

# Thickness Dependent Electrical Properties of Chemically Deposited ZnS Thin Films.

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## ABSTRACT

Thin films of ZnS were deposited on glass slides from aqueous solutions of Zinc chloride in which ammonia solution; Triethanolamine (TEA), and thiourea (TU) were employed as complexing agents. The films were studied for their electrical properties in relation to their thicknesses. The variation of the film thickness was obtained by changing the deposition time. The resistivity and the conductivity of the films were found to be thickness dependent while the results indicate that the films are semiconducting in nature.

(Keywords: chemical bath deposition, CBD, ZnS, zinc sulfide, resistivity, conductivity, thin films)

## INTRODUCTION

ZnS is a significant solid state material of both scientific and engineering interest, though fundamental investigations of ZnS was largely neglected en route to technological development. As a main group compound with a simple structure, it should be included with other main groups of sulfide, halide, and oxide materials in order to evaluate property trends and develop theories of solid state science.

Zinc sulfide belongs to group II – VI compound semiconductor materials and its thin films may be present in cubic or/and hexagonal crystal structure. Generally, the chemically deposited films are of mixed phases of cubic and hexagonal crystal structures (Pathan and Lokhande, 2004).

Zinc sulfide is an important semiconductor material with a large band gap ( $>3.5\text{eV}$ ), which has vast potential use in thin film

devices, such as photo luminescent and electroluminescent devices (Pathan and Lokhande, 2004).

Thin films of ZnS have been prepared using many deposition techniques such as chemical bath deposition (CBD) [Nair and Nair, 1992; Cheng et al., 2003], Sol – gel techniques [Bhattachagjee et al., 2002], Metal Organic Vapor Deposition MOCVD [Seo et al., 2005], pulsed Laser ablation [McLaughlin et al., 1993], Molecular Beam Epitaxy [Kitagawa et al., 1990], Vacuum Evaporation Technique (Nadeem and Ahmed, 2000), Magnetron Sputtering Technique [Zhang et al., 2004], Spray Pyrolysis Technique [Ashour et al., 1994; Pike et al., 1993; Al-Sabayleh, 2008] and Electrostatic Assisted Aerosol Jet Deposition EAAJD [Su et al. 2000].

The chemical bath deposition (CBD) technique offers the following advantages over other techniques: (1) films can be deposited on all kinds of hydrophilic substrates; (2) it is a very simple and inexpensive technique suitable for large area deposition; and (3) impurities in the initial chemicals can be made ineffective by suitably complexing them (Chopra and Kaur, 1983).

This paper reports on the investigations of electrical properties of chemical bath deposited ZnS thin films at different thicknesses.

## EXPERIMENTAL DETAILS

The CBD technique has been used in the deposition of the ZnS thin films. The technique was adopted in this work due to its simplicity, production of fairly good quality

films, cost effectiveness, convenience, and high reproducibility (Ugwu and Onah, 2007).

The reagents used for these studies are zinc chloride ( $ZnCl_2$ ), 25% ammonia ( $NH_3$ ), triethanolamine (TEA), and thiourea (TU) with all the chemicals being of analytic grade. The experimental solution of the desired concentration of the various reagents was prepared as follows: 1M of  $ZnCl_2$ , 10M of ammonia solution, 1M of TEA and 1M of TU. 10ml of the 1M  $ZnCl_2$  solution was measured into a 100ml beaker, 6ml of the 10M Ammonia solution was introduced gradually into the beaker with stirring until the white precipitates of Zinc complex formed was fully dissolved. 1ml of the 1M TEA was then added and finally 15ml of 1M thiourea was added with continuous stirring to start the reaction. Distilled water was added to make up 50ml of solution in the bath. The chemical bath composition gave a pH of 11.40.

Glass slides were used as substrates. They were cleaned together with other equipments using the following procedure in sequence:

- i. Scrubbing with liquid detergent.
- ii. Rinsing several times with distilled water
- iii. Scrubbing again with detergent.
- iv. Rinsing again with distilled water
- v. Scrubbing with trichloroethylene
- vi. Rinsing with distilled water
- vii. Scrubbing with acetone
- viii. Rinsing with distilled water
- ix. Scrubbing with alcohol
- x. Rinsing with distilled water
- xi. Drying using an oven.

After cleaning, the substrates (glass slides) were inserted into the bath and suspended vertically from synthetic foam, which covered the beaker containing the bath. Five substrates (glass slides) were inserted into the bath at the same time for an initial period of five hours. The deposition was optimized by taking a substrate out of the bath at regular interval of 3 hours starting with the initial period. The substrates which were labeled V, W, X, Y and Z had deposition time of 5, 8, 11, 14, and 17 hours, respectively.

