

Thermal and Electrical Properties of $(\text{CdS})_{1-x}(\text{ZnS})_x$ Thin-Films Deposited by Thermal Evaporation Technique

H. A. Mohamed^{1*}, W. S. Mohamed^{1,2}, Sh. S. Ali¹, and Mahrous R. Ahmed¹

¹Physics department, Faculty of Science, Sohag University, 82524 Sohag, Egypt.

²Physics Department, College of Science, Jouf University, Al-Jouf, Sakaka, P.O. Box 2014, Saudi Arabia.

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Abstract: Thin-films of CdS doped with various ZnS contents have been deposited using thermal evaporation technique. The thermal and electrical properties of the deposited films have been studied. The DC electrical conductivity of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films were calculated from the resistance measurements using two-probe method. It was found that the Seebeck coefficient (S) of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films measured at room temperature has a negative sign indicating that $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films were n-type semiconductors for different ZnS contents. The values of S found to increase with increasing ZnS content. Also, the conductivity decreased from $1646 (\Omega\cdot\text{cm})^{-1}$ to $818 (\Omega\cdot\text{cm})^{-1}$ with increasing ZnS content from $x=0$ to 0.5 , respectively. Some important parameters such as the mean free path, carrier concentration, carrier mobility, diffusion coefficient, Fermi energy and effective mass were calculated from the thermal and electrical measurements.

Keywords: CdS – CdS – Thin-Films – Electrical Properties – Thermal Properties.

1 Introduction

For the last decade, Cadmium Sulfide (CdS) thin film has attracted increased attention because of its wide direct optical band gap, good optical and electrical properties, high electron affinity, stability and n-type conductivity [1, 2]. CdS thin film is applied as a window material and as a heterojunction partner in thin films based on heterojunction solar cells such as CdTe [3], CuInS₂ [4], CuInGaS₂ [5], Cu₂ZnSn(S,Se)₄ [6] and PbS [7].

The optical band gap of CdS is relatively low (2.42 eV), hence the photons with energy higher than 2.42 eV may be absorbed by CdS layer before reaching the absorber layer. There are three ways to solve this problem: first is to reduce the CdS layer thickness, second is to substitute CdS by a wide optical band gap semiconductor like ZnS [8] and third is to increase the optical band gap of CdS. Reducing the thickness of CdS may lead directly to increase the short-circuit current density. However, the thickness must not too thin to avoid short circuit effects due to forming the pinholes [9]. On the other hand, reducing the thickness usually severely reduces the open circuit voltage and fill factor [10].

The process of doping CdS with a wider optical band gap semiconductor such as ZnS may be the best solution to improve the optical and electrical properties of CdS in order to use it as a window layer in thin-film solar cells. In this aspect, the doping type, the ratio of doping and the type of deposition techniques are considered most important factors in this process.

CdS thin films have been prepared by diverse techniques including chemical bath deposition [11], electrodeposition [12], laser ablation [13], sputtering [14], vacuum evaporation [15] etc. Thermal evaporation method is the most commonly method for constructing amorphous solid in the form of thin film due to its simplicity. The materials that are deposited by evaporation include metals, semiconductors, alloys, mixtures thereof, refractory compounds (i.e. oxides, carbides, nitrides, borides, etc.) and intermetallic compounds

In this work, thin- films of CdS doped with various ZnS contents have been prepared by a thermal evaporation technique. The effect of ZnS-content on thermoelectric

* Corresponding author E-mail: hussein_abdelhafez2000@yahoo.com

power and electrical properties of the deposited films were investigated in detail.

2 Experimental Details

Bulk samples of $(\text{CdS})_{1-x}(\text{ZnS})_x$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) have been prepared by adding different ratios of ZnS to CdS, where the mixture were ground thoroughly. Ethylene thio glycolate has been added forming paste then dried at a temperature of 130°C . Then the formed material has been ground and compressed in tablets form. To increase the homogeneity between the mixtures (CdS, ZnS), the heat treatment process has been done at temperature of 450°C in a Mini tube furnace provided by a heater around the tube under vacuum of 6×10^{-2} m bar for 4 hour.

Thin films of $(\text{CdS})_{1-x}(\text{ZnS})_x$ with thickness 150 nm have been deposited by thermal evaporation technique (using a coating machine (Edwards Ltd, Auto 306, 2016)) on FTO substrates for electrical measurements. The material vapor is condensed to form a thin film on the cold substrate surface. A pressure of 10^{-6} Torr is utilized to avoid reaction between the material vapor and atmosphere.

