BISMUTH AND ANTIMONY

(a) BISMUTH

(A) INTRODUCTION

Bismuth is a semimetal with a rhombohedral structure. Extensive investigations have been made both from the experimental and theoretical point of view on the electronic properties of bismuth.

A series of experiments have been initiated since 1930 when de Haas and Van Alphen reported an oscillatory behaviour of the susceptibility of bismuth when measured as a function of magnetic field. Such oscillatory behaviour was also observed for Hall coefficient (Cerritzen, 1940; Brodie, 1954). Further investigations (Reynolds et al, 1954; Marcus, 1955) at the liquid helium temperature definitely established that the oscillations in $R_H$ were periodic in reciprocal field and of the same period as the oscillations in the magnetic susceptibility. Thermoelectric power and thermal conductivity also showed the oscillatory behaviour (Stein and Babiskin, 1955). Even though this oscillatory behaviour was treated theoretically by Peierls as early as 1933 on the basis of free electron model, he could not explain his observations on
alkali and noble metals. Abeles and Meiboom (1956) proposed a simple many-valley model for the band structure to explain the results on single crystals of pure and tin doped bismuth and calculated the overlap between the valence and conduction band ($\approx 0.12$ eV). Cohen (1961) also proposed a nonellipsoidal model for electrons in Bi. Cardona and Greenway (1964) measured the room temperature reflectivity of the bismuth crystals over the energy range 0.5 to 2.5 eV and analysed the results using the Kramers - Kronig relation. The single crystals of Bi were found to exhibit a high degree of anisotropy (Singh, 1964), $R_H$ being more direction dependent than the magneto-resistance. Studying the diffusion size effect in bismuth at liquid helium temperature, Hattori (1967) found that at high magnetic fields recombination at the surface was dominant. For the magnetic field parallel to the trigonal axis, he found the bulk recombination time to be $\approx 6.5 \times 10^{-9}$ sec.

Considerable interest has also been shown in the properties of bismuth films especially their galvanomagnetic properties. Reimer (1957) found that for films less than 50 Å thickness, $a$ was positive whereas for thicker films it was negative, though with a larger magnitude. Suhrmann et al (1958) observed that the bismuth films had a negative T.C.R. but it became positive at higher temperatures. Bismuth films were also found to be very sensitive to the stress applied to the substrates (Colombani et al, 1960) and hence can be used as sensitive transducers, microphones, microbalances etc. When annealed above their fusion point, these
films showed a large increase in their magneto-resistance (Colombani and Huet, 1963). They also observed that though \( \frac{\Delta \sigma}{\sigma_0} \propto H^2 \) for unannealed films, magnetoresistance was more or less directly proportional to the field for annealed samples. According to Fritsche and Seufert (1963) room temperature deposits had a negative \( R_H \) whereas films condensed at very low temperature (\( < 4^\circ K \)) had a positive \( R_H \). This parameter was also dependent on the rate of evaporation, the films deposited at higher rates having a negative \( R_H \) whereas slower rates favoured a positive value (Fritsche et al. 1965). Herrman and Reimer (1965) investigated the effect of epitaxial and textured (1-d oriented) structure on the sign and magnitude of \( R_H \) and observed a change in the sign of \( R_H \) from positive to negative for deposits on glass substrates with increasing film thickness which was adduced to the change of orientation texture from \{111\} to \{111\} and \{110\}. Origin et al. (1966) reported an oscillatory behaviour of \( R_H \), \( \frac{\sigma}{\sigma_0} \) when measured as a function of thickness and attributed this to the quantum dimensional effects. Komnik and Bukhshtab (1968) also studied the quantum size effect in polycrystalline Bi films and concluded that the mean free path of electrons in the deposits is not limited by the crystal size. The negative T.C.R. of bismuth films (less than 70 \( \mu \) thickness) was attributed by Ivanov (1968) to the reduction in the mean free path by grain boundary scattering. Thermoelectric power for single crystal films deposited on mica was found to be independent of thickness (600 to 1500 \( \AA^0 \)) this being
attributed to the predominance of the specular reflection of charge carriers from the film surface (Ashalal and Duggal, 1970). Similar conclusion about specular reflection was also drawn by Hoffman and Frankel (1971) on the basis of measurements on well-ordered but twinned Bi films.

