

THERMOELECTRIC POWER OF CdTe THIN FILMS PREPARED BY VACUUM EVAPORATION METHOD

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Cadmium Telluride (CdTe) thin films of different thickness have been prepared by vacuum evaporation method on glass substrate at room temperature. X-ray diffraction and thermoelectric power (TEP) measurements were carried out on these films. The XRD pattern shows that as-deposited films are amorphous in character. Thermoelectric power (TEP) measured from room temperature to 450 K and it shows positive value at room temperature and decreases with the increase of temperature upto $T=314$ K, above which it remains almost constant. At higher temperature, $T > 410$ K, TEP becomes negative. These experimental results reveal that there are two types of carriers present in as-deposited films. In low temperature region, dominant carriers are holes and at high temperature ($T > 410$ K) it is electron. The activation energy E_0 and temperature coefficient of activation energy γ have been calculated from TEP data. E_0 and γ varies with film thickness and their values range from 0.52 to 1.21 eV and 7.05×10^{-4} to 18.4×10^{-4} eV K^{-1} respectively. It is found that TEP does not vary systematically with film thickness, which is one of the characteristics of amorphous materials reported in the text.

Keywords: Thin film, CdTe, Vacuum evaporation, XRD, Thermoelectric power, Activation energy.

1. Introduction

Cadmium Telluride (CdTe) is an II-VI compound with Wurtzite crystal structure having lattice parameters $a = 4.7$ Å and $c = 7.47$ Å. It is either n-type or p-type semiconductor with direct band gap energy 1.5 eV and is very promising material for the preparation of opto-electronic devices and solar cells [1-4]. Extensive studies have been made on the structural, electrical and optical properties of CdTe thin films, but thermoelectric behavior studies are not very abundant in the scientific literature. The measurement of thermoelectric power provides some important information about the types of carriers, nature of scattering mechanism and position of the Fermi energy in the forbidden band. Considering the immense applications of CdTe film in solar cell and opto-electronic devices, it is necessary to unveil the above characteristics. So we have prepared thin films of different thickness by vacuum evaporation method and studied the structural and thermoelectric properties of these films.

2. Experimental

CdTe films of different thickness were prepared from CdTe crystal by a vacuum-coating unit (MODEL HSV-3-30G, JAPAN) at room

temperature. Glass substrate was used to deposit CdTe films. A high vacuum of the order of 10^{-5} Torr was employed by a turbo-pump. For obtaining homogenous and uniform film thickness of large area the distance between source and substrate was kept 7 cms for all samples. A high current of about 90 amps was used to evaporate CdTe for different length of time to obtain films of different thickness. Thickness of the films was determined by Fizeau fringes method. X-ray diffraction of the films was taken using an X-ray diffractometer (MODEL- RIGAKU, Geiger flex, JAPAN) with CuK_{α} radiation at room temperature in the department of Materials Science, University of Yamanashi, Japan, to check the status of the specimens. The diffraction scan was recorded at $20 \leq 2\theta \leq 70$ with a scanning speed $2^{\circ} \text{ min}^{-1}$ and with a step sampling of 0.01° . Thermoelectric power (TEP) was measured by integral method from room temperature to about 450 K.

3. Results and Discussion

The diffraction patterns of as-deposited CdTe films were found similar for all thickness. Therefore, we have shown only the diffraction pattern of as-deposited CdTe thin film of thickness 2698 Å in Fig. 1. From XRD pattern it is seen that

