# Composition dependence of electrical properties of simultaneously evaporated Sb–Se thin films[†]

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**Abstract.** Amorphous thin films of Sb–Se are prepared using the three-temperature method. The films are prepared with atomic compositions from 5–90 at.% Sb. The electrical resistivity, Hall voltage and thermoelectric power of annealed samples have been measured in the temperature range 25 to 250°C. On heat treatment the sharp fall of resistance of the annealed films is attributed to radical structural transformation from amorphous to crystalline. Electrical resistivity, Hall constant and thermoelectric power are found to vary with thickness and composition of the film.

**Keywords.** Amorphous Sb–Se films; electrical resistivity; Hall constant; thermoelectric power.

## 1. Introduction

In recent years considerable attention has been focused on glasses of Sb and Se because of their switching effect (Luby *et al* 1971; Wood *et al* 1973). Muller and Muller (1980) report measurements on the high field conduction of Sb–Se systems as a function of composition close to the compound $Sb_2Se_3$. The electron diffraction studies (Sagara *et al* 1976) on Sb–Se films with 15, 40, 50, 75 and 85 at.% antimony show that interatomic distance and coordination number increase with increase of at.% Sb in the film. Wood *et al* (1973) point out that the addition of antimony to amorphous Se reduces the $Se_8$ ring concentration and leads to the formation of branched Se chains. They also find a peak at $Sb_2Se_3$ in the optical and thermal activation energy versus composition curve. Their results suggest that ordering into molecular units corresponding to crystalline $Sb_2Se_3$ is present in the amorphous phase. Similar results are obtained by Gilbert and Wood (1971) from the study of crystallisation temperature.

From a survey of the literature it can be seen that almost no attempt has been made to study the electrical properties of Sb–Se systems over the entire range of composition in the thin film state. Therefore it was thought that it would be of interest to investigate electrical transport properties of Sb–Se films of varying compositions and thicknesses prepared by using the three-temperature method (De-Klerk and Kelly 1965; Gunther 1966; Fleisch and Aberman 1977; George and Joseph 1982, 1984; George and Palson 1985; Yudasaka *et al* 1987).

## 2. Experimental

In the work reported here Sb–Se thin films were prepared by the three-temperature method.

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Antimony and selenium (purities 99·999%) were used as evaporants. Antimony ingots were evaporated directly from preflashed conical baskets made of nichrome wire and selenium powder from conical mica crucibles with nichrome wire windings. The coating was performed at room temperature in an IBPTORR-120 coating unit under a vacuum of the order of $10^{-5}$ torr. The substrates were perfectly clean and dry optically flat glass slides of dimensions $3·8 \times 1·2$ cm$^2$. The flux rate from each source could easily be adjusted by controlling the current through each filament. The current through the selenium source was switched on and selenium was allowed to melt in the crucible. The antimony source current was then switched on. After adjusting the flux rates from the two sources by varying the source currents films of varying compositions were obtained. There are obvious experimental difficulties in adjusting and maintaining evaporation rates of the individual components for obtaining films of different compositions with nearly the same thickness and films of different thicknesses with nearly the same composition. After several attempts we obtained films of the required compositions and thicknesses. All the films, irrespective of composition and thickness, were annealed at $\sim 95°$C for 8 h under vacuum.

The composition of the films was determined by employing absorptiometric spectroscopy at 550 m$\mu$ (Charlot 1964). To check the uniformity of the film as regards its composition, different portions of the films were subjected to absorptiometric spectroscopic analysis. The analysis confirmed that the films were of uniform composition and thickness.

Film thickness was measured using multiple beam interferometry. Films prepared for electrical measurements had compositions ranging between $Sb_5Se_{95}$ and $Sb_{90}Se_{10}$ and thicknesses between 1500 to 4500 Å. The films were continuous in this thickness range.

Electrical resistances of the films were measured at various temperatures in a vacuum of $\sim 10^{-4}$ torr by using pressure contacts similar to that used by Uen *et al* (1988). Both the heating and cooling rates were regulated at approximately 8°C min$^{-1}$.

The thermoelectric power $\alpha$ was measured by employing the integral method (Rahman Khan and Akhtaruzzaman 1982; Nikam and Pawar 1985; Sharma and Singh 1985; Moorty and Shivakumar 1986) in vacuum using pressure contacts (Goswami and Jog 1964; Dutta and Barua 1983; Sharma and Barua 1986). The distance between hot and cold ends was $\sim 3$ cm. Thermal emfs were measured by means of a microvolt potentiometer (Ajco) connected to a sensitive spot galvanometer (Ajco, P-42).

