STUDY OF LOW TEMPERATURE DC CONDUCTIVITY ON $Co_xZn_{1-x}S$ MIXED SEMICONDUCTOR COMPOUNDS

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Abstract: Polycrystalline semiconductor compounds of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) samples have been synthesized by a controlled co-precipitation technique. The samples are characterized by X-ray diffraction (XRD). DC conductivity studies were performed in the temperature region 77–300K by using a two probe method. The dc conductivity plots show the Arrhenius behavior with three different activation energies (Ea) in three different temperature regions I (300–165K), II (165–100K), III (100-77K), and they exhibited the variable range hopping conduction (VRH) mechanism at low temperature region (100-77K).

Key words: Co-precipitation technique, DC conductivity, Variable range hopping (VRH).

I. INTRODUCTION

II-VI compound semiconductors with wide energy gap and have been extensively used in optoelectronic devices, photo voltaic cells and solid state devices [1–5]. Among a variety of binary metal chalcogenides (CdTe, CdSe, ZnS, ZnSe, and CdS) the CdS – ZnS mixed system has been extensively studied. Moreover, with the compositional variation of $Cd_{1-x}Zn_xS$ it is possible to alter the electronic behavior of the mixed system and can be widely used in electronic devices. In recent years, due to the number of practical applications in the field of optoelectronics and electro-optics, a great deal of interest has been shown in the study of dielectric and conduction behavior of various semiconducting materials [6–9]. In $Cd_{1-x}Zn_xS$, which exist in single phase wurtzite structure the value of "x" plays a predominant role in altering and determining their structural, electrical and optical properties. The rapid increase in the resistivity and energy gap of $Cd_{1-x}Zn_xS$ were increases with increase in doping concentration, which leads to more usage of conductivity related applications like near infrared solar cells. So it is interesting to prepare samples of higher energy gap with reasonably good electrical conductivity [10-16].

$Co_xZn_{1-x}S$ ternary compound, a mixed compound of ZnS and CoS, is found as the most assuring material for a variety of applications in the fields such as electroluminescent optical devices, photoconductor devices and photovoltaic cells. Electrical studies on $Co_xZn_{1-x}S$ material are limited. Therefore, growth of $Co_xZn_{1-x}S$ compounds and their electrical studies are taken up. In this paper, $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) ternary compound semiconductor materials are prepared by controlled co-precipitation method and their structural, electrical properties are studied and analyzed.

II. EXPERIMENTAL DETAILS

2.1 Preparation of samples

Compounds of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) have been prepared by controlled co-precipitation method. In this method equimolar solutions of Cobalt acetate, Zinc acetate, Thiourea and Triethanolamine, all are of A.R. grade SDFCL chemicals, were taken in different compositions. The solution mixture was made alkaline by adding 30 percent liquid Ammonia under constant stirring process. The solution was heated at about 80ºC for 1 hour. The color of the solution then changed from blue to dark green indicating the starting of precipitation. Further, the solution was heated for 1 hour to complete the reaction. The reacted mixture (compound) appeared at the bottom of the flask in the form of precipitate.

The filtered precipitate was collected and dried at room temperature for 24 hour. Then the dried precipitate was heated for 2 hour at 300ºC under Nitrogen atmosphere and then slowly cooled to room temperature. The compound was ground to fine powder and the powder was made into pellets under 10 ton pressures per sq cm by using punch dye of 1.0 cm diameter. The pellets were sintered at 800ºC for 2 hour in Nitrogen atmosphere. The furnace is cooled slowly to room temperature at the rate of 2ºC per minute. XRD, electrical studies are made on the prepared samples. The reaction mechanism and other experimental details of the preparation of samples are discussed in our earlier paper [17].

2.2 X-ray diffraction studies

The X-ray diffraction studies have been carried out using PANalytical's X–ray diffractometer with CuK_α radiation (λ=1.5406 Å). Diffraction spectra were recorded at room temperature in the range of $20° \leq 2\theta \leq 80°$ at a scan speed of $0.02°$/s.