Preliminary investigations on bismuth films by Bhide (1972) showed that the type of conduction in these films (p or n-type) changed from set to set. Also, as observed from the survey of above literature different workers have reported different type of behaviour for bismuth films. In the following therefore a detailed investigation on the electrical properties of bismuth films was made.

(B) **EXPERIMENTAL**

Bismuth films were prepared by evaporating bulk bismuth (99.999% pure) from a conical silica boat heated externally by a tungsten filament which was initially flashed. All the films were deposited on glass substrates \( T_s \approx 27^\circ C \) along with suitable mask, and then annealed in vacuo at 100\(^\circ\)C. The deposition conditions for each set of evaporation were however kept more or less constant. Film thickness was estimated both by the difference in weight as well as by the interferometry method.

Electrical measurements were made by the methods described in Chapter II. These films were also subjected to electron diffraction studies for structures and orientations.
(C) RESULTS

i) Resistivity and activation energy

Resistivity of bismuth films was measured as a function of their thickness and a graph of $\rho$ vs $d$ was plotted (Fig. 4.1). It is seen that in the higher thickness region (1000 to 5000 Å), $\rho$ was almost independent of the film thickness. However at a lower film-thickness ($< 1000$ Å) range $\rho$ increased rapidly with the decreasing film thickness.

Resistivities of these films were also measured as a function of temperature (78° to about 400°K) (Fig. 4.2). It is seen that as the temperature increased from 78°K, $\rho$ decreased slowly up to a temperature of about 170°K, after which it decreased rapidly. It is interesting to see that the temperature variation of $\rho$ for bismuth films is characteristic of a semiconductor unlike the bulk Bi where the behaviour is metallic i.e. $\rho$ increased with the increase of the temperature.

Activation energy at the low temperature region was indeed very low ($\ll 7 \times 10^{-3}$ eV). In the higher temperature region however $\Delta\rho$ was larger, say about 0.05 eV. No significant thickness dependence of $\Delta\rho$ was observed for these films.

ii) Hall coefficient

Hall coefficient when measured as a function of the thickness at room temperature showed some interesting features (Fig. 4.3). As the thickness of the films increased from say
FIG 4.3

FIG 4.4

FIG 4.5
about 700 Å, \( R_H \) which was positive, increased with the increasing film-thickness up to a thickness of about 2600 Å. With a further rise of thickness \( R_H \) however started to decrease rapidly, became practically zero say around 3200 Å, eventually becoming negative. With the further rise of film thickness \( R_H \) (negative) increased in magnitude with increasing thickness and tended towards a constant value. Thus Bi films which were found to be p-type in the lower thickness region became n-type in the higher thickness region, clearly demonstrating that the nature of charge carriers was a function of film-thickness.

It was also found that \( R_H \) was independent of magnetic field (1000 to 7000 gauss) as well as current (0.05 to 2 mA) passing through these films.

The variation of \( R_H \) with temperature also showed some peculiar features as shown in Fig. 4.4. Thinner films (< 3200 Å) were p-type at room temperature but changed over to n-type. As the temperature increased from 78 K, \( R_H \) (negative) decreased, ultimately becoming zero at a particular temperature. With the further increase of temperature \( R_H \) became positive, reached a maximum and then decreased. The transition temperature at which the films changed over from n to p-type depended on thickness, thicker films having a higher transition temperature. However this type of transition was not observed for films thicker than about 3200 Å. The magnitude of \( R_H \) (negative) decreased continuously as temperature increased from 78 K and remained negative even up to the \( T_d \) temperature (\( \approx 230^\circ C \)).
**FIG 4.6**

**FIG 4.7**
At liquid nitrogen temperature all the films were n-type, irrespective of their thickness. Figure 4.5 shows the thickness dependence of $R_H$ (negative) at 780\(^\circ\)K. It is seen that $R_H$ increased with increasing thickness.

iii) Mobility

Mobility, calculated from the relation $\mu = \frac{6}{\mathcal{E}} R_H$ is shown as a function of temperature in Fig. 4.6 (log-log scale). It is seen that as the temperature was increased from 780\(^\circ\)K, mobility ($\mu$) of the majority charge carriers, here electrons because $R_H$ was negative, decreased rapidly and at the temperature corresponding to the transition temperature of the film, the mobility of the samples became effectively zero because of the predominance of the holes. However after reaching a maximum, $\mu_p$ decreased with the further rise in temperature. For films having thicknesses larger than about 3200 \(\AA\), $\mu_e$ decreased at first slowly but with the further rise in temperature it decreased rapidly though remaining dominant over $\mu_p$ throughout the temperature region.

