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Structural properties and thermoelectric power of thermally evaporated $InSbTe_3$ thin films

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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 were non-crystalline and the crystallinity was built on annealing at T ≥ 373 K .The analysis of X-ray data using a special computer program for 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 (~303-423K). Seebeck coefficient was found to be positive all over the temperature range, indicating that $InSbTe_3$ films are p-type semiconducting material. Also, the variation of the mobility with the temperature has been estimated. The results interpreted according to the grain boundary potential barrier model and the present of small polaron with energy,W_P ~ 0.05 ± 0.009 eV .

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1. Intoduction

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 and 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, $0 \le x \le 0.45$. They concluded that the increasing of In concentrationin $In_xSb_{2-x}Te_3$ system leads to the increase in the carrier density, the electrical conductivity, the Hall coefficient and the Seebeck coefficient but reduces the mobility and the band gap. To our knowledge, no reports are available on the study of the crystal structure, lattice parameters and thermoelectric power of $InSbTe_3$, for x = 1.

The present work 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, the lattice parameters and Miller׳s indices for the prepared $InSbTe_3$ 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 considered.

2. Experimental technique

The ternary compound, $InSbTe_3$, was grown by direct fusing of the constituent elements (In, Sb and Te with 99.999% purity) of stoichiometric proportions into an evacuated quartz ampoule .The temperature was raised at 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 different thickness (~ 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 material is allowed 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 obtained compound and the prepared films were checked by energy dispersion X-ray spectro-scopy (EDX) using a scanning electron microscope (Jeol 5400). An X-ray diffractometer (Philips x, pert), using Cu radiation 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 616A). The thermoelectric power was measured using the differential technique based on the following equation [11]:

$$(d\Delta E/dT) = S_{12} = S_2 (T_{12}) - S_1 (T_{12}) \qquad (1)$$

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 temperature 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 has 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 microvoltometer.

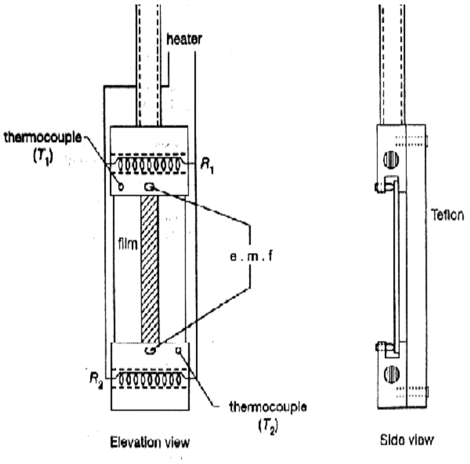

Fig. 1. Holder used for the thermoelectric power measurement.

3. Results and discussion

X-ray diffractograms obtained for $InSbTe_3$ in powder form, as a starting material, as well as thin film form(~150 nm thickness) either as deposited or after being annealed, at 323 ,373 ,423 and 473K),are shown in Fig. 2. The as deposited films have amorphous nature while those annealed in vacuum for two hours at $T \geqslant 373$ K have polycrystalline nature. The degree of crystallinity were found to increase with increasing temperature. The observed diffraction angle, Θ_{obs}, the calculated diffraction angle ,Θ_{cal} , inter-planner 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 InSbTe3 compound has Orthorhombic structure with lattice constants, a =16.394 ± 0.00045 Å, b=10.216 ± 0.0006 Å, c = 3.98 ± 0.00019 Å and the cell volume, V = 666.64± 0.00043 Å^3.

