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Study of transport properties co – evaporated lead telluride (PbTe) thin films

Thin films of lead telluride (PbTe) of thicknesses ranging from 1000 Å to 2500 Å have been prepared by co-evaporation (three temperature) technique, onto precleaned amorphous glass substrates at various temperatures. The deposited samples were annealed and annealed samples were used for characterization. Resistivity of these samples was measured by four-probe technique as a function of thickness and temperature. Activation energy for charge transport have been evaluated and found in the range of 0.09 to 0.106 eV. Thermoelectric power has been measured and found to be positive indicating that the samples are p-type semiconducting material. Mobility variation with temperature has been estimated (evaluated) and correlated with scattering mechanism in the entire range of temperature studied. The X-ray diffraction analysis confirmed that films are polycrystalline having cubic structure cell and lattice parameters are reported.

Keywords: co-evaporation, lead telluride, thermoelectric power, activation energy, mobility

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1. Introduction

Among the II-IV compounds, the lead chalcogenides with narrow energy gap have been extensively studied due to their device applications in many fields like IR detectors photoconductors, thin film transistor etc. [1-3] The lead chalcogenides exhibit very interesting photoelectric, photoconducting, thermoelectric, optical and semiconducting properties. Many workers have been reported on the transport properties of these chalcogenides in the bulk state but very little is known about their properties in the thin film state. The electrical properties of these compounds have been studied by many workers [4-7]. The surfaces of polycrystalline films of PbTe condensed onto amorphous substrates have been studied by hot wall technique [8], RF magnetron sputtering [9], and thermal evaporation [7,10,11]. There has been some work on the thermoelectric power of impurity doped lead telluride films but very little on pure undoped samples in the thin film form. Barisova has measured the thermoelectric power of bulk PbTe doped with Bi, Sb, Cr and Ag in amounts of 0.1 - 0.5 at %. He found that undoped PbTe was p-type whereas those doped with Bi, Sb and Cr was n-type. The room temperature value of thermoelectric power for pure undoped PbTe bulk was quoted [12] as around 30μv/k. The electrical properties of thallium and silver doped PbTe films were also reported [13,14].

Thus it is seen that there has been very little study on transport properties of undoped PbTe films The present work on the resistivity, carrier concentration, carrier mobility,

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thermoelectric power and structural information of PbTe films have been studied and an attempt is made to explain the charge transport on the basis of scattering mechanism.

2. Experimental Details

Polycrystalline PbTe co-evaporated films have been deposited via sublimation of the two basic ingredients by three-temperature technique, under vacuum about 10^{-5} torr. The deposition was controlled by adjusting the rate of both sources of sublimations. The substrates to source distance was 20cm. The substrate temperature was varied from the range 300K-423K. The glass substrates were cleaned with warm dilute chromic acid, detergent solution, distilled water and acetone in that order. The samples of different thicknesses at constant substrate temperature (373K) were deposited under similar conditions. The samples having almost same thickness of about 1500 Å were deposited at various substrate temperatures, 303K, 323K, 373K and 423K. The films were annealed at reduced pressure 10^{-5} torr and at temperature 523K for the period of three hours. The thicknesses of films were controlled by using quartz crystal thickness monitor model No.DTM-101 provided by Hind-High Vac. The deposition rate was maintained 20-40 Å/sec. throughout sample preparations.

The X-ray diffractograms (Rigaku, Miniflex Japan) were obtained of these samples to obtain the structural information and to identify the film structure qualitatively. The scanning angle (2θ) range was from 20° to 80° (CuKα line). The X-ray shows that all the films prepared were polycrystalline with cubic structure. Resistivity of the samples was measured by four-probe technique using model No. DEP-02. "Scientific Equipment Roorkee", as a function of thickness and temperature.The thermoelectric power has been measured by the integral method, [7] the set up is used for this measurement provided by "Puspha Scientific Co., Hydrabad".