The values of different electrical parameters at room temperature for bismuth films are shown in Table 4.1.

iv) Thermoelectric power

Thermoelectric power of bismuth films was measured by the differential method. All the films behaved as n-type
<table>
<thead>
<tr>
<th>Thickness d (Å)</th>
<th>$R_H \times 10^{-2}$ cm$^2$ g$^{-1}$</th>
<th>$\sigma \times 10^{-4}$ ohm-cm</th>
<th>$\mu$ cm$^2$/V-sec</th>
</tr>
</thead>
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<tr>
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<td>29.8</td>
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<tr>
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<td>+2.4</td>
<td>5.90</td>
<td>45.0</td>
</tr>
<tr>
<td>2662</td>
<td>+3.6</td>
<td>4.90</td>
<td>77.5</td>
</tr>
<tr>
<td>2800</td>
<td>+2.4</td>
<td>4.90</td>
<td>49.0</td>
</tr>
<tr>
<td>3100</td>
<td>+1.0</td>
<td>4.90</td>
<td>20.4</td>
</tr>
<tr>
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<td>-1.0</td>
<td>4.70</td>
<td>21.7</td>
</tr>
<tr>
<td>3800</td>
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<td>54.0</td>
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</tr>
<tr>
<td>4820</td>
<td>-4.6</td>
<td>4.70</td>
<td>97.2</td>
</tr>
</tbody>
</table>
FIG 4.8

FIG 4.9

FIG 4.10
whether measured at room temperature or liquid nitrogen temperature without indicating any transition from n to p-type contrary to the Hall effect observation. Fig. 4.7 shows $\alpha$ as a function of temperature. At low temperatures $\alpha$ increased with increasing temperature and after about 200°K, it was almost constant. However, after 360°K, $\alpha$ decreased with the further rise of temperature. Thinner films, in general, had lower $\alpha$ than the thicker films at a particular temperature.

v) T.C.R.

The T.C.R. for all the films (700 to 5000 Å) was negative. Figure 4.8 shows the temperature variation of T.C.R. It is seen that the thicker films had slightly higher magnitude of T.C.R. as compared to the thinner films. Also T.C.R. decreased gradually at low temperatures (90 to 240°K) but sharply at higher temperatures (240° to 400°K).

vi) Magnetoresistance

The variation of the magnetoresistance ($\Delta\rho / \rho_0$) with the magnetic field is shown in Fig. 4.9. It is seen that thinner films had lower $\Delta\rho / \rho_0$ as compared to the thicker films. However, the slope of the curve $\log \Delta\rho / \rho_0$ vs $\log H$ was about 2 thus indicating the square law dependence of magnetoresistance for both thick and thin films. It is interesting to see that $\Delta\rho / \rho_0$ at a fixed magnetic field was larger in magnitude at 73°K as compared to the room temperature value.

vii) Structure

Bismuth films deposited on polycrystalline NaCl at room
temperature and annealed in vacuo at 100°C yielded pattern shown in Fig. 4.10. The d values for various reflections correspond to a hexagonal structure \((a = 4.54 \, \text{Å}, \, c = 11.86 \, \text{Å})\), having a basic rhombohedral unit cell \((a = 473.6 \, \text{Å}, \, \alpha = 57^\circ 14' 13'\) ). Deposits of bismuth on collodion produced continuous rings corresponding to the hexagonal (rhombohedral) structure. However, thicker deposits invariably developed 1-orientations.

