Bismuth forms two well known oxides viz. Bi₂O₃ and Bi₂O₅. Out of these Bi₂O₅ has three crystallographic forms viz. α, β and γ. α-Bi₂O₅ has a monoclinic unit cell (a = 5.83 Å, b = 8.14 Å, c = 7.48 Å and α = 64.07°), β-form is tetragonal (a = 10.63 Å, c = 10.93 Å) whilst γ-Bi₂O₅ has a b.c.c. structure with a = 10.24 Å (Schumb and Rittner, 1943). The structure of bismuth oxide as discussed above has been investigated by several workers. However, not much attention has been paid to the formation and structure of the sub-oxide of bismuth.

Schneider, as early as 1953 reported the formation of a bismuth sub-oxide but could not establish its structure. The presence of a sub-oxide of bismuth in powder and colloidal bismuth was reported by Bhatnagar (1930) who found it to be weakly diamagnetic or even paramagnetic. Bridge and Howell (1954) attributed the spectral observation of bismuth vapours to BiO. An electron diffraction study of thin layers in the Bi-O system during the initial stages of oxidation of bismuth suggested the existence of a hexagonal (rhombohedral) phase.
of BiO with $a = 3.8 \pm 0.024 \text{ Å}$, $c = 9.71 \pm 0.05 \text{ Å}$ (Zavyalor, 1965). The formation of BiO and its structure have recently been established from the electron diffraction studies (Gadgil and Goswami, 1970).

Mansfield (1949) measured the thermoelectric power of bismuth oxide at high temperatures and found it to be p-type. Konosylov et al. (1955) on the other hand found an n-type of conduction using the same technique as above. Fidyre et al. (1960) found the type of conduction in $\text{Bi}_2\text{O}_3$ to be temperature dependent, with p-type conduction in the temperature range 250 to 300°C and n-type at higher temperatures. Electrical conductivity and thermal e.m.f. of solid and liquid bismuth oxide were measured by Zolyan and Regel (1963). It was observed that at the transition temperature $\alpha - \beta$ phase, the conductivity of $\beta$-$\text{Bi}_2\text{O}_3$ increased by 3 orders of magnitude, this increase being attributed to an ionic component of the conductivity.

Investigations on the electrical properties of thin films have been essentially on oxide films formed by evaporation of $\text{Bi}_2\text{O}_3$ in oxygen atmosphere or sometimes by further oxidising in air. Doyle (1958) prepared bismuth sesqui oxide by the oxidation of vacuum deposited bismuth films in oxygen atmosphere. The absorption spectra of $\text{Bi}_2\text{O}_3$ films thus prepared was characterised by a stray absorption in the ultraviolet, the threshold photo energy being 3.2 eV. Thermal energy gap
of polycrystalline $\mathrm{Bi}_2\mathrm{O}_3$ films, determined from the conductivity measurements in the temperature range of 400 to 500°C was about $2.07 \pm 0.007$ eV (Mattix, 1960). Lieberman and Medrud (1969) prepared bismuth oxide films by crystallization of the highly absorbing, amorphous, reactively sputtered films. These films had high refractive index ($n = 2.4$ to 2.7) and low optical absorption ($k = 0$ to 0.004). Halford and Harker (1969) investigated the dielectric properties of bismuth trioxide films, prepared by the vacuum evaporation of $\mathrm{Bi}_2\mathrm{O}_3$ from platinum boat and its subsequent annealing in oxygen atmosphere. Detailed investigations on various properties of bismuth oxide films, prepared by the electron beam evaporation of $\mathrm{Bi}_2\mathrm{O}_3$ in oxygen atmosphere were done by Gobrecht et al. (1969). Measurements of the dependence of the electrical conductivity on temperature as well as transmission and reflection measurements indicated a band gap $= 2.91$ eV for the direct optical transitions and 2.60 and 2.15 eV (optical and thermal results respectively) for the indirect one. They also concluded on the basis of conductivity changes under the influence of chemisorbed oxygen, that films prepared by oxidation of bismuth in air show n-type of conductivity and those prepared by the electron beam evaporation method show a p-type of conduction.

Bismuth oxide films have also been used in fabricating devices like Vidicon (Weimer, 1950) where they are used after being doped by certain materials.