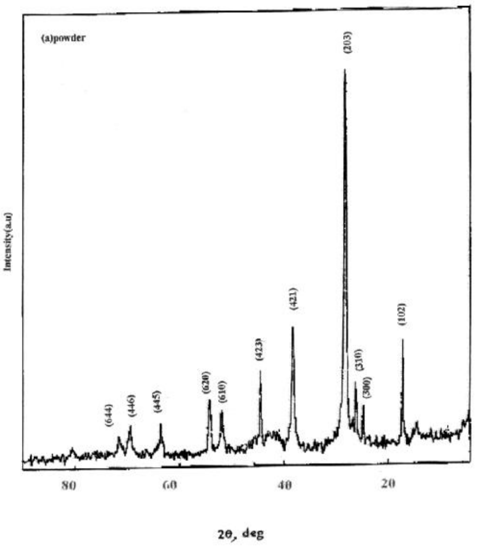

Fig. 2. X-ray diffraction patterns for $InSbTe_3$ a) in powder form and thin film form ; b) as deposited ;c) an annealed at 323K ;d)an annealed at 423 K and e)an annealed at 473K for two hours in vacuum.

The electrical resistivities, of as deposited InSbTe3 thin films with different thickness (~ 50 - 150 nm), were measured in a temperature range (~ 300 - 423 K). Fig. 3 shows that the dark electrical resistivity decreased 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 semiconductor properties of the prepared $InSbTe_3$ thin films. A decreasing in the resistivity from ~ $1.3x10^7$ to ~ $8.5x10^6$ Ωm was detected corresponding to a change in the film thickness from (~ 50 to 150 nm), this may be due to the kinetic of the film growth and decreasing in the density of structural defects [15]. In addition, as shown in Fig. 3, distinct line was observed in log (*p) vs.* 1000/T relation for each thickness, a trend as such is commonly seen in many semiconductor thin films [14,16-17].This behaviour of the resistivity supporting the applying of the following well known relation to describe the temperature dependence of the resistivity of as deposited $InSbTe_3$ thin films[14].

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

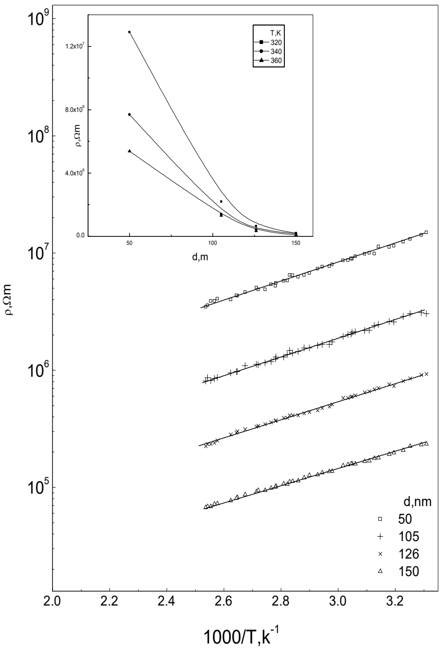

Fig. 3.Temperature dependence of the resistivity ,ρ of as deposited $InSbTe_3$ thin films with thicknesses 50,105,126 and 150nm; the inset figure;The thickness dependence of the resistivity of as deposited $InSbTe_3$ thin films at T = 320,340 and 360 K.

Where k_B is the Boltzmann' s constant, ΔE_ρ is the thermal activation energy and ρ_o is the pre-exponential resistivity. According to Equ. 2, the thermal activation energy, ΔE_ρ could be obtained. It has been found that the values of the thermal activation energy, $\Delta E_\rho \approx 0.176 \pm 0.002$ eV, where ΔE_ρ represented an independent on the film thickness within the experimental error. The calculated values of ΔE_ρ, ρ_o are listed in Table 1 .According to the structural studying, the investigated films, of $InSbTe_3$ till T ≈ 373 K, have an amorphous nature . Therefore, during the low-temperature range some sort of aggregation might occur. Such aggregation might cause a reduction in the electrical resistivity. At higher temperatures, the film might be started transferring from the amorphous state into crystalline state as shown in Fig.2 (d-f).

