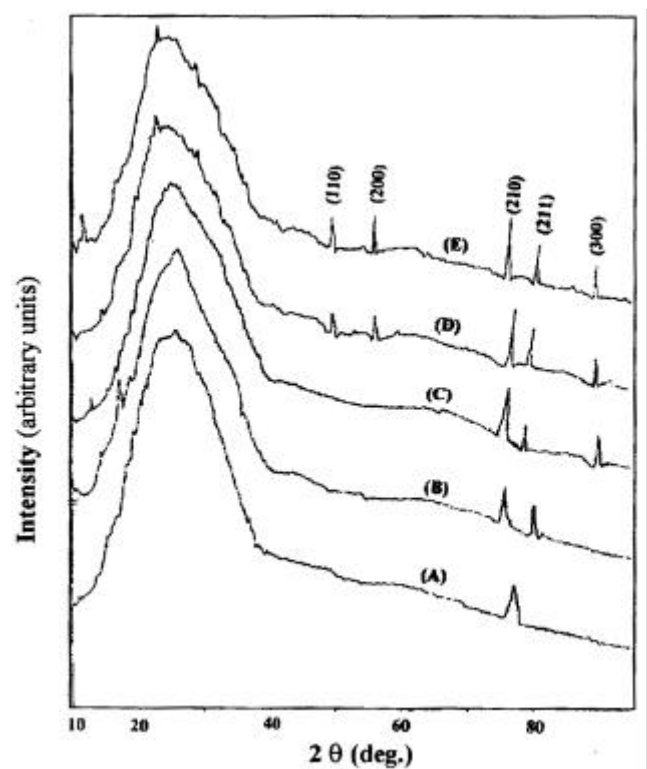


Figure 3. X-ray diffraction patterns of ZnS thin films for different thicknesses. (Film thickness: (A) 76 nm; (B) 141 nm; (C) 207 nm; (D) 272 nm and (E) 332 nm).

Comparison of XRD data for ZnS films is shown in tables 2–6.

The XRD patterns show small crystallites. The crystallinity of the films was improved with thickness. The XRD patterns matched well with the standard patterns of ZnS, which possess hexagonal structure.

3.4 Electrical resistivity studies

The electrical resistivity of ZnS films with different thicknesses was measured using the d.c. two-point probe method in air. Figure 4 shows the variation of log of resistivity ($\log r$) with reciprocal of temperature ($1/T$) $\times 10^3$. For all films it was seen that resistivity decreases with temperature indicating semiconducting nature of films. For all the films, resistivity follows the relation

$$r = r_0 \exp(E_0/KT), \quad (7)$$

Table 2. Comparison of d -values with ASTM data ([A] Film thickness, 76 nm).

Sl. no.	Standard d -value (Å)	Observed d -value (Å)	Reflection plane (hkl)
01	1.251	1.2504	(210)

Table 3. Comparison of d -values with ASTM data ([B] Film thickness, 141 nm).

Sl. no.	Standard d -value (Å)	Observed d -value (Å)	Reflection plane (hkl)
01	1.251	1.2584	(210)
02	1.226	1.2252	(211)

Table 4. Comparison of d -values with ASTM data ([C] Film thickness, 207 nm).

Sl. no	Standard d -value (Å)	Observed d -value (Å)	Reflection plane (hkl)
01	1.251	1.259	(210)
02	1.226	1.2343	(211)
03	1.1023	1.1017	(300)

Table 5. Comparison of d -values with ASTM data ([D] Film thickness, 272 nm).

Sl. no.	Standard d -value (Å)	Observed d -value (Å)	Reflection plane (hkl)
01	1.911	1.8333	(110)
02	1.654	1.6502	(200)
03	1.251	1.2488	(210)
04	1.226	1.231	(211)
05	1.1023	1.1096	(300)

where r is resistivity at temperature, T , r_0 is a constant, K the Boltzmann constant (1.38×10^{-23} J/K) and E_0 the activation energy required for conduction.

Table 6. Comparison of d -values with ASTM data ([E] Film thickness, 332 nm).

Sl. no.	Standard d -value (Å)	Observed d -value (Å)	Reflection plane (hkl)
01	1.911	1.9662	(110)
02	1.654	1.6323	(200)
03	1.251	1.2421	(210)
04	1.226	1.2290	(211)
05	1.1023	1.1066	(300)

Table 7. Variation of activation energy with film thickness.