Hall voltage was measured at room temperature in air at fields varying between 2·4 and 8·4 K Gauss (Polytronic, EMP-100, SR. NO-116) and current ranging between 2 and 4 mA using a sensitive microvolt potentiometer and a spot galvanometer (both Ajco) as described before (Deokar and Goswami 1968; Nikam and Pawar 1985). For the Hall effect measurements, films had length to breadth ratio $\sim 7$.

## 3. Results and discussion

Figure 1 shows the variation of resistance with temperature of measurement for the film deposited on a glass substrate at room temperature. The resistance decreased with increase of temperature and displayed a minimum near 169°C. The change of resistance with temperature was reversible in the region AB (25 to 169°C). The resistance of the

film in the region AB was found to fit the relation

$$R_F = R_B \exp \Delta E / KT \tag{1}$$

characteristic of semiconducting transport process. The electrical resistance showed a sudden decrease from $6 \cdot 2 \times 10^6$ to $2 \cdot 7 \times 10^3$ ohms when the film was heated from 169 to 240°C (region BC). The variation of $R$ with temperature was irreversible in region BC. After 240°C the film was cooled to room temperature (region CD). In the region CD the resistance changed reversibly with temperature obeying (1).

Figure 2 shows the variation of resistivity $\rho$ with thickness $d$ of the films deposited on glass at room temperature. Similar plots were obtained for the films of any composition studied. The resistivity increased continuously with decrease of film thickness.

Figure 3 shows the dependence of resistivity of films with the Sb atomic fraction $x$. It is seen that the resistivity of the film decreased sharply up to $x = 0 \cdot 13$ and then decreased
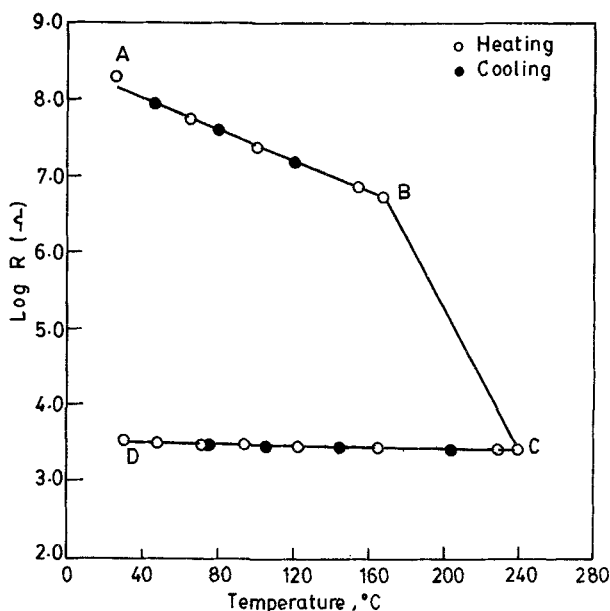


**Figure 1.** Variation of $\log R$ with temperature $T$ for $Sb_{26}Se_{74}$ film of thickness $\sim 1500 \, \text{Å}$ deposited at room temperature.
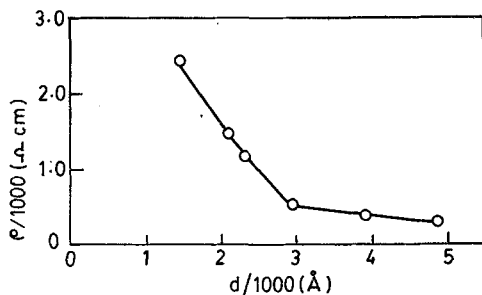


**Figure 2.** Variation of resistivity $\rho$ with thickness $d$ for $Sb_{35}Se_{65}$ films.

gradually up to $x = 0.4$. Resistivity decreased very sharply for antimony concentrations ranging from 0.42 to 0.52 atomic fraction and then slowly for $x > 0.52$.

The energy of activation (region AB) was found to decrease with increase of thickness and antimony concentration. Tables 1 and 2 include variation of $\Delta E$ with thickness and composition of the film respectively. The $\Delta E$ values of second reversible cycle (region CD) were found to be very small.

