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Effect of excess tin on the electrical properties of SnTe thin films

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The influence of temperature and thickness on the electrical transport properties of 10% excess tin-doped polycrystalline SnTe thin films were investigated. From the observed variation of electrical resistivity and Seebeck coefficient it is concluded that the material exhibits a p-type degenerate behaviour. Using the size effect data, different physical parameters such as Fermi energy, effective mass and scattering parameter were evaluated and compared with the results on SnTe thin films to understand the effect of excess tin.

1. Introduction

SnTe is a narrow-band gap semiconductor [1] which finds application as an infrared detector [2] and radiation receiver [3]. It forms a series of solid solutions with PbTe and the resulting alloys are used as tunable lasers and infrared detectors over a wide range of wavelengths [4]. The bulk form of SnTe is always deficient in tin because of the low chemical diffusion constant of tin [5] and this results in a very high carrier concentration [6]. Various dopants such as copper, tin and bismuth have been tried by Brebrick [7] to reduce the carrier concentration in SnTe. In general bulk samples of varying concentrations have been prepared by earlier researchers by heating the SnTe sample with an overlayer of tin in the presence of tin or tellurium vapour.

The electrical and optical properties of SnTe were found to depend critically on the carrier concentration values. Efinova *et al.* [8, 9] and Allgaier and Houston [10] have observed that the carrier mobility increases with reduction in carrier concentration. Allgaier and Schie [11] and Brebick and Strauss [12] have observed an anomalous dependence of thermoelectric power with carrier concentration and their work led to the two valence band models for SnTe. Even the observed phase transition at low temperatures in bulk SnTe is distinguished by its clear dependence on carrier concentration [13, 14]. While the bulk form of SnTe has been extensively investigated, detailed studies on SnTe thin films are rather limited and confined to epitaxial films.

Thus studies of the properties of SnTe thin films with varying carrier concentration should be of great interest. In this aspect, the only notable study has been done by Dawar *et al.* [15] and they have studied the effect of excess tin on the electrical conductivity and Hall coefficient of SnTe epitaxial films of thickness 0.7 μm grown on mica and NaCl substrates. In the present paper, the results obtained from the studies on electrical resistivity and Seebeck coefficient of 10% excess tin-doped SnTe polycrystalline thin films are discussed. The effect of annealing, adsorption and electrical contacts were investigated first to optimize the sample preparation conditions. The electrical resistivity and Seebeck coefficient were studied as a function of temperature (300 to 450 K) and thickness (50 to 200 nm). Low-temperature variation of resistance in the temperature range (100 to 300 K) was also studied on few samples. Using the obtained experimental data different physical parameters such as a Fermi energy (E_F), effective mass (m^*) and scattering parameter (b) have been evaluated. The results obtained were compared with the values for undoped SnTe films to understand the influence of excess tin.

2. Experimental techniques

The compound SnTe with 10% excess tin was prepared by the fusion of a mixture of high-purity elements tin and tellurium (99.999% purity) in a vacuum sealed quartz ampoule taken in the correct ratio. The films for studies were prepared using a thermal evaporation technique at a vacuum of 10^{-5} torr in a Leybold–Heraus coating unit and the substrates used were pyrex glass. The substrates were initially cleaned using freshly prepared chromic acid, and then by ultrasonic agitation in the presence of Teepol solution. After cleaning well with doubly distilled water, the substrates were degreased with isopropyl alcohol and finally the substrates were subjected to ion bombardment in vacuum for 5 min using a 5 kV source before deposition. The thickness of the films was measured using a quartz crystal thickness monitor. To study the effect of adsorption, air was introduced in a controlled manner into the chamber immediately after deposition and the resistance was monitored as a function of pressure. Annealing of the films was done by heating the samples in a separate copper enclosure. The resistance measurements taken to within an accuracy of $\pm 0.001\,\Omega$. The carrier concentration was calculated from the Hall coefficient measurements and the length to width ratio of the sample was kept above four to avoid geometry effects. For thermo e.m.f. measurements, the integral method was employed. One end of the sample (6.5 cm × 0.8 cm) was fixed to a massive copper block which remains at room temperature, serving as the cold end, and the other end temperature

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could be varied gradually using a strip heater. The e.m.f. was measured between the ends and the temperature measurements were taken using a copper–constantan thermocouple. The Seebeck coefficient was evaluated to within an accuracy of $\pm 0.2\,\mu V$ from the recorded data of thermal e.m.f. as a function of ΔT by least square error analysis using spline functions.

