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## Effect of Zinc Nano-particles on CdS Thin Films grown by Solution Technique

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### ABSTRACT

This research paper investigated the effect of Zinc nano-particles on cadmium sulphide thin film's electrical properties as a function their as-deposited thicknesses. Solution technique was used to grow thin films on ordinary microscope substrate slides from aqueous solutions of  $Zn^{+2}$  and  $Cd^{+2}$  with  $S^{+2}$  ions in the presence of TEA. By varying its deposition time only to obtain eleven (11) samples, resistance was measured using a two point probe while its conductivity type was measured using a Gauss meter as a function of their thicknesses. The thin films were found to be n-type semiconductors with a very high valence electron density, a band gap of 2.43 eV, an average transmittance above 79% on in the VIS - NIR region and a resistivity of  $9.5 \times 10^1 - 1.22 \times 10^2 \Omega\text{-cm}$ . Sheet resistivity increased with an increase in Zn ion concentration.

**Keywords:**  $Cd_{0.3}Zn_{1.1}S_{0.7}$ , Band gap, Complexing Agent, n-type, Semiconductor

## 1. INTRODUCTION

A composite of inorganic ternary stable non-stoichiometric compounds containing zinc, cadmium and sulfur is attracting research attention for application in thin film solar cells (Mosiori *et al.*, 2015). These element belongs to group II – VI compound semiconductor materials. Further still, this ternary semiconducting material has shown a considerable application in photoluminescent (ref) and electroluminescent devices (ref). Such greater attention has been attracted because this compound can be prepared by solution a technique which allows thin films to be grown on all kinds of hydrophilic substrates (ref). It is also a very simple, inexpensive method suitable for applications large area deposition requirements.  $Cd_{0.3}Zn_{1.1x}S_{0.7}$  thin films start from CdS binary thin films (Mosiori *et al.*, 2015). Certain treatments done to binary CdS, such as incorporating Zn onto CdS produces ternary thin films. This third impurity has direct influence on the electrical properties of the resulting material. Some of these properties are useful for applications in single hetero-junction solar cells (ref). In this work, CdS was doped with Zn by varying  $x$  to produce  $Cd_{0.3}Zn_{1.1x}S_{0.7}$  to lower minority carrier recombination if this material was to be used a window layer in solar cells. The concept used in this work was that the chemical bath deposition of CdS is based on the ion-to-ion model (Mosiori *et al.*, 2014) in which growth takes place by condensation of  $Cd^{+2}$  and  $S^{-2}$  that results in thin film formation. Hence, the growth of  $Cd_{0.3}Zn_{1.1x}S_{0.7}$  thin films results from the incorporation of the Zn ions in the CdS precipitate.

## 2. Theoretical Considerations

### 2.1 Resistivity in thin films

Sheet resistance in thin films depends only on thickness. Any change in thickness cause large change in resistance without change of properties. Hence the total resistance (ref) is given as:

$$R = R_s \times A \quad (1)$$

where  $R_s$  is the surface resistance,  $A$ , is the number of squares or from the relation:

$$R = R_s \left( \frac{BW}{Qh^2} + \frac{1}{Qh} - 2(0.46) \frac{B}{Qh} \right) \quad (2)$$

hence;  $\frac{R_s BW}{nh^2} \approx 1$  where  $Q = \frac{s}{h} + 1$ , where  $h = s$  width of each line,  $W$  is intervals between the lines.

This gives resistance as (ref):

$$R = \frac{\rho}{h} \times A \quad (3)$$

## 2.2 Measurement of Conductivity Type

The Hall coefficient is function of the material and its impurity concentration. Hall Effect is observed when a magnetic field is applied at right angles to a rectangular sample of a material carrying an electric current so that a voltage appears across the sample due to an electric field that is at right angles to both the current and the applied magnetic field (ref). The the drift field ( $J_x$ ) cause carriers to flows in the x-direction. The carriers move with an average drift velocity which is vector of Lorentz force as:

$$F = q(E + v \times B) \quad (4)$$

where  $\mathbf{F}$  is the force on the carriers,  $q$  is the charge of the carriers,  $\mathbf{E}$  is the electric field acting on the carriers and  $\mathbf{B}$  is the magnetic field. The charge may be positive (“holes”) or negative (“electrons”).