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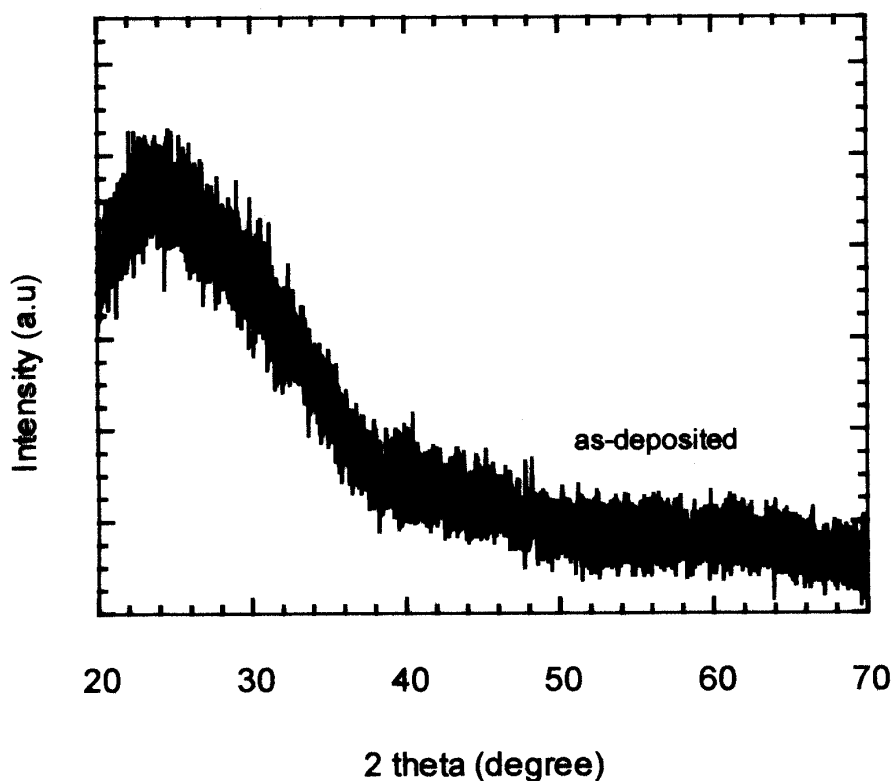


Figure 1. XRD pattern of as-deposited CdTe thin film.

there is no crystalline peak which suggests the amorphous nature of the films.

The thermal emf as a function of temperature difference between hot and cold ends for both heating and cooling cycles of as-deposited CdTe thin film of thickness 2698 Å is shown in Fig. 2. The thermal emf values of heating and cooling cycles are slightly different, though the pattern is same which indicates that the film undergoes an irreversible process. This irreversible transformation reveals the amorphous character of CdTe films as suggested by Damodara et al. for Sb₂Te₃. Our X-ray diffraction experiment strongly supports the result obtained in the thermal emf measurement. Similar patterns of the emf were observed for other films of different thickness prepared by vacuum evaporation method. For better understanding we have taken the average value of thermal emf for evaluating thermoelectric power, S , of the samples and is calculated using the relation $\Delta V = \pm S \cdot \Delta T$, where S is the Seebeck coefficient. Since the value of Seebeck coefficient of connecting copper wire is very small ($S = 1.7 \mu\text{V/K}$) compared to CdTe, we have neglected this value during the calculation of Seebeck coefficient.

The change of TEP for CdTe thin films of different thickness with increase in temperature difference is shown in Fig. 3. The value of TEP at room temperature is positive which decreases with the increase in temperature up to $T \sim 314$ K, after which it remains almost constant for a wide range of temperature (314 K-410 K). At $T \sim 410$ K, TEP crosses zero value and then goes to negative values indicating a switching over from p-type to n-type conductivity. The above result can be explained by two-carrier model [5],

$$S = \frac{S_h \sigma_h + S_e \sigma_e}{\sigma_h + \sigma_e} \quad (1)$$

where S_h and S_e are Seebeck coefficients due to hole and electron, σ_h and σ_e are the conductivities due to holes and electrons. In low temperature region ($T < 314$ K), high value of TEP indicates that holes in the valence band mainly responsible for the charge transport. The drop of S with increase of temperature indicates that the electrons are excited into conduction band, which yield minor contribution to the charge transport