3. Results and discussion

The preliminary adsorption studies indicated that there is no apreciable change in resistivity even for films kept in the atmosphere for few days. This type of behaviour is in total contrast to PbTe films, where even n–p transition has been observed. Thus adsorption does not seem to have any effect and the excess tin-doped SnTe films are highly stable. Gold and copper were found to be the best electrical contact materials. To obtain good polycrystalline films, annealing at different temperatures was attempted for different periods of time. The results clearly indicated that the films annealed at 463 K for 90 to 120 min gave perfect retraceable behaviour of both electrical resistance and Seebeck coefficient in both the heating and cooling cycles. The polycrystalline nature of the films was verified using X-ray and electron diffraction studies.

3.1. Temperature variation of resistance and thermoelectric power

Fig. 1 gives $\log_{10} R$ against $1/T$ plots for 10% excess tin-doped SnTe films of different thicknesses in the temperature range 300 to 450 K and it can be seen that all films exhibit identical behaviour with a positive TCR. Fig. 2 represents the typical resistance variation at low temperatures in the range 100 to 350 K. From Figs 1 and 2 it can be clearly seen that the material SnTe (10% excess tin) exhibits a degenerate metallic behaviour. Fig. 3 depicts the variation of Seebeck coefficient of excess tin-doped SnTe films and it is clearly seen that the Seebeck coefficient increases with increasing temperature and the sign of the thermoelectric power is positive, thus indicating that the films are p-type in nature. The carrier concentration value has been found to be of the order of 4 to $5 \times 10^{20}\,cm^{-3}$ from Hall effect studies. The presence of such a large number of carriers can result in a degenerate behaviour. But in a normal degenerate semiconductor where the ionized impurity scattering is predominant, the mobility should be independent of temperature. In the case of SnTe, Allgaier and Houston [10] have observed a temperature variation of mobility as $T^{-1.3}$ for $P > 10^{19}\,cm^{-3}$. This suggests that the lattice defect scattering is the main dominant scattering mechanism and this has been verified from the evaluation of scattering parameter using the size-effect data. Hence through the combination of a very high carrier concentration and the dominance of lattice scattering mechanism, the temperature variation of resistance and Seebeck coefficient exhibits a metallic behaviour.

3.2. Thickness dependence of ϱ_F and S_g

In thin films where the thickness is low, in addition to the bulk scattering, we have scattering centres spaced by a distance of the order of the mean free path and thin films will have a greater resistivity than the bulk. Even though there are various models available to take into account the surface scattering, most of the experimental data on electrical transport properties have been fitted to the Fuchs–Sondheimer function [16, 17]. In thin films the structure does not approximate to a single crystal, rather it consists of randomly oriented polycrystallites. The linear dimensions of the crystallites in the plane of the film itself is often comparable to the carrier mean free path. Hence there will be an additional deviation in Matthisen's rule due to the scattering at the grain boundaries. If the grain-boundary scattering also is taken into account one can use the Mayadas model [18, 19]. However, the expressions are highly complex for practical usage and the integrals involved have to be evaluated numerically. Hence linearized forms were attempted and in this regard the works of Tellier, Tosser and Pichard are outstanding [20–30]. They have developed different models applicable for different situations and for polycrystalline thin films, the effective mean free path model can be used [20, 22]. All the available models can be used for metals and degenerate semiconductors and in the present studies, the material being

