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STRUCTURAL PROPERTIES AND THERMOELECTRIC POWER OF THERMALLY EVAPORATED $InSbTe_3$ THIN FILMS

H. E. Atyia, A. M. A. El-Barry

Ain Shams University, Faculty of Education, Physics Department, Cairo, Egypt

Stoichiometric thin films of different thickness (~50 – 150 nm) of $InSbTe_3$ were prepared by thermally evaporated technique, onto pre-cleaned glass substrates at ~ 298 K. The as-deposited films are non-crystalline and the crystallinity occurs on annealing at T ≥ 373 K. The analysis of X-ray data using a special computer program for an unknown system confirmed that $InSbTe_3$ compound has orthorhombic structure with lattice constants a = 16.39 ± 0.004 Å, b = 10.21 ± 0.0063 Å, c = 3.98 ± 0.0019 Å, and cell volume, V = 666.64 ± 0.0043 $Å^3$. Both dark electrical resistivity ρ and thermoelectric power were measured in the temperature range (~303-423 K). Seebeck coeficient was found to be positive over entire temperature range, indicating that $InSbTe_3$ films are p-type semiconducting materials. Also, the variation of the mobility with the temperature has been estimated. The results were interpreted acording to the grain boundary potential barrier model and the presence of small polaron with energy, W_P ~ 0.05 ± 0.009 eV.

Keywords: $InSbTe_3$, Thin films, Thermal evaporation, Thermoelectric power, Seebeck coefficient

1. Introduction

Samples of the Sb_2Te_3-In_2Te_3 systems i.e. $In_xSb_{2-x}Te_3$ solid solutions, have been studied in a number of papers [1-3]. Considerable attention has been devoted to determine the phase diagram an mutual solubility of these systems [1-4]. Several authors studied the optical properties [5-7] and the electrical properties [8-10] of $In_xSb_{2-x}Te_3$ solid solution where, 0 ≤ x ≤ 0.45. They concluded that the increasing amount of In atoms in $In_xSb_{2-x}Te_3$ system gives an increasing value of the carrier density, of the electrical conductivity, of the Hall coefficient and of the Seebeck coefficient but reduces the mobility and the band gap. To our knowledge, no data are available on the crystal structure, lattice parameters and thermoelectric power of $InSbTe_3$.

The paper aims to investigate some characteristics of $InSbTe_3$ thin films. The investigation concerns the analysis of X-ray patterns to determine the type of the crystal structure and the lattice parameters of $InSbTe_3$ compound. The thermoelectric power for the thermally evaporated $InSbTe_3$ films, the type and the concentration as well as the mobility of the majority carriers and the temperature dependence of the diffusion coefficient were also investigated.

2. Experimental

The ternary, $InSbTe_3$, was prepared by mixing the constituent elements (In, Sb and Te with 99.999 % purity) in stoichiometric proportions into an evacuated quartz ampoule. The temperature was raised at a rate of 50 Kh^{-1} to 1003 K. It was kept constant for 48 hours. The ampoule was cooled slowly at a rate of 180 Kh^{-1} [6]. Thin films of various thicknesses (~50-150 nm) of $InSbTe_3$ were thermally evaporated onto optically flat glass substrates, using a high-vacuum coating unit (Edwards type E 306 A). The substrate temperature was fixed at 298 K during the deposition. When the vacuum chamber is pumped to 10^{-4} Pa, the materials start to evaporate. The film thickness and the rate of deposition are controlled using a quartz thickness monitor (FTM4 Edwards). The chemical composition of both the bulk compound and of prepared films were checked by energy dispersion

X-ray spectroscopy (EDX) using a scanning electron microscope (Jeol 5400). An X-ray diffractometer (Philips x, pert), using Cu radiation from a target operating at 40 kV and 30 mA, was used to investigate the structure. The electrical resistivities of $InSbTe_3$ thin films of different thickness (sandwiched between two Al electrodes) were measured in a temperature range (~300 – 423 K), using an electrometer with high input impedance (Keithley 616 A). The thermoelectric power was measured using the differential technique based on the following equation [11]:

$$(d\Delta E/dt) = S_{12} = S_2 (T_{12}) \qquad (1)$$

where S_{12} is the relative thermoelectric power between the materials 1 and 2 at temperatures T_1 and T_2, $S_2(T_2)$ and $S_1(T_1)$ are the thermoelectric power between the film and the contact material [12]. A special holder (see Fig. 1) was used. The temperatures T_1 and T_2 of the two ends were increased by using two different high power resistance R_1 and R_2 as a heat source and heat sink across the thin film under test. The sample had a dimension ~ 6 × 0.5 cm^2. The electromotive force, ΔE, associated with the temperature gradient along the film was measured using an electrometer (Keithly 616). The temperature was measured using a cromel – alumel thermocouple monitored by a microvoltmeter.