The Hall voltage was generated only for films with $x > 0.5$. The Hall coefficient $R_H$ and Hall mobility $\mu_H$ increased with increase of thickness and $x$ (figures 4 and 5). $R_H$ values were found to be independent of magnetic and electric fields.
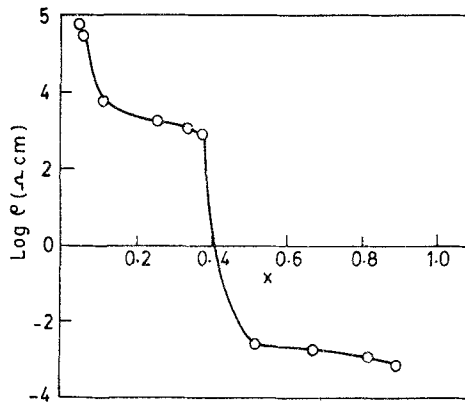


**Figure 3.** Variation of $\log \rho$ with atomic fraction $x$ of Sb for thickness $\sim 2000$ Å.

**Table 1.** Variation of activation energy ($\Delta E$) with thickness ($d$) for $Sb_{40}Se_{60}$ films.

| $d$ (Å) | $\Delta E$ (eV) |
|---------|-----------------|
| 1484 | 0.36 |
| 1962 | 0.34 |
| 2168 | 0.33 |
| 2297 | 0.32 |
| 2915 | 0.26 |

**Table 2.** Variation of activation energy ($\Delta E$) with atomic fraction ($x$) of Sb for $d \sim 3000$ Å

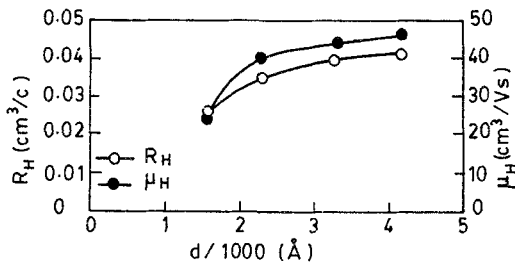| $x$ (Å) | $\Delta E$ (eV) |
|---------|-----------------|
| 0.05 | 0.78 |
| 0.06 | 0.71 |
| 0.26 | 0.36 |
| 0.30 | 0.32 |
| 0.35 | 0.33 |
| 0.39 | 0.32 |
| 0.77 | 0.07 |

**Figure 4.** Variation of $R_H$ and $\mu_H$ with thickness $d$ for $Sb_{67}Se_{33}$ films.
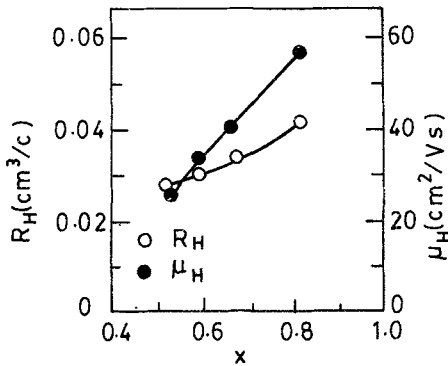


**Figure 5.** Variation of $R_H$ and $\mu_H$ with atomic fraction $x$ of Sb for thickness $\sim 2200$ Å.
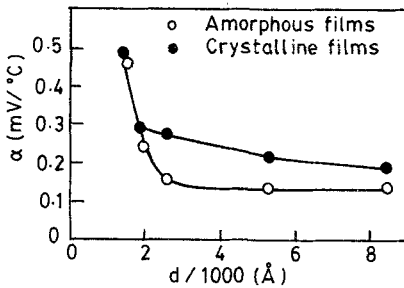


**Figure 6.** Variation of thermoelectric power $\alpha$ with thickness $d$ for $Sb_{60}Se_{40}$ films.
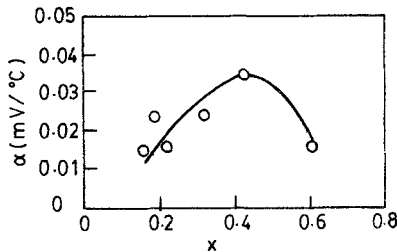


**Figure 7.** Variation of thermoelectric power $\alpha$ with atomic fraction $x$ of Sb for thickness $\sim 5000$ Å.

Thermoelectric power $\alpha$ decreased with the increase of thickness up to $2500\,\text{Å}$ and then remain almost constant. As regards the composition dependence of $\alpha$, it showed a maxima at $x = 0.4$. Figures 6 and 7 show variation of $\alpha$ with thickness and composition of the film. All the samples irrespective of composition and thickness of the film were $p$-type which is in conformity with the Hall-effect measurements.

The high resistance of the films in the region AB is explained on the basis of the disordered amorphous structure of the films. The high resistivity activation energy $(0.07-0.78\,\text{eV})$ obtained in this region is ascribed to the intrinsic conduction. The sharp fall of resistance in the region BC is accounted for by the radical structural transformation from amorphous to crystalline on heat treatment of the film. This is in agreement with previous work (Chopra 1969; Blum and Feldman 1972; Persin *et al* 1972; Webb and Brodie 1975; Das and Banerjee 1987; Chandrashekhar *et al* 1987). This structural transformation is likely to be accompanied by appearance of donor or acceptor states which contribute towards the observed conductivity. The low resistance and low $\Delta E$ of crystalline films in the region CD can be explained by assuming that the conduction is extrinsic involving deep donor or acceptor impurity or imperfection levels in the forbidden energy gap.