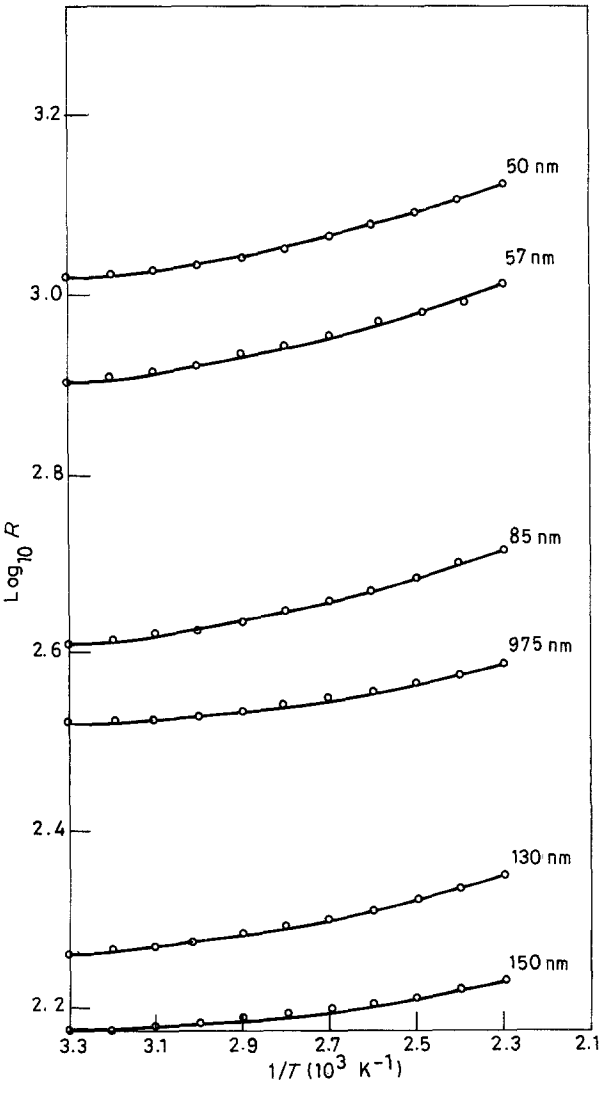

Figure 1 $\log_{10} R$ against $1/T$ plots for 10% excess tin-doped SnTe films.

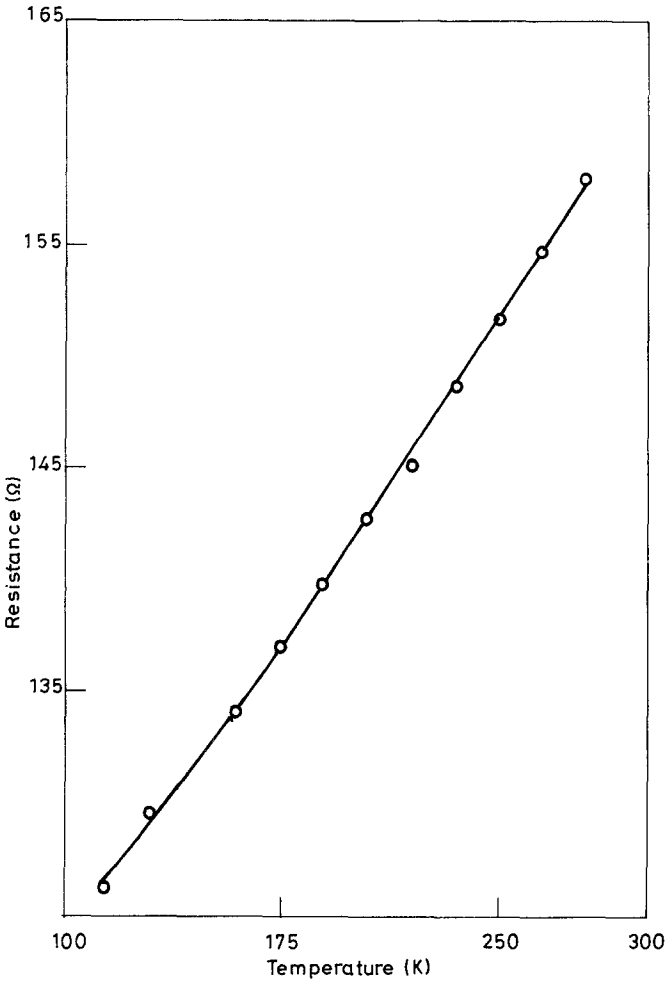

Figure 2 Low-temperature variation of resistance of excess tin-doped SnTe films, thickness '180 nm.

polycrystalline and degenerate with a very small grain size, the effective mean free path model is considered to take into account both surface and grain-boundary scattering.

In the Tellier's model, by defining a term effective mean free path, l_g, the expression for film resistivity is obtained as

$$\varrho_F = \varrho_g\left[1 + \frac{3}{8K_g}(1 - p)\right] \qquad (1)$$

where $K_g = t/l_g$, ϱ_g and l_g are the resistivity and effective mean free path of an infinitely thick polycrystalline film, t is the film thickness and p is the specularity parameter.