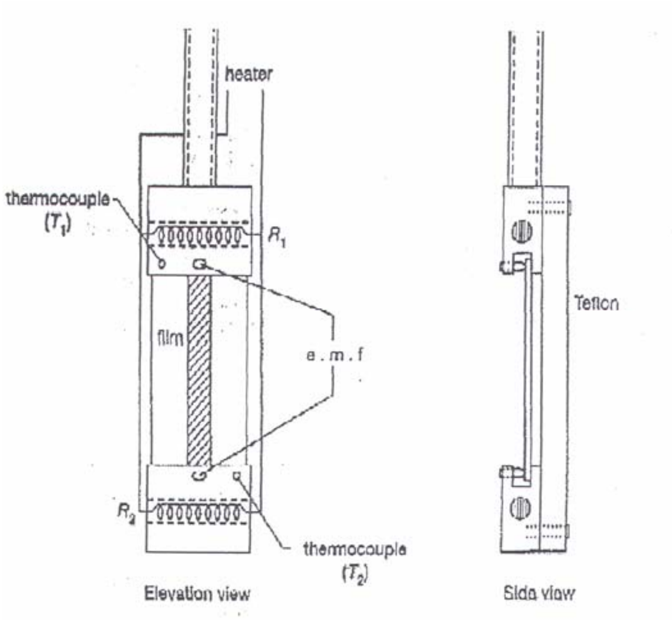

Fig. 1. Holder used for the thermoelectric power measurement.

3. Results and discission

X-ray diffractograms obtained for $InSbTe_3$ in powder form, as a starting material, as well as thin film form (~150 nm thickness) either freshly deposited or after being annealed, at 323, 373, 423 and 473 K), are shown in Fig. 2. The as deposited films have amorphous structure while those annealed in vacuum for two hours at T ≥ 373 K have polycrystalline structure. The degree of crystallinity was found to increase with increasing temperature. The observed diffraction angle, Θ_{obs}, the calculated diffraction angle, Θ_{cal}, interplanar spacing, d_{hkl}, and Miller indices, hkl, were determined, using special computer program for unknown systems [13] (see Table 1). The analysis of X-ray data confirmed that $InSbTe_3$ compound has orthorhombic structure with the lattice constants, a = 16.394 ± 0.00045 Å, b = 10.216 ± 0.0006 Å, c = 3.98 ± 0.00019 Å and the cell volume is V = 666.64 ± 0.0043 $Å^3$.

Table 1. $2\Theta_{obs}$, $2\Theta_{cal}$, d_{obs}, I/I_o and Miller indices, hkl for $InSbTe_3$ compound.

2Θ (observed)	2Θ (calculated)	d (observed)	I/I_o	hkl
17.339	17.339	5.1104	0.4	102
24.988	24.983	3.5606	0.2	300
26.345	26.358	3.3802	0.24	310
28.388	28.410	3.1414	1.00	203
38.418	38.435	2.3412	0.43	421
44.538	44.502	2.0327	0.29	423
52.019	52.023	1.7566	0.2	610
54.229	54.257	1.6901	0.21	620
63.406	63.366	1.4658	0.14	445
69.360	69.395	1.3538	0.14	446
71.396	71.38	1.3201	0.11	644

