

Electrical transport in amorphous $\text{Se}_{1-x}\text{Sb}_x$ thin films

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Amorphous $\text{Se}_{1-x}\text{Sb}_x$ ($x=0.1, 0.15$ and 0.2) films of different thicknesses were prepared by the electron gun evaporation technique. Their structure was studied using reflection or transmission electron diffraction patterns. The d.c. electrical conductivity, thermoelectric power and magnetoresistance measurements, were made in the temperature range 80–300 K. These measurements confirm intrinsic conduction in the entire range of investigation, and were found to be independent of the film thickness. The effect of antimony impurity on electrical transport properties of selenium is understood in terms of the reduction of the Se_8 ring population.

1. Introduction

As the potential uses for selenium for device fabrication have grown, so have the attempts to modify some of its properties by alloying. Electron transport in selenium is associated with Se_8 rings and chains. The alloying elements produce characteristic effects depending upon whether the alloying material is univalent such as chlorine or thallium, isoelectronic such as tellurium and sulphur, or capable of producing chain branching such as antimony, arsenic, bismuth or germanium. The latter group of additives disturb the ring-chain equilibrium and modify both the chain length and the chain branching. It may be mentioned here that in addition to the structural properties, the conductivity activation energy of a-Se can be effectively controlled by the introduction of suitable additives. Besides introducing structural changes, the additives may also provide new acceptor or donor states [1].

It is thus quite interesting to study the effect of chain-branching additives on transport properties of selenium such as d.c. conductivity, thermoelectric power and magnetoresistance.

2. Experimental procedure

The thin films of a- $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ used in the present work were grown by the electron gun evaporation technique [2, 3]. For these films a charge was prepared by the melt-quenching technique as described elsewhere [4]. The parent material was evaporated by an electron gun in high vacuum (10^{-4} Pa) on to Corning glass substrate kept at room temperature. The rate of growth of these films was adjusted to around 50 nm s^{-1} using a quartz crystal monitor. The thickness of the films was determined by an optical measurements technique and the composition of the thin films was confirmed from electron probe microanalysis (EPMA) analysis. The films were found to be homogeneous and the composition was

found to be within 5% of the parent constituents. For electrical measurements, gold contacts were evaporated on to the films to provide a coplaner configuration.

For d.c. conductivity measurements, the films were mounted on a copper block (electrically insulated) in a vacuum cryostat in which cooling of the film was achieved by conduction through the copper block. Liquid nitrogen was used as a coolant and the temperature of the films was increased from liquid nitrogen to room temperature (80–300 K) with the help of a 25 W heater coil wrapped directly to the copper block. Change in the current through the film on the application of a voltage was found by measuring the change in voltage drop across a standard resistance (in series with the sample), with a Keithley nanovoltmeter model 148. For magnetoresistance (MR) measurements, the change in current through the samples on the application of magnetic field was measured by observing the change in voltage drop across the standard resistance.

Measurement of thermoelectric power (TEP) was carried out using a copper–constantan thermocouple to measure ΔT . The measurements were made in the coplaner configuration with an electrode spacing $\approx 1 \text{ cm}$. The TEP or Seebeck coefficient is obtained as $\Delta V/\Delta T$ where ΔV is the voltage developed across the film and ΔT is the temperature gradient [5].

3. Results and discussion

3.1. Electron microscopic studies

Films of different thickness, t , were used ranging from 25–160 nm: the thin films, $t < 50 \text{ nm}$, were studied using transmission electron diffraction (TED) patterns while relatively thick films, $t > 50 \text{ nm}$, were studied with the help of reflection electron diffraction (RED) patterns. The TED/RED patterns for amorphous $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ films were found to be completely diffused irrespective of thickness,

showing that all these films are amorphous in nature. One such TED pattern for a thin-film a-Se₈₅Sb₁₅ is shown in Fig. 1.

