SUMMARY AND CONCLUSIONS

The electron transport properties of vacuum deposited films, both semiconducting as well as semimetallic, have been investigated in details with a view to understand the conduction mechanism operative in films and compare these with their bulk properties. For this, electrical properties such as Hall effect, conductivity, magnetoresistance, thermoelectric power etc. of deposits formed at different substrate temperatures were measured at a wide range of temperature (73° to about 600°K). Various electrical parameters such as Hall coefficient, carrier concentration, mobility, activation energy, T.C.R., were then evaluated. These studies also quite often revealed the type of conduction and scattering mechanism predominant in thin film state. The evaporating conditions such as, substrate temperature, annealing, rate of deposition etc. were found to have a pronounced influence on different electrical parameter. Many a time crystallographic structures, phase-composition etc. of these films differed considerably from the starting bulk material as revealed by the electron diffraction studies, which also served to control the nature of the deposits and eventually correlate them with the electrical properties.

Tellurium films (p-type) showed some peculiar features. The Hall coefficient, instead of saturating at low temperature, as expected for an impurity semiconductor,
decreased at low temperatures, invariably showing a peak. This behaviour has been explained on the basis of the impurity band conduction mechanism (Goswami and Ojha, 1973). Another important conclusion drawn was that the dominant scattering mechanism in tellurium films was due to the charged impurities since mobility followed the Conwell-Weiskopf law viz. $\mu \propto T^{3/2}$. Such scattering for the Te films was observed at a comparatively higher temperature region in contrast to the bulk single crystals of Te, where it was effective only at the liquid helium temperature region. Activation energy was a function of the film thickness, thinner films having higher values. $R_\eta$, $\mu$ and $\sigma$ were also considerably affected by thickness but unlike the case of $\Delta E$, thicker films had higher magnitude. With the help of electron diffraction studies, it was found that the semiconducting properties of tellurium were neither significantly affected by either normal or oblique incidence of the Te vapours on the substrates nor from the fact that they were polycrystalline or 1-d orientated.

Although bismuth is a semimetal in the bulk form, it showed a different conduction mechanism in the thin film state. All the films ($700 \, \AA$ to about $5000 \, \AA$) had a negative T.C.R. as against positive T.C.R. observed in the case of bulk. The activation energy for these films was however very small ($\approx 0.05 \, \text{eV}$). The type of conduction in thin films was found to be essentially a function of thickness, thinner films ($< 3000 \, \AA$) showing p-type behaviour, whereas the thicker films were n-type at room temperature. The temperature
variation of $R_H$ showed an interesting feature viz. a transition from $n$ to $p$-type as the temperature increased from 78°K, the transition temperature being a function of the film thickness. This transition from $n$ to $p$-type conduction suggested the dominance of electrons or hole mobility depending upon the temperature of measurement. The magnetoresistance followed a square law dependence on magnetic field and was higher at 78°K as compared to that at room temperature.

Antimony films, unlike bismuth films, had a positive T.C.R. thus indicating a semimetallic behaviour. All the films were $p$-type indicating the dominance of acceptor type of impurities. $R_H$ was constant at low temperature but decreased rapidly at higher temperatures. The mobility behaviour for the room temperature and higher temperature deposits was different, whilst the former showed $T^{-1}$ dependence of mobility, the latter showed a $T^{-1.5}$ dependence, this being no doubt due to the predominance of lattice scattering at higher temperature. The thickness dependence of $R_H$ and $\sigma$ was similar to tellurium films.

Mercury selenide, however showed a semi-metallic type of behaviour, similar to the bulk single crystal. All the films, epitaxial or polycrystalline, were $n$-type and had a positive T.C.R. which indicates the overlapping of valence and conduction bands. $R_H$ and $\mu$ were constant at low temperatures but decreased at higher temperatures. Mobility in the higher temperature region followed the relation $\mu \propto T^{-x}$ where $x$ varied
from 2.5 to 2.83, thicker films favouring higher values, thus suggesting that the scattering mechanism in HgSe films was dependent on the carrier concentration as was also observed in the case of bulk. Magnetoresistance was proportional to the square of magnetic field for all the films. Thermoelectric power, showing all films to be n-type, increased considerably with temperature (40 to 140 μV/°C). It was found that for the films deposited on mica substrates, the electrical parameters such as $R_H$, $\sigma$, $\mu$ etc. had higher magnitudes as compared to those formed on glass substrates, thus suggesting a better perfection of crystallites in the former case.