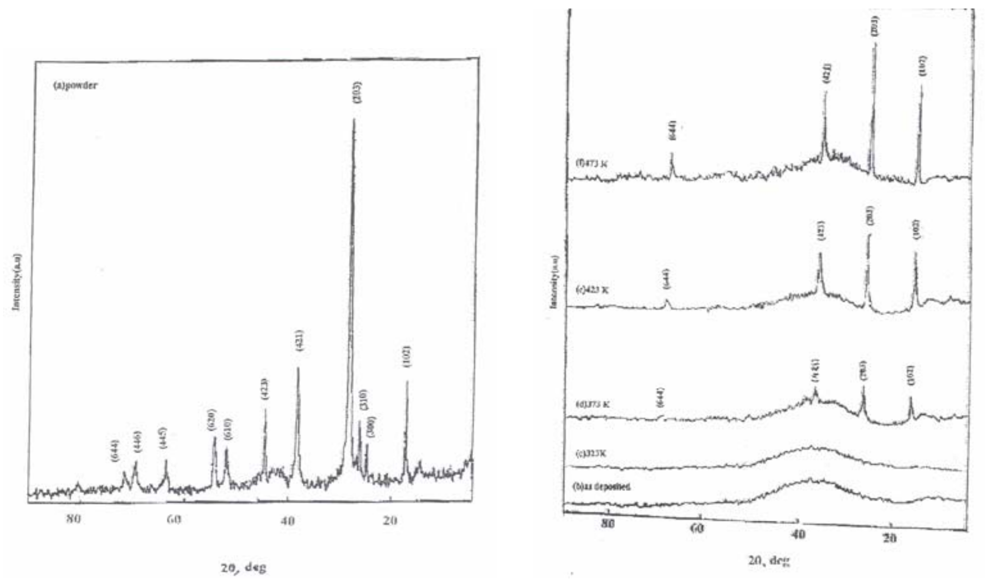

Fig. 2. X-ray diffraction patterns for $InSbTe_3$ a) in powder form and thin film form; b) as-deposited; c) annealed at 323 K; d) annealed at 423 K and e) annealed in vacuum at 473 K for two hours.

The electrical resistivities, of as-deposited $InSbTe_3$ thin films with different thickness (~50-150 nm), were measured in the temperature range (~300 – 423 K). Fig. 3 shows that the dark electrical resistivity decreases with increasing both temperatures and thickness (see the inset of Fig.3). This behaviour is in agreement with that reported for other compounds [14], indicating the presence of semiconductor properties of the $InSbTe_3$ thin films. A decrease in the resistivity from $\sim 1.3 \times 10^7$ to $\sim 8.5 \times 10^6$ Ωm was detected and this corresponds to a change in the film thickness from ~50 to 150 nm. This may be due to the kinetic of the film growth and diminishing in the density of structural defects [15]. This trend is commonly observed in many semiconductor thin films [14, 16, 17]. This behaviour of the resistivity in as-deposited $InSbTe_3$ thin films [14] corresponds to the well known relation (2) that describes the temperature dependence of the resistivity:

$$\rho = \rho_0 \exp (\Delta E_\rho / k_B T) \qquad (2)$$

where k_B is the Boltzmann's constant, ΔE_ρ is the thermal activation energy and ρ_0 is the pre-exponential resistivity. Using the Eq. 2, the thermal activation energy, ΔE_ρ could be obtained. There was found that the value of the thermal activation energy is $\Delta E_\rho \approx 0.176 \pm 0.002$ eV, where ΔE_ρ

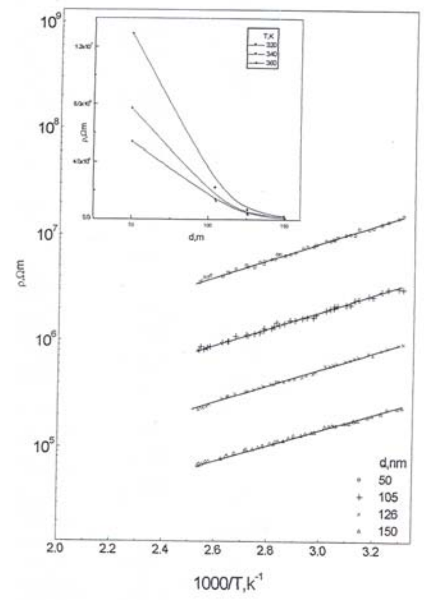

Fig. 3. Temperature dependence of the resistivity, ρ of as deposited $InSbTe_3$ thin films with thicknesses 50, 105, 126 and 150 nm; Inset: the thickness dependence of the resistivity of as-deposited $InSbTe_3$ thin film at T = 320, 340 and 360 K.

represents an energy independent on the film thickness within the experimental error. The calculated values of ΔE_ρ, $\rho_{0,}$ are listed in Table 1. According to the structural results, the investigated films of $InSbTe_3$ up to $T \approx 373$ K have an amorphous nature. Therefore, during the low-temperature regime some sort of aggregation might occur. Such aggregation might cause a reduction in the electrical resistivity. At higher temperatures, the film could start to transform from the amorphous state into crystalline state as shown in Fig. 2 (d-f).