3.2. D.c. conductivity measurements

The observed variation of d.c. conductivity as a function of temperature ($\ln \sigma$ versus T^{-1}) for Se₉₀Sb₁₀, Se₈₅Sb₁₅ and Se₈₀Sb₂₀ films, is shown in Fig. 2. The conductivity for all the films over the entire temperature range (80–300 K) was found to exhibit an activated-type temperature dependence with a single activation energy. The conductivity was found to increase with increasing antimony concentration. No thickness dependence of conductivity for these films was observed. The data in Fig. 2 correspond to two different thickness: 25 nm (minimum) and 160 nm (maximum).

The conductivity of the films was found to satisfy the relation

$$\sigma = \sigma_0 \exp(-E_\sigma/KT) \quad (1)$$

where E_σ and σ_0 represent the conductivity activation energy and pre-exponential factor, respectively. The values of σ_0 and E_σ for different compositions are shown in Table I. The values of E_σ and σ_0 for a-Se are also included for comparison.

It can be seen from Table I that there is a sharp decrease in activation energy and the pre-exponential factor up to 15% Sb after which no appreciable change is observed with increasing antimony concentration in selenium. This can be attributed either to a large decrease in the optical band gap of the Se–Sb system or to the increase in width of the localized states region. Lucovsky has shown that a-Se contains both polymeric chain and Se₈ ring molecules [6]. It has been further shown that the incorporation of a branching additive, namely arsenic, reduces the Se₈ ring population sharply up to 20% As and produces deep hole presumably at branch points on polymeric chains. The reduction of the Se₈ ring population causes a decrease in the mobility of the carrier. However, at higher concentration, the branch points coalesce and produce a new network. Because antimony is also one of the branching additives, a sharp change in the transport parameter up to certain percentage of antimony in selenium is expected, as is observed in the present case, i.e. up to 15% Sb in Selenium. The observed decrease in the value of σ_0 with the increase of antimony content also indicates the decrease in the conductivity mobility with reduction of Se₈ rings.

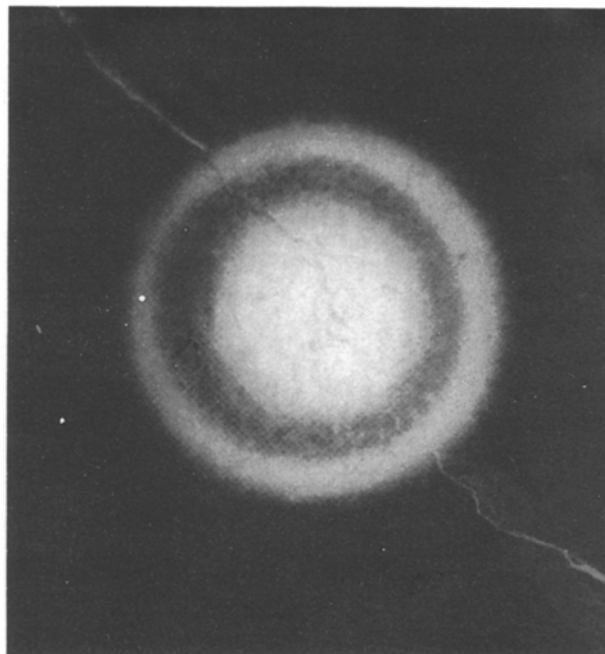


Figure 1 TED pattern for a-Se₈₅Sb₁₅ film of thickness 160 nm.