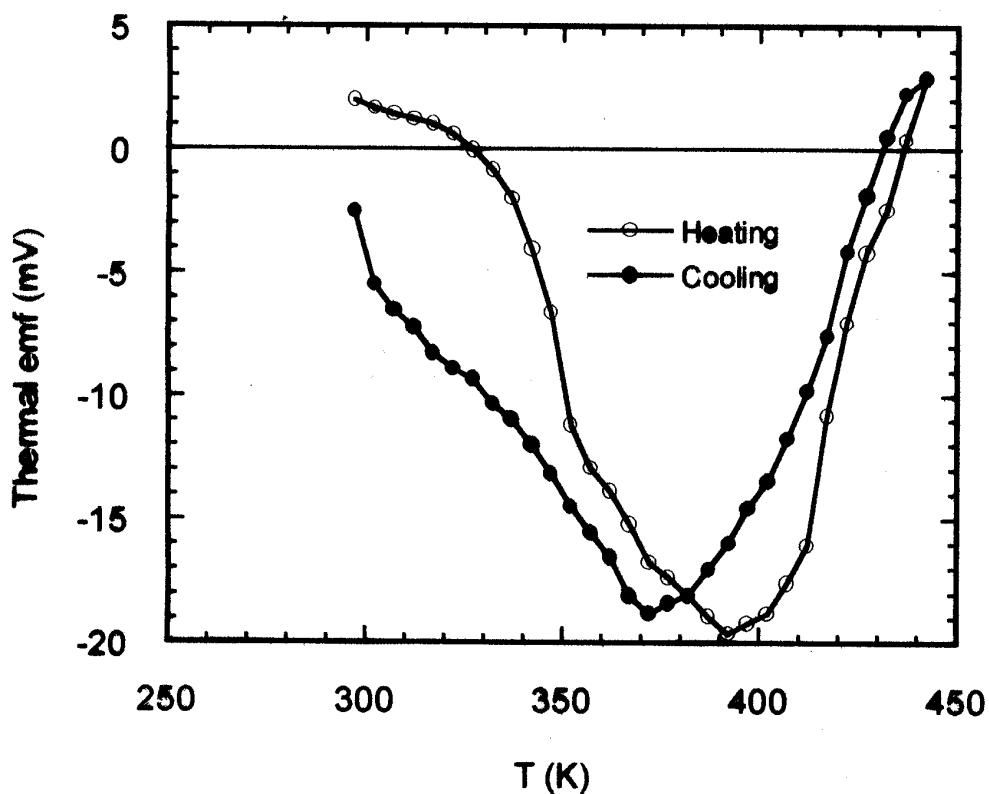


Figure 2. Variation of thermal emf with temperature difference of hot and cold ends.

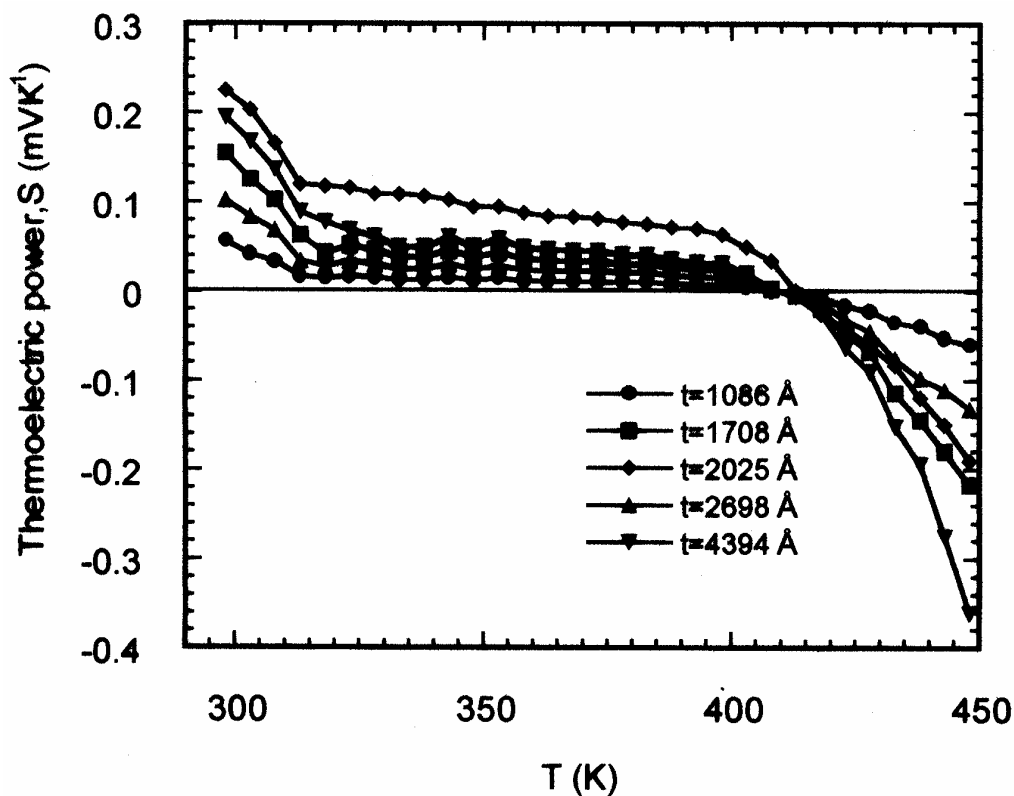


Figure 3. Temperature dependence of thermoelectric power S of CdTe films.