Sl. no.	Film thickness (nm)	Activation energy (eV)
(A)	76	1.29
(B)	141	1.07
(C)	207	0.94
(D)	272	0.91
(E)	332	0.81

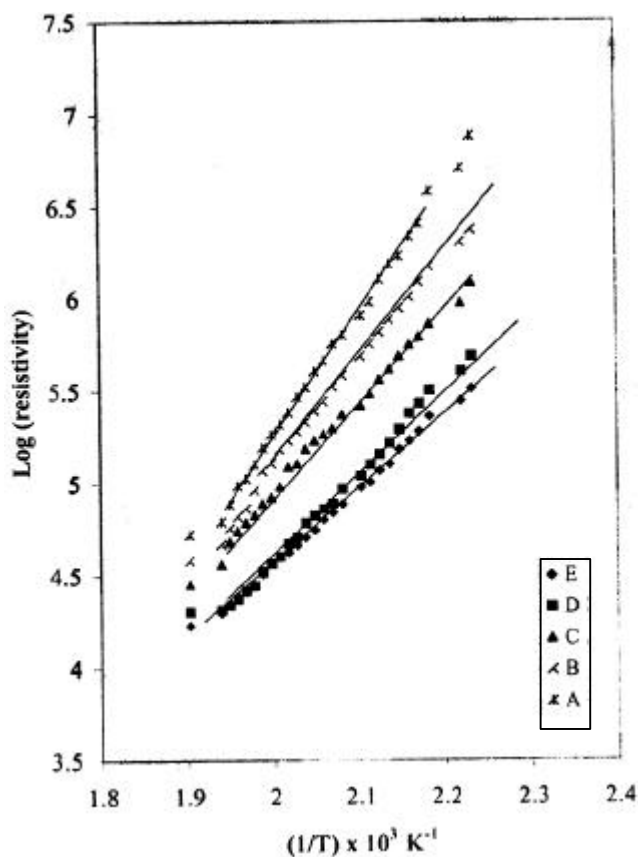


Figure 4. Variation of $\log(r)$ vs $1/T \times 10^3$ (K^{-1}) for different thicknesses of ZnS films (Film thickness: (A) 76 nm, (B) 141 nm, (C) 207 nm, (D) 272 nm and (E) 332 nm).

Figure 5 shows variation of electrical resistivity, r (Ω -cm), with film thickness. Resistivity of ZnS film decreases from 1.832×10^5 (Ω -cm) to 0.363×10^5 (Ω -cm) as film thickness decreases from 76 to 332 nm at temperature, 505.5 K. This decrease in resistivity is due to the improvement in crystallinity of the films as the film thickness was increased from 76 to 332 nm. This observation is attributed to the size effect observed in semiconductor thin films. A similar behaviour of nanocrystalline materials prepared by different methods was reported by several workers (Liu *et al* 1993, 1994; Wang *et al* 1993; Kale *et al* 1996).

From the resistivity plots, the thermal activation energies were calculated using (7). Table 7 shows activation energies at different thicknesses of ZnS film. Activation energies are of the order of 0.81–1.29 eV as film thickness was decreased from 332 to 72 nm.

4. Conclusions

The ZnS thin films have been chemically deposited from an aqueous alkaline bath and thickness of film was varied from 76 nm to 332 nm, by changing deposition time. The structural and electrical properties of ZnS are found to be thickness dependent. The resistivity measurement shows that films are semiconducting in nature.

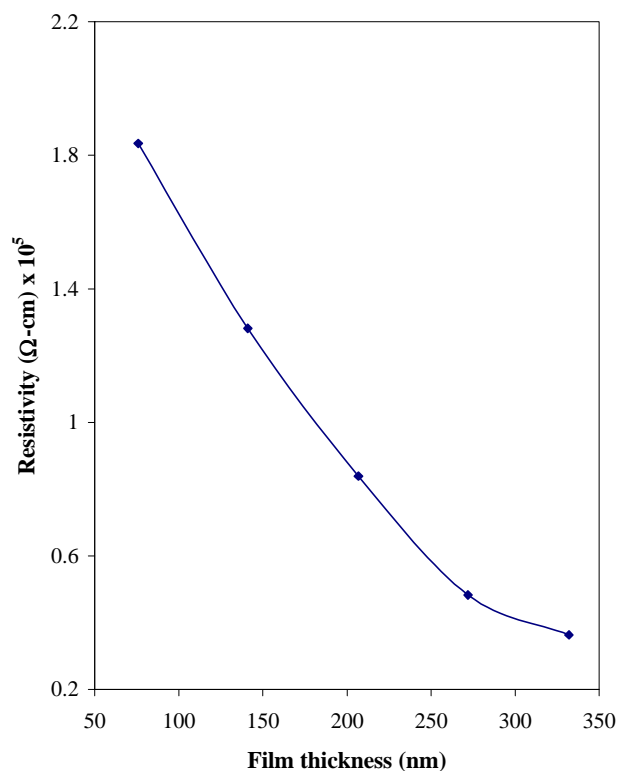


Figure 5. Plot of variation of electrical resistivity (r) (Ω -cm) $\times 10^5$ with ZnS film thickness at 500.5 K temperature.

Acknowledgement

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