\section*{(D) DISCUSSION}

The semiconductor-like behaviour of bismuth films as compared to the bulk bismuth which is a semi-metal emphasized the fact that the properties of thin films differ to a large extent from the starting bulk material. Although the pure single crystals of bismuth has a n-type of conduction at room temperature, the conduction mechanism in bismuth films is essentially a function of thickness. At room temperature thinner films (less than about 3000 Å) were found to be p-type as compared to the thicker films which were n-type. The p-type behaviour for thinner films is likely to be due to the creation of acceptor levels which increase the number of holes. These acceptor levels can arise from different defects such as grain boundaries and voids which are present in larger amount in thinner films than thicker films. As the film becomes thicker these defects reduce and so do the acceptor levels making the film n-type as is the case for bulk Bi. This process appears to make the films n-type from p-type with increasing thickness.
It is well known that electrical properties of bismuth are anisotropic (Singh, 1964), and hence it is likely that the ordering of crystallites i.e. their orientation and perfection may influence these properties. It has also been noted from the electron diffraction studies that bismuth deposits tend to develop and orientate much more easily even for very thin films, compared to other vacuum deposited materials. The change from the p-type of conduction for thinner films to n-type may also be adduced to this.

Another interesting feature of the properties of Bi films was that the deposits which were p-type at room temperature were no longer p-type at low temperatures but changed over to n-type, the transition temperature depending upon thickness of the films (Fig. 4.4). This effect, however, cannot be attributed to the crystalline perfection or otherwise. Apparently other factors play a dominant role in this case.

At low temperatures it was found that the mobility of electrons ($\mu_e$) was much larger than that of holes ($\mu_h$). However, as the temperature increases $\mu_e$ reduces whereas $\mu_p$ increases. Now for a mixed type of conduction $R_H$ is given by

$$ R_H = \frac{1}{e} \frac{p \mu_h^2 - n \mu_e^2}{(p \mu_h + n \mu_e)^2} $$

Thus at low temperatures where $R_H$ is negative, $n \mu_e^2 > p \mu_p^2$.

At the transition temperature $R_H = 0$ so that $p \mu_h^2 = n \mu_e^2$. 
However above the transition temperature \( n/\mu_n^2 < p/\mu_p^2 \) so that \( R_H \) is positive. The decrease in \( R_H \) (positive) after attaining a peak indicates approach of intrinsic region.

It was seen that all the films had a negative T.C.R. and a finite activation energy, though small (\( \approx 0.05 \) eV). This behaviour, contrary to the bulk may be due to the separation of valence and conduction bands as was suggested by Asbel and Brandt (1965). Such a feature may also be due to the presence of different defects and impurities that might cause separation of valence and conduction level (Jain, 1959).

Magnetoresistance whether measured at room temperature or low temperature was proportional to the square of magnetic field. This behaviour is analogous to a typical semiconductor.

The thermoelectric power behaviour was anomalous in the sense that all the films were found to be n-type in the complete temperature range investigated whereas the Hall effect measurements indicated both p and n-type of behaviour depending upon thickness of the films. This anomaly is not yet fully understood.
Bulk antimony, like bismuth, is a semimetal. It has a rhombohedral structure with two pentavalent atoms in each unit cell. The semimetallic behaviour of antimony results from small overlaps between the fifth and sixth energy bands creating an equal number of holes and electrons in small, nearly ellipsoidal, pockets.

The de Haas-van Alphen effect, as for bismuth, was also observed for Sb single crystals (Shoenberg, 1952). Magneto-resistance and Hall effect also showed the oscillatory dependence upon magnetic field between 15° to 4.2°K (Steele, 1955). Freedman and Juretschke (1961) deduced the energy band structure of antimony from room temperature galvanomagnetic measurements and their interpretation was in terms of a theoretical model. They found that the calculated galvanomagnetic effects assuming a simple, independent three-valleyed band for both the valence and conduction bands and isotropic relaxation times for both holes and electrons fitted well with the experimental observations. The Fermi surface of antimony has been studied through the de Haas–Van Alphen effect (Shoenberg, 1952, Saito, 1963), Shubnikov-de Haas effect (Ketterson and Ekstein, 1963; Lener and Eastman, 1963), cyclotron resonance (Detars and Vanderkooy, 1964), infrared absorption (Nanney, 1963) etc. The above measurements indicated that carriers occupy at least two bands, with each of these two bands containing either three or six...
nearly ellipsoidal pockets arranged in accordance with the rhombohedral symmetry of the crystal. According to Oktu and Saunders (1967) the electron and hole mobilities in Sb single crystals were found to be proportional to $T^{-1.48}$ and $T^{-1.42}$ respectively.

