

Studies on Co-Sn-Te thin films

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Abstract. Electrical and galvanomagnetic properties of $\text{Co}_x\text{Sn}_{1-x}\text{Te}$ thin films have been studied. On the basis of small positive temperature coefficient of resistance, small and constant resistivity, low Hall coefficient and negligible magnetoresistance, it was concluded that CoTe-SnTe system is metallic. Discussion employing the Sondheimer's model further corroborated the metallic nature of the thin films.

Keywords. Electrical properties; galvanomagnetic properties; thin films; Co-Sn-Te alloys; Hall coefficient.

1. Introduction

Since the inception of solid state circuit technology, thin film devices have become an essential feature of integrated electronics. Transition metal chalcogenides, alloys and related compounds in the thin film state are potential device materials in micro-electronics. Several workers have reported the electrical and galvanomagnetic properties of SnTe in the bulk and thin film state. SnTe is variously described as a semi-conductor conforming to a two-valence band model (Allgaier and Scheie 1961; Brebrick and Strauss 1962; Houston and Allgaier 1964; Efimova *et al* 1965) or as a metal (Sagar and Miller 1962; Damon *et al* 1963). On the other hand, CoTe is a confirmed metal (Kamat Dalal 1972). Further, CoTe has the NiAs structure while SnTe exhibits the NaCl symmetry. Therefore, an interesting variation in structural, electrical and galvanomagnetic properties of CoTe-SnTe system might be expected. A preliminary report on CoSnTe_2 was published by Bamane and Biswas (1979). The present paper gives the details of our results.

2. Experimental

2.1 Preparation and X-ray analysis

Cobalt, tin and tellurium (each of 99.999% purity) were taken in atomic ratios 1:1:2, 1:3:4 and 1:7:8 respectively in an ultrasonically cleaned and completely dried quartz capsules, which were sealed at a dynamic air pressure of $< 10^{-5}$ torr and heated for 60 hr at 900°C and quenched in liquid nitrogen. Compounds thus formed were carefully pulverised to 200–300 mesh grain size and used to prepare thin films.

X-ray powder diffraction patterns were recorded on a Philips X-ray diffractometer (model PW 1010) and employing CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) with nickel filter.

All the compounds were found to possess the NaCl structure with almost the same lattice parameter:

$$\text{CoTe} : \text{SnTe} \quad (\text{CoSnTe}_2) \quad a = 6.32 \pm 0.02 \text{ \AA}$$

$$\text{CoTe} : 3\text{SnTe} \quad (\text{CoSn}_3\text{Te}_4) \quad a = 6.33 \pm 0.02 \text{ \AA}$$

$$\text{CoTe} : 7\text{SnTe} \quad (\text{CoSn}_7\text{Te}_8) \quad a = 6.34 \pm 0.02 \text{ \AA}$$

$$\text{SnTe} \quad a = 6.31 \pm 0.02 \text{ \AA}$$

It is difficult to explain the close similarity in the lattice parameters at the present juncture.

2.2 Preparation and properties of thin films

In order to minimise problems arising out of vapour pressure differences in the constituents, the flash evaporation technique was employed. The pulverised powder was allowed to fall onto a tungsten strip maintained at $\sim 2000^\circ\text{C}$. Clean microscope glass slides having flat, smooth and scratch-free surfaces were used as substrates. A typical deposition rate of $10 \text{ \AA}/\text{sec}$ was maintained. The films were annealed *in situ* at 300°C for ~ 7 hr. X-ray diffractograms of sufficiently thick films were recorded to ensure that no degradation during vacuum evaporation had taken place.

Transmission electron micrographs (TEM) and selected area diffraction (SAD) patterns were recorded (Philips electron microscope, model EM 301) to assess the crystalline nature of the samples.

The film thickness was measured using an oscillating (6 mHz) quartz crystal thickness monitor, while the calibration was performed with a multiple-beam interferometer (precision $\pm 10\%$).

I-V characteristics were checked over the ranges of 0–1 mA and 0–350 mV.D.C. resistance/resistivity was measured by the conventional four-probe method. For temperature coefficient of resistance (TCR) measurements, resistance at room temperature and ice temperature was measured at a pressure of 10^{-2} torr using indium contacts.

