JOURNAL OF MATERIALS SCIENCE 22 (1987) 3522–3528

Electrical conductivity and thermoelectric power of amorphous Sb_2Te_3 thin films and amorphous–crystalline transition

V. DAMODARA DAS, N. SOUNDARARAJAN, MANJUNATHA PATTABI
Thin Film Laboratory, Department of Physics, Indian Institute of Technology, Madras 600 036, India

The results of electrical conductivity and thermoelectric studies on antimony telluride, a promising thermoelectric material, in the thin film state are reported. Films were vacuum-deposited on to clean glass substrates with thickness between 50 and 200 nm and studied in the temperature interval 300 to 470 K. On heating the as-grown films, there is a sharp fall both in the Seebeck coefficient and the electrical resistivity at around 340 to 370 K for all the films. This is attributed to an amorphous to crystalline transition, which is confirmed by X-ray diffractogram and electron diffraction patterns.

1. Introduction

Antimony telluride is a narrow band gap semiconductor and has been the subject of great interest during recent years because of its potential application as a thermoelectric material. However, little work has been carried out on thin films of Sb_2Te_3.

Rajagopalan and Ghosh [1] measured the Hall constant, the resistivity and the Seebeck coefficient of thin films 160 to 800 nm thick. They found that all the above parameters were thickness dependent. From their studies, it was found that thin films also were p-type. Gadgil and Goswami [2] studied the epitaxial growth of thin films on single-crystal substrates such as mica and rocksalt, while Kremnev *et al.* [3] investigated the structure changes as a function of substrate temperature. Gol'tsman and Komissarchik [4], Boikov *et al.* [5], and Lidorenko *et al.* [6] studied the transport properties of thin films of solid solutions of antimony telluride and bismuth telluride. It is seen from the above that only a very limited amount of work has been carried out on Sb_2Te_3 thin films, especially with respect to the phase transition in them and also the thickness and temperature dependence of electrical conductivity and thermoelectric power. The present studies were carried out in an attempt to make a detailed analysis of the behaviour regarding the phase transition in Sb_2Te_3 thin films.

It is known that the as-grown antimony telluride films undergo irreversible structural changes. Therefore the influence of the structural changes over the transport properties, such as the Seebeck coefficient and the electrical resistivity, can be understood from studies of the Seebeck coefficient and resistivity of unannealed films as a function of temperature. Therefore, Seebeck coefficient and resistivity of unannealed films of different thicknesses were studied in the temperature interval 300 to 470 K. From these studies and also X-ray and electron diffraction studies, it was found that the as-grown films were amorphous and underwent an amorphous–crystalline transition when heated to around 350 K.

2. Experimental techniques

Antimony telluride films were prepared by the evaporation of Sb_2Te_3 alloy. The films were of different thicknesses varying from 50 to 200 nm. They were prepared at a pressure of about 2×10^{-5} torr using a conventional vacuum system, and were grown over well-cleaned glass substrates held at room temperature (about 300 K) during deposition. The substrates were kept at a distance of 30 cm vertically above the evaporation source. The films were deposited at a constant rate of 1 nm sec^{-1}, and their dimensions were 3.0 cm × 1.0 cm × t cm for the electrical conductivity measurements and 6.5 cm × 0.5 cm × t cm for the Seebeck coefficient measurements, where t is the thickness of the film. In each deposition a given quantity of the Sb_2Te_3 alloy was taken in the boat and this material was completely evaporated to avoid fractionation. Tin contact film was used for conductivity measurements as silver and copper films were found to react with antimony telluride films at the areas of contact. The films of a given thickness for the Seebeck coefficient and resistivity measurements were prepared in a single evaporation using suitable masks.

The Seebeck coefficient and the electrical resistivity measurements were carried out on unannealed films in a high vacuum of 2×10^{-5} torr. To determine the Seebeck coefficient, the integral method was employed, in which the thermal e.m.f. developed because of the temperature gradient across the specimen was measured as a function of temperature difference between the ends, keeping the cold end at a constant temperature. The Seebeck coefficient, the derivative of the developed thermal e.m.f. function with respect to temperature, was calculated at different temperatures using spline functions which are local. Both the temperature and the thermal e.m.f.

