Effect of Cu Doping on the Electrical Properties of ZnTe by Vacuum Thermal Evaporation

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Abstract

In this study, the ZnTe thin films were deposited on a glass substrate at a thickness of 400nm using vacuum evaporation technique (2×10^{-5}mbar) at RT. Electrical conductivity and Hall effect measurements have been investigated as a function of variation of the doping ratios (3,5,7%) of the Cu element on the thin ZnTe films. The temperature ranges of (25-200°C) is to record the electrical conductivity values. The results of the films have two types of transport mechanisms of free carriers with two values of activation energy (E_{a1}, E_{a2}), expect 3% Cu. The activation energy (E_{a1}) increased from 29meV to 157meV before and after doping (Cu at 5%) respectively. The results of Hall effect measurements of ZnTe , ZnTe:Cu films show that all films were (p-type), the carrier concentration (1.1×10^{20} m^{-3}) , Hall mobility ($0.464m^2/V.s$) for pure ZnTe film, increases the carrier concentration ($6.3\times10^{21}m^{-3}$) Hall mobility ($2m^2/V.s$) for doping (Cu at 3%) film, but decreases by increasing Cu concentration.

Keywords: ZnTe thin films, Electrical conductivity, Hall Effect and Cu doping.

1. Introduction

ZnTe is a material promising for pure-green light emitting diode since where a band gap of 2.26eV at room temperature and the band structure is of direct optical transition type. However, it is difficult to realize p-n junctions because of the well-known compensation effect specific to II—VI materials. P-type ZnTe can be easily obtained but n-type ZnTe cannot be realized because of self-compensation. The possibility of n-type ZnTe has been studied.

The N-type materials are obtained by these techniques but the carrier concentrations have been limited to high 10^{16} up to low $10^{17}cm^{-3}$. ZnTe crystals were annealed in molten Zn with n-type dopants and it was reported that n-type conductivity was obtained, but the resistivity was high in the range of 10^5 to $10^7\Omega$.cm [1,2,3]. For most semiconductor devices, formation of a low-resistance ohmic contact requires a heavily doped region adjacent to the metal contact in order to establish a tunneling current transport across the interface. Regarding II–VI compound semiconductors, ZnTe can be doped to rather high levels of 10^{18} cm^{-3} (or more) with copper and most column V elements for p-type conductivity and Al for n-type doping. Copper-doped ZnTe has been used as an ohmic contact to CdTe in CdS/CdTe solar cells. However, copper is known to be a fast diffuser in most materials which results in degradation of solar cells.[4] In this research, we have examined the electrical properties of the undoped and copper doped ZnTe polycrystalline thin films deposited by vacuum evaporation.

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2. Experimental

2.1. Alloy and Film Preparation

ZnTe powders were prepared by the alloy which was obtained by mixing of the appropriate quantities of high purity (99.999 %) material of zinc (1.693 gm) and tellurium (3.306 gm) in evacuated fused quartz ampoules, heated at (1573 K) for 1h, according phase diagram of ZnTe **Figure 1.** [5]. We left the ampoules in the furnace until it gradually cooled to room temperature.

Undoped and Cu doped ZnTe thin films have been prepared onto glass substrate by thermal evaporation technique in a high vacuum system. The base pressure during the evaporation is (2×10^{-5} mbar) using (Coating Unit; Edwards Vacuum Ltd, Model: E306) from molybdenum boat with thickness (400nm). The distance from molybdenum boat to sample holder was about (18cm), Al electrodes of thickness (250 nm) were used as contact material for making the electrical connections.

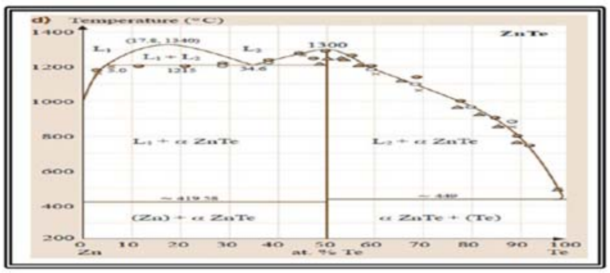

Figure 1. Phase diagram of ZnTe [5].