Irrespective of the size effect function, the Seebeck coefficient of thin films can be written as

$$S_F = \frac{-\pi^2 k^2 T}{3eE_F}\left[1 + U\frac{\beta_F}{\beta_0}\right] \qquad (2)$$

where $U = (\mathrm{d}\ln l/\mathrm{d}\ln E)_{E=E_F}$, and β_F and β_0 stand

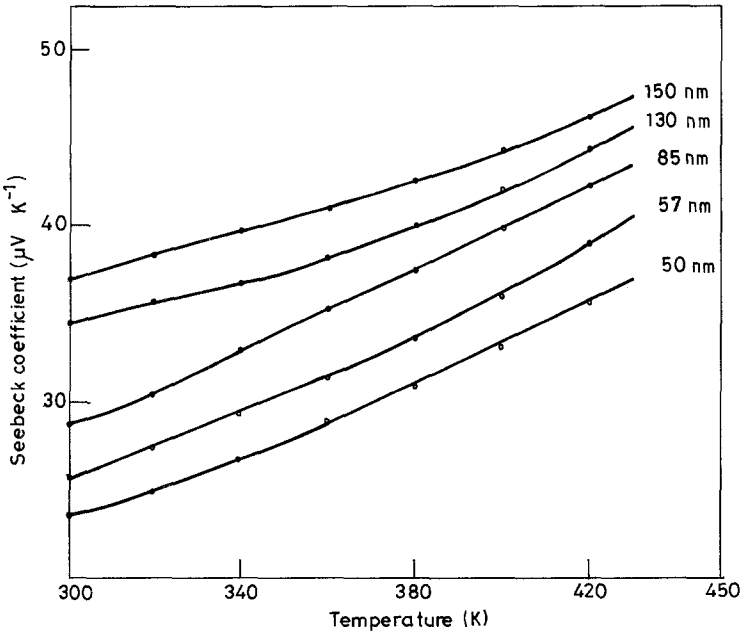

Figure 3 Seebeck coefficient variation with temperature of excess tin-doped SnTe films.

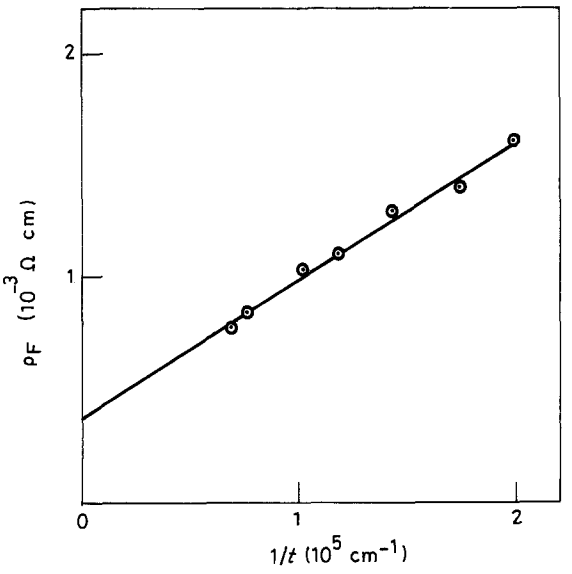

Figure 4 ϱ_F against $1/t$ plot for excess tin-doped SnTe films.

for film and bulk TCR. In Tellier's model

$$S_F = \frac{-\pi^2 k^2 T}{3eE_F}\left(1 + U\frac{\beta_F}{\beta_g}\right) \quad (3)$$

Substituting for β_F/β_g and rearranging we have

$$S_F = S_g\left[1 - \frac{3l_g}{8t}(1-p)\frac{U_g}{1+U_g}\right] \quad (4)$$

where

$$S_g = \frac{-\pi^2 k^2 T}{3eE_F}(1 + U_g)$$

Fig. 4 gives the plot of ϱ_F against $1/t$ and the plot is linear as required by Equation 1. The values of ϱ_g and l_g from the above fit are calculated assuming diffused scattering ($p = 0$) for polycrystalline films. Thus $\varrho_g = 4.5 \times 10^{-4}\,\Omega$cm and $l_g = 4.7 \times 10^{-5}$ cm. Fig. 5 gives the S_F against $1/t$ plot and this is also linear as required by Equation 4. From this plot $S_g = 44.5\,\mu$V K^{-1} and $U_g = 0.17$.

Using the expression for S_g, the value of E_F is calculated to be equal to 0.19 eV. As the value of carrier concentration is known, using the expression for E_F, the value of effective mass, m^*, can be calculated. The value of m^* is estimated to be equal to $1.2m_0$.

