

Electrical properties of tin-chalcogenide films*

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A study has been made on some electrical properties such as resistivity (ρ), activation energy (ΔE), thermoelectric power (ϵ), temperature coefficient of resistance (TCR) etc., of vacuum deposited films of SnSe, Sn₂Se₃, SnS and SnTe. While the selenides and sulphide in film-state behaved as semiconductors, the telluride had a semi-metal character. The decrease of resistance of SnSe, Sn₂Se₃ and SnS films with an increase of T_{max} appears to be associated with the gradual phase change occurring in them.

INTRODUCTION

In a series of papers, Goswami and his coworkers (1962, 1964, 1966) have shown that vacuum deposited films of semiconducting materials behave often in a different manner from the bulk and also that some of the semiconducting properties are considerably affected by variables such as rate of deposition, substrate temperature, thickness, annealing etc. The following is a report of our study on vacuum deposited films of SnSe, Sn₂Se₃, SnS and SnTe.

EXPERIMENTAL

The selenides and telluride of tin were prepared by mixing the constituent elements in their stoichiometric proportions and melting the mixture after sealing them in vacuo ($\approx 10^{-5}$ mm of Hg) in silica tubes in a furnace. The heating of the samples was carried out in stages and the final temperature was about 50°C above the melting point of the individual compounds. The molten samples were kept at these temperatures for about 4-6 hours while the contents were mixed by occasional shaking. These were then removed and suddenly plunged into water. Solid compounds thus obtained were then used for evaporation in vacuo ($\approx 10^{-5}$ mm of Hg).

SnS powder was, however, prepared by passing a stream of H₂S gas through a solution of stannous chloride obtained by warming in HCl (A.R.) containing a small amount of metallic tin, as described previously (Dadachhane & Goswami 1964). The precipitate thus formed was then washed with distilled water till free from chloride, then with alcohol and finally dried in vacuo.

The chalcogenides of tin thus prepared were evaporated from micro-conical silica baskets and deposited on glass substrates of dimensions 4 cm × 0.5 cm in the usual way. Specimens of different thicknesses were obtained not only from the same set of evaporation, but also from

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different sets. The thickness of each film was estimated from the difference in weight before and after deposition and from the known area of deposit, assuming that the density of deposited film is the same as that of the bulk material.

The experimental set-up and techniques for measuring resistivity (ρ), thermoelectric power (α) etc., was similar to those described previously (Goswami & Jog 1964). Resistance measurements were carried out both by ac and dc methods with the help of suitable bridges during heating and cooling cycles. Heating of specimens was made by an external heater provided with a control. Thermoelectric power was determined from the potential difference due to the thermal gradient, created with the help of two micro-heaters attached at the two ends of the experimental film. The emf developed was measured by a vernier potentiometer and temperatures at different positions of film by chromel-p-alumel thermocouples. In the case of high resistance films, ambient temperature was also raised

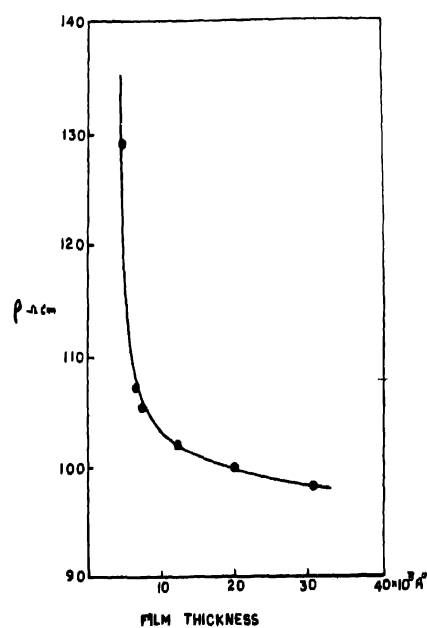


Figure 1. Variation of resistivity with film-thickness.

by an external heater to a measurable emf. All measurements of resistance, thermoelectric power etc., were carried out in vacuo ($\approx 10^{-5}$ mm of Hg) to minimise the oxidation or adsorption of gases.