*Table 1. $2\Theta_{obs}$,$2\Theta_{cal}$, d_{obs} ,I/I_0 and miller indices, hkl for **$InSbTe_3$** compound.*

2Θ (observed)	2Θ (calculated)	d- observed	I/I_0	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

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 experimental data indicated that the Seebeck coefficient, S is positive for all studied thickness all 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 substituted for Sb in the cation lattice of Sb_2Te_3, while the Te sublattice remains unchanged .Eeach substitution of In atom for Sb atom deletes two electrons 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 temperature. At certain range of temperature ~ 350 K , a maximum broad peak of the thermoelectric power started to appeare. Behined this broadening peak in (S) tends to decrease .This behaviour 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, may be described by the following relationship [19];

$$S = -[k_B/e]\,[(\Delta E_s/k_BT) - (\gamma/K_B) + 1] \qquad (3)$$

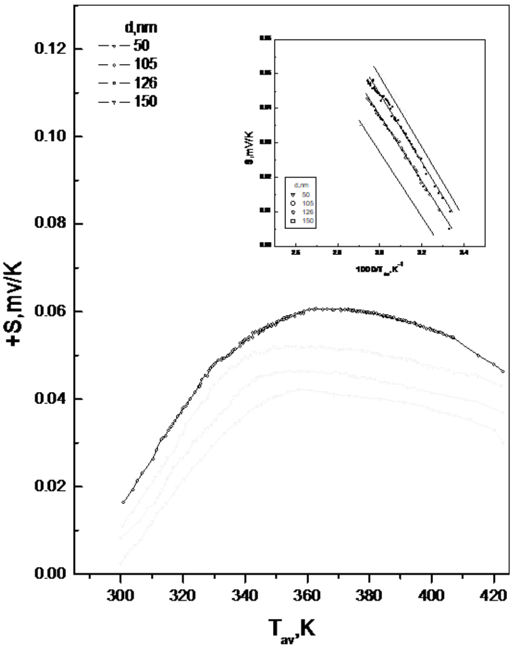

Fig. 4. Temperature dependence of Seebeck coefficient, S for as deposited $InSbTe_3$ thin films with thicknesses 50,105,126 and 150 nm, the inset figure; S vs. 1000/T.

Where ΔE_s is the Seebeck activation energy, γ is the temperature coefficient of the activation energy and e is the electronic charge. The representation of S vs. 1000/T,see the inset of Fig. 4, gave the ability 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, $\Delta E_s \approx 0.12 \pm 0.027$ eV. The obtained values of ΔE_s and γ for each thickness are listed in Table.1 .The difference between the thermal activation energy and the Seebeck activation energy , (ΔE_ρ - ΔE_s). can be attributed to the present of small polarons with energy W_H [22].The average activation energy of the small polarons ~ 0.0595 ±0.0245 eV. (ΔE_ρ - ΔE_s), μ_o and γ are listed in Table 1.

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

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

Where m* is the effective mass, which was taken as 0.11 m_e [23], $M = [2\prod m^*k_BT/h^2]$ 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 the film thickness. These results may be consistent with the transition from amorphous to polycrystalline state [19-21].

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 In $SbTe_3$ thin films.

t,nm	ρ_o ,Ωm	ΔE_ρ ,eV	ΔE_S,eV	ΔE_ρ -ΔE_S, eV	γ ,eV/K	μ_o ,m^2/v.sec
50	5.94x10^4	0.178	0.143	0.035	3.73x 10^{-4}	6.02x10^{-12}
105	6.55x10^3	0.179	0.133	0.046	3.34x 10^{-4}	5.94x10^{-11}
126	1.5x10^3	0.175	0.1	0.075	3.25 x-10^{-4}	1.53x10^{-10}
150	2.26x10^2	0.172	0.087	0.082	3.24 x10^{-4}	5.64x10^{-10}

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 made use of the free-charge-carrier concentration calculated from the 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 the 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.