0022–2461/87 $03.00 + .12

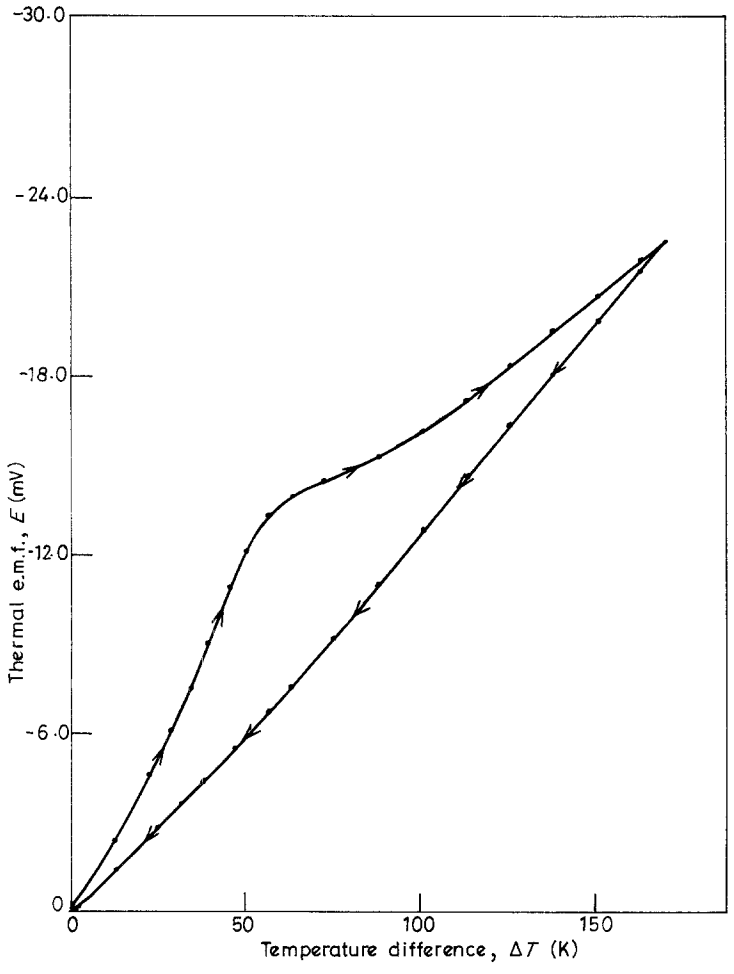

Figure 1 The variation of thermal e.m.f. as a function of temperature difference for unannealed film of thickness 107 nm during heating and cooling cycles.

were measured using potentiometers and sensitive null detectors (10^{-9} A/div.). The thermal e.m.f. was measured to within an accuracy of 1 μV. The measurements were taken in the temperature range 300 to 470 K for every variation of 2 K.

The electrical resistance was measured in the temperature interval 300 to 470 K for each step of ~ 2 K both during heating and cooling. A Keithley electrometer (610 C type) and a Wheatstone network were used to record the resistance. When the resistance was in the MΩ range, an electrometer was used to measure it, but if the resistance was in the kΩ range, the Wheatstone network was used. When the Keithley electrometer was used, the measurements were accurate to 1%. When the Wheatstone network was used the accuracy was 0.1% to 1% depending on the resistance. The unannealed films were examined in the electron microscope using low and high beam current densities and also after annealing. The corresponding electron diffraction patterns (Figs 6b, 7b, 8b) do not show any rings corresponding to oxidation of the alloy or its components.

3. Results

Fig. 1 shows the thermal e.m.f. data on an unannealed Sb_2Te_3 film of thickness 107 nm during the heating and cooling cycles as a function of temperature difference. The thermal e.m.f. values during heating and cooling are different, confirming that the unannealed film undergoes an irreversible transformation during heating. The developed e.m.f. measured with respect to copper is negative, and therefore, the Seebeck coefficient is positive. The Seebeck coefficient was calculated from the thermal e.m.f. data by finding the derivative as a function of temperature. Fig. 2 shows a plot of the variation of Seebeck coefficient for the unannealed film of thickness 107 nm during heating and cooling cycles as a function of temperature. It can be seen from the figure that the thermoelectric power (which is positive) increases initially as a function of temperature, reaches a maximum value and then falls sharply to a very low value (still positive) in a very narrow range of temperature and then again increases with increasing temperature. While cooling, there is a monotonic uniform decrease of thermoelectric power with a decrease in temperature.