ZnTe powder and Copper are placed in two molybdenum boat troughs in the Vacuum system. The Copper doped ZnTe (contains 3, 5, 7 wt % Cu) films were deposited at a rate of ($3.5 nms^{-1}$). For dc conductivity and Hall measurement, a 30V dc fixed bias is maintained. A power supply (Heath kit, 5A, 0-30V Adjustable DC) is used to pass a constant dc current through the test sample. An electrometer (Fluke, Model: 8845A) is used to monitor the current through the sample and a digital multimeter (DMM Model: MT -1820) is used to measure the potential differences across each sample.

2.2. Characterization of ZnTe and ZnTe: Cu Thin Films

For D.C. measurement the variation of electric resistance (R) with temperature range (25-200)^{o}C, were measured using digital multimeter, then calculated the conductivity (σ) by Equation (1) [6]:

$$\sigma = \frac{1}{\rho} = \frac{L}{R.b.t} \qquad (1)$$

Where: ρ resistivity, t is film thickness, b is electrodes width; L is distance between two Al electrodes.

Hall effect measurements have been carried out to investigate the type of charge carriers, carrier concentrations (n_H) and Hall mobility (μ_H) using the Hall measurement system. The sign of the Hall coefficient (R_H) of semiconductor is determined by the sign of the charge carriers. If the conduction is due to one carrier type, we can measure the carrier concentration according to the Equation (2) [7]:

$$n_H = \pm 1 / R_H.e \qquad (2)$$

The mobility is related to the Hall coefficient by Equation (3) [7]:

$$\mu_H = \sigma / n_H .e = \sigma . \left| R_H \right| \qquad (3)$$

The films thickness were measured by using the weighing method according to the Equation (4):[8]

$t = m / A . \rho_o$ (4)

Where: m is mass of film, ρ_o is density of film, A is films area. Using a sensitive balance whose sensitivity of the order (10^{-4}).

3. Results and Discussion

Figure 2. shows d.c electrical conductivity as a function of the reciprocal temperature ($10^3/T$) for ZnTe films pure and different percentage ratio of Cu (3, 5, and 7%) at (R.T). We observe from **Figure 2.** that there are two regions where continuous conductivity changes ($\ln(\sigma_{dc})$). In the sense that there are two values of activation energy as we see in Table 1 a low temperature, $\ln(\sigma_{dc})$ increases gradually when temperature increases (high $10^3/T$) within the range (28-85 °C) and (28-133 °C) for pure ZnTe and doping Cu thin films (5,7%) Respectively. In this region the conductivity depends entirely on the type and concentration of the impurities added is called extrinsic region. It increases sharply within a narrow temperature range. At high temperatures, the conductivity gradually increases with increasing temperature (low $10^3/T$).