2.3 DC conductivity measurements

The DC conductivity of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) compounds were measured by two probe method using a conductivity cell fabricated in the laboratory. Keithley nano Voltmeter (Model 2000), constant current source (Model 6220) were used for conductivity measurements. A constant current of 0.1mA is passed through the samples. Conductivity measurements were made at different temperatures ranging 77-300K.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Figure 1 shows X-ray diffraction patters of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) compound semiconductor samples and confirms the formation of the compound with polycrystalline nature. Inter-planar distances (d values) of all the observed peaks of a compound are compared with JCPDS data (Card No. 892347) and found that they match well and imply Hexagonal structure. It is observed from the diffractograms that the intensities of prominent peaks (d=3.1280Å (1 0 8), 1.9129Å (1 1 0), 1.6314Å (0 2 8)) and all other peaks remained almost same with the increase in cobalt concentration (x = 0-0.1). From the observed XRD peaks, each peak possessing some width is an indicative of polycrystalline nature of samples. Further, the peak positions shifted slightly with cobalt concentration. This clearly implies lattice compression consistent with the replacement of Co^{2+} smaller ionic radius (0.058nm) compared to that of Zn^{2+} (0.064 nm). This confirms the incorporation of Cobalt into ZnS lattice [18-19]. The observed 'd' values of all compounds are compared with JCPDS data (Card No. 892347) of Hexagonal ZnS structure.
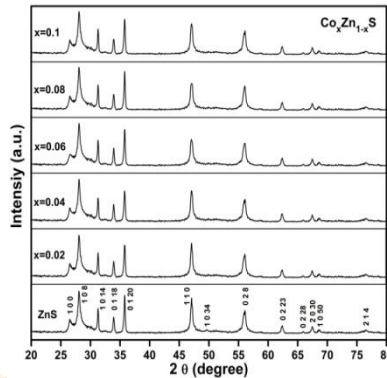

Fig.1 XRD diffractograms of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) compounds.

The average crystalline size of all the compounds are calculated from the recorded X-ray data i.e., Bragg angle and FWHM of a prominent peak by using Scherrer's formula [20] and is found to lie between 30.59 to 39.97 nm.

3.2 DC conductivity studies of $Co_xZn_{1-x}S$ compounds

The DC electrical conductivity of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) samples was measured in the temperature region 77-300K and the plot drawn between Log σ and $10^3/T$ for all the samples is shown in Fig 2. Each plot shows three linear regions of conductivity shown explicitly for $Co_{0.02}Zn_{0.08}S$ Fig 3. The plot exhibits Arrhenius behavior in different temperature regions (i) 300-165K , (ii) 165-100K and (iii) low temperature region (77-100 K) obeying the relation [21-22].

$$\sigma = \sigma_o \, exp(\frac{-E_a}{k_BT}) \qquad (3.1)$$

Where E_a is the activation energy, k_B is the Boltzmann's constant and T is temperature in kelvin.

In general, the electrical conductivity follows different types of mechanisms. They are, the ordinary conductivity due to drifting of charge carriers in the applied field which usually occurs at higher temperatures (above room temperature), and below room temperature, the conductivity due to thermally assisted hopping, the conductivity due to hopping of charge carriers with the localized states and the conduction due to variable range hopping (VRH) [23]. It is observed that $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) compounds exhibit three types of conduction below room temperature. In Log σ versus $10^3/T$ plot the deviation from the straight line part below 100K, indicates the existence of VRH conduction. The Greaves conductivity expression for the VRH model [24], applicable at low temperature is

$$\sigma T^{1/2} = C \, exp\left[\frac{-To_o}{T}\right]^{1/4} \qquad (3.2)$$

Where, C and T_o are the constants related to the density of localized states and $N(E_F)$ is given by,

$$T_o = \frac{16\alpha^3}{K_B(E_F)} \qquad (3.3)$$

The activation energies of all the samples of different compositions of $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) samples were calculated for two regions and tabulated in Table 1 and also shown in a graphical way Fig. 4. Below 100K the conductivity is almost constant representing the freezing of charge carriers. From Fig. 2 the DC conductivity increases with increase in cobalt content. This increase can be attributed to the fact that the addition of cobalt in ZnS creates defect levels close to the conduction band within the forbidden energy gap. This result is almost similar to that of copper addition in ZnS which infers that cobalt is going into the lattice of ZnS as divalent similar to copper. As concentration of cobalt increases the defects created are such that their corresponding energy levels move closer to the conduction band and hence, there is a change in the activation energy.

Plots of Log ($\sigma T^{1/2}$) versus $T^{-1/4}$ (Fig. 5), in the temperature region 100-77K are drawn for all $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) samples. The graphs are found to be straight lines indicating the legitimacy of hopping conduction mechanism and are in good agreement with Mott's VRH procedure. The slopes of these curves give the values of characteristic temperature coefficient T_o and these estimated values are shown in Table 1.

It may be observed that the activation energies of all the compounds in the temperature region 300-165K vary from 49.92-16.79meV and this proposes conduction due to the thermally assisted hopping. In the temperature range 165-100K the conduction due to hopping of charge carriers is because of existence of localized states around E_F and is supported by the activation energy values ranging from 24.26-105.09meV. The graphical variations of activation energies (E_{a1} and E_{a2}) corresponding to temperature regions (i) and (ii) of $Co_xZn_{1-x}S$ with x are also shown in Fig. 4. Obviously, the figure shows that E_{a1} decreases rapidly from 49.92meV (corresponding to ZnS) to 11.39meV (corresponding to $Co_{0.02}Zn_{0.08}S$). When small fraction of Zn is replaced with cobalt and it increases gradually, by small amounts and reaches 16.79meV by the

