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Thermal Investigations of Vacuum Evaporated $Cd_{1-x}Zn_xTe$ Heterojunction Thin Films*

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Abstract: The $Cd_{1-x}Zn_xTe$(x=0.02,0.04,0.06,0.08) binary compounds and their pseudo-binary solid solutions crystallize into homologous layered structures parallel to the C-axis and are highly anisotropic. Among these $Cd_{0.96}Zn_{0.04}Te$ crystal is a p-type narrow band gap semiconductor with the direct band gap of 0.16 eV. In order to tune the band gap, a third substitution element may be added. The present study aims at resistivity, charge carrier mobility and concentration measured on $Cd_{0.96}Zn_{0.04}Te$ thin films. Digital meters were used for all electrical measurements. The dependence of resistivity of the film on thickness and substrate temperature has been measured. Effect of film thickness and substrate temperature on carrier concentration and mobility has also been studied.
Keywords*:* carrier concentration, glass transition, mobility, resistivity.

1. Introduction

Physical properties of semiconductor in the form of thin film have become an active field in semiconductor physics. For many years the crystalline solid has been studied and a high degree of understanding of its various physical properties has been attained. Cadmium telluride and Zinc telluride structure has attracted much interest in the study of these materials in the heterojunction thin film state, because of its application in optoelectronic devices [1-2]**.** Binary semiconductors are the basic materials for schottky barriers, solar cells and other electronics engineering devices. Similar works have been done on the thin films of alloys of different

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compositions of selenium and tellurium regarding the amorphous-crystalline transitions[3-4]. Structural and electrical properties of CdTe/ZnTe heterojunction thin film have also been studied[4-5]. There have been various studies on the bulk and thin film characteristics of $Cd_{0.96}Zn_{0.04}Te$ including optical and electrical properties. $Cd_{1-x}Zn_xTe$ binary compounds (x=0.02, 0.04, 0.06, 0.08, 0.10) and their pseudobinary solid solutions are highly anisotropic and crystallize into homologous layered structure parallel to C-axis and are known to find applications ranging from photoconductive targets in T.V. cameras to IR Spectroscopy [6-7]. $Cd_{1-x}Zn_xTe$ is the most potential material for thermoelectric devices such as thermoelectric generators, thermocouples, thermo coolers and IR Sensors with the best figure of merit near room temperature [8-10]. It also finds applications in electronic, microelectronic, optoelectronic and electro-mechanical devices [11]. Its melting point is 846^o K and is a p-type semiconductor. There have been various studies on the bulk and thin film characteristics of ZnTe including optical and electrical properties [12]. However, there is no report on effect of substrate temperature on resistivity, carrier concentration and mobility of Cd_{1-x} Zn_xTe thin films. We hereby report the effect of substrate temperature on resistivity, carrier concentration and mobility of $Cd_{1-x}Zn_xTe$ thin films. Thermo-emf measurement has also been carried.

2. Experimental Details

The material was synthesized using stoichiometric mixtures of the respective elements of 5^N purity. The vacuum pressure used to seal the quartz ampoule containing the charge was of the order of 10^{-5} torr. The sealed ampoule was kept in an alloy mixing furnace, providing rotation and rocking of the charge at 896^o K, i.e., 50° above the melting point. After 48 hours of mixing, the molten charge was slowly cooled to room temperature over a period of two days. Thin films of Cd_{1-x} Zn_xTe (x=0.04) were prepared on the (001) NaCl crystal substrate, using thermal evaporation method under a pressure of 10^{-5} torr. at room temperature, i.e., at 300K using the vacuum coating unit model 12A4 (Hind Hivac, Bangalore). The thickness of the film was measured employing Tolansky's multiple-beam interferometric method [13]. In present study, the integral method was employed for the measurement of the thermo-e.m.f. The experimental set-up for the thermo-e.m.f. measurement consisted a massive copper heat sink and a copper holder to which a heater was attached. With this set-up, one end of the film can be kept at a constant temperature while the temperature of the other end of the film can be varied. Damodars and Mohanty have given a detailed description of the set-up[14]. The temperature of the hot end was varied from

300 to 450 K while the cold end temperature is maintained at 300 K. The temperature of the hot end of the film was measured with copper constantan thermocouple making contact with the film [15]. The substrate was heated by a radiant heater and the temperature was controlled by a digital temperature controller. The thermo-e.m.f. developed across the film was measured with respect to copper as a function of hot end temperature with a Aplab d.c. micro-voltmeter (model-5056) having high input impedance of 100 MΩ. The thermo-e.m.f. of the thermo couple recording the hot end temperature was measured using a digital milivoltmeter. In order to study the effect of substrate temperature on the electrical properties like resistivity and carrier concentration, the thin films were prepared under identical conditions keeping other parameters constant, viz., evaporation rate of about 0.5 nm/s and residual pressure of 10^{-5} torr. The thickness was varied in the range 50 nm to 200 nm. The substrate temperature was controlled by a digital temperature controller. Digital meters were used for all electrical measurements [16-17].