The set up is such that one end of the film can be connected to a heater attachment and the other end to a massive copper block in order to ensure a constant temperature. It was found that the cold end temperature was maintained at room temperature (~300K) within ±0.5K. The temperature of other end could be varied from 300 to 473K. The temperature of both the ends were measured using copper-constantan thermocouple fixed right on to the film. The thermo emf (electromotive force) developed across the film was measured with respect to copper, as a function of hot-end temperature using high impedance digital micro-voltmeter model No. DMV-001 provided by "Scientific Equipment Roorkee".

3. Results and Discussions

Two sets of film samples have prepared, one set of samples of thickness 1500 Å at various substrate temperatures and other set of samples of various thicknesses at 373K-substrate temperature. The thicknesses of the films have been controlled using quartz crystal thickness monitor during film deposition and are crosschecked using Tolansky's technique. Film thicknesses found correct within ±50Å.

The resistivities of film samples have been measured as a function of thickness and temperature. Variation of resistivity with thicknesses of films indicates that size effect [15,16] is followed by film material. This fact is further confirmed from the plot of ρ against 1/d [Fig-1] that represent straight-line graph following the Sondheimer's relation

$$\rho = \rho_0 [1 + 3\lambda/8d (1-P)] \quad (1)$$

Where ρ_0 and P are respectively the bulk resistivity and specular reflection coefficient at the surface of the film. If surface scattering be assumed entirely nonspecular so that P=0, the bulk mean free path λ_o and bulk resistivity ρ_0 may be computed from the observed slope and intercept. The values of ρ_0 and λ_o so obtained may be used calculate the electron density from the relation by [17]

$$(1/\rho_0\lambda_0) = (8\pi/3)^{1/3} (e^2/h) n^{2/3} \quad (2)$$

Where e and h are respectively electron charge and Plank's constant. The evaluated value of carrier concentration is found to be 0.71×10^{18} cm^{-3} . This value is very close to those reported by Mandale for films having thicknesses of the order of 3 to 7 μm. [18,19] Vaya have also reported the carrier concentration to be 1.1×10^{18} cm^{-3} from the hall measurement [20].

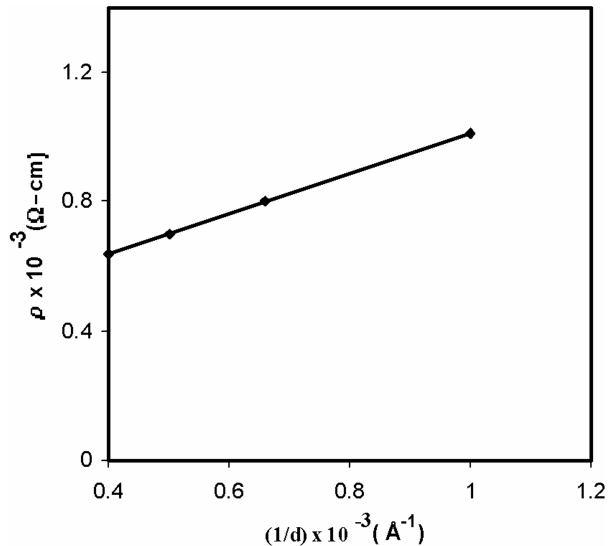

Fig. 1: Plot of resistivity Vs reciprocal of thickness.

The variation of resistivity as a function of temperature [Fig-2 and Fig-3] Log ρ against 1/T indicates that all the film sample have negative temperature coefficients of resistivity, which suggested their semiconducting nature. These graphs shows linear variation in the temperature range (303-450) K. From these graphs using Arrhenius relation [10] the thermal activation energies ΔE have been evaluated and varied from 0.09 to 0.120 eV., which was found random as a function of thickness. However for the samples of constant thickness (1500 Å) deposited at various substrate temperatures, the activation energies evaluated as 0.099, 0.109 and 0.120 eV (± 0.010) for substrate temperatures 323K, 373K and 423K respectively. Activation energies evaluated are very close to those reported by Terra [10] ΔE=0.106 ± 0.004 eV for the low temperature range.