Resistance measurements of proposed deposited $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films on FTO substrates are implemented in air at room temperature applying the stadered two-probe points. Electrical contacts are made by placing silver paste over the films surface with a 2 mm separation. The sample resistance is measured by an Ohmmeter (UT71E-TRUE RMS MULTIMETERS).

In order to determin the type of carriers; Seebeck coefficient measurement is carried out for $(\text{CdS})_{1-x}(\text{ZnS})_x$ films. The developed Seebeck voltage (ΔV) of the sample is measured by micro voltammeter and the temperature of the specimen is determined by means of thermal contact using chromel-alumel thermocouple in contact with with the specimen surface.

3 Results and Discussion:

For inspecting the type of carriers; Seebeck coefficient was measured for $(\text{CdS})_{1-x}(\text{ZnS})_x$ films of various ZnS contents ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) with 150 nm thick, deposited on FTO, and calculated using the following equation: [16].

$$S = \Delta V / \Delta T \quad (1)$$

where, S is the Seebeck coefficient which is the value of the developed electromotive force between the two ends of the thin film when the temperature difference ΔT between them equals to five degrees. Figure (1) illustrates the Seebeck coefficient (S) measured at room temperature as a function of ZnS content of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films.

It is clear that S has a negative sign indicating that $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films are n-type semiconductors for different ZnS contents. The S values (absolute values) increase with

increasing the ZnS content. These results agree well with many studies such as [17].

Firstly, the resistance of the formed film is measured from which the conductivity is calculated. Figure (2) represents the variation of electrical conductivity (σ) with increasing ZnS content of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films deposited into FTO substrates. Firstly, the resistance of the formed film is measured at room temperature using two probe points methods and then the conductivity is calculated.

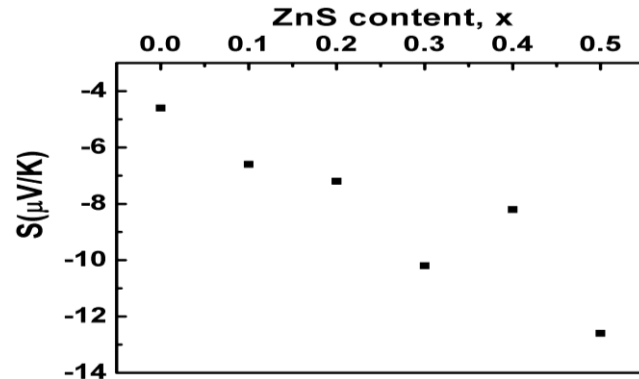


Fig.1: The Seebeck coefficient at room temperature as a function of ZnS content ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin film.

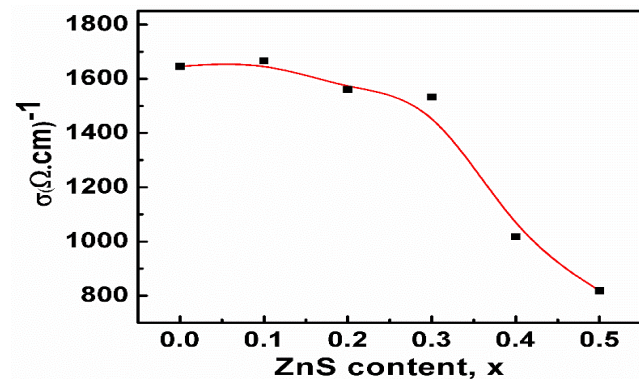


Fig.2: Variations of electrical conductivity with ZnS content of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films.

The figure displays that the electrical conductivity of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films decreases with increasing ZnS content. The conductivity decreases from $1646 (\Omega.\text{cm})^{-1}$ to $818 (\Omega.\text{cm})^{-1}$ with increasing ZnS content from $x=0$ to 0.5 , respectively. This decreasing in the electrical conductivity can be accredited on the effect of carrier mobility and/or carrier concentration. The smaller grain size increases grain boundary surface area, which is responsible for the decrease of carrier mobility and it acts as a trap of the free carries [18]. In addition, the increase in film disordering with increasing ZnS content may be led to decrease in carrier mobility. According to this discussion, quantitative measurements of carrier mobility and carrier concentration are required and will be discussed in the next section.