Thus from the above survey of literature it is seen that though some amount of work has been carried out on the electrical
properties of $\text{Bi}_2\text{O}_3$ films, prepared mostly in oxidizing environment, hardly anything is reported about the properties of the directly evaporated bismuth oxide films, without any further treatment and their correlation with the ones obtained after their thermal oxidation in air. In the present investigations a detailed study of the electrical and structural properties of both the types of films mentioned above has been carried out to throw some light on their basic properties and possible correlation with their structures.

(B) EXPERIMENTAL

Initial experiments with $\text{Bi}_2\text{O}_3$ (supplied by M/S Bigot-Sharfe & Co., Hamburg) powder which was yellowish in colour showed that deposits obtained by evaporation in vacuo were blackish in appearance. Further these deposits when heated in air changed to yellowish colour. Suspecting that the nature of these black deposits might be different from those of oxidised in air and also that the evaporation source might have some effect, a detailed study on these deposits for their structure and electrical properties was made.

Bismuth oxide powder was thermally vacuum deposited either from a conical silica basket heated externally by a tungsten wire (hereafter called A-films) or directly from molybdenum boat (hereafter B-films) on glass substrates of appropriate size at room temperature. Both the tungsten filament as well as the molybdenum boat were initially flashed.
These films were then annealed in vacuo at 225° C which was much lower than the temperature of discontinuity.

Electric parameters viz. resistivity, Hall coefficient, mobility, carrier concentration, thermoelectric power, T.C.R. etc. were measured between the temperature range of about 73° to 525° K in the manner described before (cf. Chapter 2). Measurements of all the parameters were repeated several times and found to be in agreement with one another.

A-films were also oxidized in air at about 400° C for eight hours (hereafter C-films). These oxidized films were found to have shiny yellowish tinges in contrast to the blackish appearance of A and B films. These oxidized deposits were then subjected to the resistance measurements 1) in air between the temperature range of about 300° to 770° K and (ii) in vacuo in the same temperature range after treating C-films at about 770° K (also in vacuo) for four hours.

Film-thickness in all cases was estimated by the multiple beam interference method. Electron diffraction studies were also made on the A, B and C-films formed on glass or polycrystalline NaCl tablets for their structural features. Both the bulk powder as well as the residues remaining on silica baskets and molybdenum boats were also examined by the X-ray powder technique. It may be mentioned here that the residues from the silica basket were pale yellowish in
FIG 6.2

FIG 6.3
appearance whereas those from molybdenum boats were blackish
in nature.

(C) RESULTS

(a) A and B films:

i) Resistance and activation energy

Figure 6.1 shows the variation of resistivity with film-thickness for the two types of evaporated films of A
and B. Even though B-films had slightly higher resistivity
than A-films, the trend of the thickness variation of
resistivity in both the cases was similar, with the thicker
films tending to a constant value.

The temperature variation of resistance in A and B-films
was slightly different. Figure 6.2 shows the variation of R
with 1/T (semilog scale) for different A-films. It is seen
that each curve showed different slopes in the three tempera­
ture regions viz. (a) the high, (b) the intermediate, and
(c) the low temperature region. Activation energy for A-films
varied widely in these regions. $\Delta E$ was quite large (about
2.60 eV) in the A-region but low ($\approx 0.036$ eV) in the
B-region and in the C-region it was indeed very low
($\approx 10^{-5}$ eV). These were true for all A-films thus showing
the thickness independence of activation energy.

The variation of $R$ vs $1/T$ for B-films is shown in
Fig. 6.3. Here only two slopes can be seen viz. (a) and
(b) compared to the three for A-films. The activation
FIG 6.7

FIG 6.8
energies of B-films were respectively $\sim 0.056$ and $\sim 10^{-3}$ eV for these regions and were close to (b) and (c) regions respectively of A-films. The steep slope as observed in A-films (cf. Fig. 6.2) was not observed even when measurements were extended up to the temperature of discontinuity $T_d$ of B-films ($\approx 230^\circ$C).

(ii) Hall coefficient

It was found that $R_H$ was independent of the magnetic field (1000 - 6000 gauss) and current (0.1 to 2 mA) throughout the temperature range ($78^\circ$ - $525^\circ$K) for both A and B-films. Both the types of films were n-type.