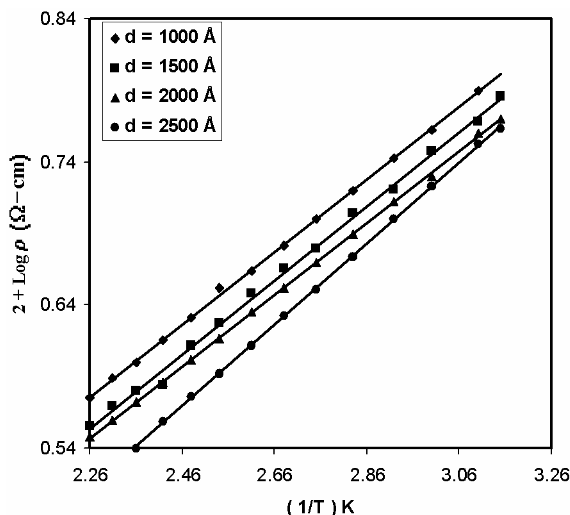

Fig. 2: Variation of Log r Vs reciprocal of temperature for various film thicknesses.

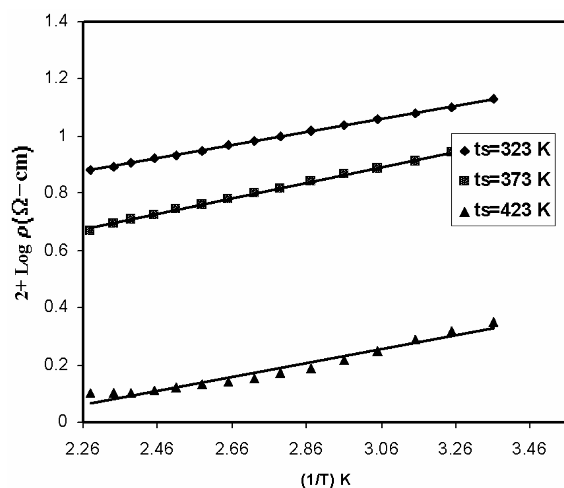

Fig. 3: Plots of Log r Vs reciprocal of thickness.

To explain dependence of resistivity or conductivity of a semiconducting material using the relation $\rho = 1/e\mu_p p$ and $P = Nv \exp[- Eg/2KT]$ and assuming $m^*_{hh}=0.29m_0$ [21], the charge carrier concentration at various temperatures have been hence mobility at different temperatures. From these data, graphs of

(i) Log p Vs log T
(ii) Log μ Vs log T

have been plotted and presented in figures Fig. 4, 5. Fig. 6 respectively.

From the graphs of log p Vs 1/T the band gaps have been evaluated these values are very close to activation energies evaluated previously from the graphs of log ρ Vs 1/T. They are presented in the Table 1.

Table 1: Comparison of thermal band gap energies: -

Substrate Temp. (K)	From ρ Vs 1/T Eg (eV)	From nVs 1/T Eg (eV)	Fermi Energy (eV)	$Eg=2E_F$
323	0.099	0.084	0.0307	0.062
373	0.109	0.088	0.0425	0.085
423	0.120	0.092	0.0445	0.089
Thickness (Å)				
1000	0.099	0.084	--	--
2000	0.095	0.084	--	--
2500	0.105	0.088	--	--