3. Results and Discussion

The resistivity of the film was found to decrease with increasing thickness and substrate temperature. This is attributed to increasing grain size at higher substrate temperatures. It was found that, the carrier concentration as well as mobility increases with increasing film thickness. Also the carrier concentration is larger whereas the mobility is smaller in the films deposited at higher substrate temperatures. The detail results are reported and discussed.

3.1 Electrical properties

Many semiconductors change their resistance when subjected to magnetic field; the effect being known as magnetoresistivity. In this case usually the fractional change of the resistivity due to applied magnetic field with respect to zero field value is obtained. In the case of thin films since the resistance is usually high, van der Pauw [18] method is not practical due to small value of voltage, which usually can not be measured accurately. So instead, the linear four probe method described by Goswami and Ojan [19] was used in the present study. The sample was prepared in rectangular geometry with pre-evaporated Ag (Silver) films as the ohmic electrodes. The resistivity was calculated using the formula,

$$\rho = \frac{RW\alpha}{l} \tag{3.1.1}$$

where, R = resistance of the film, l = length of the film, W = breadth of the film, α = thickness of the film,

The measurements were carried out on films of different thicknesses at different substrate temperatures. Fig. 1 & 2 show the plots of electrical resistivity versus thickness of the film deposited at 423K and 498K, for $Cd_{0.96}$ $Zn_{0.04}Te$ and $Cd_{0.94}Zn_{0.06}Te$ films. The resistivity of the film is found to decrease with increasing thickness and substrate temperature. It may be due to increase in grain size with increase in substrate temperature. Such a variation in resistivity is explained by Patritz's barrier model. Because the crystallites do not grow sufficiently at low temperatures, the intercrystalline barriers are wide, offering a high resistance to the motion of charge carriers. Whereas, at higher substrate temperatures, large crystallite size is obtained which ultimately decreases the intercrystalline barrier. The charge carriers therefore have to cross comparatively narrow intercrystalline barriers and this result in a decrease of resistivity. The variation of carrier concentration and mobility of $Cd_{0.96}$ $Zn_{0.04}Te$ film, deposited at two different substrate temperatures with film thickness is shown in Fig.3 (a) and 3 (b).

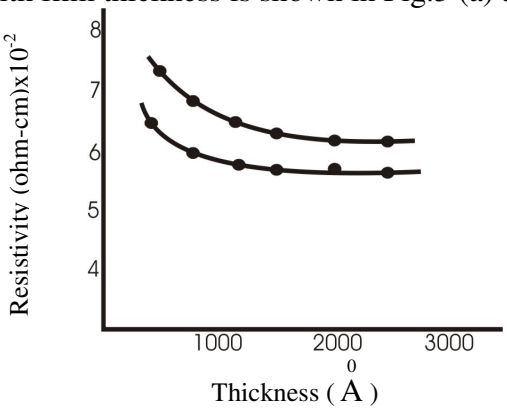

Fig.1: Resisitivity vs thickness of $Cd_{0.96}$ $Zn_{0.04}Te$ heterojunction thin film for different substrate temperature (a) 423 K, (b) 498 K

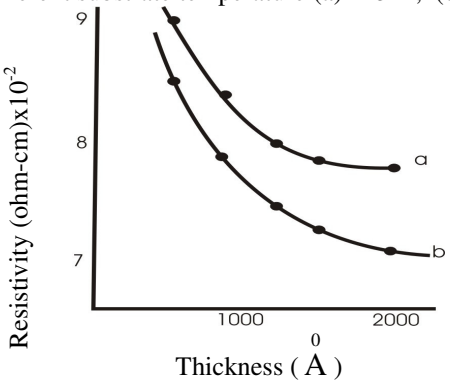

Fig.2: Resisitivity vs thickness of $Cd_{0.94}$ $Zn_{0.06}Te$ heterojunction thin film for different substrate temperature (a) 423 K (b) 498 K