The variation of thermal e.m.f. as a function of temperature difference for unannealed films of different thicknesses during the heating cycle is shown in Fig. 3. Similarly, the temperature dependence of the Seebeck coefficient is plotted in Fig. 4 for the above unannealed films during the heating cycle. The Seebeck coefficient is positive in all cases. One can see that there is a sharp decrease of the Seebeck coefficient at around 340 to 370 K for all films.

The variation of log resistivity as a function of temperature for unannealed films during heating and cooling cycles is shown in Fig. 5. It is interesting to note that here also there is a sharp fall in the resistivity around the same temperatures (between 340 and 370 K) during heating, while during cooling, resistivity increases monotonically with a decrease of temperature without any singularities. Figs 6a, b and 7a, b show, respectively, typical electron micrographs and

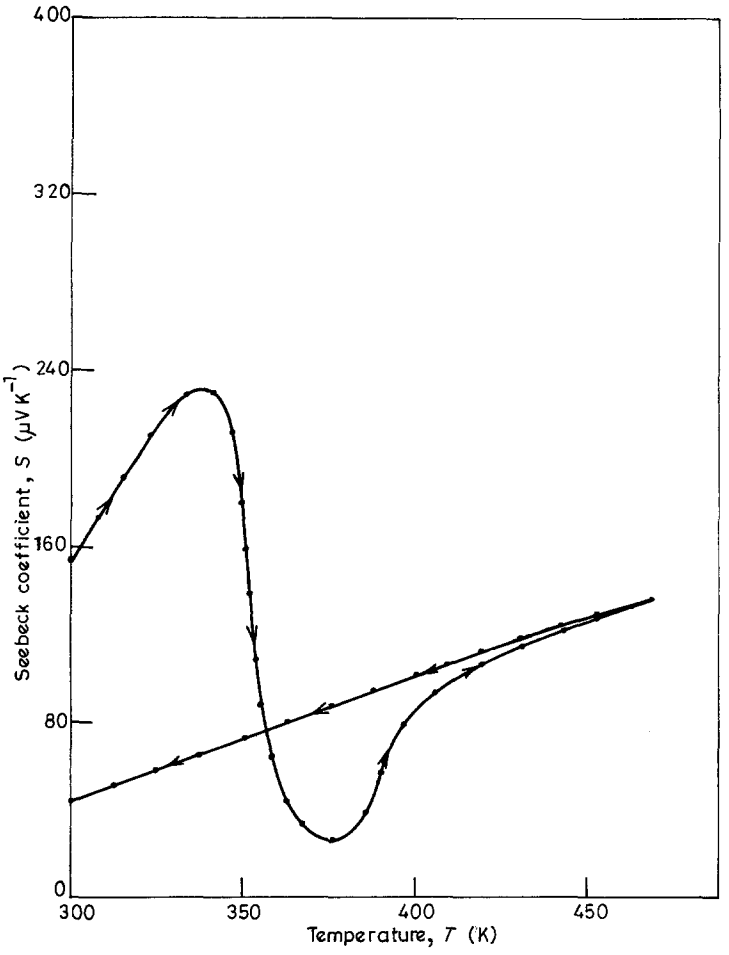

Figure 2 The variation of Seebeck coefficient as a function of temperature for unannealed film of thickness 107 nm during heating and cooling cycles.