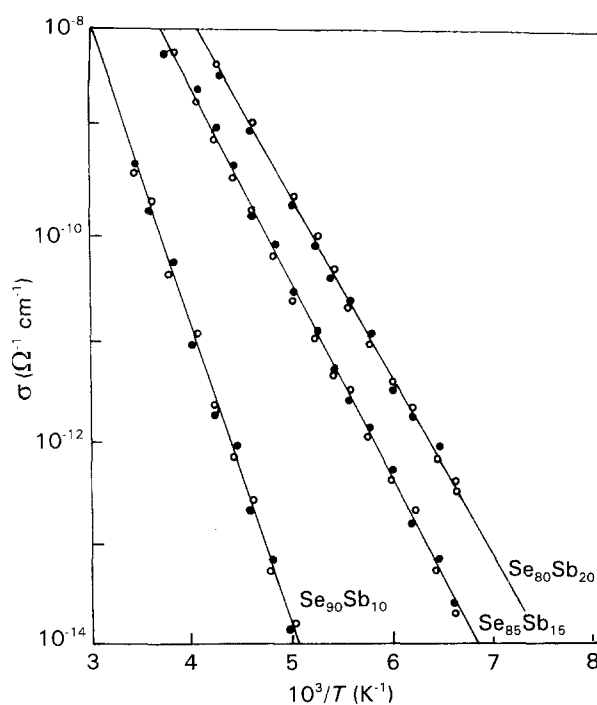


Figure 2 Semilog plots of conductivity versus reciprocal temperature for a-Se₉₀Sb₁₀, Se₈₅Sb₁₅ and Se₈₀Sb₂₀ films of various thicknesses: (●) 25 and (○) 160 nm.

TABLE I Various transport parameters for a-Se₉₀Sb₁₀, Se₈₅Sb₁₅ and Se₈₀Sb₂₀ films

Sample	Sample composition	Conductivity activation energy, E_σ (eV)	TEP activation energy, E_a (eV)	Pre-exponential factor, σ_0 ($\Omega^{-1} \text{cm}^{-1}$)	A
1	Se	0.82	–	80.0	–
2	Se ₉₀ Sb ₁₀	0.58	0.43	6.0	2.6
3	Se ₈₅ Sb ₁₅	0.39	0.36	0.21	2.6
4	Se ₈₀ Sb ₂₀	0.35	0.31	0.19	2.1

3.3. Thermoelectric power (TEP) measurements

The variation of TEP with the reciprocal temperature (S versus T^{-1}) for films of a- $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ is shown in Fig. 3. The TEP was found to be positive, indicating that the conduction occurs due to holes in the valence band. The magnitude of TEP decreases with increasing antimony concentration. TEP is found to be independent of the film thickness. The variation of TEP with temperature is found to obey the relation

$$S = \frac{k}{e} \left(\frac{E_a}{Kt} + A \right) \quad (2)$$

where E_a is the TEP activation energy and A is a constant which represents thermal energy transported by charge carriers. The values of E_a and A are also listed in Table I. The values of the activation energy pre-exponential factor and the sign of thermopower indicate that the conduction is in the localized states at the valance band edge. It can be observed from Table I that the conductivity activation energy is much greater than the TEP activation energy for $\text{Se}_{90}\text{Sb}_{10}$ film, indicating a thermally activated mobility. The physical basis of the thermally activated mobility could not be provided by a small polaron model [7] owing to the dependence of the potential barrier ($E_\sigma - E_a$) on sample composition (Table I). The other possibility is that the conduction is not a single channel process [8] but involves two bands of states simultaneously, such as extended states beyond the mobility edge and in localized states below the edge, as in the Davis and Mott model [9]. It may be mentioned that for $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ the ($E_\sigma - E_a$) is very small (≈ 0.03 eV) thereby indicating that the single channel conduction is dominating.

3.4. Magneto resistance (MR) measurements

The variation of MR with magnetic field, B , at ambient temperatures 300 and 80 K for $\text{Se}_{90}\text{Sb}_{10}$,

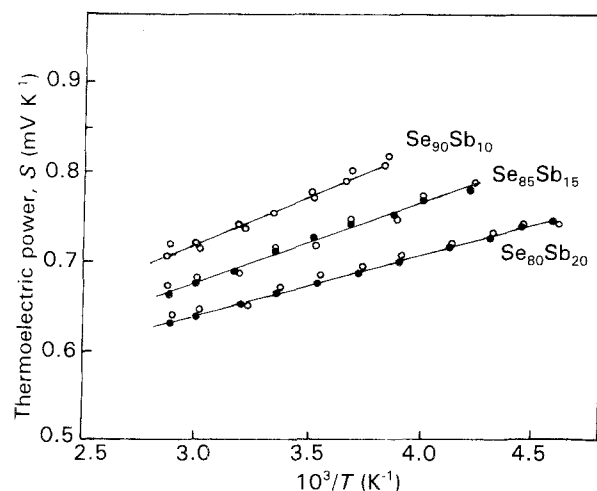


Figure 3 Plot of thermoelectric power against reciprocal temperature for a- $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ films of various thicknesses (see Fig. 2).