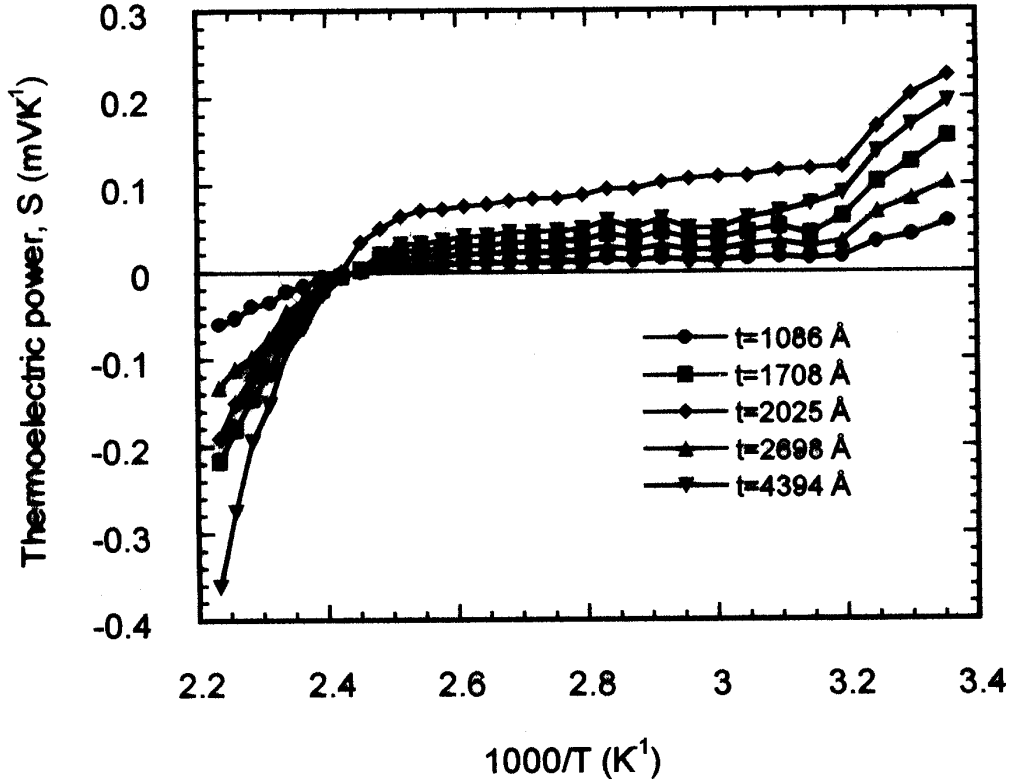


Figure 4. Dependence of thermoelectric power S on 1/T.

process. The negative TEP at temperature $T > 410$ K reveals that the sample goes into n-type semiconductor and therefore the electrons in the conduction band mainly contribute to the charge transport process.

Figs. 4 and 5 show the plot of thermoelectric power, S , plotted against $1/T$ and Peltier coefficient, Π , against T respectively. From these two plots, E_0 and γ for the films have been estimated by the following way:

The inverse temperature dependence of S is observed to follow the relation [6]

$$S = \pm \frac{k}{e} \left(\frac{E_F - E_V}{kT} + A \right) \quad (2)$$

or,

$$S = \pm \frac{k}{e} \left(\frac{E_0}{kT} - \frac{\gamma}{k} + A \right) \quad (3)$$

Here it is assumed that $E_F - E_V = E_0 - \gamma T$ for a limiting range of temperature, where E_F is the

Fermi energy, E_V is the top valence band energy, γ is the temperature coefficient of activation energy, k is the Boltzmann constant and A is a constant related to the scattering mechanism. For amorphous semiconductor A is assumed to unity.

Peltier coefficient, Π , is assumed to follow the relation [6],

$$\Pi = ST = \frac{E_0}{e} - \frac{1}{e}(\gamma - kA)T \quad (4)$$

The value of E_0 has been calculated from the intercept of Π versus T plot (in y-axis at $T = 0$ K). The value of γ was found out from the intercept of S versus $1/T$ plot (in y-axis at $1/T = 0$ K). The obtained values of E_0 and γ for CdTe thin films of different thickness are shown in Table 1. It is observed that the value of E_0 varies on film thickness. It is well known that the value of maximum activation energy would be half of the forbidden energy. The forbidden energy of CdTe crystal is 1.5 eV as reported previously [3, 4]. The activation energy obtained in this study is comparable to the half of the forbidden energy of CdTe crystal. The value of activation energy