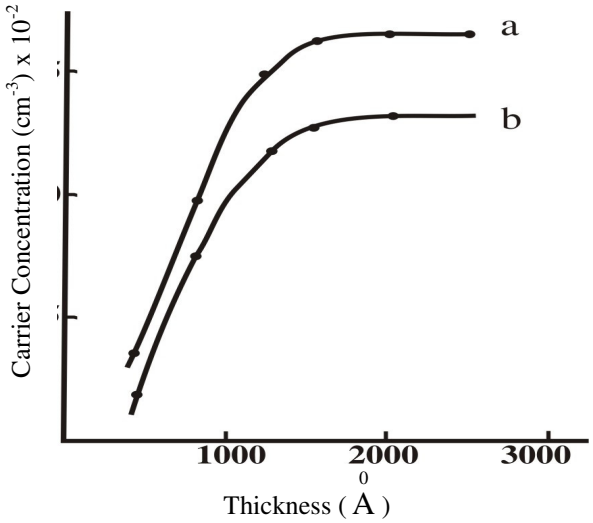

Fig.3(a): Carrier concentration vs thickness of $Cd_{0.96}$ $Zn_{0.04}Te$ heterojunction thin film at different substrate temperature (a) 423 K, (b) 498 K

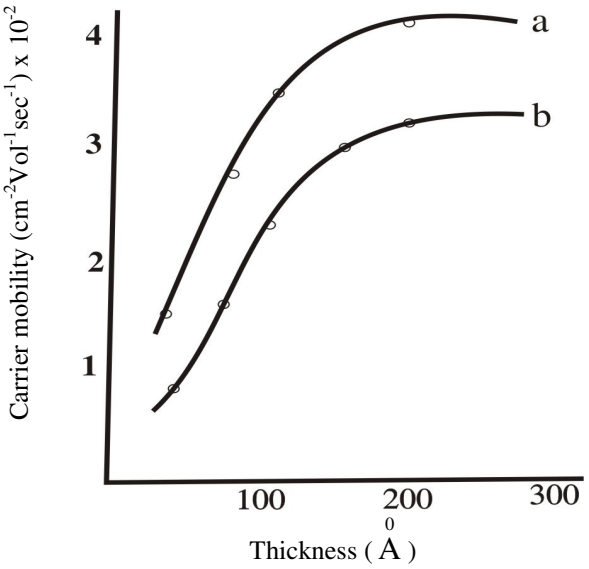

Fig. 3(b): Carrier mobility vs thickness of $Cd_{0.96}$ $Zn_{0.04}Te$ heterojunction thin film at different substrate temperature (a) 423 K (b) 498 K

3.2 Thermal properties

3.2.1 Differential Scanning Calorimetry

Figure 4 shows DSC thermograms for $Cd_{0.96}$ $Zn_{0.04}Te$ and $Cd_{0.94}Zn_{0.06}Te$ thin film. The general features of DSC thermograms (glass

transition temperature T_g, and crystallization peaks T_p) were determined and reported in Table 1. It is noticed that both T_g and T_p increase with increasing value of x.

Table 1.
The glass transition temperature Tg and the crystallization temperature Tp at different values of x.

Value of x	T_g(K)	T_{p1} (K)	T_{p2}(K)
0.02	376	436	---
0.04	383	441	455
0.06	390	463	572
0.08	404	491	---

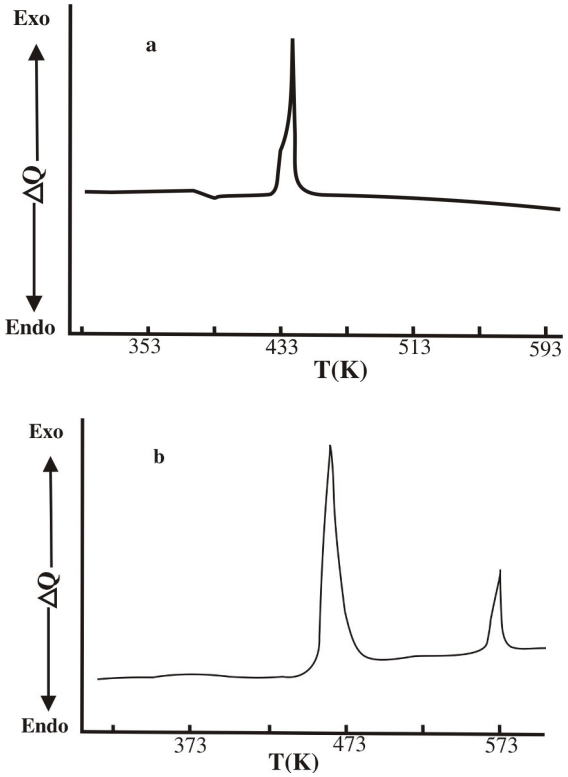

Fig 4: DSC thermo-grams for (a) $Cd_{0.096}Zn_{0.04}Te$ (b) $Cd_{0.94}Zn_{0.06}Te$ heterojunction thin film

3. 2.2. x Dependence of Thermoelectric Power

Figure 5. shows a typical plot of thermoelectric power (S) versus reciprocal temperature for Cd_{1-x} Zn $_x$ Te heterojunction thin film for different values of x. It is seen from the plots that for all the films

thermoelectric power S is linear function of the reciprocal temperature, decreases with decreasing temperature, in the temperature range studied (300 to 600 K). Thermoelectric power increases with increasing value of x. It is evident from Fig.5 that for $Cd_{1-x}Zn_xTe$ heterojunction thin film for different values of x = 0.02, 0.04, 0.06, 0.08, the thermoelectric powers (S) versus reciprocal temperature plots are linear.