Seebeck coefficient was measured at a dynamic air pressure of $< 10^{-5}$ torr. Hall coefficient (R_H) and magnetoresistance were measured by imposing a direct and reverse magnetic field by changing the polarity of magnet and feeding direct and reverse currents through the film by changing its direction and subsequently taking the average. Magnetic fields up to 23 kOe were employed.

The details of the experimental apparatus have been described elsewhere (Bamane 1980).

3. Results and discussion

Figures 1–5 depict the results of the electrical and galvanomagnetic properties of CoSnTe_2 , CoSn_3Te_4 , CoSn_7Te_8 and SnTe respectively.

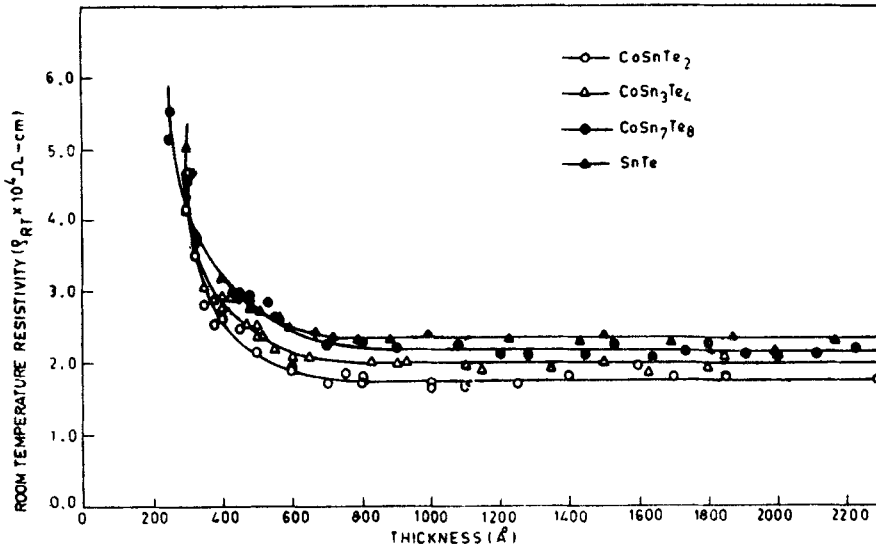


Figure 1. Room temperature resistivity variation with film thickness for Co-Sn-Te system.

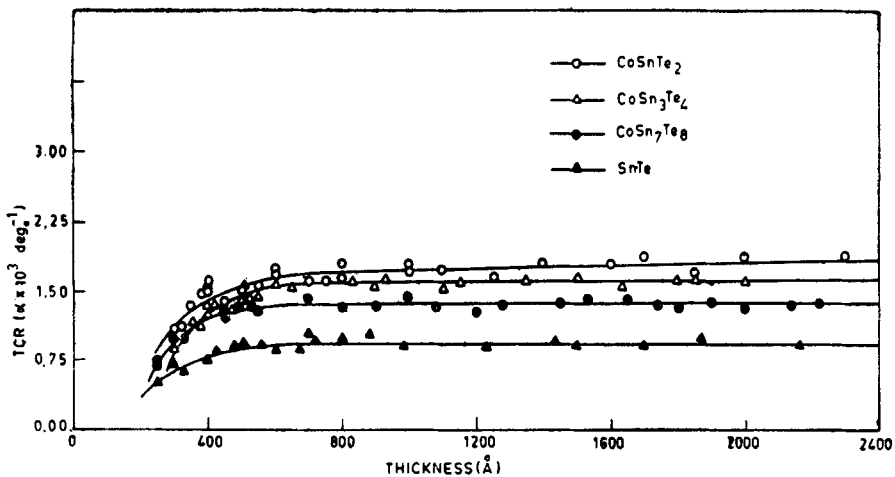


Figure 2. Temperature coefficient of resistance variation with film thickness for Co-Sn-Te system.