To understand the main bulk scattering mechanism involved, the Jain-Verma theory [31] is employed to evaluate the scatterng parameter b. In this model, the relaxation time $\tau = aE^b$, and the size-effect function S_F for diffused scattering is given by the expression,

$$S_F = S_0\left[1 - \frac{(b+\frac{1}{2})}{(b+\frac{3}{2})}\left(1 + \frac{\beta_F}{\beta_0}\right)\right] \quad (5)$$

Based on Tellier's model, Equation 5 can be modified as,

$$S_F = S_g\left[1 - \frac{(b+\frac{1}{2})}{(b+\frac{1}{2})}\frac{3}{8K_g}\right] \quad (6)$$

To evaluate the value of b, a family of curves of the Seebeck coefficient ratio S_F/S_g against reduced thickness, K_g, are drawn for different values of b according to Equation 6. The experimental points are also plotted here and Fig. 6 gives such a plot for excess tin-doped SnTe films. From Fig. 6 it is clear that the best fit is obtained for $b \sim -0.3$.

3.3. Comparison of the evaluated physical parameters with that of SnTe films

Table I gives the values of the evaluated physical parameters of excess tin-doped SnTe films and the undoped SnTe polycrystalline films [32]. In the case of excess tin-doped film the carrier concentration is found to be less than that of undoped SnTe. The carrier concentration has been reduced from 10^{21} cm^{-3} to 5×10^{20} cm^{-3} and this can be attributed to the reduction in tin vacancies due to the addition of excess tin. In SnTe it has already been established that the mobility of charge carriers is enhanced with reduction in carrier concentration. In the present investigation,

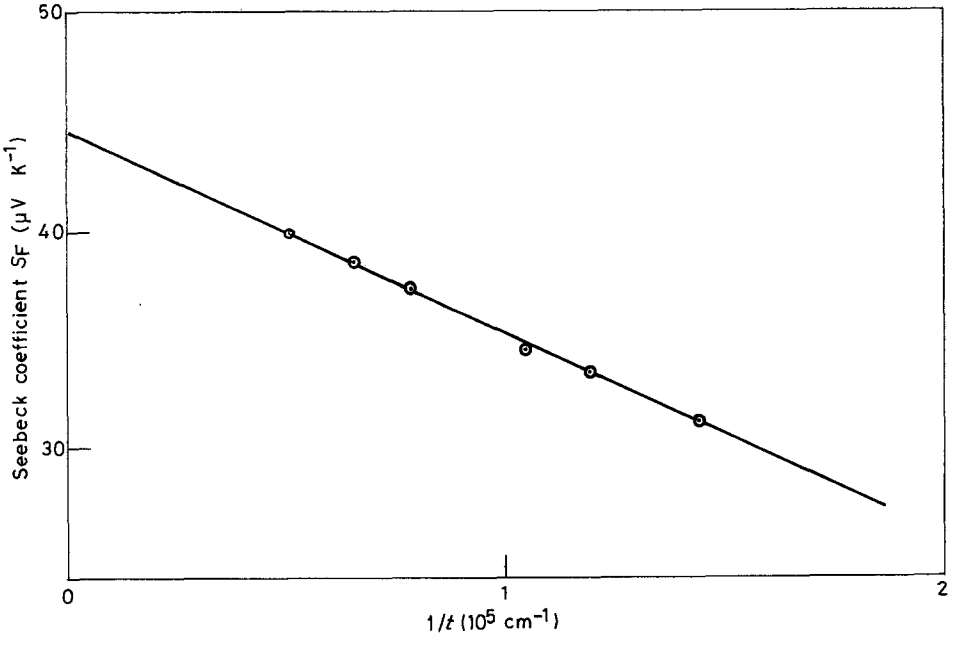

Figure 5 S_F against $1/t$ plot for excess tin-doped SnTe films.