RESULTS

(a) Resistivity (ρ) and film thickness (t)

The variation of ρ with T was measured for all the above chalcogenide films and figure 1 shows a typical graph for SnSe films. Similar was also the nature of Sn_2Se_3 , SnS and SnTe films. It is seen that ρ is very much dependent on film thickness.

(b) Temperature effect on Resistance (R) and activation energy (ΔE)

(i) SnSe films

A typical $\log R$ vs $1/T$ graph for the first heating cycle of an unannealed film ($\approx 31000 \text{ \AA}$) beyond the range of discontinuity temperature T_d , (Coswami & Jog 1964) is shown in figure 2. It is seen that the curve has two distinct slopes in two regions of temperatures, A and B, while an additional

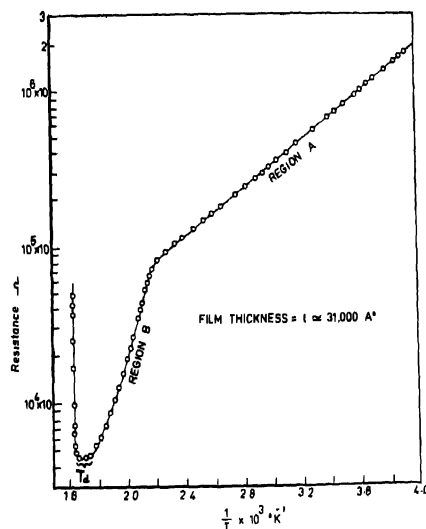


Figure 2. Variation of $\log R$ vs $1/T$ for an unannealed SnSe film ($t \approx 31,000 \text{ \AA}$)

change occurs at the T_d region, the last being no doubt due to a break in the continuity of the film. The change of slope of the graph from A to B

region occurred between 150°C to $\approx 180^{\circ}\text{C}$, depending upon the film-thickness, T_d being $\approx 310^{\circ}\text{C}$.

In some preliminary experiments, contrary to our general expectation, resistance of any film during heating and cooling cycles was considerably dependent on the temperature of annealing. Even simply heating specimens in vacuo to any temperature beyond the region A, caused a significant change in the cooling path, which was quite different from the heating one. Subsequent heating and cooling paths followed the initial cooling path provided the temperature did not exceed the maximum temperature (hereafter called T_{max}) reached in the first heating cycle. These features of $\log R$ vs $1/T$ curves are quite in contrast with those of other vacuum deposited films previously reported (Goswami & Jog 1964, Goswami & Koli 1966, Deokar & Goswami 1966). The temperature effect was there-

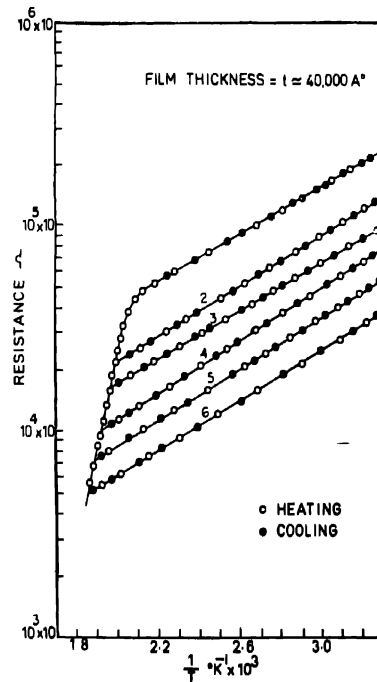


Figure 3. Variation of resistance with T_{max} of Sn_1Se_3 films.

fore studied by measuring film resistance under the following conditions viz. (i) in the temperature region A, during both the heating and cooling cycles repeating several times with varying T_{max} upto the upper limit of region A ; (ii) raising T_{max} to any temperature beyond the region A and continuing the measurements as in (i) ; (iii) increasing T_{max} after measurements as in (ii) in the region B and continuing the process.