Using the measured values of both Seebeck coefficient S and electrical conductivity σ at room temperature, some important parameters can be calculated such as Fermi energy E_f , carrier concentration N , carrier mobility μ , diffusion coefficient D , mean free path ℓ and effective mass m^* .

According to Benco and Koffyberg [19], the energy of Fermi level E_f can be correlated to Seebeck coefficient S by the Boltzmann transport equation;

$$\frac{E_f}{k_B T} = \frac{S |e|}{k_B} - A_s \quad (2)$$

where e is the electron or hole charge value, k_B is Boltzmann's constant and A_s is a dimensionless parameter, dependent on the carrier scattering mechanism and assumed to be unity of semiconductors. According to Eq. (2), energy of Fermi level E_f has been calculated and listed in Table (1). The small and negative values of E_f indicate that the Fermi-level lies in the optical band gap lower the bottom of the conduction band by the values 0.022- 0.024 eV.

Table (1): Fermi level energy E_f , diffusion coefficient D and mean free path ℓ of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films with different ZnS contents.

x	E_f (eV)	D (cm^2/s)	ℓ (nm)
0.0	0.0245	14.1	29.3
0.1	0.0239	14.6	30.2
0.2	0.0237	13.8	28.5
0.3	0.0228	14.1	28.6
0.4	0.0234	9.1	18.7
0.5	0.0221	7.7	15.6

To deduce the carrier concentrations, the following relation can be used;

$$N = \frac{2(2\pi m_e k_B T)^{\frac{3}{2}}}{h^3} e^{\frac{E_f}{k_B T}} \quad (3)$$

where m_e is the electron mass.

In order to deduce the carrier effective mass, the relation of the Fermi energy of a free-electron gas has been used [20], on the assumption of parabolic band edges, i.e.

$$E_f - E_c = \frac{h^2 (3\pi^2 N)^{\frac{2}{3}}}{2m^*} \quad (4)$$

where E_c is the bottom of conduction band, which E_c is assumed to be zero. From the slope of E_f vs $N^{\frac{2}{3}}$ plot shown

in Fig. (3), the effective mass m^* has been deduced to be $m^* = 0.71 m_0$.

Using the values of E_f , the dependence of free carrier concentration on ZnS content is shown in Fig. (4-a). It can be seen that N decreases from $1.90 \times 10^{19} \text{ cm}^{-3}$ to $1.71 \times 10^{19} \text{ cm}^{-3}$ with increasing ZnS content from $x=0$ to $x=0.5$, respectively. This is may be due to a decrease of the grain size and the electrons trapped in grain boundaries that act as major scattering centers of the electronic conduction.

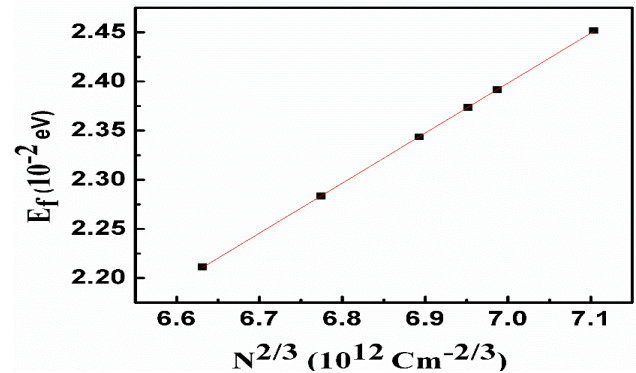


Fig. 3: E_f Vs $N^{2/3}$ plot of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films.

Moreover, the mobility is calculated by the known formula $\mu = \frac{\sigma}{Ne}$ at room temperature and its dependence on ZnS content is plotted in Fig.(4-b).