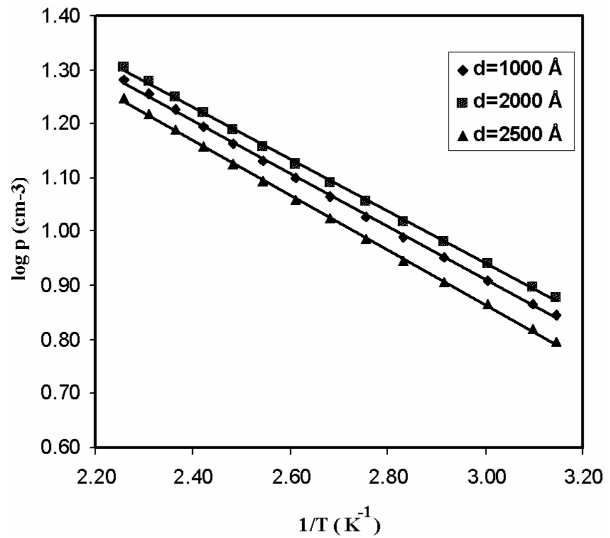

Fig. 4: Variation of carrier concentration p with (1/T) for various film thicknesses.

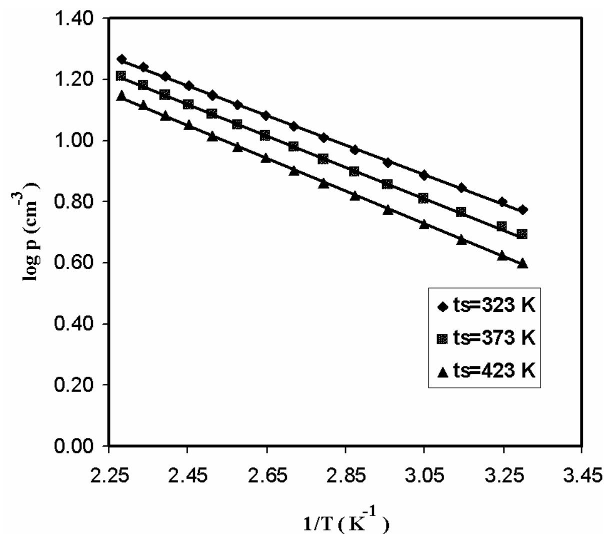

Fig. 5: Variation of carrier concentration p with (1/T) for various substrates temperature.

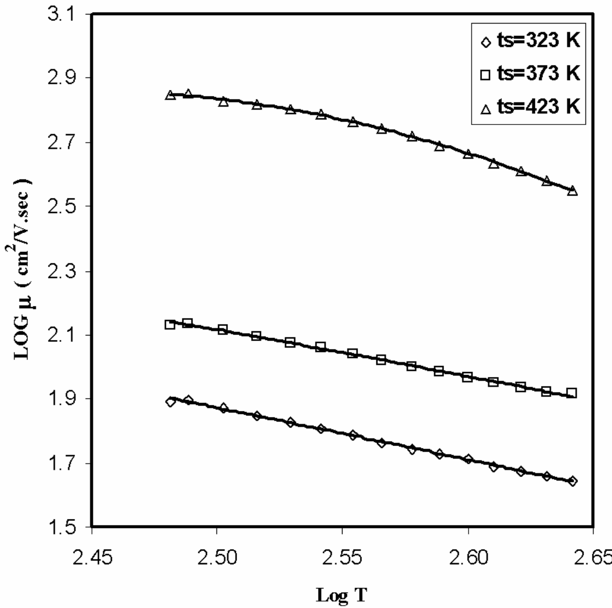

Fig. 6: Variation of mobility m with temperature LogT for various substrates temperature.

Figure-6 represents the variation of log μ Vs log T. These graphs are linear having negative slopes with magnitudes very close to 3/2 i. e. ~ 1.5. Therefore it may be concluded with certainly the scattering mechanism in these films is due to acousting phonon. Hence these graphs suggest that scattering mechanism of charge carrier transport is due to acousting phonon. As the mobility due to acoustic phonon m_l is given by

$$m_l \propto [\, m^* \,]^{-5/2}\, T^{-3/2} \tag{3}$$

Plots of thermo emf versus temperature difference for PbTe films deposited at various temperatures and annealed are displayed in figure-7. It is seen that thermo emf increases linearly with increasing temperature. It is also clear from Fig-7 that the emf developed for the same temperature difference is higher for low substrate temperature while for the sample deposited at room temperature is lowest. Thermo emf of PbTe was found to be positive (high temperature end is at positive potential) indicating PbTe is p – type material.