It was found that $R_H$ increased with the increasing thickness (Fig. 6.4), with B-films having thicknesswise slightly higher $R_H$ than the A-films. Figs. 6.5 and 6.6 for A and B-films show the temperature variation of $R_H$. It was almost constant at low temperatures ($78^\circ$ to $170^\circ$K), but decreased gradually with the further rise of temperature.

(iii) Carrier concentration

Figs. 6.7 and 6.8 show the variation of $n$ with temperature for A and B-films respectively. $n$ was constant at low temperatures but it increased gradually at higher temperatures.

(iv) Mobility

Mobility increased with increasing film-thickness with the A-films having slightly higher $\mu$, thicknesswise (Fig. 6.4). The variation of $\mu$ with temperature for different thickness
of A and B-films is shown in Figs. 6.9 and 6.10 respectively (log-log scale). \( \mu \) decreased with increasing temperature following the relation \( \mu \propto T^{-x} \) where \( x \) varied from 0.9 to 1.0 in both the sets of films. The dotted line shows a hypothetical case following the relation \( \mu \propto T^{-3/2} \) for scattering due to lattice vibrations.

Table 6.1 shows the values of different electrical parameters, both for A and B films measured at room temperature.

(v) **Thermoelectric power**

Thermoelectric power, measured both by integral and differential methods, was found to be in good agreement. Fig. 6.11 shows the variation of \( \alpha \) with temperature for both A and B-films. It is seen that \( \alpha \) increased slowly with the temperature, attained a peak at about 400\(^{0}\)K and then decreased with the further rise of temperature. All the films were found to be n-type by this method also.

(vi) **T.C.R.**

The variation of T.C.R. (\( \% \)) for both A and B-films is shown in Fig. 6.12. It is seen that for A films T.C.R. was almost constant (about 0.1\( \% \)) in the temperature region 78\(^{0}\) to 300\(^{0}\)K. However, after 300\(^{0}\)K, T.C.R. started increasing with the further increase in temperature and after about 440\(^{0}\)K the increase was steep, its magnitude being about ten times larger than the value at low temperatures. In the case of B-films, the T.C.R. varied more or less in the same manner as A-films,
### Table 6.1

**Deposits from silica boat**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Thickness d Å</th>
<th>( R_H ) cm(^3) C(^{-1})</th>
<th>( \phi ) ohm-cm</th>
<th>( \mu ) cm(^2)/V-sec</th>
<th>( n ) cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>0.020</td>
<td>6.0x10(^{-3})</td>
<td>3.3</td>
<td>3.12x10(^{20})</td>
</tr>
<tr>
<td>2</td>
<td>1649</td>
<td>0.045</td>
<td>5.62x10(^{-3})</td>
<td>8.0</td>
<td>1.39x10(^{20})</td>
</tr>
<tr>
<td>3</td>
<td>2200</td>
<td>0.072</td>
<td>5.00x10(^{-3})</td>
<td>14.4</td>
<td>8.70x10(^{19})</td>
</tr>
<tr>
<td>4</td>
<td>2620</td>
<td>0.068</td>
<td>4.44x10(^{-3})</td>
<td>15.3</td>
<td>9.20x10(^{19})</td>
</tr>
<tr>
<td>5</td>
<td>3140</td>
<td>0.080</td>
<td>4.26x10(^{-3})</td>
<td>13.9</td>
<td>7.80x10(^{19})</td>
</tr>
<tr>
<td>6</td>
<td>3500</td>
<td>0.100</td>
<td>4.16x10(^{-3})</td>
<td>21.7</td>
<td>6.25x10(^{19})</td>
</tr>
<tr>
<td>7</td>
<td>4050</td>
<td>0.104</td>
<td>3.91x10(^{-3})</td>
<td>26.6</td>
<td>6.00x10(^{19})</td>
</tr>
<tr>
<td>8</td>
<td>4330</td>
<td>0.115</td>
<td>3.81x10(^{-3})</td>
<td>30.3</td>
<td>5.45x10(^{19})</td>
</tr>
</tbody>
</table>