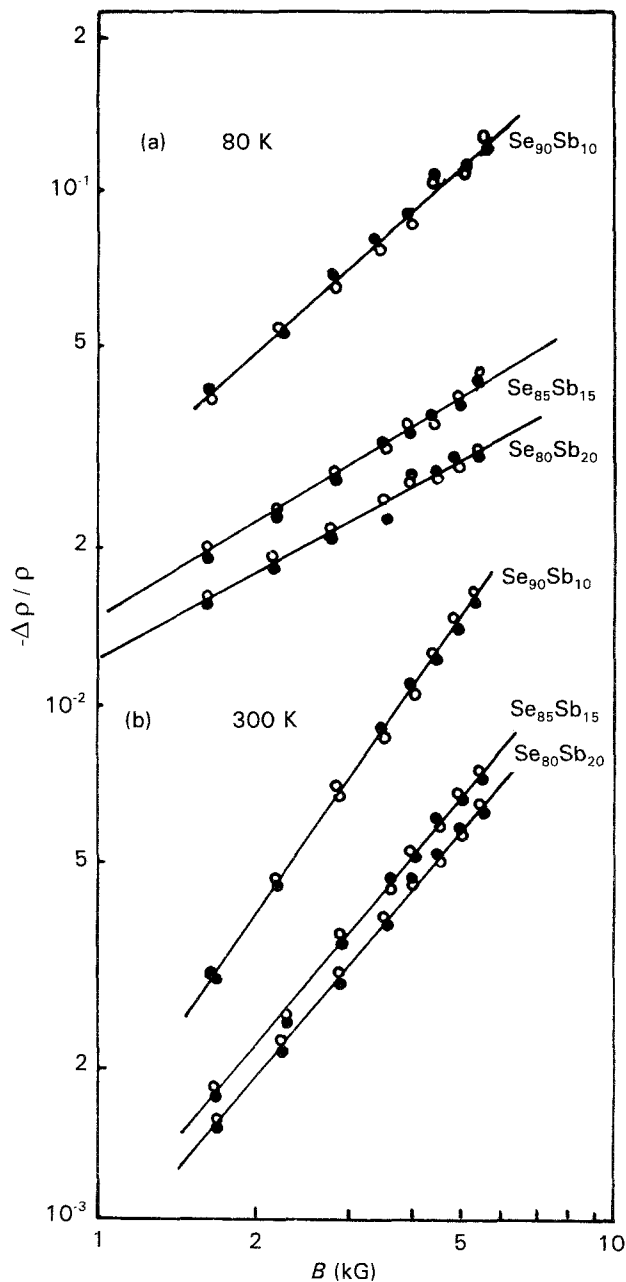


Figure 4 Plots of magnetoresistance versus magnetic field for a- $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ films of various thicknesses at (a) $T = 80$ K and (b) $T = 300$ K (see Fig. 2).

$\text{Se}_{85}\text{Sb}_{15}$, and $\text{Se}_{80}\text{Sb}_{20}$ films are shown in Fig. 4a and b, respectively. No thickness dependence of MR is observed for these films and the data in Fig. 4a and b corresponds to two different thickness (25 and 160 nm) of the films. It can be seen from Fig. 4a and b that the MR is negative (i.e. the conductivity is found to increase with increasing magnetic field). The magnitude of negative MR is found to be independent of angle between current and the magnetic field. The negative MR is found to vary in accordance with the relation

$$-\Delta\rho/\rho \propto B^n \quad (3)$$

The values of exponent n for different compositions at both the ambient temperatures are given in Table II.