Figure – 8 shows the plots of thermoelectric power against temperature for the films of thickness 1500 Å deposited at various substrate temperatures and it is found that thermoelectric power developed at the same temperature depends clearly on the substrate temperature being smallest for room temperature deposition. While it being largest for the sample substrate temperature 323K.

These results can be explained as detailed below.

In a non – degenerative p- type semiconductor the thermoelectric power S_F is given by the expression [7]

$$\begin{aligned} S_F &= K/e\,[5/2 + S - (E_F - Ev/KT)] \\ &= K/e\,[A + \ln (Nv/p)] \\ &= K/e\,[A - E_F/KT] \end{aligned} \tag{4}$$

Where $Nv = 2\left[2\pi m^*_h KT/h^2\right]^{3/2}$, E_F is the fermi energy, Ev is the energy of top valence band, K is the Boltzman's constant, e is the charge of electron or hole, T is absolute temperature, p is hole concentration and s is defined by $\tau(E) = \tau_o E^S$ where τ, the relaxation time, is considered to be a function of energy and τo is constant. Nv is the effective density of states in the valance band. Since Nv > p the expression inside the bracket is positive and hence signs of the carrier. It is found that in the case of PbTe films SF is positive throughout temperature range used suggesting that the sample to be p- type in nature.

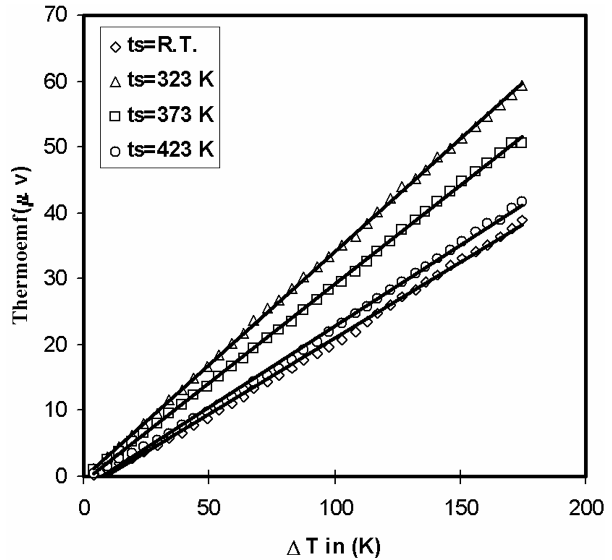

Fig. 7: Thermo emf as a function of temperature difference.

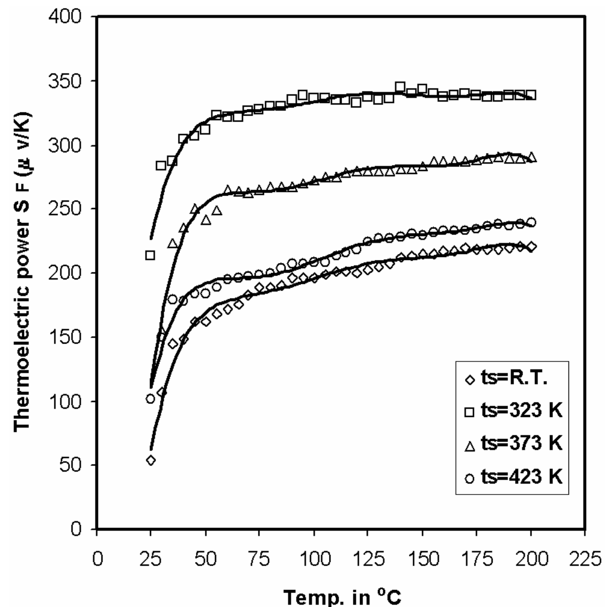

Fig. 8: Temperature varition of the TEP for PbTe thin films.