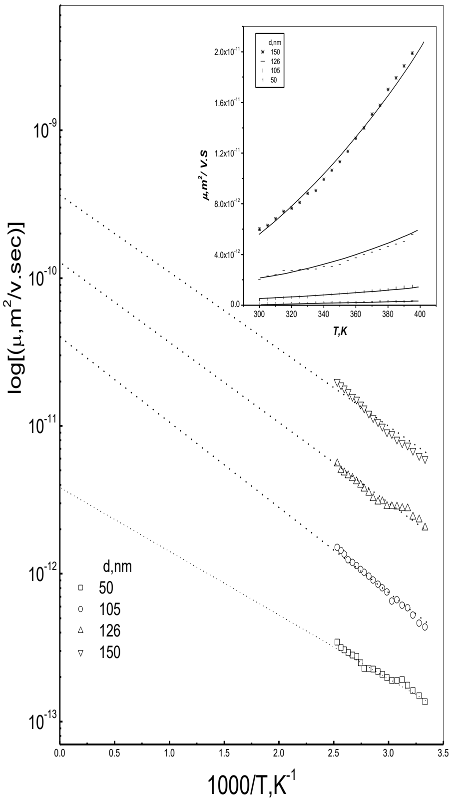

Fig. 5. Temperature dependence of the carriers mobility as log(μ) vs 1000/T ;the inset Figure: μ vs T (of as deposited $InSbTe_3$ thin films with thicknesses 50,105,126 and 150 nm).

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. T and Fig. 5 (log (μ) vs. 1000/T). The log (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]: -

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

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 the intercept of the straight lines in Fig. 5. The average calculated value of $\Delta E\mu \approx 0.11 \pm 0.009$ eV.

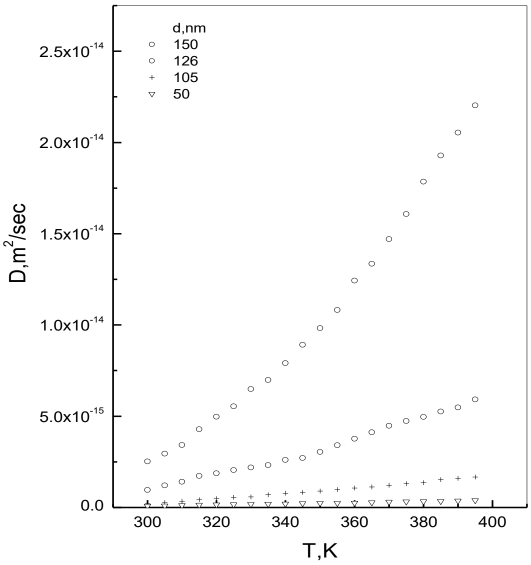

Fig. 6. Temperature dependence of the Diffusion coefficient, D of as deposited In $SbTe_3$ thin films, with 50,105,126 and 150 nm thickness.

Since Einstein relation give the ability [11] to determine the diffusion coefficient when the mobility of charge carrier calculated .The diffusion coefficient, $D = (k_BT\mu) /n$ [11], of the majority carrier through $InSbTe_3$ films was calculated .The obtained data exhibited in Fig. 6 . The figure shows a curvature increasing in the diffusion coefficient, with both temperature and film thickness.

4. Conclusions

The structure of $InSbTe_3$ compound, in both powder and thin film form, was studied by analysis of X-ray patterns using a special computer program. The obtained data indicated that the powder as well as annealed films at $T \geqslant 373$ K have polycrystalline natures with an orthorhombic structure.The as-deposited and annealed films at T< 373k have an amorphous nature. The studying of the dc-electrical resistivity ,of as deposited film, supporting the semiconductor behaviour.The average thermal activation energy, ΔE_p ,was found to have a single value~ 0.176 ± 0.002 eV independent 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 all over the whole range of temperature(~300 –423 K), where as deposited $InSbTe_3$ thin films behave as p-type semiconductor. 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 obtained, incorporating the results of the Seebeck coefficient and the resistivity at the same temperature .The slight increasing (of the evaluated thermal activation energy, ΔE_ρ over the Seebeck activation energy value ,ΔE_s.) was interpreted in the present work by the present of small polaron with average energy,$W_P \sim 0.05 \pm 0.009$ eV .

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