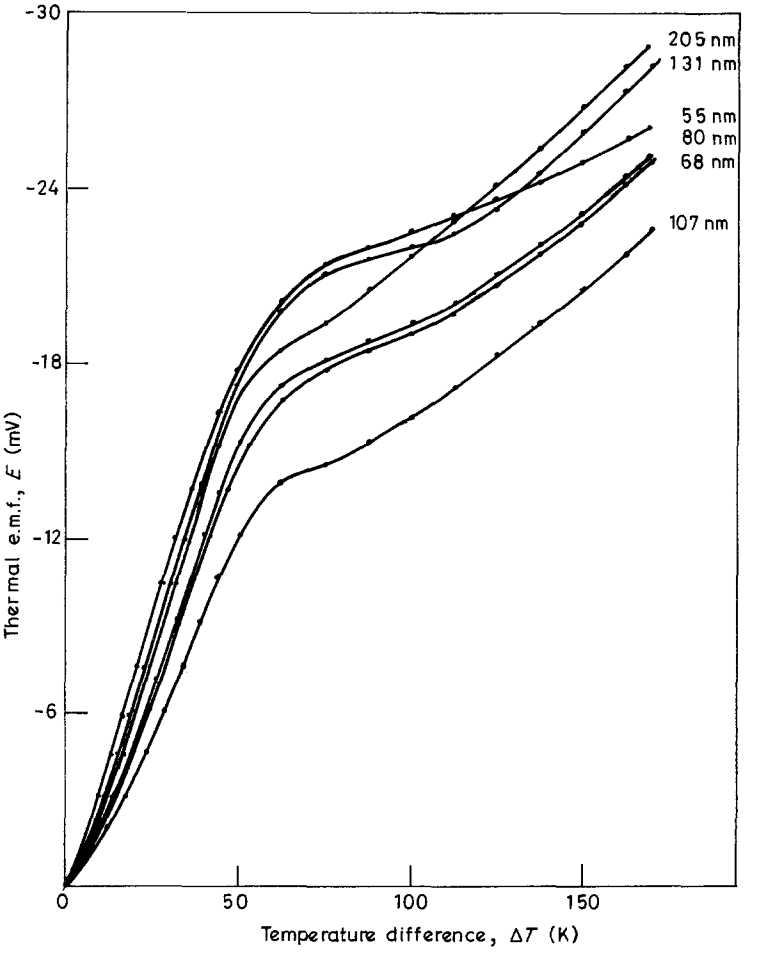

Figure 3 The variation of thermal e.m.f. as a function of temperature difference for unannealed films of different thicknesses during heating cycle.

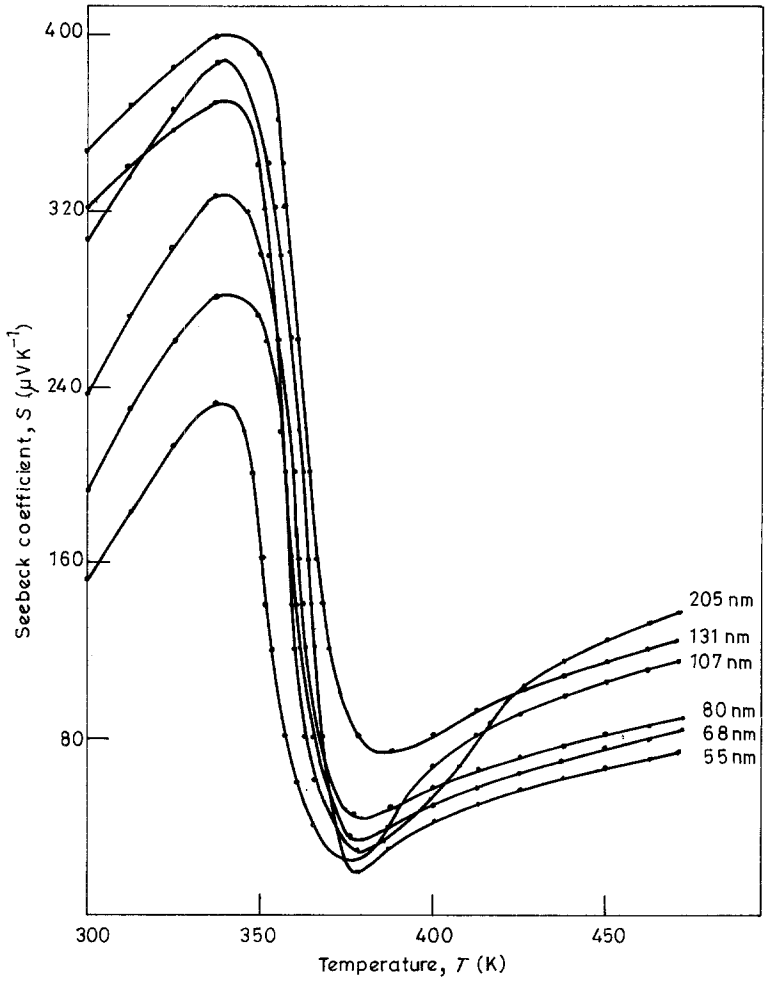

Figure 4 The variation of Seebeck coefficient as a function of temperature for unannealed films of different thicknesses during heating cycle.