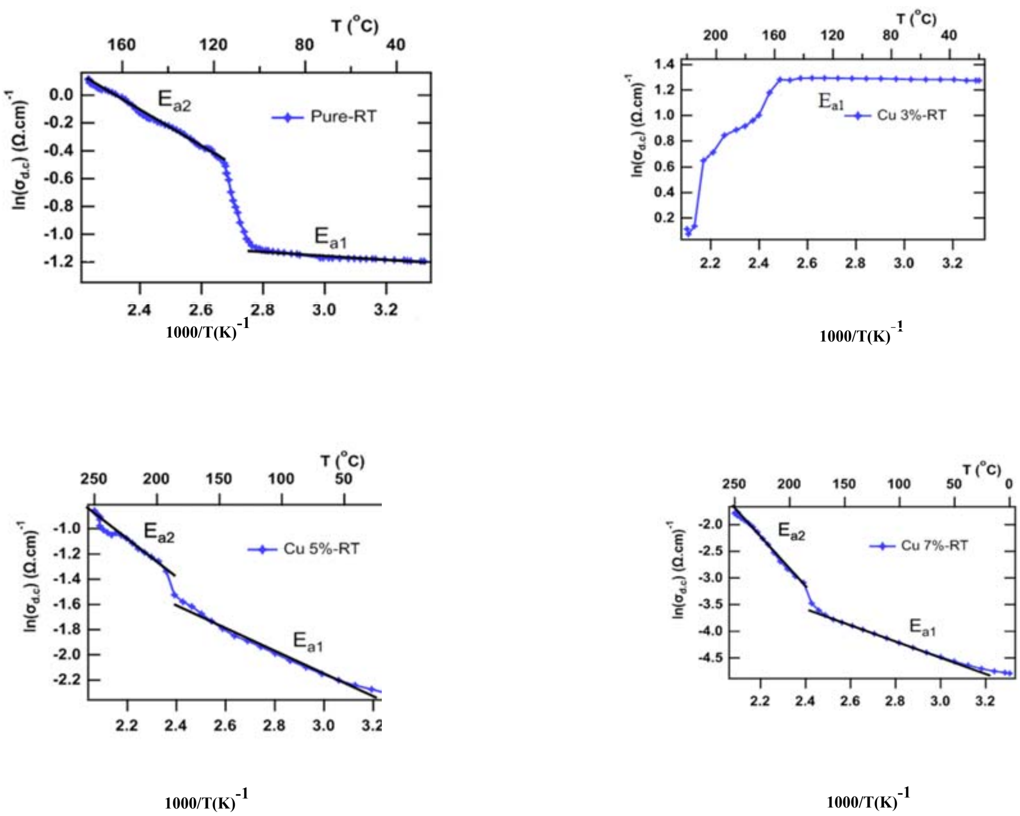

Figure 2. ln ($\sigma_{d.c}$) versus $10^3/T$ for ZnTe films at different ratio of Cu.

Within the range (103-175°C) and (152-204°C) for ZnTe and ZnTe: Cu respectively. This region is called the intrinsic region. We also note that the conductivity of the thin films doping (Cu 3%) showed a completely different behavior from the rest. At the high temperature the conductivity decreases i.e. the thin film exhibits the behavior of the conductor. This may be due to a change in the preparation condition for this ratio. The doping was completed in two stages during and after evaporation of the Cu, the copper becomes a layer above the ZnTe.

The activation energy is calculated by plot between ln($\sigma_{d.c}$) as function (10^3/T) depending on the relationship 5 [9] [10].

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{K_B T}\right) \tag{5}$$

Where (σ_o) is the minimum electrical conductivity at [0 K], (Ea) is the activation energy which corresponds to (Eg /2) for intrinsic conduction. (T) is the absolute temperature and (k_B) is the Boltzmann's constant. Note from Table 1 that the values of the activation energy (E_{a1}) equal to 157 meV and less than that value [3] [11] at the intermediate temperature are approximately equal to the copper ionization energy of 150 meV. Meaning most impurities is ionized at room temperature or higher.

Table 1. The activation energy for thin ZnTe films for different ratio of Cu at R.T.

Cu %	T (°C)	Temp. range (°C)	Ea_1 (meV)	Temp. range (°C)	Ea_2 (meV)
0	RT	(28-85)	29	(103-175)	253
3	RT	(29-110)	6	-	-
5	RT	(27-133)	157	(162-202)	218
7	RT	(27-134)	119	(152-204)	211

Figure 3. shows the linear relationship between the Hall voltage (V_H) produced by the effect of the magnetic field on the thin films prepared and the current (I) passing through the thin film under the bias of the external voltages within range (0-30).

It can be seen that for all undoped and doped thin films, there is directly proportional between the voltage of the hall and the passing current. This indicates that the carriers are the majority of the positive type (p-type). This is consistent with all published literature on this article [12-14]. Except for thin films doping Cu-3% (**Figure 3.**), they showed different behavior when the voltages from (0-15) volts were recorded inversely proportional i.e. the type of charge is negative (n-type). After this voltage until (30 volts), the carrier has become a positive type. This may be due to the incomplete diffusion of the added impurities due to the difference in the mechanism of preparation of these thin films as shown in the study of conductivity. In other words, the Hall effect appears are behavior of the conductor for the added impurities and increase in the electric field show the effect of holes for the thin film ZnTe semi-conductor.