The thermoelectric power of p-type semiconductor is given by the equation

(3.2.2.1) $$S = \frac{k}{e}\left[2.5 + p - \left(E_F - \frac{E_v}{kT}\right)\right]$$

or

(3.2.2.2.) $$S = \frac{k}{e}\left[2.5 + p + \ln\left(\frac{N_v}{n}\right)\right],$$

where, $$N_v = 2\left(\frac{2n\pi kT}{h^2}\right)^{\frac{2}{3}}.$$

E_F and E_v are Fermi energy and the energy of the top of the valence band respectively, k is Boltzman's constant and e is the charge of the carrier. T denotes absolute temperature, n is the hole concentration and p is the scattering parameter. N_v denotes the effective density of state in the valence band. It is clear from the Eq. (3.2.2.1) that, in the case of nondegenerate semiconductor, the thermoelectric power varies as the reciprocal temperature and hence a plot of thermoelectric power S against reciprocal temperature will be linear. The height of the Fermi level from the valence band top edge i.e. $E_F = E_v + E_H$ can be evaluated from the slop of S versus 1/T plots. It is evident from Fig. 5 that the slope of the plots varies within a narrow range for the different value of x. The height E_H of the Fermi level from the top edge of the valence band is found to vary between the limits 52 and 67 meV. It can also be noted that in entire temperature region studied, the S versus 1/T plot is linear and hence has the same slope at all the temperatures, these heights E_H of the Fermi level from the top edge of the valence band does not change with temperature. That is to say, the Fermi level is pinned at a particular energy in the entire temperature region studied, which indicates that conduction is due to holes[20].

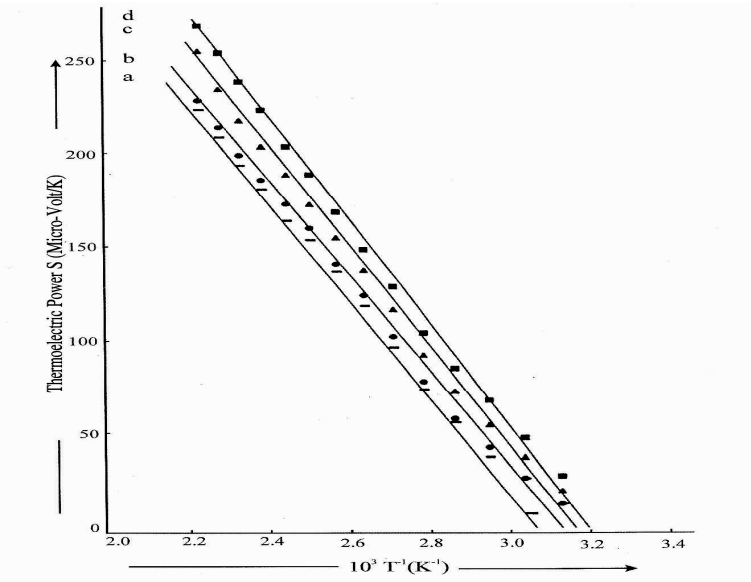

Fig. 5: Thermoelectric power (S) vs reciprocal temperature of heterojunction thin film for different values of x (a) 0.02, (b) 0.04, (c) 0.06 (d) 0.08

Conclusion

$Cd_{1-x}Zn_xTe$ heterojunction thin films have been successfully deposited by vacuum evaporation technique. Electrical and thermal measurements have been carried out. It has been found that the resistivity of the film decreases with increasing film thickness and substrate temperature. Carrier concentration and mobility increases with film thickness. It has been observed that thermoelectric power is linear function of reciprocal temperature. $Cd_{1-x}Zn_xTe$ thin film has shown tantalizing potential for low cast area module fabrication. But successful large area commercial production has been elusive. Some of these advantages are particularly relevant as polycrystalline thin film community addresses issues related to the challenges of fabricating tandem film with efficiencies over 25%. The major objectives of thin film solar cell research and development programmes are to improve the efficiency, stability and life time of photovoltaic devices.

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