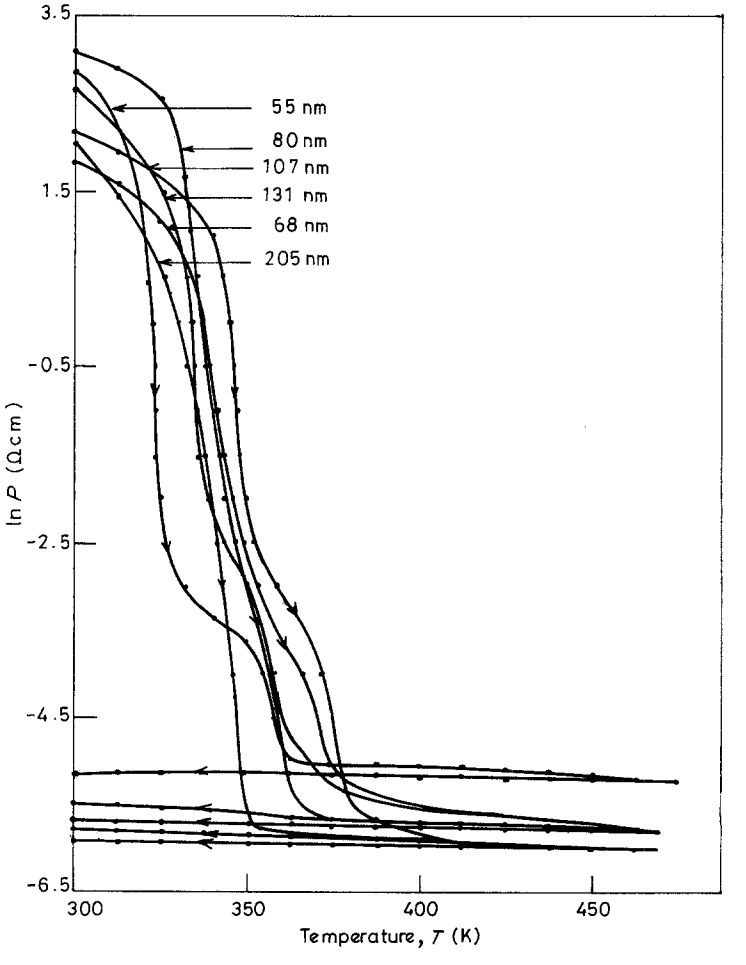

Figure 5 The logarithmic variation of resistivity as a function of temperature for unannealed films of different thicknesses, during heating and cooling cycles.

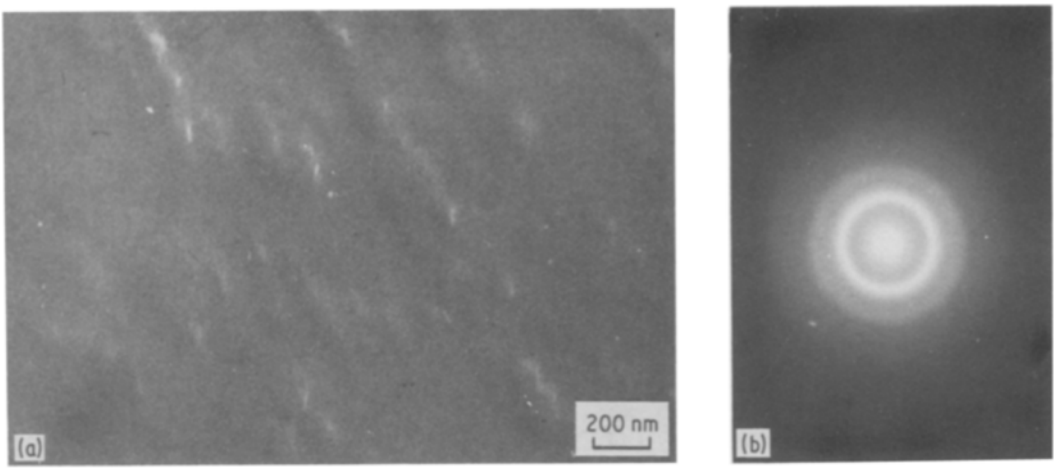

Figure 6 (a) A typical electron micrograph and (b) electron diffraction pattern, of as-grown film at low beam current densities.

electron diffraction patterns of an as-grown Sb_2Te_3 thin film and a film annealed at 120° C for 1 h. Both the above films were prepared in a single evaporation and were of the same thickness. Both the electron micrographs and the electron diffraction patterns were taken at a very low electron beam current density ($< 0.5\,A\,cm^{-2}$) because it was found that high beam current densities produce damage in amorphous Sb_2Te_3 thin films, as is evident from Figs 8a and b. Figs 8a and b show the electron micrograph and diffraction pattern of the as-grown Sb_2Te_3 film of Figs 6a and b at high electron beam intensities ($> 15\,A\,cm^{-2}$) which incidentally show that the as-grown, amorphous film of Sb_2Te_3 has undergone an amorphous–crystalline phase transition due to electron beam damage. Fig. 9 shows the X-ray diffractograms of as-grown, thick Sb_2Te_3 film and a film annealed at 120° C for 1 h.