In order to detect the type of the majority carrier in $InSbTe_3$ thin films the Seebeck coefficient, S, was measured as a function of temperature. Fig. 4 depicts the variation of Seebeck coefficient, S vs. Average temperature, T_{av} for different thickness of $InSbTe_3$ thin films. The experimetnal data indicate that the Seebeck coefficient, S is positive for all studied thickness over the whole range of temperature (~300 – 423 K). Accordingly, the conduction in $InSbTe_3$ thin films occurs via the holes i.e., $InSbTe_3$ behaves as p-type semiconductor, because according to the simplest model for the solid solutions, In is substitued for Sb in the cation lattice of Sb_2Te_3, while the Te sublattice remains unchanged. Each substitution of In atom for Sb atom eliminates two electron s from the lattice. From the conventional point of view these electrons would be removed from the valence band, and the free hole concentration would rise accordingly [18]. Fig. 4 shows that the thermoelectric power, S in the low temperature region increases with the temperature. At certain temperature, ~350 K, a maximum broad peak of thermoelectric power started at appear. Behind this broad peak in (S) tends to decrease. This beaviour of S has been observed before [19-21]. The range of temperature at which a maximum in S appeared is recognized as the transition temperature from extrinsic to intrinsic conduction [19-21]. The decreasing in S, at higher temperature, may be attributed to the large mobility of the generated electrons associated with intrinsic conduction [20]. The Seebeck coefficient S, in the lower temperature range, could be described by the following relationship [19].

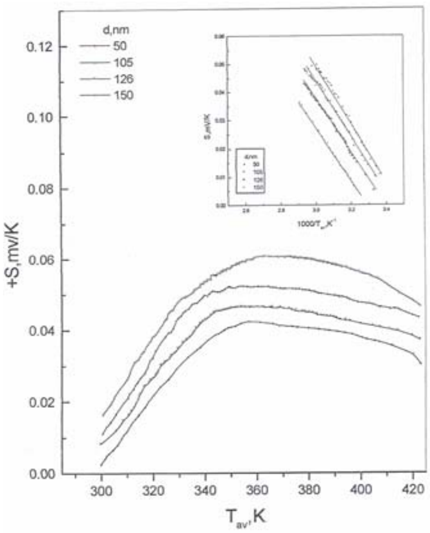

Fig. 4. Temperature dependence of Seebeck coefficient, S, for as deposited $InSbTe_3$ thin films with thicknesses 50, 105, 126 and 150 nm. The inset figure shows S vs. 1000/T.

$$S = - [k_B/e][(\Delta E_S/k_BT) - (\gamma/K_B)+1] \quad (3)$$

where ΔE_S is the Seebeck activation energy, γ is the temperature coefficient of the activation energy and e is the electronic charge. The plot of S vs. 1000/T (see the inset of Fig. 4), gives the possibility to determine the values of ΔE_S and γ for each thickness in the lower temperature range. The average value of the Seebeck activation energy is $\Delta E_S \approx 0.12 \pm 0.027$ eV. The obtained values of ΔE_S and γ for each thickness are listed in Table 1.

From the thermoelectric measurements, S, the free charged carrier concentration, n, was calculated according to the following equation [23-24].

$$n = 2\,M^{3/2}\,[(\exp\,(2k_B + S)/k_B)] \quad (4)$$

where m^* is the effective mass, which was taken as 0.11 m_e [23], $M = [2_{\Pi}\ m^*k_BT/h^2]$ and h is Planck's constant. It has been found that n increased from 3.65×10^{24} to 4.88×10^{24} as the temperature increased from ~ 300 to 423 K, regardless of film thickness. These results may be consistent with the transition from amorphous to polycrystalline state [19-21].

fig(5)