The results of the above measurements are shown in figure 3. Under the condition (i), the curve follows the path 1, for all repeated heating and cooling cycles, even when T_{max} varies from room temperature to the maximum temperature of the range A thus suggesting that heating and cooling paths in this region were more or less the same and independent of T_{max} . For the condition (ii), on the other hand, the cooling path differed considerably from the first heating one. Subsequent heating and cooling paths were the same as the initial cooling path and it was characteristic of T_{max} as shown by curves 2, 3, 4, 5 or 6 (figure 3). With increasing T_{max} as in (iii) the cooling paths changed from 2 to 5, each time resistance of the film decreasing with the rise of T_{max} . It is also seen that

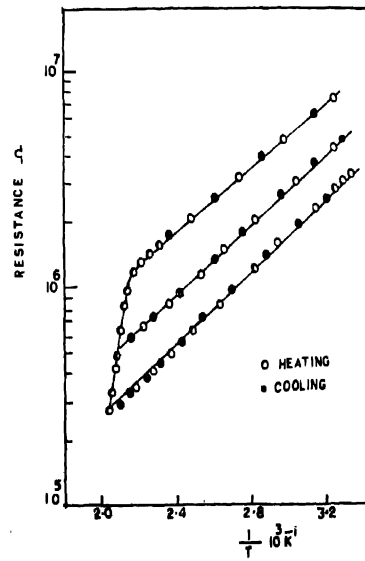


Figure 4. Variation of resistance with T_{max} of Sn_3Se_3 films.

the effect of increasing T_{max} was a new $\log R$ vs $1/T$ curve independent of the previous history of heating of the sample. Even a slight variation of T_{max} by $5-7^\circ\text{C}$ was sufficient to show a significant change in the above curve. It is interesting to mention that any change in T_{max} or time of heating in the region A had no effect on the path.

Similar results were also observed for different film thicknesses, though the value of the slope slightly differed, thinner films having higher values. The activation energy thus observed for SnSe films varied from 0.30 eV to 0.23 eV for film thicknesses ranging between $15,000\text{\AA}$ to $\approx 40,000\text{\AA}$.

(ii) Sn_2Se_3 film

Figure 4 shows $\log R$ vs $1/T$ curves for a film ($\approx 32,000\text{\AA}$), for different T_{max} . Here also it is seen that paths changed considerably with T_{max} . Similar results were also obtained for other film-thicknesses. T_d and the change of slope were found to occur in the same range as for SnSe films.

(iii) SnS films

These films had higher resistances compared to selenide films of corresponding thicknesses. Figure 5 shows the variation of $\log R$ vs $1/T$

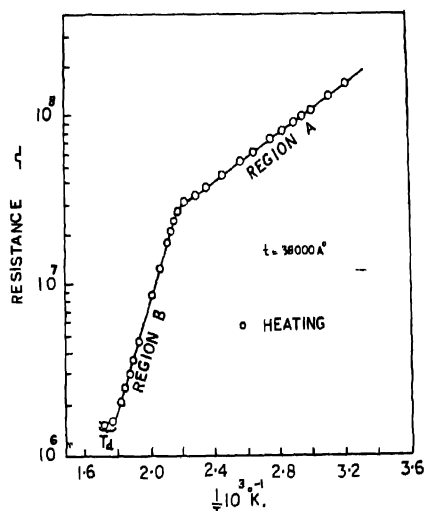


Figure 5. Variation of $\log R$ vs $1/T$ of SnS films (unannealed).

for a film of thickness $\approx 38,000\text{\AA}$. The change of paths with T_{max} was also observed for these films.