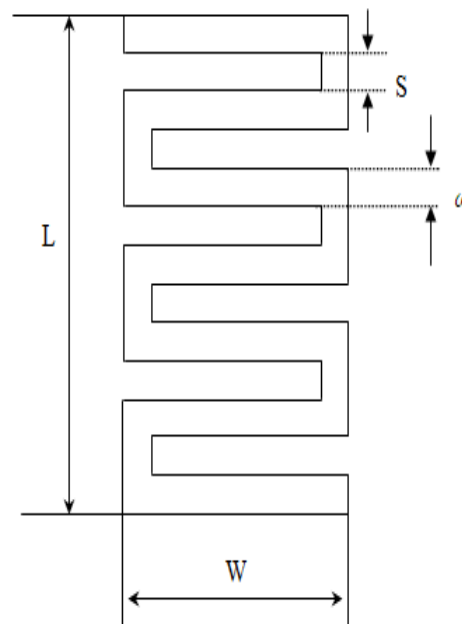
The films were characterized for electrical resistivity using the direct current (DC) two point probe method in air. From the values of the resistivities of the films, the conductivities were deduced.

## THEORY AND CALCULATIONS

To characterize the resistance of the thin films by normalized parameter, called surface resistivity ( $R_s$ ), two basic configurations of the film resistance (Glaser and Subak, 1977), as shown in Figure 1, are considered. The resistance ( $R$ ) can be expressed by considering the rectangular section of the film (Figure 1) (Glaser and Subak, 1977) and given as:

$$R = \rho L/dw \quad (1)$$

where ( $R$ ) is the resistance, ( $\rho$ ) is the resistivity, ( $L$ ) is the length of the rectangular substrate, and ( $dw$ ) is the element of the width.



**Figure 1:** Rectangular Section of the Film.

If  $L=W$ , then:

$$R = \rho/d = R_s \quad (2)$$

Therefore, the resistance ( $R_s$ ) of one square of a film depends not on square the size, but on the resistivity and thickness. ( $R_s$ ) is the resistance of the film layer and is expressed in ohms-square. This value is widely used for film comparison, in particular films of one material deposited under identical conditions. If the thickness is known, the resistivity ( $\rho$ ) is obtained from the equation (Glaser and Subak, 1977):

$$\rho = dR_s \quad (3)$$

A change in thickness provides variation of resistance value without change in the basic properties of a material. However, resistivity and temperature coefficient of resistance (TCR) on the depend surface resistance ( $R_s$ ) and the number of squares, (N) (Glaser and Subak, 1977), i.e.:

$$R = R_s \cdot N \quad (4)$$

The configuration is characteristic of many thin films and the resistance of such material is determined by the equation (Glaser and Subak, 1977) are given by the relation:

$$R = R_s (LW/nw^2 + 1/nw - 2(0.46)L/nw) \approx R_s LW/nw^2 \quad (5)$$

where  $n = s/w + 1$ ,  $w = s$  the width of lines, and (S) is the width of intervals between the lines. Therefore, the parameters of a film which can be used for operational development of resistance (Glaser and Subak, 1977):

$$R = \rho/s \cdot N \quad (6)$$

Hence, the temperature coefficient of resistance is described by the equations:

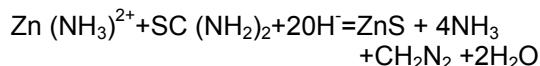
$$\alpha = \frac{1}{R} \frac{dR}{dT} \quad (7)$$

$$\alpha = R - \frac{R_0}{R_0(T - T_0)} \quad (8)$$

where (R) is the resistance at certain temperature, T, and  $T_0$  is the temperature at 0K.

## RESULTS AND DISCUSSION

The reaction governing the formation of the ZnS can be represented:



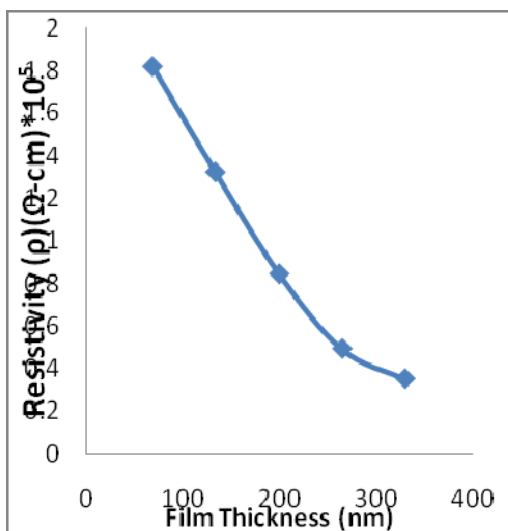
The optimization of the volume of sulphide ion source was achieved with the concentration of zinc chloride (1M), pH (11.40) of the bath at room temperature and deposition time kept constant, in a similar way demonstrated by Ubale and Kulkani (2005).