4. Discussion

The variation of Seebeck coefficient and resistivity as a function of temperature for unannealed films of different thicknesses as seen from Figs 1 to 5 show that both the parameters S and ϱ of as-grown films show irreversible variation with temperature during the first heating. A similar kind of variation was observed by Rajagopalan and Ghosh [1] in the resistivity and the Seebeck coefficient of antimony telluride films of thicknesses between 160 and 800 nm. They discussed their results on the basis of intercrystalline barriers. According to them, during the first heating, irreversible reduction in the height of intercrystalline barriers results in the sharp irreversible variation of physical properties.

However, it is well established that as-grown films are amorphous. Structural studies of as-grown antimony telluride films were carried out by Andrievskii *et al.* [7]. They found that as-grown films were amorphous and subsequent heating led to loosening of the amorphous structure accompanied by an increase in the radius of the first coordination group. Above about 350 K the film changed to the crystalline state.

We attribute the sharp fall in S and ϱ during heating, to the amorphous–crystalline transition. To analyse the structure of the Sb_2Te_3 thin films and to show conclusively that the as-grown films are amorphous and crystallize on heating, we analysed the as-grown Sb_2Te_3 thin films by electron diffraction and microscopy in the case of thinner films, and by X-ray diffractometry in the case of thicker films. It was necessary to work with low electron beam current densities ($< 0.5\,A\,cm^{-2}$) because it was found that the as-grown Sb_2Te_3 amorphous thin films crystallized on electron bombardment at high beam current densities ($> 15\,A\,cm^{-2}$). It is clearly seen from Figs 6a and b that the as-grown Sb_2Te_3 thin films are amorphous

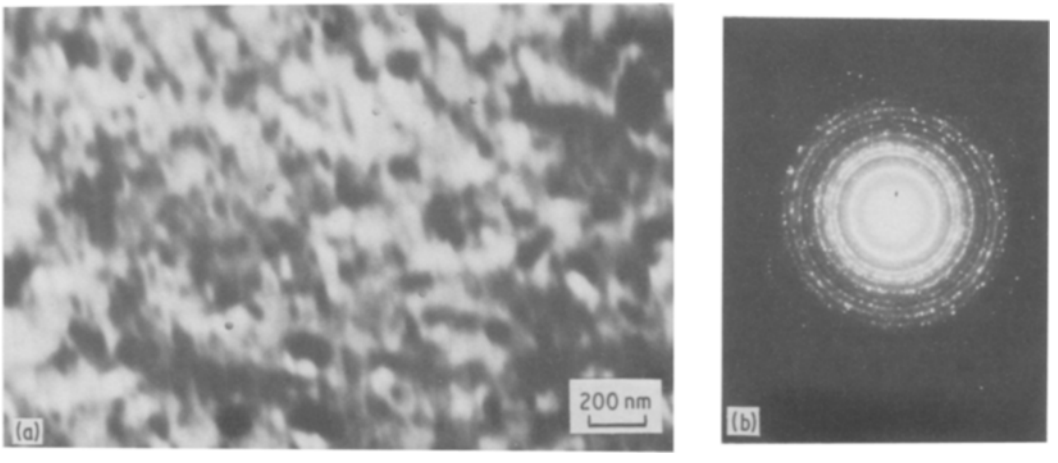

Figure 7 (a) Electron micrograph and (b) electron diffraction pattern, for annealed film at low beam current densities.