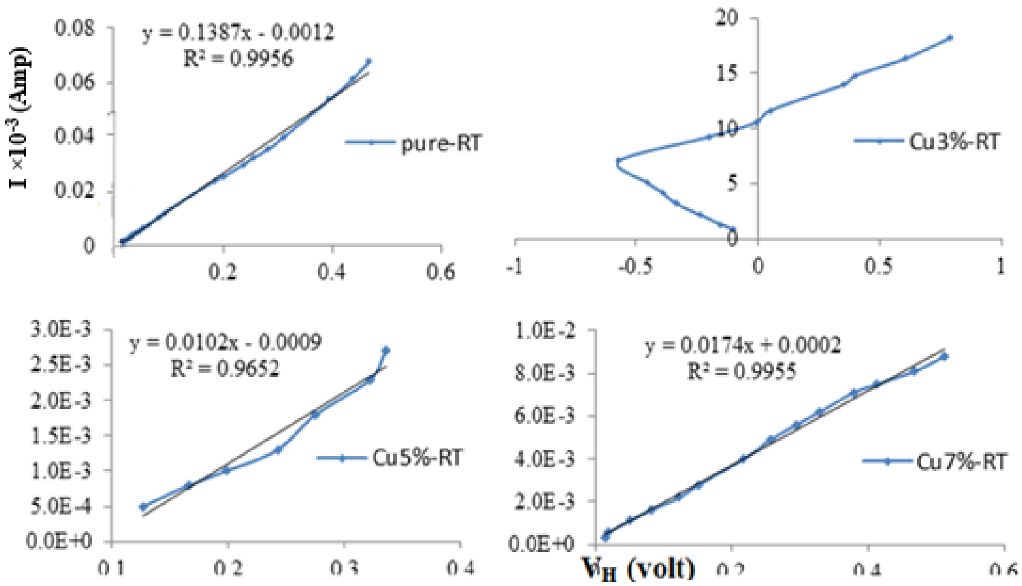

Figure 3. Hall voltage relationship and the current passing through pure and doping Cu thin films prepared at room temperature

The type of charge carriers, concentration and Hall mobility, have been estimated from Hall measurements as shown in **Table 2**. The positive sign of Hall coefficient indicates the conductivity nature of the film is p-type. In addition, **Table 2.** carrier's concentration decreased with increasing ratio Cu doping, in general.

Table 2. Summary of Hall Effect Results

Sample	ρ (Ω.m)	σ (Ω.m)$^{-1}$	R_H (m^3C^{-1})	μ_H (m^2/V.s)	N_A (m^{-3})
pure-RT	0.125	8.000	0.0580	0.4640	1.1E+20
Cu3%-RT	0.0005	2000.0	0.0010	2.0000	6.3E+21
	0.0006	1666.67	-0.0007	-1.1670	-8.9E+21
Cu5%-RT	1.474	0.678	0.7840	0.5316	8.0E+18
Cu7%-RT	0.980	1.020	0.4600	0.4690	1.4E+19

4. Conclusion

In this study, the researcher succeeded in doping ZnTe thin films in different ratio of Cu simultaneously, by placing both ZnTe and Cu at two Molybdenum boats separate in the vacuum evaporation system. We have shown through measurements of both conductivity and the effect of Hall that thermal evaporation is a good way to prepare thin films ZnTe of alloy material prepared. Electrical conductivity shows that the thin films before and after doping of the copper, increase exponentially with increasing temperature. The thin films also contain two activation energies that are interpreted on the basis two types of transport mechanisms, Except for doping Cu-3%. The Hall Effect tests showed that all thin films are positive (p-type). And that the doping resulted in decreasing the concentration of the carriers and the hall mobility.

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