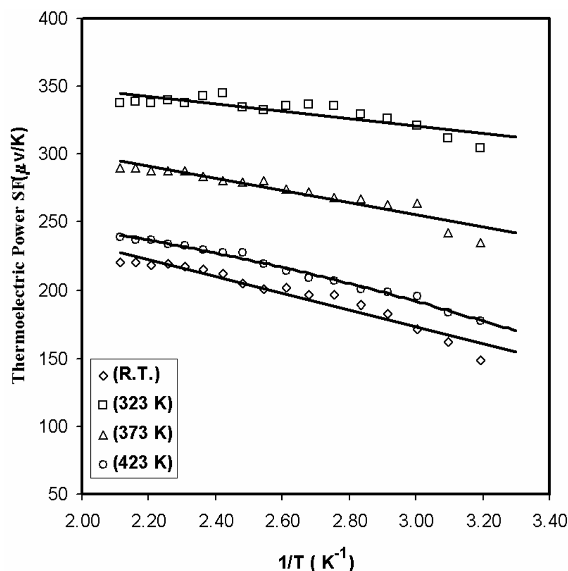

Fig. 9: Variation of Thermoelectric power with reciprocal of temperature.

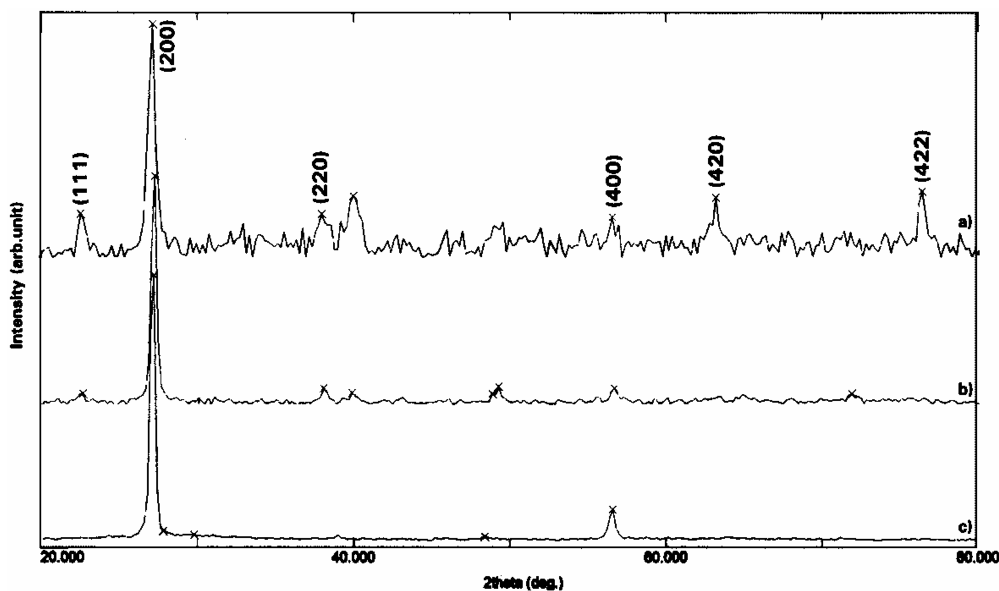

Fig. 10: X-ray diffractogram of PbTe co-evapurated thin films of different substrate temperature a) R.T., b) 323 K, c) 423 K

Also from the above expression it is expected that S_F should vary as 1/T. The plots presented in Fig-9 are in good agreement as expected from the above expression. Further from slopes of these graphs the values of E_F are evaluated. These values are very close to Eg/2 or $\Delta E/2$ obtained from log ρ Vs 1/T and log p Vs 1/T plots. All these parameters are presented in Table-1. This clearly indicates validity of the experimental results.