Bismuth oxide films prepared from silica and Mo boat, showed structures which were slightly different from each other. Electrical properties of the two types of films were also different. $R_H$ and $\sigma$ were slightly higher for films deposited from the Mo boat. Activation energy for films deposited from silica boat was about 2.60 eV as compared to 0.05 eV for films deposited from Mo boat. The temperature variation of $\mu$ followed the relation $\mu \propto T^{-1}$ and the deviation of this relation from the lattice vibration scattering mode ($\mu \propto T^{-3/2}$) was attributed to the dominance of defects and impurities.

The oxidised films however showed some interesting properties. The activation energy of these films when measured in air was $\approx 1.80$ eV but was much higher ($\approx 2.60$ eV) when measured in vacuum. The above feature together with the fact that conductivity of the vacuum heated films was higher than
the untreated ones, no doubt suggests the dissociation of the oxide in vacuo and the formation of intermediate products like BiO (Goswami and Ojha, 1973).

Structural and electrical properties of Tl2Te films deposited by the flash evaporation method were also studied in detail. X-ray powder and electron diffraction analysis of the bulk and films respectively established that Tl2Te had a tetragonal structure \((a = 8.62 \text{ Å} \text{ and } c = 12.64 \text{ Å})\). All the films were found to be p-type. It was found that substrate temperature had a pronounced effect on the properties of Tl2Te films. Films deposited at room temperature had lower values of \(R_H\), \(\sigma\), and \(\mu\) as compared to those formed at higher substrate temperatures. Activation energy for room temperature deposits was about 0.14 eV as compared to about 0.70 eV for the higher substrate temperature deposits. Both \(R_H\) and \(\sigma\) were almost constant at low temperatures but decreased rapidly at high temperatures. Mobility behaviour in the two cases was also different. For higher temperature deposits \(\mu\) was constant in the low temperature region \((78^\circ \text{ to } 140^\circ \text{K})\) above which it decreased continuously following the \(\mu \propto T^{-x}\) when \(x\) was about 1.30. Even though the room temperature deposits followed a similar trend upto a temperature of about 270\(^\circ\text{K}\) but beyond this region it followed a different relation i.e. \(\mu \propto T^{+x}\).

High mobility films of InSb \((8000 \text{ cm}^2/\text{V-sec})\) were prepared with the help of the flash evaporation technique. Thickness dependence of \(R_H\), \(\mu\) and \(\sigma\) was similar to the tellurium films.
Activation energy was found to be about 0.26 which agreed well with that reported for the bulk. It was found that the substrate temperature had a considerable influence on the properties of these films, higher substrate temperatures favouring higher mobility films. The temperature variation of $R_H$ and $\rho$ was characteristic of an impurity semiconductor. $\mu$ was found to increase initially at low temperature but after about 700 K it showed a gradual decrease.

Thus the present investigations on the electrical properties of semiconducting and semimetallic films reveal that the transport mechanism is often altered in thin film state. Some of these can be adduced to factors such as evaporation conditions, annealing, film thickness and much more so to the presence of impurities and defects which are invariably present in the evaporated films, as mentioned earlier. Effect of vacuum conditions, not only in causing phase changes but also a possible dissociation of the compounds have been clearly brought out in some of our results.

The study also showed that electrical parameters which are constant for a bulk material are no longer so in the film state, these being strong functions of evaporating conditions and thickness etc. These variations have posed severe problems for any quantitative evaluation on the basis of a theoretical model usually assumed for the bulk. This difficulty has further been enhanced because of a lack of precise knowledge of the variation, if at all, of the effective mass of electrons.
and holes in the film state. It is quite likely that these parameters are also thickness dependent as observed for other parameters. Consequently further investigations of the effective mass of charge carriers for thin films would be of great interest. With the precise knowledge of the effective mass along with other transport parameters, it would be possible to quantitatively propose a theoretical model for the conduction mechanism in thin films.