Antimony films however have not been subjected to as rigorous experimental treatment as for the bulk. Suhrmann and Berndt (1940) evaporated antimony at liquid air temperature and found that the films had negative T.C.R. which became +ve upon heating. Harris and Sheaffer (1949) measured resistivity of Sb deposits as a function of thickness at different temperatures. They concluded from their results that the trapping of electrons in the surface becomes important for thicknesses less than 1000 A. Levertan and Dekker (1950) measured Hall coefficient and resistivity by a.c. method and attributed the observed increase in $R_H$ and $\sigma$ with annealing due to a partial recombination of electrons and holes. Cohen (1954) prepared semiconducting films of Sb (amorphous) by depositing them at low temperature and calculated activation energy to be about 0.07 eV at low temperature and 0.13 eV at high temperatures. This result is contrary to those reported by many workers for films deposited at room or high temperature wherein these films showed metallic behaviour. Bonfilioli and Malvano (1958) measured the conductivity modulation in antimony films and confirmed the existence of localized and conducting surface states at the metal/dielectric
interface. Harris and Corrigan (1964) calculated the mean free paths of electrons and holes from $R_H$ and data on Sb films (330 to 15,000 Å) to be 1890 Å and 1220 Å respectively. They also found that the thermo-electric power of these films (positive) was thickness dependent; thinner films having smaller magnitude. Recently Bhide (1972) studied electrical properties of Sb films and found them to be p-type by Hall effect and thermal e.m.f. tests.

The above survey of literature shows a lack of systematic work on the properties of antimony films, especially their temperature dependence. In the following therefore the electrical properties of antimony films were studied in detail.

(B) EXPERIMENTAL

Antimony (99.999 % pure) was evaporated from a conical silica basket, heated externally by a tungsten filament. Cleaned glass pieces of appropriate size were used as substrates. Films with different thicknesses were obtained in each of the different sets of evaporation as described previously (Chapter 2). The rate of deposition was kept more or less constant for all the sets of depositions. All the films, whether deposited at room temperature or higher substrate temperature were annealed in vacuo at about 100°C for two hours. Only then the films were subjected to different electrical measurements. Film thickness was measured by the interferometry method. Antimony films deposited under different conditions were also examined in
FIG 4.11

FIG 4.12
an electron diffraction camera for their structural and orientation.

In all the figures filled circles (●) correspond to 
\( T_s = 100^\circ C \) and empty circles to \( T_s = 27^\circ C \).

(C) RESULTS

1) Resistivity

Resistivity of antimony films decreased with the increasing film thickness (Fig. 4.11) as observed for other films. Further the films deposited at substrate temperature \( (T_s) = 100^\circ C \) had a lower resistivity than those deposited at room temperature.

The temperature variation of \( \phi \) showed the metallic behaviour (Fig. 4.12), with \( \phi \) increasing with the increasing temperature. However for room temperature deposits the variation of \( \phi \) with temperature (78° to 370°K) was rather insignificant though the trend was the same.

ii) Hall coefficient and carrier concentration

The Hall coefficient of antimony films was independent of the current (0.1 to 2 mA) and the magnetic field (1000 - 6000 gauss) whether measured at room temperature or at liquid nitrogen temperature. However, \( R_H \) was thickness dependent, increasing with the increasing thickness and above 3000 \( A^o \) it tended to saturate (Fig. 4.13). \( R_H \) was also a function of the substrate temperature, deposits formed at higher \( T_s \) having higher values.
FIG 4.13

FIG 4.14
The variation of Hall coefficient with temperature is shown in Figure 4.14. It is seen that as the temperature increased, \( R_H \) increased sharply up to about 250 K after which it increased slowly and was practically constant in the low temperature range (78 K - 170 K).

The carrier concentration though constant in the low temperature region (78° to 170°K) increased with the further rise in temperature (Fig. 4.15). It may be noted that carrier concentration at a particular temperature was also thickness dependent similar to \( R_H \), thinner films having higher carrier concentration than thicker films.

iii) Mobility (\( \mu \))

Mobility was also thickness dependent, as observed in the case of \( R_H \) and \( \phi \). \( \mu \) increased considerably with the increasing film thickness (Fig. 4.13). Also, thicknesswise higher substrate deposits had much higher \( \mu \) than room temperature deposits.