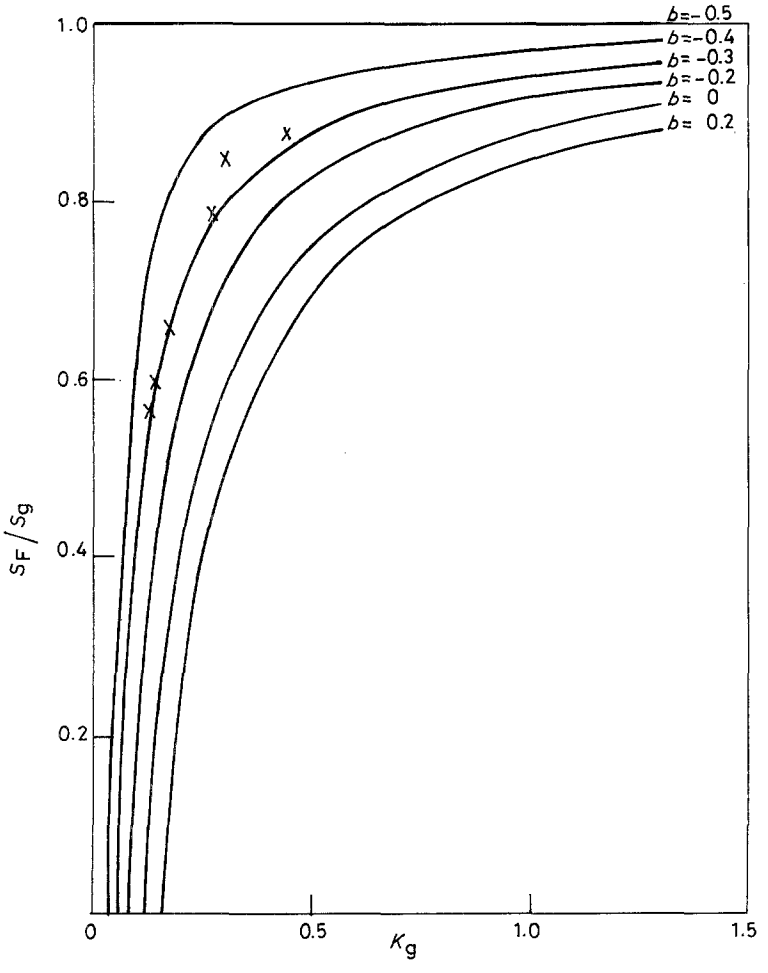

Figure 6 Thermoelectric power ratio (S_F/S_g) against reduced thickness ($K_g = t/l_g$) for different values of b. (——) Jain–Verma expression, (x) experimental points.

based on structural studies, it is observed that the crystallinity is more in the case of excess tin-doped SnTe films than that of undoped SnTe films. This contributes only a small increase in ϱ_g. The effective mean free path, l_g, is a function of $l_0 f(\alpha)$ and the reduction in $f(\alpha)$ can result in a decrease in the value of l_g.

The Seebeck coefficient value, S_g, has increased considerably in comparison with SnTe. The rise in S_g can be attributed mainly to the reduction in the carrier concentration. The value of Fermi energy, E_F, is less than that of undoped SnTe films and this is due to the reduction in carrier concentration.

The effective mass, m^*, has been reduced significantly in comparison with that of SnTe films and the m^* value has actually been reduced to $1.2m_0$ with addition of excess tin. In bulk SnTe it is a known fact that in the carrier concentration region 10^{20} to 10^{21} heavy holes are the majority carriers, and the total domination of a light hole starts at $n < 10^{19}\,\text{cm}^{-3}$.

TABLE I Comparison of the values of the different parameters evaluated for SnTe (10% excess tin) with that obtained for SnTe

Quantity	SnTe (10% excess tin)	SnTe
n	$4\text{–}5 \times 10^{20}\,\text{cm}^{-3}$	$10^{21}\,\text{cm}^{-3}$
ϱ_g	$4.5 \times 10^{-4}\,\Omega\text{cm}$	$4 \times 10^{-4}\,\Omega\text{cm}$
l_g	$4.7 \times 10^{-5}\,\text{cm}$	$8 \times 10^{-5}\,\text{cm}$
S_g	$44.5\,\mu\text{V K}^{-1}$	$39\,\mu\text{V K}^{-1}$
E_F	0.19 eV	0.2 eV
m^*	$1.2m_0$	$1.78m_0$
b	−0.3	−0.4

The values of effective mass for heavy holes and light holes are 1.5 to $2.0m_0$ and $0.4m_0$, respectively [33]. In the present case, with addition of tin the carrier concentration is reduced, and the reduction in m^* clearly indicates the transfer towards the light hole band. However, the value of m^* is still high enough to conclude that heavy holes are the majority charge carriers.