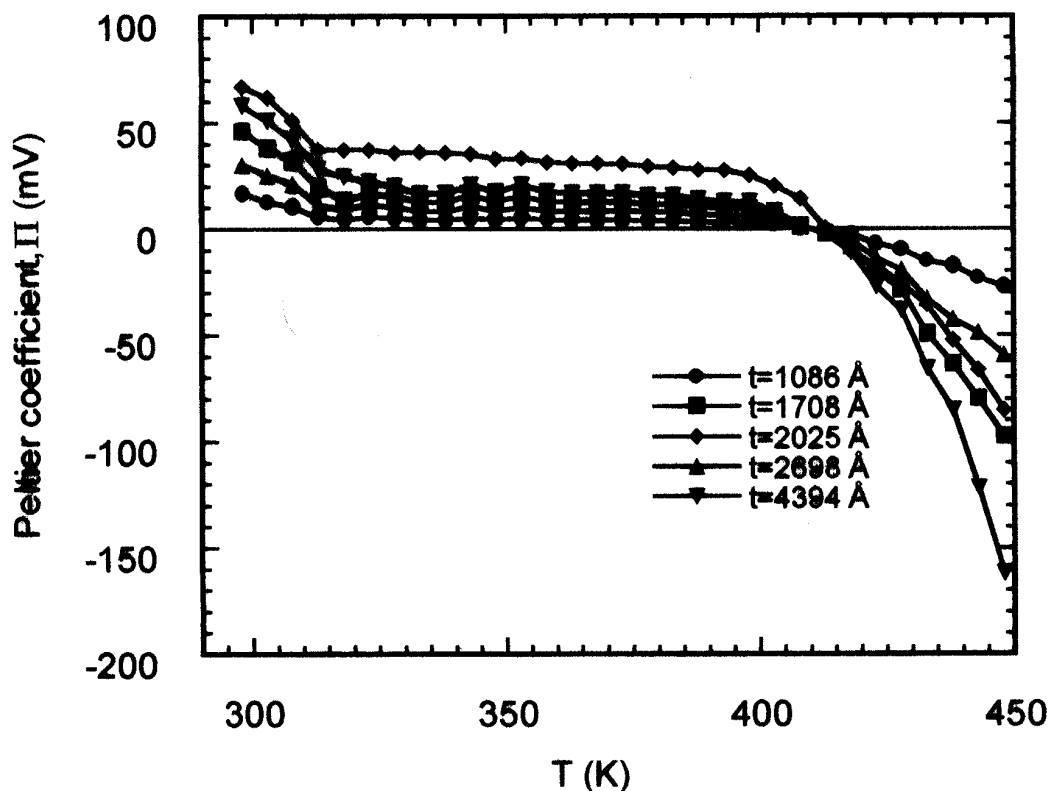


Figure 5. Temperature dependence of Peltier coefficient Π of CdTe films.

Table 1. Thermoelectric power S , activation energy E_0 and temperature coefficient of activation energy γ of CdTe thin films of different thickness.

Film thickness, t (Å)	Thermoelectric power, S (μVK^{-1})		E_0 (eV)	$\gamma \times 10^{-4}$ ($\text{eV} \cdot \text{K}^{-1}$)
	at 300 K	at 400 K		
1086	50.5	6.50	0.526	7.05
1708	145	20.5	1.080	14.4
2025	220	60.0	0.879	11.6
2698	96.5	15.5	0.978	8.50
4394	180	25.5	1.210	18.4

($E_0 \gg kT$) obtained in this study indicates the deep level localized states in the forbidden energy band. From Table 1 it is observed that the value of γ does not vary systematically with thickness, since the activation energy, E_0 and temperature coefficient of activation energy, γ depend not only on the thickness of the films but also on other parameters like film growth conditions, defect states and nature of scattering etc.

The temperature dependence of Fermi energy, ($E_F - E_V$), with respect to the top of the valence band is calculated from the relation $E_F - E_V = E_0 - \gamma T$ and the variation of ($E_F - E_V$) with temperature for the films of different thickness is shown in Fig 6. It is seen from the plot that the value of $E_F - E_V$ decreases with the increase of temperature indicating that the Fermi energy E_F shifts towards the valence band edge.