3.1 Thickness dependence of resistivity (ρ) and temperature coefficient of resistance (TCR)

A noticeable scatter was observed in the experimental data (cf figures 1 and 2). This is understandable in view of the subtle variations in film composition, degree of oxidation or contamination in different runs of the evaporation process. However, it is gratifying to note that the scatter is not unusually large so that reasonably smooth curves could be drawn through the experimental points. It may be seen that a sharp change in ρ and TCR occurs below a certain thickness range.

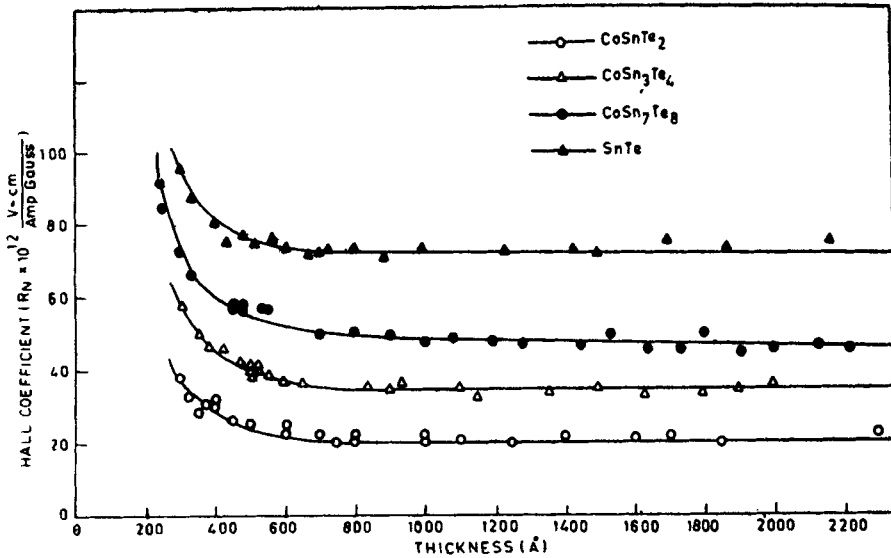


Figure 3. Hall coefficient variation with film thickness for Co-Sn-Te system.

It may be recalled that the Matthiessen's rule states that

$$\rho_{\text{film}} = \rho_{\text{ideal bulk}} + \rho_{\text{impurities}} + \rho_{\text{imperfections}} + \rho_{\text{thickness}}$$

where the last term arises because some of the carrier mean free paths (MFP) get reduced by termination at the film surface, when the thickness becomes comparable to the carrier MFP. In order to analyse the interaction of electrons with surface, one should determine whether the reflections are specular, diffuse or a combination of the two. Sondheimer (1952) has developed a theory for diffuse scattering by considering an electron at an arbitrary point in the film and noting what would happen if its velocity were in a certain direction. He then integrated over all positions in the film and over all directions for one velocity and showed that

$$\rho_f/\rho_0 = 1 + \frac{3}{8K} \text{ for } K \gg 0.1$$

where ρ_f is the film resistivity, ρ_0 the bulk resistivity and $K = d/l_0$ with d the film thickness and l_0 the bulk mean free path of the carrier. Thus in the region of validity of the 'thick film' approximation

$$\rho_f \cdot d = \rho_0 \cdot d + \frac{3 \rho_0 l_0}{8} \quad (1)$$

Therefore, the $\rho_f \cdot d$ vs d plot should be linear. This is a convenient method for determining l_0 and ρ_0 for a set of films of varying thickness, provided that they all have smooth surfaces with no agglomeration.