When the ionic product (IP) of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  exceeds the solubility product (SP) of ZnS (i.e.,  $S > 1$ ), ZnS is formed (Ubale and Kulkani, 2005). Ions form ZnS nuclei onto substrate and in solution which grows with time to give the film (Ubale and Kulkani, 2005). The rate of deposition becomes zero when  $S < 1$  and the film attains terminal thickness (Ubale and Kulkani, 2005).

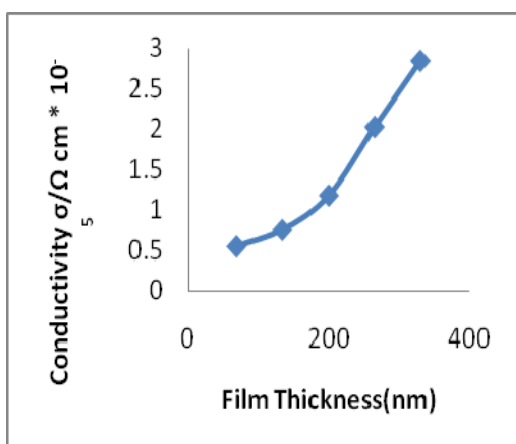
The rate of deposition is high in the initial process of growth due to high concentrations of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  (Ubale and Kulkani, 2005). As more and more ZnS is formed, the solution becomes deficient in ions giving lower rate of deposition (Ubale and Kulkani, 2005). Rate of deposition becomes zero when  $S \leq 1$ , and film attains terminal thickness (Ubale and Kulkani, 2005). Further addition of thiourea does not increase the thickness of the film as the appropriate volume of thiourea (15 ml) is utilized.

The variation of electrical resistivity ( $\rho$ ) ( $\Omega\text{-cm}$ ), with the thickness is presented in Figure 2. The resistivity of ZnS film decreases from  $1.822 \times 10^5$  ( $\Omega\text{-cm}$ ) to  $0.363 \times 10^5$  ( $\Omega\text{-cm}$ ) as the film thickness increases from 69 to 300nm.

Figure 3 presents the variation of electrical conductivity  $\sigma$ , ( $\Omega^{-1}\text{-cm}^{-1}$ ), with film thickness. The conductivity of the ZnS film increases from  $0.549 \times 10^{-5}$  ( $\Omega^{-1}\text{-cm}^{-1}$ ) to  $2.841 \times 10^{-5}$  ( $\Omega^{-1}\text{-cm}^{-1}$ ) as the film thickness increases from 69 to 300nm.



**Figure 2:** Plot of Variation of Electrical Resistivity ( $\rho$ )( $\Omega$ -cm)  $\times 10^5$  with ZnS Film Thickness.

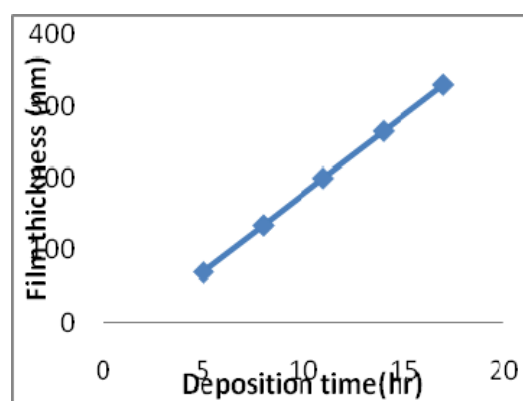


**Figure 3:** Plot of Variation of Electrical Conductivity  $\sigma/\Omega$ -cm  $\times 10^{-5}$  with ZnS Film Thickness.

The above results confirmed that the decrease in resistivity and the increase in conductivity are due to the improvement in crystallinity of the films as the film thickness was increased from 69 to 300nm, and this observations is attributed to the size effected observed in semiconductor thin films (Ubale and Kulkani, 2005).

A similar behavior was reported by Ubale and Kulkani (2005), when they used zinc acetate as the source of  $Zn^{2+}$ , and by several other workers among other whom are Liu et al., (1994); Wang et al., (1993); and Kale et al. (1996) who used different deposition methods.

The variation of ZnS film thickness with deposition time is presented in Figure 4. The deposition time is optimized by taking a substrate out of bath at regular interval of 3 hrs. The film thickness increased with deposition time.



**Figure 4:** Variation of ZnS Film Thickness (nm) with Deposition Time (hr).

## CONCLUSION

ZnS films with thickness that ranged from 69 to 330 nm have been successfully deposited on glass substrates at room temperature using chemical bath deposition, technique. The variation of the film thickness was obtained by changing the deposition time. The resistivity and the conductivity were found to be thickness dependent and the results showed that the films are semiconducting in nature.

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