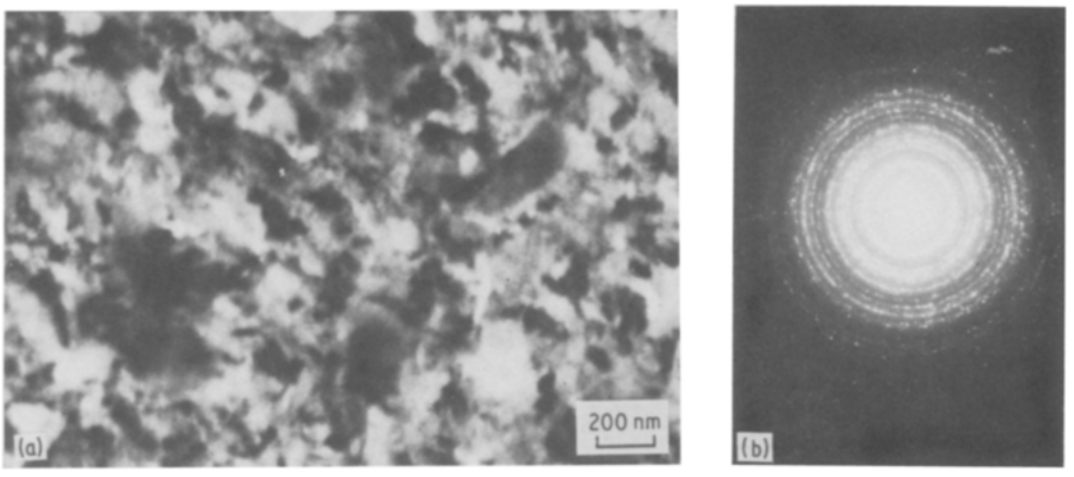

Figure 8 (a) Electron micrograph and (b) electron diffraction pattern, at high beam current densities for unannealed film.

and show the typical micrograph and diffraction pattern of an amorphous film. Figs 7a and b show that the annealed films are polycrystalline. The graininess of the ring pattern in Fig. 7b shows that the film grains are bigger. Thus, it can be conclusively said that the as-grown films are amorphous and crystallize on heating. Therefore, the idea of irreversible intercrystalline barrier height reduction of Rajagopalan and Ghosh [1] causing reduction in the resistance can be ruled out. From Figs 8a and b one can see that the amorphous Sb_2Te_3 film has been transformed to a polycrystalline film by the electron bombardment. This shows that the Sb_2Te_3 amorphous thin films can also be crystallized by electron bombardment. From the X-ray diffractograms (Fig. 9), again we see that also in the case of thicker Sb_2Te_3 thin films, as-grown films are amorphous while the annealed ones are polycrystalline with a tendency towards single crystallinity.

Mahan and Bube [8] studied the temperature dependence of the field effect in antimony telluride. It was observed that there was a very high density of localized states at the Fermi level. Because the states are localized at the Fermi level, the carrier movements are only by hopping from one localized state to another. Therefore, it is expected that the conductivity will vary with temperature as $\exp(-T_0/T)^{1/4}$. If, in amorphous materials, only hopping conduction is present, then the Seebeck coefficient is given by

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

Because, for localized states, $\partial \ln \sigma(E)/\partial E$ is higher than for free carriers, it is expected that in amorphous materials the Seebeck coefficient will be high and temperature dependent, increasing with increasing temperature. That is what has been observed in the present studies on unannealed films before irreversible reduction in the Seebeck coefficient takes place. Thus, it can be concluded that the irreversible changes taking place around 340 to 370 K are the result of the structural change from the amorphous to the crystalline state and not due to changes in the heights of the intercrystalline barriers as suggested by Rajagopalan and Ghosh [1].

The sharp fall in resistivity near 340 K observed for films of all thicknesses in Fig. 5 is certainly due to the structural change from the amorphous to the crystalline state as was also true in the case of the Seebeck