(iv) *SnTe* films

Unlike the selenides and sulphide, resistance of these films increased, though slightly, with the rise of temperature. Figure 6 shows the variation

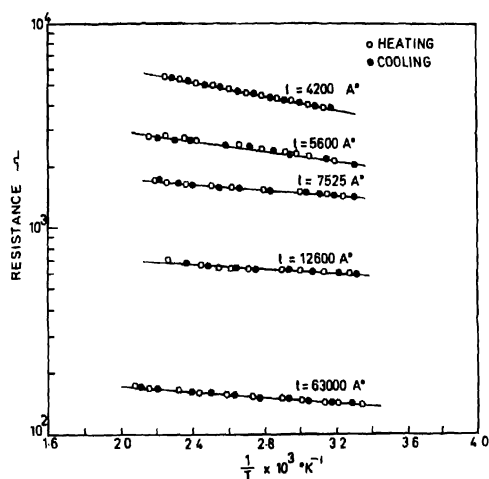


Figure 6. Variation of R vs $1/T$ of SnTe films.

of $\log R$ vs $1/T$ for different film thicknesses. It is interesting to note that T_{max} had no effect at all on the heating or cooling paths.

(c) *Thermoelectric power* (α)

For selenides and sulphide films ambient temperature was raised to 150°C and the thermoelectric power was measured in the usual way. Figure 7 shows a typical emf vs temperature difference curve. Similar graphs were also obtained for different film-thicknesses. For SnTe films also similar graphs were obtained even when the ambient temperature was the same as the room temperature. It may be mentioned here that α remained more or less constant for each of the compounds even

though the thickness range varied from $15,000 \text{ \AA}$ to $\simeq 40,000 \text{ \AA}$ and the values were found to be about 160, 150 and $42 \mu\text{V}/^\circ\text{C}$ respectively, for SnS, Sn_2Se_3 , SnS and SnTe films.

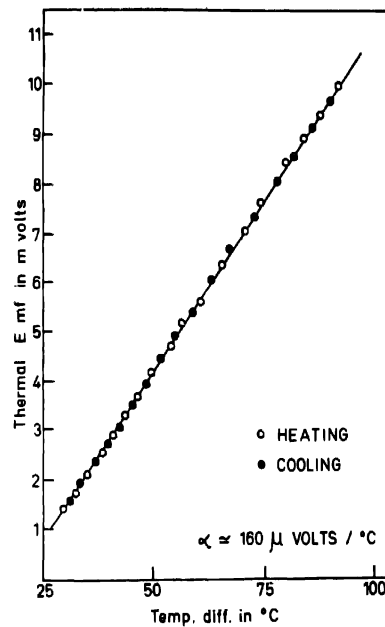


Figure 7. Thermal emf vs temperature difference between two ends of SnSe film.

(d) *Temperature coefficient of resistance (TCR)*

TCR given by $\left(\frac{1}{R} \cdot \frac{dR}{dT}\right)$ was calculated at different temperatures from the graph of resistance vs temperature. Figures 8–10 show the variation of TCR with temperature for selenides and sulphide films. It will be seen that TCR was negative in all cases. Another feature of above graphs is that, the magnitude of TCR decreased with the increase of temperature

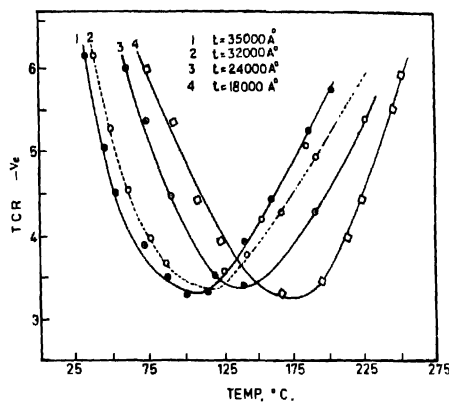


Figure 8. Variation of TCR with temperature of SnSe films.

upto a minimum value and again increased with a further rise of temperature, the exact temperature region for this change, however, depended on the film-thickness. TCR for SnTe films was found to be positive.