Films deposited at higher substrate temperature $(t_s = 150°\text{C})$ do not show amorphous to crystalline transformation on heat treatment. This is presumably due to removal of defects and formation of the crystalline phase during deposition of the film itself.

The variation of resistivity $\rho$ with thickness of the film deposited at room temperature is shown in figure 2. The sharp increase of $\rho$ for thinner films may be mostly due to the island structure of the film. The effect of the film thickness can also be explained in terms of the Mathiessen rule $\rho_{\text{total}} = \rho_{\text{ideal}} + \rho_{\text{residual}} + \rho_{\text{thickness}}$, where $\rho_{\text{ideal}}$ depends on the amplitude of thermal motion of ions, $\rho_{\text{residual}}$ is the component strongly dependent on the lattice defects but independent of temperature as long as these lattice defects are not affected by temperature changes, and $\rho_{\text{thickness}}$, the component of $\rho_{\text{total}}$ that depends on the thickness of the film.

Since selenium films of thickness $\sim 1800\,\text{Å}$ have specific resistivity (Sharma and Singh 1983) of the order of $10^7\,\Omega\,\text{cm}$ and that of antimony films of the same thickness is $10^{-5}\,\Omega\,\text{cm}$ (El-Shazly *et al* 1983) the observed resistivities are in the expected range for the Sb–Se binary system for all the values of $x$. The gradual decrease of resistivity in the region $0.06 \leqslant x \leqslant 0.4$ appears to be due to the ordered structure of the film. Further it can be seen from the graph (figure 3) that the resistivity decreases sharply from $10^3\,\Omega\,\text{cm}$ to $10^{-2}\,\Omega\,\text{cm}$ between $0.4 \leqslant x \leqslant 0.52$. It is known that pure selenium vapour when quenched on glass substrate at room temperature yields selenium films consisting of $Se_8$ rings. On the contrary antimony vapours when quenched under similar conditions transform to polycrystalline trigonal films (Ojha 1973; Patel and Shivakumar 1978). Wood *et al* (1973) have found that the addition of antimony to amorphous salenium film reduces $Se_8$ ring concentration and leads to the formation of Se chains. It is, therefore not surprising that as the Sb fraction in $Sb_xSe_{1-x}$ alloy increases, the ring–chain equilibrium is continuously affected through the phase transformation $mSe_8 \rightarrow nSe_y$ and there comes a point $(x = 0.5)$ when addition of more Sb results in a loss of ring-forming ability and the vapour-quenched alloys has ordered into molecular units of amorphous $Sb_2Se_3$ corresponding to crystalline $Sb_2Se_3$ (Wood *et al* 1973). The observed critical fraction of $mSe_8 \rightarrow nSe_y$ transition in the vicinity of $x = 0.4$ is in good agreement with independent evidence from electrical and optical

measurements as a function of composition by Wood *et al* (1973). The resistivity of the film decreases further with the addition of antimony dopant.

Decrease in $\Delta E$ with increase of thickness of the film (table 1) may be accounted for by increase in the ordered structure of the film with increase of thickness. As seen from table 2, the addition of Sb to Se appreciably lowers the activation energy which implies that either there is large decrease in the optical band gap of the Sb–Se system or the width of the localised state region increases or both. These results are in conformity with those of Mehra *et al* (1979).

Measurements of Hall effect in the amorphous material are very difficult and uncertain (Chopra 1969). Hall effect measurements were not possible on films with $x < 0.5$ due to their high resistivity. Increase in $\mu_H$ and $R_H$ with thickness is attributed to removal of imperfections in thicker films. The addition of antimony to amorphous selenium semiconductor changes the mobility of charge carriers or introduces the structural change (Twaddell *et al* 1972), accordingly the addition of antimony to selenium increases the ordered structure of the films resulting in the increase of $\mu_H$ and $R_H$ with increase of $x$.

Thermoelectric power has two distinct values in different temperature regions presumably due to the amorphous and crystalline phases of Sb–Se system. The $\alpha$ for the crystalline phase is higher than that for the amorphous phase due to more ordered and less defect density in crystalline films. $\alpha$ values for crystalline as well as amorphous phase decrease with increase of thickness up to 2500 Å and then remain constant. It is suggested that at 2500 Å thickness the majority of defects are removed keeping $\alpha$ constant (figure 6). It is interesting to note from figure 7 that $\alpha$ increases with $x$ and reaches a maximum at $x \sim 0.4$ corresponding to the ordered phase $Sb_2Se_3$. This observation is in good agreement with that reported by Wood *et al* (1973).

## Acknowledgement

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