The total current gives a drift current  $J_x$  (ref) is given by;

$$J_x = nqv_x \quad (5)$$

where  $n$  is the number density and thus we can measure the carrier density in terms of mobility,  $\mu$  from carrier drift velocity per unit electric field obtained from;

$$v = \mu E \quad \text{or,} \quad \mu = \frac{v_x}{E_x} \quad (6)$$

Giving current density as;

$$J = \sigma E, \text{ or } \Rightarrow J_x = nqv_x = nq\mu E_x \quad (7)$$

and conductivity  $\sigma$  as (ref);

$$\sigma = nq\mu = \frac{1}{\rho} \quad (8)$$

where  $\rho$  is the resistivity.

## 3. METHODOLOGY

### 3.1 Reagents and Chemicals

Analytic grade chemicals of about 99.9% purity were purchased and used without further purification. These included zinc chloride, thiourea, cadmium chloride, absolute ammonia and triethanolamine (TEA) among others. The substrates were ordinary microscope slides.

### 3.2 Cleaning of substrates

The microscope slide substrates were prepared and cleaned according to the procedure given by Mosiori *et al.* 2014 and stored for use.

### 3.3 Experimental Procedures

All solutions were prepared according to Mosiori *et al.*, 2014. The substrate were inserted at a small angle to the vertical and suspended vertically from synthetic foam and the bath composition was maintained at pH of 10. The as deposited films were removed at intervals of 3, 8, 13, 18, 23, 28, 33, 38, 43, 48 and 53 hours to obtain eleven samples as tabulated below respectively cleaned and dried before characterized as deposited for electrical resistivity using a two point probe and a Gauss meter for conductivity type. Therefore the variation  $x$  was meant to produce  $Cd_{0.3}Zn_{1.1x}S_{0.7}$  thin films whose thickness was to vary with growth time.

## 4. RESULTS AND DISCUSSION

### 4.1 Chemical Process mechanisms

The following formulae were used to calculate the various concentrations of the solutions used;

$$\text{Molarity} = \frac{\text{No. of moles} \times \text{volume used}}{1000} \quad (9)$$

Concentration as;

$$\text{Concentration} = \frac{\text{mass used}}{\text{RMM} \times 1000} \text{ in moles per litre} \quad (10)$$

The films were cleaned from one side using cotton wool soaked in dilute hydrochloric acid, dried in air and then characterized as-deposited according to Mosiori *et al.* 2014. In the chemical reaction governing the formation of the  $Cd_{0.3}Zn_{1.1x}S_{0.7}$ , the values of  $x$  was determined by using the formula;

$$x = \frac{[Zn^{2+}]}{[Cd^{2+} + Zn^{2+}]} \quad (11)$$

When the ionic product of  $Zn^{2+}$  and  $S^{2-}$  exceeds the solubility product ( $Cd_{0.3}Zn_{1.1x}S_{0.7}$ ), precipitation starts and overall nuclei start to coagulate onto the substrate (Mosiori *et al.*, 2014). The overall general deposition expression can be represented as:



At the initial process, the rate of deposition was high and this was attributed to the high concentrations of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  in the bath solutions forming a thicker film per unit time spent. As time goes on, precursor solution becomes deficient in ions and this resulted into slower rates of film growth. Though in our work, we did not achieve the rate of deposition where it is zero or when  $S \leq 1$ , it was expected if the deposition time as increased to attain terminal thickness hence stopping further deposition.

#### 4.2 Thin films Sheet Resistivity

A direct current two point probe was used to measure the electrical sheet resistivity, ( $\rho$ ) in ohm metre ( $\Omega\text{-cm}$ ) as a function of thickness. The results were tabulated in table 1 which shows that sheet resistivity decreased exponential from  $1.822 \times 10^5$  to  $0.323 \times 10^5$  ( $\Omega\text{-cm}$ ) as the film thickness increases from 69 to 300nm. The results were plotted in figure 2.