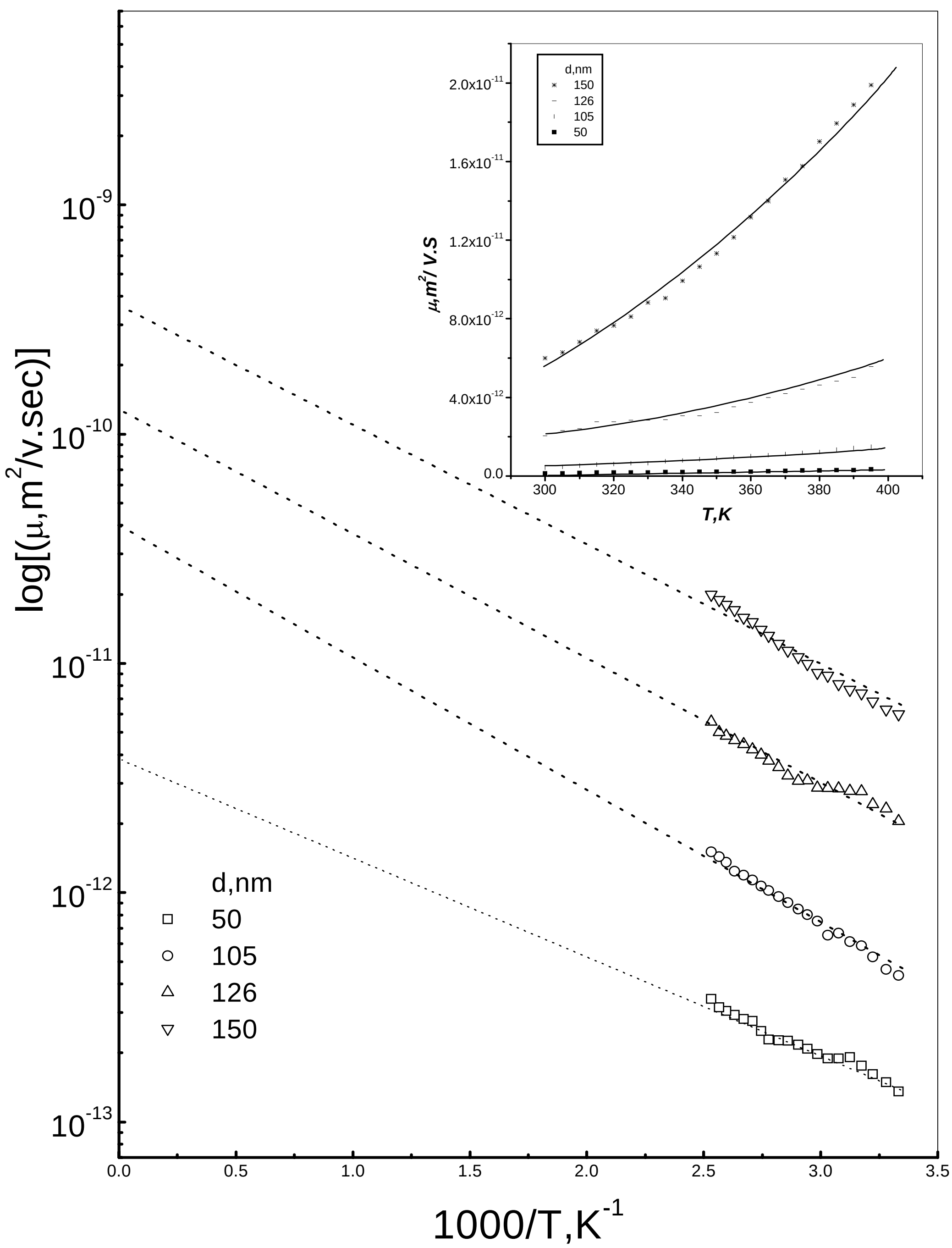

Fig. 5. Temperature dependence of the carriers mobility as log(μ) vs 1000/T. The inset figure: μ vs T (of as deposited $InSbTe_3$ thin films with thicknesses 50, 105, 126 and 150 nm).

The estimation of the carrier density gave us the ability for calculating the carriers mobility, μ, of as deposited $InSbTe_3$ thin films. The resistivity and thermoelectric power data were incorporated at different temperatures. A number of authors [26-27] have used the free-charge-carrier concentration calculated from Hall coefficient measurements that are connected with the conductivity measurements at the same temperature. To determine the carrier mobility, in the present work the free-charge-carrier concentration, obtained from thermoelectric power measurements, were connected with the resistivity measurements to calculate μ at any given temperature according to the relation, $\rho = 1/(n\ e\ \mu)$ [14, 21], where, e is the electronic charge, ρ is the electrical resistivity, n is the carrier concentration and μ is the carrier mobility.