The change in the value of the scattering parameter from −0.4 to −0.3 in the case of tin-doped SnTe films, clearly indicates the reduction in lattice scattering. With the addition of tin atoms the lattice defects are also reduced, thus decreasing the lattice scattering. However, the values of b in both undoped and excess tin-doped SnTe film clearly indicate the dominance of lattice scattering and this must be the reason for the observed metallic behaviour of electrical transport properties.

4. Conclusions

Resistance and thermoelectric power variation with temperature of excess tin-doped SnTe films clearly indicate degenerate behaviour. On addition of tin the values of ϱ_g and S_g are increased. The values of E_F and m^* are reduced due to the reduction in carrier concentration. However, heavy holes are still the dominant charge carriers. The value of b suggests a clear decrease in lattice scattering.

References

1. L. ESAKI and P. J. STILES, *Phys. Rev. Lett.* **16** (1966) 1108.
2. A. G. MIKOLAICHUK and D. M. FREIK, *Sov. Phys. Solid State* **11** (1970) 2033.

3. D. M. FREIK, G. M. GAIDUCHOK, V. V. VOITKIV and S. P. OLES'KIV, *Sov. Phys. Crystallogr.* **16** (1970) 390.
4. T. C. HARMAN, "Physics of IV–VI Compounds and Alloys", edited by S. Rabi (Gordon and Breach, London, 1971) p. 141.
5. H. T. SAVAGE, *Phys. Rev.* **6** (1972) 2292.
6. N. J. PRADA and G. N. PRATT, *Phys. Rev. Lett.* **22** (1969) 180.
7. R. F. BREBRICK, *J. Phys. Chem. Solids* **24** (1963) 27.
8. B. A. EFINOVA, T. S. STAVISKAYA, L. S. STILBANS and L. M. SYSOERA, *Sov. Phys. Solid State* **1** (1959) 1217.
9. B. A. EFINOVA, V. I. KAIDANOV, B. YA. MOIZHES and I. A. CHERNIK, *ibid.* **7** (1966) 2032.
10. R. S. ALLGAIER and B. B. HOUSTON, *Phys. Rev.* **B5** (1970) 1004.
11. R. S. ALLGAIER and P. O. SCHIE, *Bull. Am. Phys. Soc.* **6** (1961) 436.
12. R. F. BREBRICK and A. J. STRAUSS, *Phys. Rev.* **131** (1963) 104.
13. K. L. I. KOBAYASHI, Y. KATO, Y. KATAYAMA and K. F. KONTSUBARA, *Solid State Commun.* **17** (1975) 875.
14. A. D. C. GRASSIE, J. A. AGAPITO and P. GONZALEZ, *J. Phys. C* **12** (1979) L925.
15. A. L. DAWAR, P. C. MATHUR, A. O. MOHAMMED and O. P. TANEJA, *Thin Solid Films* **82** (1981) 273.
16. K. FUCHS, *Proc. Camb. Phil. Soc.* **34** (1938) 100.
17. E. H. SONDHEIMER, *Adv. Phys.* **1** (1952) 1.
18. A. F. MAYADAS, M. SHATZKES and J. F. JANAK, *Appl. Phys. Lett.* **14** (1969) 345.
19. A. F. MAYADAS and M. SHATZKES, *Phys. Rev.* **B1** (1970) 1382.
20. C. R. TELLIER, A. J. TOSSER and C. BOUTRIT, *Thin Solid Films* **44** (1977) 201.
21. C. R. TELLIER, *ibid.* **51** 311 (1978).
22. C. R. TELLIER and A. J. TOSSER, *ibid.* **61** (1979) 349.
23. *Idem, ibid.* **70** (1980) 225.
24. C. R. TELLIER, C. R. PICHARD and A. J. TOSSER, *ibid.* **76** (1981) 129.
25. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *ibid.* **62** (1979) 189.
26. *Idem, Phys. Status Solidi* **A65** (1981) 327.
27. *Idem, J. Mater. Sci.* **15** (1980) 2236.
28. *Idem, ibid.* **15** (1980) 2991.
29. *Idem, Rev. Phys. Appl.* **14** (1979) 743.
30. E. E. MOLA and J. M. HERAS, *Thin Solid Films* **18** (1973) 137.
31. G. C. JAIN and B. S. VERMA, *ibid.* **15** (1973) 191.
32. N. GANESAN, PhD thesis, Indian Institute of Technology, Madras (1986).
33. L. M. ROGERS, *J. Phys. D.* **1** (1968) 845.

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