**Table 1: Variation of sheet resistivity with thickness**

Sample Label	Thickness (nm)	Resistivity ( $\Omega\text{-cm}$ ) $\times 10^5$
A	69	1.924
B	120	1.613
C	143	1.262
D	156	0.936
E	166	0.793
F	189	0.736
G	214	0.633
H	237	0.613
I	269	0.542
J	283	0.427
K	300	0.323

This variation in sheet resistivity was attributed to the increase in thickness as well as the increase in Zn concentration in the thin film. Zinc is a good electron conductor and its presence as a dopant increase the degree of conductivity hence the films showed a decrease in resistivity. The presence of

Zn was also attributed to crystallinity. The presence of Zn may have improved the relationship of Zn impurities and with CdS crystals in the films. A similar observation was obtained by Mosiori *et al.* 2014 who attributed it to the increase in size of crystals that end up modifying resistivity in  $Cd_xZn_{1-x}S_x$  thin films (Mosiori *et al.*, 2014). Similar curves were observed by (ref) and (ref) who used different deposition methods but similar reagents.

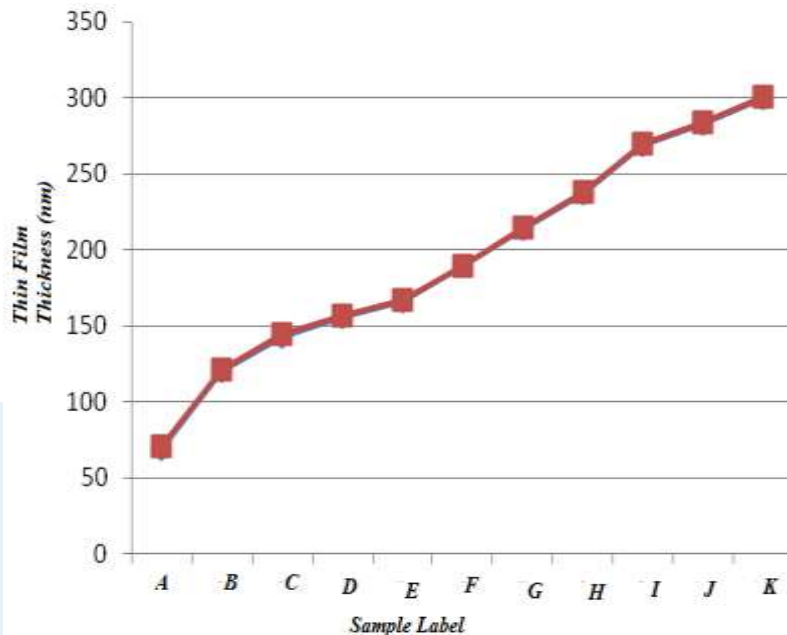


Figure 2: Plot of sheet resistivity against sample label

### 4.3 Conductivity measurement

The Gauss meter used in this work was programmed to use LabView measure  $R_H$ , by controlling the drift current in the samples. The V-I data was recorded from the two volt meters in the gauss meter. The computer labview program was set to have steps of the driving voltage recorded from each of its meters and output the results when the program terminates. The sheet dimensions were set follows: width, ( $w$ ) was set at 0.15 cm, length, ( $L$ ) at 0.37cm = 0.381 cm and thickness of  $d = 166$  nm. The choice of thickness was done by assuming that the average thickness was the optimized thin film. Analysis showed that the thin films had intrinsic electron carrier density and hence n-type. This density of valance electrons were calculated as follows (ref): Density of Valance Electrons (DVE) at  $E_g$  of 2.41 eV with  $kT$  at room temperature being 0.025 eV was;

$$\rho_{electronc} = 7 \times 10^{28} \left[ e^{-\frac{E_g}{kT}} \right] = 7 \times 10^{28} \times e^{-96.4} \text{ electrons} \quad (13)$$

## CONCLUSION

In this work, the effect of Zn nanoparticles on CdS was investigated by solution method on ordinary microscope substrates at room temperature. It was found that thickness range from 69 nm to 300 nm and sheet resistivity was dependent on thickness. The thin films were n-type with very high density valence electrons and had an average band gap of 2.41 eV, transmittance of above 79% in the VIS - NIR region with sheet resistivity of  $1.924 \times 10^2 - 0.323 \times 10^2 \Omega\text{-cm}$  that increased with Zn nanoparticle concentration. The films were proposed to be suitable for solar cell applications.

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