Table 2. The variation of $\rho_o(\Omega m)$, ΔE_ρ (eV), ΔE_S (eV), ΔE_ρ-ΔE_S (eV) γ, eV/K and $\mu_o(m^2/v.sec)$ with the thickness (t, nm) of $InSbTe_3$ thin films.

t, nm	$\rho_o(\Omega m)$	ΔE_ρ (eV)	ΔE_S (eV)	ΔE_ρ-ΔE_S (eV)	γ, eV/K	$\mu_o(m^2/v.sec)$
50	5.94×10^4	0.178	0.143	0.035	3.73×10^{-4}	6.02×10^{-12}
105	6.55×10^3	0.179	0.133	0.046	3.34×10^{-4}	5.94×10^{-11}
126	1.5×10^3	0.175	0.1	0.075	3.25×10^{-4}	1.53×10^{-10}
150	2.26×10^2	0.172	0.087	0.082	3.24×10^{-4}	5.64×10^{-10}

A reasonable increasing in the calculated mobility, μ was observed due to the variation of the film thickness from 50 to 150 nm as the temperature increase from ~ 300 to 423 K. See the inset of Fig. 5, which illustrates the temperature dependence of the carrier's mobility through as deposited $InSbTe_3$ thin films as (μ) vs. 1000/T relation represented by a family of straight line. This linearity is supporting the exponential temperature dependence of the mobility, which can be explained by the grain boundary potential barrier model [23,28]. The grain boundary potential barrier model as proposed by Petriz [28] is based upon the consideration that the grain boundaries have an inherent space-charge region due to the interface. The carrier mobility can be represented by the following relation [28]:

$$\mu = \mu_o \exp(-\Delta E_\mu / k_B T) \qquad (5)$$

Where μ_o is the grain boundary limited mobility and ΔE_μ is the mobility activation energy. According to Equ. 5 the mobility activation energy, ΔE_μ and the grain boundary limited mobility, μ_o can be estimated from the slope and intercept of the straight lines in Fig. 5. The average calculated value of $\Delta E_\mu \approx 0.11 \pm 0.009$ eV.

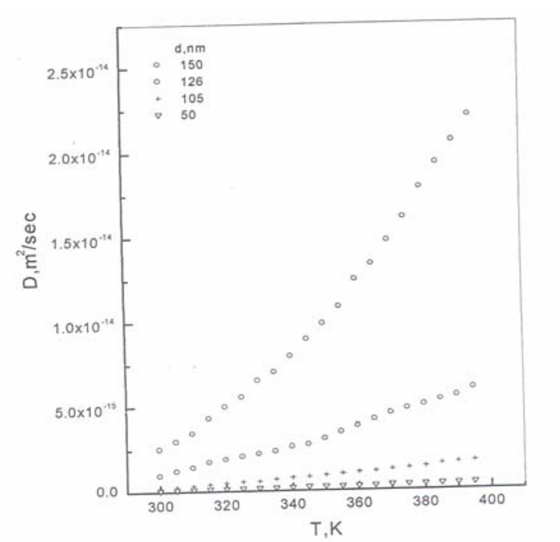

Fig. 6. Temperature dependence of the diffusion coefficient, D of as deposited $InSbTe_3$ thin films, with 50, 105, 126 and 150 nm thickness.

Since Einstein relation gives the possibility [11] to determine the diffusion coefficient when the mobility of charge carriers is calculated. The diffusion coefficient, $D = (k_B T \mu)/n$ [11] of the majority carriers through $InSbTe_3$ films was calculated. The obtained data are shown in Fig. 6. The figure shows an increasing curvature in the diffusion coefficient, with both temperature and film thickness.

4. Conclusions

The structure of $InSbTe_3$ compound, in the powder and thin film form, was studied by analysis of X-ray patterns using a special computer program. The obtained data indicate that the powder (bulk) material as well as annealed films at $T \geq 373$ K are polycrystalline with an orthorhombic structure. The as-deposited and annealed films at $T < 373$ K are amorphous. The study of the dc-electrical resisitivity, of as deposited films, supports the semiconductor behaviour. The average thermal activation energy, ΔE_p, was found to have a single value ~ 0.176 ± 0.002 eV, regardless on the film thickness, (~50 -150 nm), within the experimental error. Also, it was found that Seebeck coefficient, S is positive for all studied thicknesses over the whole range of temperatures (~300 - 423 K), where the as-deposited $InSbTe_3$ thin films behave as p-type semiconductors. The density of charge carriers was found to be in the range of 10^{24} m^{-3}. The carriers' mobility and the diffusion coefficient were determined, by incorporating the results of the Seebeck coefficient and the resistivity at the same temperature. The slight increase of the evaluated thermal activation energy, $\Delta E_{p,}$ over the Seebeck activation energy value, ΔE_s, was interpreted by the presence of small polaron with average energy, W_p ~ 0.05 ± 0.009 eV.

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