Temperature variation of \( \mu \) showed slightly different features for deposits formed at different \( T_S \) (Fig. 4.16). For room temperature deposits, \( \mu \) was constant in the temperature region 76° to about 200°K, but decreased with the further rise of temperature, following the relation \( \mu \propto T^{-x} \) where \( x \) was about 1. However, for higher substrate deposits \( \mu \) decreased continuously throughout the temperature range. It did not follow any definite power law.

The values of different electrical parameters at room temperature are shown in Table 4.2.
### $T_a = 30^\circ C$

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness $d$ (Å)</th>
<th>$R_H \times 10^{-2}$ cm$^3$ C$^{-1}$ cm</th>
<th>$\zeta \times 10^{-4}$ ohm-cm</th>
<th>$\mu$ cm$^2$/V-sec</th>
<th>$n \times 10^{20}$ cm$^{-3}$</th>
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<td>0.99</td>
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<td>3.70</td>
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### $T_a = 100^\circ C$

<table>
<thead>
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<th>No.</th>
<th>Thickness $d$ (Å)</th>
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<th>$\zeta \times 10^{-4}$ ohm-cm</th>
<th>$\mu$ cm$^2$/V-sec</th>
<th>$n \times 10^{20}$ cm$^{-3}$</th>
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<td>2.30</td>
<td>1.11</td>
<td>193</td>
<td>2.72</td>
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</table>
iv) T.C.R.

T.C.R. for all the films was positive, thicker films having higher value as compared to thinner films. The variation of T.C.R. with temperature is shown in Figure 4.17 where it is seen that T.C.R. increased with increasing temperature.

v) Thermoelectric power

Thermoelectric power of antimony films was measured by differential method. All the films were found to be p-type by this method as was also observed by Hall effect measurements. It is seen from Fig. 4.18 that a increased with the rise in temperature upto about 300°K but tended to decrease with the further increase in temperature.

vi) Structure

Thinner films of antimony were polycrystalline in nature as compared to thicker films which showed 1-d orientation (Fig. 4.19). Thus the deposits were crystalline in nature and had normal rhombohedral structure. (a = 4.29 Å, c = 11.26 Å).

(D) DISCUSSION

All the antimony films (700 to 5000 Å) showed a metallic (or rather semimetallic, p-type) behaviour as is also the case for bulk Sb. It is interesting to note that bismuth though a semimetal in the bulk form behaved like a semiconductor in the thin film form. Thus although bismuth and antimony are structurally similar in the thin films form (rhombohedral), the conduction mechanisms in these films are quite different.
It is well known that outer electrons in the semimetal antimony (bulk) are distributed between two overlapping energy bands. The electrons overlapping into the upper conduction band behave as negatively charged carriers \( (n_e) \) whilst the unfilled energy levels in the lower band behave as positively charged one \( (n_p) \). Thus the conductivity equation for metals becomes

\[
\sigma = \frac{ne^2 \ell}{m^* v} \text{hole} + \frac{ne^2 \ell}{m^* v} \text{electron}
\]

If some amount of impurity is present, the relative distribution of charge carriers will differ significantly depending upon the type of impurities (acceptor or donor). The fact that antimony films are p-type suggests the dominance of acceptor type of impurities. Such impurities are likely to be in the form of numerous defects and imperfections invariably present in thin films.

The dependence of Hall coefficient and resistivity on the film-thickness was similar to tellurium films (cf Chapter 3), with the latter increasing whilst the former decreasing with increasing film thickness.

Although the T.C.R. for the films deposited at room temperature and higher substrate temperature was positive, the variation of \( \sigma \) with temperature was much less for the former than the latter. This is mainly because of the higher carrier concentration in the case of room temperature deposits. The Hall coefficient like resistivity was constant at low temperature but decreased rapidly at high temperatures.
The mobility behaviour for the room temperature deposits followed the relation $\mu \propto T^{-1}$, as compared to the higher substrate deposits which though did not follow any particular law at higher temperatures, however, tended to follow approximately $\mu \propto T^{-1.5}$ relation. This perhaps suggests scattering due to lattice vibration as was also suggested for the bulk Sb single crystal (Okkut and Saunders, 1967) where for holes the relation $\mu \propto T^{-1.48}$ was valid.