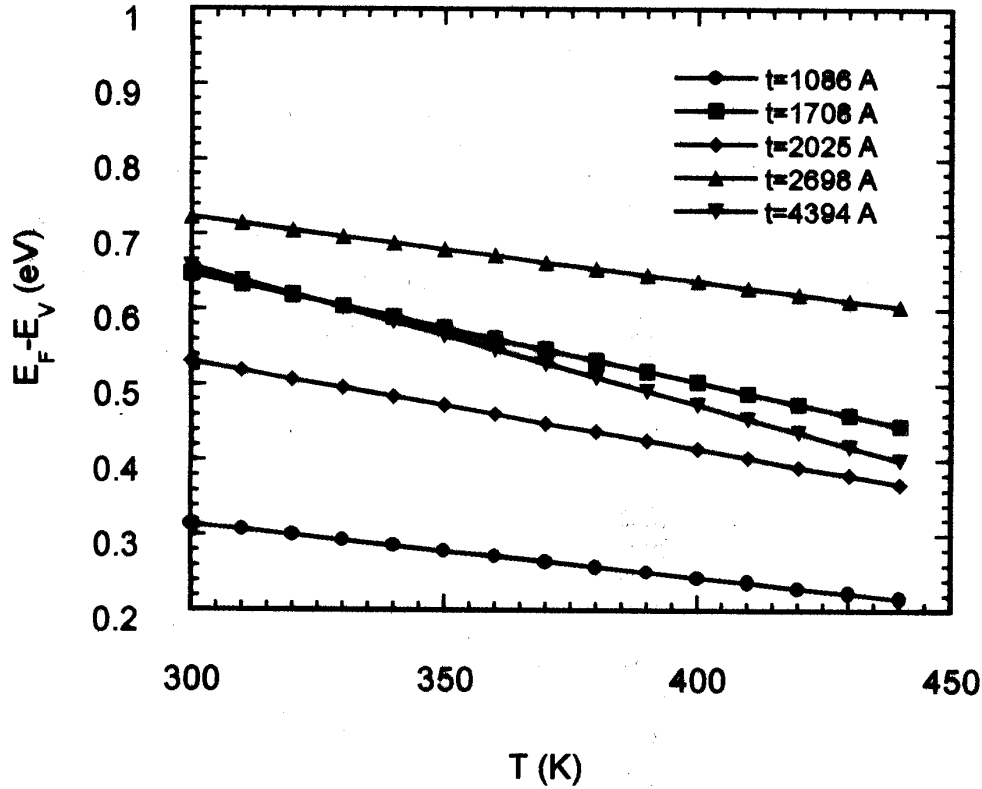


Figure 6. Variation of $(E_F - E_V)$ with temperature T .

The non-systematic variation of TEP with thickness at 300 K and 400 K, as can be revealed by Figs. 3 & 4, is not unexpected for amorphous materials and can be explained by the following expressions [7, 8],

$$S = S_g \left[1 - \frac{3}{8} (1-P) \frac{l_g}{t} \left(\frac{U_g}{1+U_g} \right) \right] \quad (5)$$

Here, S_g is the Seebeck coefficient for bulk crystal and is given by

$$S_g = - \frac{\Pi^2 k^2 T}{3eE_F} (V + U_g) \quad (6)$$

where,

$$V = \left(\frac{\delta \ln A}{\delta \ln E} \right)_{E=E_F} \approx 1, \quad U_g = \left(\frac{\delta \ln l_g}{\delta \ln E} \right)_{E=E_F} \quad (7)$$

Here, U_g is the energy dependence of mean free path of the charge carriers, A is the Fermi surface

area and P is the specularity parameter giving the fraction of charge carriers that are specularly scattered from the surface, T is the temperature in Kelvin, l_g is the effective mean free path, t is the thickness of the film and E_F is the Fermi energy. The non-systematic variation of TEP with film thickness may be attributed to the absence of diffuse scattering at the surface, so that the specularity parameter $P=1$ [7]. When $P=1$, the expression for TEP becomes,

$$S = - \frac{\Pi^2 k^2 T}{3eE_F} (1 + U_g) \quad (8)$$

At a constant temperature T , E_F and U_g are constants, therefore TEP becomes independent of thickness. Furthermore, the random variation in S observed with thickness may be due to some small differences in deposition parameter such as degree of vacuum, deposition rate, structural defects etc. It should be pointed out here that Damodara et al. did not find any thickness dependence of TEP in $Pb_{0.8}Sn_{0.2}Te$ thin film, which corresponds to our observed results for CdTe films.

4. Conclusions

The XRD and thermoelectric power measurements reveal that investigated CdTe thin films are p-type amorphous materials at room temperature. In high temperature region, the sign reversal of TEP indicates the switching over of materials from p-type to n-type. The variation of TEP is non-systematic with the film thickness. The high activation energy ($E_0 > kT$) attributes the deep level localized states of the films.

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