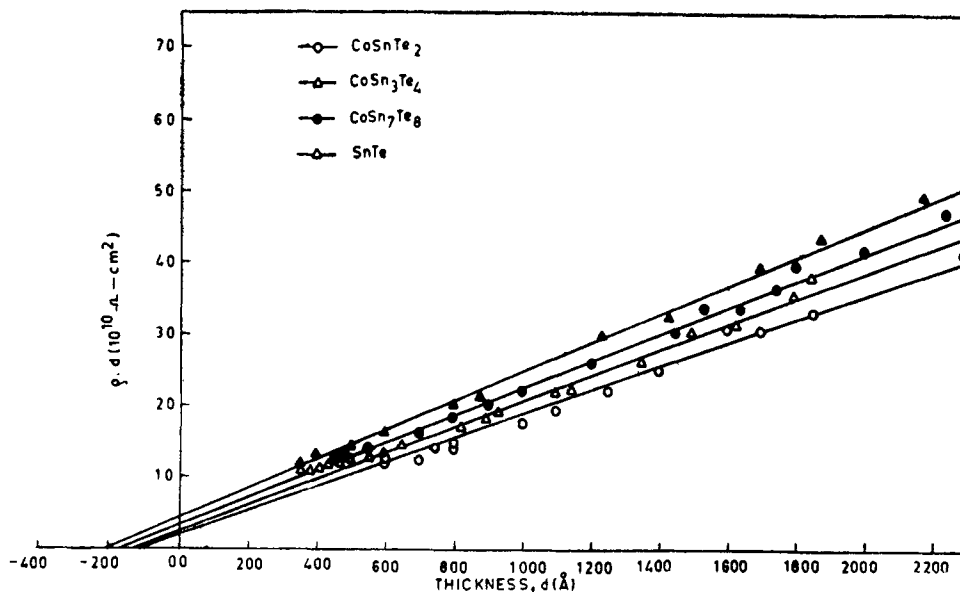


Figure 4. $\rho_f \cdot d$ vs d plots for Co-Sn-Te system.

Figure 4 shows that $\rho_f \cdot d$ vs d plots are indeed linear and the calculated values of l_0 and ρ_0 are

$$\text{CoSnTe}_2 \quad l_0 = 345 \text{ \AA} ; \rho_0 = 1.7 \times 10^{-4} \text{ ohm-cm}$$

$$\text{CoSn}_3\text{Te}_4 = 400 \text{ \AA} ; \rho_0 = 1.9 \times 10^{-4} \text{ ohm-cm}$$

$$\text{CoSn}_7\text{Te}_8 = 400 \text{ \AA} ; \rho_0 = 2.1 \times 10^{-4} \text{ ohm-cm}$$

$$\text{SnTe} = 560 \text{ \AA} ; \rho_0 = 2.2 \times 10^{-4} \text{ ohm-cm}$$

respectively.

TEM and SAD patterns indicated that all the compositions were primarily polycrystalline; however, the validity of the Sondheimer theory is independent of whether the resistivity in the bulk is caused by phonons, impurities, grain boundaries or anything else.

3.2 Thickness dependence of Seebeck coefficient

Variation of Seebeck coefficient (S) as a function of film thickness for typical compositions is shown in table 1. Surprisingly, S values were consistently positive, *i.e.*, holes were the majority charge carriers. The observed p -type behaviour may be explained by presuming distortion of the Fermi surface. According to Mott and Jones (1958)

$$S = - \frac{\pi^2 k^2 T}{3e} \left| \frac{\partial \log \sigma(E)}{\partial E} \right|_{E=E_F}$$

Table 1. Seebeck coefficient for some typical films of Co-Sn-Te system.

CoSnTe ₂		CoSn ₃ Te ₄		CoSn ₇ Te ₈		SnTe	
Film thickness (Å)	S (μV/°C)	Film thickness (Å)	S (μV/°C)	Film thickness (Å)	S (μV/°C)	Film thickness (Å)	S (μV/°C)
225	15	250	30	300	35	250	48
500	20	550	38	520	42	530	65
900	20	900	40	980	45	980	61
1310	22	1320	40	1380	47	1350	62
1620	20	1650	40	1660	45	1700	63
2000	22	2050	40	2150	45	2050	64

From the observation that S is positive for copper at high temperatures, Gold *et al* (1960) inferred that $\partial\sigma(E)/\partial E$ is of opposite sign to that predicted for free electrons. They believed that this sign reversal is connected with the Fermi surface distorting to the extent of contacting the Brillouin zone boundary. S is also positive for silver and gold where the Fermi surface is known to contact the zone faces.

The S value was found to decrease in the order CoSn₇Te₈-CoSn₃Te₄-CoSnTe₂. This may be considered as indicative of increasing metallic character with increasing CoTe content. Further evidence for metallic behaviour is obtained from linearity of $S.d$ vs d plots (cf figure 5).