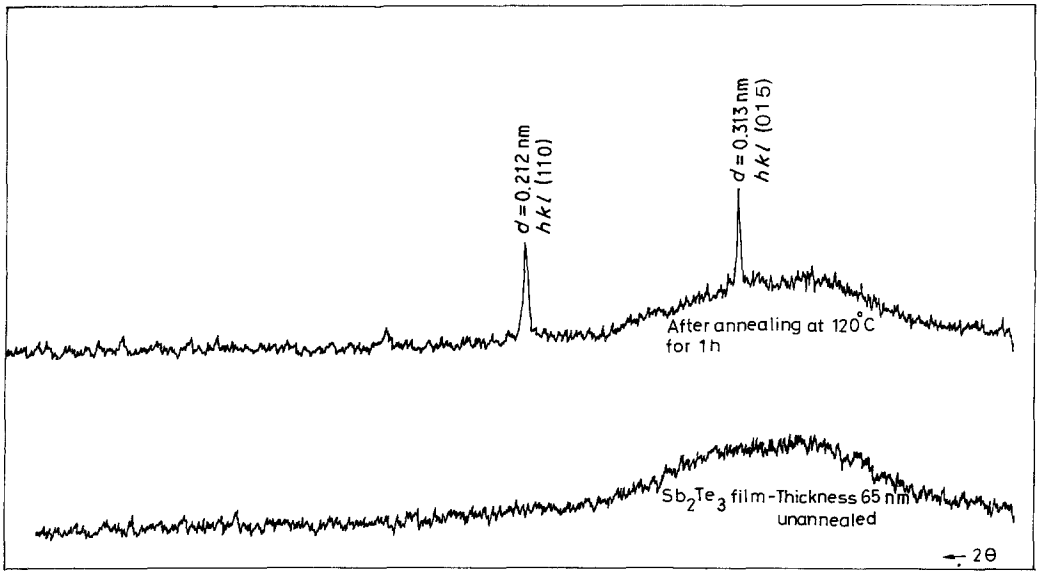

Figure 9 Typical X-ray diffractograms of as-grown and annealed films.

coefficient. In the region 300 to 340 K, where the film is amorphous, the resistivity decreases with temperature. Because in antimony telluride, the localized states are distributed about the Fermi level, the temperature dependence of conductivity is given by

$$\sigma = \sigma_0 \exp - \left(\frac{T_0}{T}\right)^{1/4}$$

However, in the present study, the fall in resistivity with increasing temperature is more than that expected from the above equation. This is mainly because during heating, the loosening of the amorphous structure and increase in the radius of first group are taking place as the temperatures above room temperature are close to the transition temperature as observed by Andrievskii *et al.* [7]. Thus, during the interval 300 to 340 K, the resistivity changes are due not only to the increase in hopping conduction, as given by the above equation, but also because of the onset of amorphous to crystalline transition which modifies the behaviour. At 340 K, the film resistivity decreases sharply by two to three orders of magnitude. This is because the film undergoes the phase change from the amorphous to the crystalline state.

It is also very interesting to note that the amorphous–crystalline transition, as observed from both the Seebeck coefficient and resistivity measurements, takes place at slightly different temperatures for films of different thicknesses. The change in the phase-transition temperature of films of different thicknesses may be due to the size effect influencing the phase equilibrium as observed in polycrystalline Ag_2Te and Ag_2Se films by Damodara Das and Karunakaran [9].

5. Conclusions

Antimony telluride thin films of different thicknesses between 50 and 200 nm were studied. The unannealed films were used to study the Seebeck coefficient and the electrical resistivity behaviour in them at different temperatures in the range 300 to 470 K. The unannealed films exhibited anomalous behaviour, which has been explained by showing that the as-grown films are amorphous and during heating the films undergo an irreversible structural change to a crystalline phase at about 350 K.

References

1. N. S. RAJAGOPALAN and S. K. GHOSH, *Physica* **29** (1963) 234.
2. L. H. GADGIL and A. GOSWAMI, *J. Vac. Sci. Technol.* **6** (1969) 591.
3. V. A. KREMNEV, P. A. LEONT'EV and A. I. PLATOV, *Kristallogr.* **16** (1976) 411.
4. B. M. GOL'TSMAN and M. G. KOMISSARCHIK, *Sov. Phys. Solid State* **15** (1973) 219.
5. YU. A. BOIKOV, B. M. GOL'TSMAN and S. F. SINENKO, *ibid.* **17** (1976) 2046.
6. N. S. LIDORENKO, V. N. GALEV, Z. M. DASHEVSKII and N. V. KOLOMOETS, *Sov. Phys. Dokl.* **20** (1975) 699.
7. A. I. ANDRIEVSKII, E. D. NABITOVICH and YA. V. DUTCHAK, *Sov. Phys. Crystallogr.* **7** (1963) 704.
8. J. E. MAHAN and R. H. BUBE, *J. Non-Cryst. Solids* **24** (1977) 29.
9. V. DAMODARA DAS and D. KARUNAKARAN, *J. Phys. Chem. Solids* **46** (1985) 551.

Received 17 September 1986
and accepted 11 February 1987