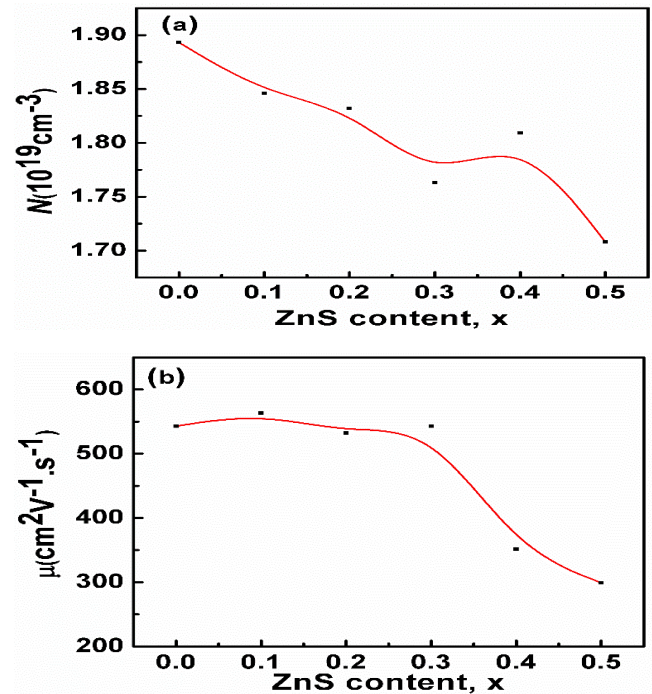


Fig.4: Dependence of carrier concentration (a), and mobility(b) on ZnS contents ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films.

This figure denotes that the mobility decreases with increasing ZnS content as expected before. At $x=0.0$, μ records a value of $543 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and at $x=0.5$, μ records a value of $299 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. From the values of N and μ we can conclude that the decrease in electrical conductivity is attributed to the decrease of both free carrier concentration and carrier mobility and the later plays the significant role in decreasing the conductivity.

Using the mobility, the diffusion coefficient $D = \frac{k_B T}{e} \mu$ is calculated and listed in Table (1) as functions of ZnS content. It can be seen, D decrease with increasing ZnS content and has the same behavior of mobility.

In order to determine the main scattering mechanism, whether the scattering on the grain boundaries or the scattering on the impurities is the responsible for μ and N variations, the mean free path ℓ is calculated using [21]:

$$\ell = \frac{h}{2e} (3N/\pi)^{1/3} \mu \quad (5)$$

The calculated values of ℓ are listed in Table (1). It can be noted that the mean free path decreased from 29.3 nm to 15.6 nm with increasing ZnS content from $x=0.0$ to $x=0.5$, respectively. While, the values of grain size D_L decreases from 26 nm to 14 nm as shown in Table (1) at the corresponding values of ZnS. This suggests that the grain boundary scattering has a major effect on the carrier transport since the values of ℓ are in general in the range of grain size for all films. Therefore, it is thought that the increase in grain boundaries scattering is the main reason for the decrease in mobility.

Conclusion

From the obtained results we can conclude that:

- 1- Thermal evaporation technique is suitable to deposit $\text{CdS}_{1-x}(\text{ZnS})_x$ with different ZnS contents onto different types of substrates.
- 2- The DC electrical conductivity σ of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films are calculated from the resistance measurements using standered two-probe method. The conductivity decreased from $1646 (\Omega \cdot \text{cm})^{-1}$ to $818 (\Omega \cdot \text{cm})^{-1}$ with increasing ZnS content from $x=0$ to 0.5 , respectively.
- 3- The Seebeck coefficient (S) of $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films measured at room temperature had a negative sign indicating that $(\text{CdS})_{1-x}(\text{ZnS})_x$ thin films are n-type semiconductors for different ZnS contents. The S values increased with increasing the ZnS content.
- 4- Some important parameters such as the mean free bath ℓ (nm), carrier concentration N (cm^{-3}), carrier mobility μ ($\text{cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$), diffusion coefficient D (cm^2/s), Fermi energy E_f (eV) and effective mass m^* were calculated from the S and σ . These results of these parameters revealed that:

- Small and negative values of E_f indicated that the Fermi- level layed in the energy gap below the bottom of the conduction band by the values 0.022- 0.024 eV.
- The effective mass m^* was deduced to be $m^* = 0.71 m_0$.
- The carrier concentration N decreased with increasing ZnS content from $1.90 \times 10^{19} \text{ cm}^{-3}$ for $x=0$ to $1.71 \times 10^{19} \text{ cm}^{-3}$ for $x=0.5$.
- The mobility decreased with increasing ZnS content. At $x=0.0$, μ records a value of $543 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and at $x=0.5$, μ recorded a value of $299 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.
- Both free carrier concentration and carrier mobility play the significant role in decreasing the electrical conductivity.
- The diffusion coefficient decreased with increasing ZnS content and has the same behaviour of mobility.
- The mean free bath ℓ decreased from 29.3 nm to 15.6 nm with increasing ZnS content from 0.0 to 0.5, respectively. The values of ℓ are generally in the range of grain size for all films, this suggested that the grain boundary scattering has a major effect on the carrier transport.

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