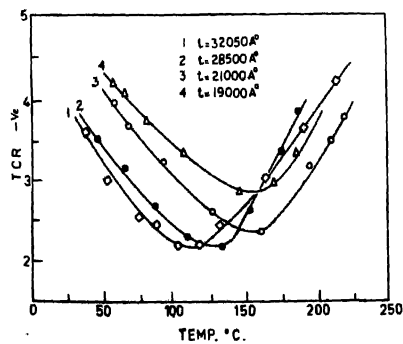


Figure 9. Variation of TCR with temperature of Sn₄Se₃ films.

(e) *Electron diffraction study*

The deposit films were also examined by electron diffraction methods. It was observed that similar to SnS (Badacchape & Goswami 1964), the

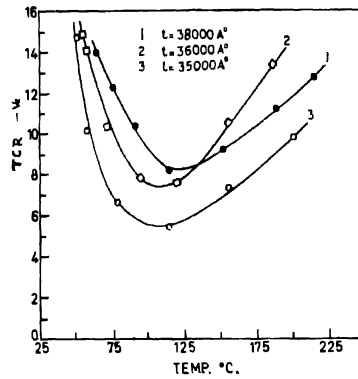


Figure 10. Variation of TCR with temperature of SnS films.

selenide SnSe developed an orthorhombic structure (figure 11) when deposited at room temperature. But at a higher substrate temperature say about 300°C and above, a cubic phase along with the orthorhombic

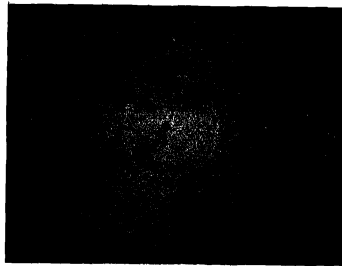


Figure 11. Polycrystalline SnSe (orthorhombic).

was formed (figure 12). This transformation was found to be irreversible as was the case for SnS.



Figure 12. Single crystal SnSe (cubic & orthorhombic)

DISCUSSION

From the above study it is seen that films of SnSe, Sn_2Se_3 and SnS are semiconducting in nature as shown by the decrease of resistance with the increase of temperature and by the high value of negative TCR. But the reverse is the case for SnTe films, showing a semi-metallic behaviour. The distinguishing feature of selenides and sulphide films in contrast with telluride is the dependence of the heating and cooling paths on T_{max} beyond the region A. This effect does not seem to be related to the annealing of defects such as dislocations, microtwins etc., which are invariably present in evaporated films, since in that case heating to any T_{max} such as 2 or 3 in the region B would not affect the heating as well as the cooling paths, as shown in curves 4, 5 or 6 when T_{max} was further raised (cf. figure 3). The temperature effects observed for SnSe, Sn_2Se_3 and SnS appear to be associated with a phase change occurring during the heating of deposits. Our observation of transformation of orthorhombic SnSe to a cubic phase at higher temperature and also of SnS (Dadachape & Goswami 1964) lends support to this view. Since the phase change was an irreversible process and dependent on temperature, the shift of $\log R$ vs $1/T$ curve with T_{max} can easily be understood. It seems likely that similar process may also take place for Sn_2Se_3 films. It may be mentioned here that no new phase could be observed for SnTe films even though the deposition was made at various substrate temperatures.

There is no satisfactory theory as yet to explain the various semiconducting behaviours of vacuum deposited films having thicknesses in the ranges studied in this paper. Island structure theory (Naugebauer 1962, 1964) proposed for very thin films, takes into account the growth process leading to the formation of discrete islands of average radius (r) separated by a mean distance (d). With the increase of film thickness there will be an increase in island size r and a corresponding decrease of d . The expression for conductivity (σ) takes these into account. During our studies of resistance of many vacuum deposited films of low thicknesses it was observed that the activation energy changed with film thickness, thinner films having higher values (Goswami & Jog 1964). Surprisingly enough similar trend was also observed in the present cases, where island structure theory is not valid as these films are no longer discontinuous. The variation of TCR with temperature in thicker films is similar to those of very thin films.

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