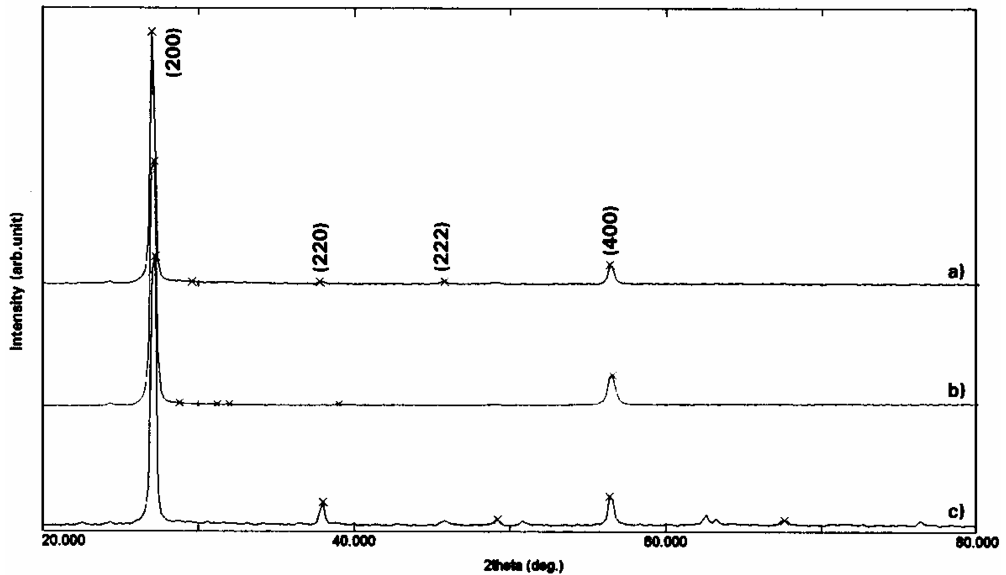

Fig. 11:

Table 2: Experimental valves of interplanar spacing and the corresponding data of the standard card.
Experimental Standard Card of PbTe no.8-28

d (Å) for R.T.	I/I_1	d(Å) for 50°C	I/I_1	d(Å) for 150°C	I/I_1	d(Å)	I/I_1	h k l
3.93	19	3.93	5	--	--	3.74	10	111
3.27	100	3.27	100	3.27	100	3.23	100	200
2.25	270	2.262	5	--	--	2.28	80	220
--	--	1.864	5	1.879	5	1.858	30	222
1.624	18	1.624	7	1.624	14	1.609	20	400
1.245	29	1.313	5	--	--	1.314	40	422
d=1000 Å	I/I_1	d=2000Å		d=2500 Å				
3.29	100	3.27	100	3.27	100	3.23	100	200
2.37	3	2.30	2	2.36	11	2.28	80	220
1.979	3	--	--	1.850	5	1.858	30	222
1.630	10	1.624	13	1.630	13	1.609	20	400

The X-ray diffractogram of various samples are presented in Fig-10 and Fig-11. Which clearly indicate that film material is polycrystalline. The observed data is compared with the standard ASTM Card No.8-28 having cubic structure cell. The comparison of observed d values and normalized intensities and standard ASTM values are presented in Table-2. It is seen from this table that prominent observed peaks and d values are in good agreement with standard values indicating the PbTe films have cubical structure cell. [9,22] Furthermore the d values have also matched with standard calculated by the computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program version 2.2). The

value of lattice constant was evaluated as 6.5514 Å which matches with standard lattice constant 6.443 Å. In addition it was found that peak intensity of (200) reflection increases with substrate temperature and thickness of samples. As the peak intensity of (200) reflection change appreciably with thickness and substrate temperature growth of film taken place in the same direction, which is perpendicular to substrate surface i. e. film growth, is preferred orientation having homogeneous single phase. Similar results were reported by Sahay [9].

Conclusion

In conclusion, homogeneous single-phase thin films of PbTe have been successfully deposited by three-temperature technique using basic Pb and Te elemental starting materials. Resistivity measurement as a function of thickness suggests film material obeys size effect. Evaluated thermal energy gaps are very closely agrees with those evaluated from the calculated carrier concentration and those evaluated from thermoelectric power measurement. This suggests validity of experimental measurements

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