The presence of a negative MR in amorphous chalcogenide Se-Sb samples cannot be explained in terms

TABLE II Magnetoresistance mobility, μ_{MR} , of a- $\text{Se}_{90}\text{Sb}_{10}$, $\text{Se}_{85}\text{Sb}_{15}$ and $\text{Se}_{80}\text{Sb}_{20}$ films

Sample	Composition	Exponent, n		μ_{MR} ($\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$)	
		300 K	80 K	300 K	80 K
1	Se	1.96	1.35	5000	4900
2	$\text{Se}_{90}\text{Sb}_{10}$	1.4	1.1	923	2850
3	$\text{Se}_{85}\text{Sb}_{15}$	1.15	0.6	237	86
4	$\text{Se}_{80}\text{Sb}_{20}$	1.13	0.55	195	32.2

of Toyozawa's localized spin moment model [10] and the semi-classical random-walk hopping model [11] because of the absence of localized magnetic states in the chalcogenides and the absence of Mott's VRH conduction in the present Se-Sb system [12]. The effect of electron correlation and the shrinkage of the localization length of a doubly occupied space due to magnetic field could account for the anomalous behaviour of MR in hydrogenated a-Si [13]. In the present system, the anomalous behaviour of MR, i.e. the presence of positive components of MR, is not observed, so the effect of electron correlation is not considered. The two-band model of Hedgcock and Raudorf [14], which does not require the existence of localized magnetic states can, however, be applied to these chalcogenide films. It assumes the existence of a band with higher mobility over a band with lower mobility with a sharp mobility edge in between the two. The negative MR is attributed to the dumping of the charge carriers (holes in this case) with the application of magnetic field, from the localized states to the extended states. The amorphous chalcogenide Se-Sb samples also possess extended states separated from the localized states by a mobility edge. The conduction mechanism in these samples is found to be via thermally assisted tunnelling of the carriers in the localized states at the mobility edges. The negative MR in these samples, therefore, can be attributed to magnetic field-induced dumping of the carriers from the localized states to the extended states.

It can be seen from Fig. 4a and b that the magnitude of the negative MR is higher at 80 K compared to that at 300 K. The increase in the magnitude of the negative MR with decreasing temperature is due to the shift of the carriers to the localized states region away from the mobility edge. The change in the mobility due to dumping of the carriers with the magnetic field will, therefore, be more.

It can be noted from Table II that the value of exponent n at 80 K is less than the value at 300 K. The exponent n is, however, found to decrease sharply up to 15% Sb in the Se-Sb system. This is due to a sharp decrease in the activation energy up to $\text{Se}_{85}\text{Sb}_{15}$ films. The values of magnetoresistance mobility, μ_{MR} , have been determined [15] using the relation

$$\Delta\rho/\rho = \left(\frac{\mu_{MR}H}{C}\right)^n \quad (4)$$

where $C = 10^8$ and H is the applied magnetic field

(gauss). The calculated values of μ_{MR} for all the samples are given in Table II. The value of μ_{MR} for a-Se films is also included in the table for comparison. The value of μ_{MR} is found to decrease with increasing antimony content. A similar decrease in the conductivity mobility has been inferred from the compositional dependence of σ_0 in the present system. It may be mentioned that the values of μ_{MR} are found to be abnormally high. High values of μ_{MR} have also been observed in other Se-Te chalcogenide glasses [16, 17]. The physical significance of such high values of μ_{MR} is intriguing and requires further study of another type.

4. Conclusion

The transport properties of a- $\text{Se}_{1-x}\text{Sb}_x$ ($x = 0.1, 0.15, 0.2$) are sensitive to antimony content. The d.c. conductivity measurements show a singly activated conduction throughout the temperature range 80–300 K. The TEP is found to be a positive, indicating holes as the majority charge carriers. The conductivity activation energy exceeds the TEP activation energy, representing a thermally activated mobility, the physical basis of which is probably provided by two-channel conduction. Magnetoresistance is found to be negative and best interpreted on the basis of the two-band model of Hedgcock and Raudorf. All the above electrical transport properties are found to be independent of the thickness of Se-Sb films.

Acknowledgements

Professor P.C. Mathur and Dr R. M. Mehra, Department of Electronics Science, University of Delhi, Delhi, are thanked for providing the laboratory facilities and fruitful discussions, and the help extended by Dr S.C. Agarwal in the experimental work is greatly appreciated.

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*Received 15 December 1992
and accepted 9 September 1993*