3.3 Thickness dependence of Hall coefficient

The Hall coefficient (R_H) was positive for all the compositions, in agreement with Seebeck coefficient studies. Further, it increased from CoSnTe₂-CoSn₃Te₄-CoSn₇Te₈ films having the thickness range from 250-2300 Å. The low R_H values are typical of metals. For example $R_H \sim 10 \times 10^{-12}$ Vcm/A gauss for potassium (Kittel 1971).

3.4 Magnetoresistance

There was no observable change in the resistance on applying magnetic fields up to 24 kOe for all the films of different compositions. This is understandable because, in metallic materials, magnetoresistance is a second order effect.

4. Conclusion

The system CoTe-SnTe is almost metallic and this conclusion is based on the following experimental findings:

- (i) The temperature coefficient of resistance is positive and has a small value ($\sim 10^{-3}/^\circ\text{C}$).

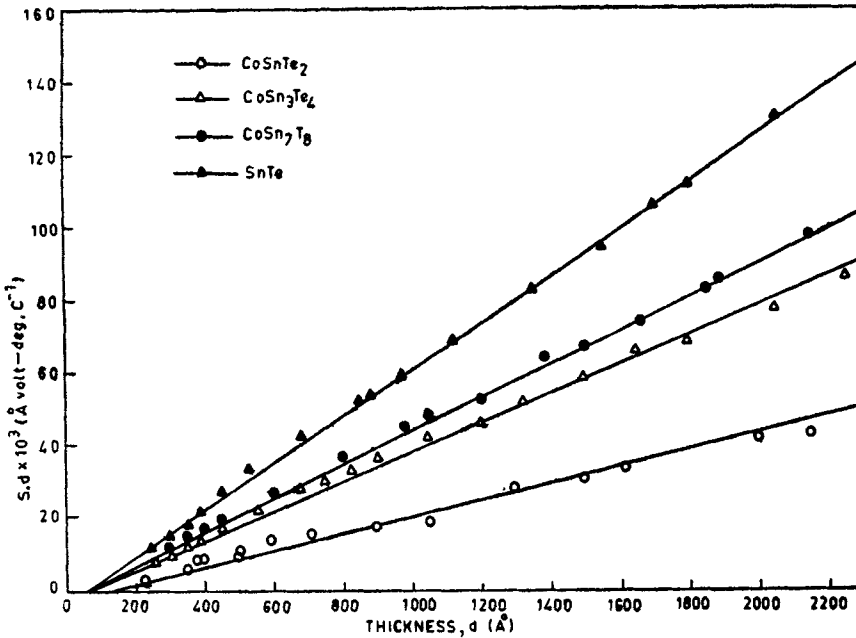


Figure 5. $S.d$ vs d plots for Co-Sn-Te system.

- (ii) The resistivity values are constant at low values $\sim 10^{-4}$ ohm-cm. Further, the charge carrier concentration is high ($\sim 10^{19}/\text{cm}^3$).
- (iii) The Hall coefficient, R_H is of the same order of magnitude ($\sim 10^{-11}/\text{Vcm/A gauss}$) as that of typical metals like potassium.
- (iv) No magnetoresistance is observed.

Further, transmission electron micrographs (TEM) and selected area diffraction patterns (SAD) indicated polycrystalline nature of the films. Therefore, Sondheimer's theoretical model predicting the variation of electrical resistivity with film thickness could be tested. Good agreement with the theoretical predictions not only indicated metallic nature of the Co-Sn-Te films but also enabled determination of the bulk mean free path for the charge carriers.

In spite of the above, the majority charge carriers were not electrons but holes, both from Seebeck coefficient and Hall effect studies. This observation may be attributed to the distortion of the Fermi surface, presumably to the extent of touching the Brillouin zone boundary.

In conclusion, it may be stated that since the electrical and galvanomagnetic properties of SnTe in the pure state as well as in the CoTe-SnTe system indicate metallic character, it supports the observations of Sagar and Miller (1962) and Damon *et al* (1963); the two-valence band model does not seem to be applicable.

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