time x is equals to 0.1. Since cobalt replacement causes a small variation in E_{a1} the variation in conductivity may be considered as due to thermally assisted hopping conduction. In the temperature range 165-100K the activation energy, E_{a2}, increases with the increase in cobalt concentration i.e., from 24.26meV (for ZnS) to 105.09meV for $Co_{0.1}Zn_{0.9}S$. It can also be seen from Fig. 2 that there is an overall rise in conductivity in the temperature range 165-100K. In spite of an increase in activation energy with increase in cobalt concentration the rise in conductivity indicates that the hopping of charge carriers in the localized states around E_f is predominant. This results, $Co_xZn_{1-x}S$ compounds are more favorable for hopping conduction mechanism.
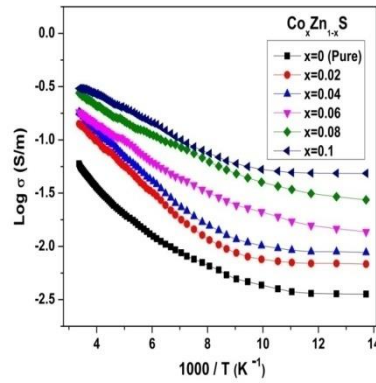

Fig. 2 Variation of Log σ versus $10^3 / T$ for $Co_xZn_{1-x}S$ ($0 \le x \le 0.1$) compounds.
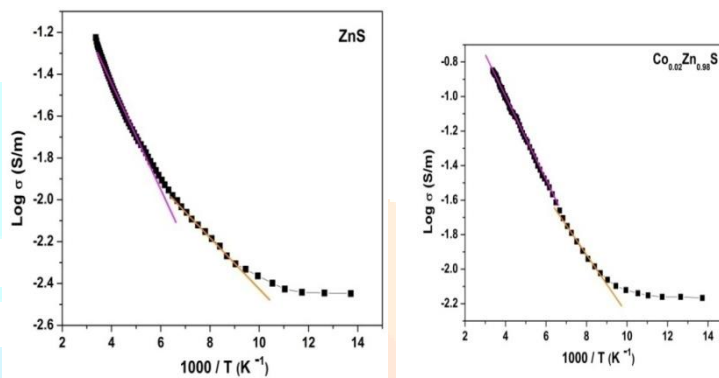

Fig.3 Variation of Log σ versus $10^3 / T$ for x=0, 0.02 compositions, showing three conduction mechanisms.

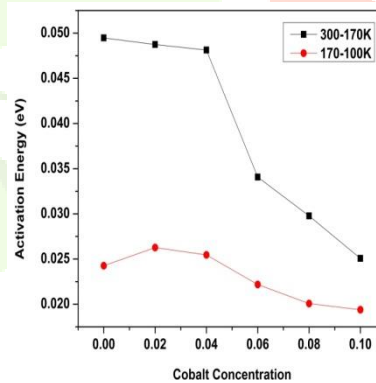Fig.4 Variations of activation energy with cobalt concentration in $Co_xZn_{1-x}S$ ($0 \le x \le 0.1$) compounds in two temperature regions.
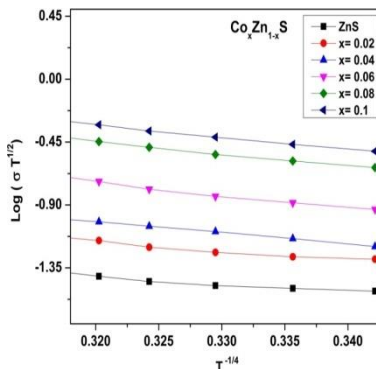

Fig.5 Log ($\sigma T^{1/2}$) versus $T^{-1/4}$ for $Co_xZn_{1-x}S$ (x=0-0.1) compounds.

Table 1. Activation energies (E_a) and T_0 values of $Co_xZn_{1-x}S$ ($0 \le x \le 0.1$) compounds.

Sample	Activation Energy (E_a) (meV)		T_0
$Co_xZn_{1-x}S$	E_{a1} (300-165K)	E_{a2}(165-100K)	VRH (100-77K)
x = 0	49.92	24.26	2.87
x = 0.02	11.39	81.01	3.05
x = 0.04	12.48	88.78	3.33
x = 0.06	12.65	93.22	3.43
x = 0.08	15.73	102.69	3.41
x = 0.1	16.79	105.09	3.87

IV. CONCLUSIONS

1. Bulk polycrystalline $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) mixed semiconductor compounds are prepared by controlled Co-Precipitation method.

2. XRD studies showed that $Co_xZn_{1-x}S$ ($0 \leq x \leq 0.1$) compounds have hexagonal structure and the structure remained same with increase of cobalt concentration.

3. The dc electrical conductivity increases with increase in cobalt content in all the samples and also increases with temperature, which confirms the semiconductor nature of the samples.

4. The increase in conductivity of $Co_xZn_{1-x}S$ compounds and increase in activation energies in region (ii) with increase in cobalt concentration suggests a vigorous hopping of charge carriers in defect localized states around E_F.

V. ACKNOWLEDGEMENTS

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