**Deposits from molybdenum boat**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Thickness d Å</th>
<th>( R_H ) cm(^3) C(^{-1})</th>
<th>( \phi ) ohm-cm</th>
<th>( \mu ) cm(^2)/V-sec</th>
<th>( n ) cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1623</td>
<td>0.15</td>
<td>5.91x10(^{-2})</td>
<td>2.5</td>
<td>4.16x10(^{19})</td>
</tr>
<tr>
<td>2</td>
<td>2857</td>
<td>0.22</td>
<td>2.51x10(^{-2})</td>
<td>8.9</td>
<td>2.84x10(^{19})</td>
</tr>
<tr>
<td>3</td>
<td>3350</td>
<td>0.31</td>
<td>2.14x10(^{-2})</td>
<td>14.5</td>
<td>2.02x10(^{19})</td>
</tr>
<tr>
<td>4</td>
<td>4233</td>
<td>0.37</td>
<td>1.57x10(^{-2})</td>
<td>23.6</td>
<td>1.69x10(^{19})</td>
</tr>
<tr>
<td>5</td>
<td>5000</td>
<td>0.48</td>
<td>1.45x10(^{-2})</td>
<td>33.1</td>
<td>1.30x10(^{19})</td>
</tr>
<tr>
<td>6</td>
<td>5333</td>
<td>0.52</td>
<td>1.39x10(^{-2})</td>
<td>37.4</td>
<td>1.20x10(^{19})</td>
</tr>
</tbody>
</table>
FIG 6.12

FIG 6.13

FIG 6.14
except that in this case there was no sharp increase as observed for A-films.

(vii) Structure

Electron diffraction studies made on A and B-films were not very conclusive regarding the phase composition of the materials except that the observed reflections for both the types of films were similar to some of the reflections of Bi₂O₅. Even then there was a considerable intensity variation in different reflections of A and B-films. Fig. 6.13 shows a typical pattern obtained from A-films suggesting the cubic structure (a = 10.8 Å). The intensity of the reflections of B-films (Fig. 6.14) could, however, be better explained with a cubic cell (a = 5.4 Å) which is half that of the normal γ-Bi₂O₅ cell. X-ray powder patterns from the bulk as well as those of residues from A and B (Fig. 6.15 and 6.16 respectively) were broadly similar except that the number of reflections for A and B residues were lesser than those of bulk γ-Bi₂O₅ (Fig. 6.17). A general consideration suggests that B-film residue had a = 5.4 Å whereas residues from A-films consisted of a mixture of species having a = 5.4 Å and 10.8 Å.

(b) C-films

(i) Resistance and activation energy

Films measured under the condition (i) had high resistance. Fig. 6.18 shows a typical R vs 1/T curve (semilog scale) between
the temperature range 300 to 770°K (curve 1). As the film resistance was very high no measurement below room temperature could be carried out. The same film under the conditions (ii) showed a considerable change not only in resistance (cf curve 2 Fig. 6.18) but also in appearance and the film became greyish. When further treated in vacuo for 4 hours and measured under conditions (ii), a considerable lowering in resistance was observed (cf curve 3, Fig. 6.18). It is seen that the curve 1 had two distinct linear slopes, one at the higher temperature range \( \Delta \varepsilon = 1.80 \text{ eV} \) and the other at lower temperature region \( \Delta \varepsilon = 1.20 \text{ eV} \). Curve 2 corresponding to (ii) has steeper slope \( \Delta \varepsilon = 2.56 \text{ eV} \) between the narrow temperature range (620 to 660°K). At the lower temperature region the slope was no longer constant. A similar value of \( \Delta \varepsilon \) \( (= 2.60 \text{ eV} ) \) between the temperature range 610 to 650°K was observed for the curve 3.

It may also be mentioned here that the resistance of C-films continuously decreased with the vacuum treatment, tending towards values similar to those of A-films and the appearance of such films became greyish to blackish. Both C(i) and C(ii) films were found to be n-type similar to the A-films.

(ii) Structure

Fig. 6.19 shows electron diffraction pattern for the oxidized films C(i). This pattern corresponds to \( \gamma \)-Bi\(_2\)O\(_3\) (b.c.c., \( a = 10.8 \text{ Å} \)).
The above study has clearly demonstrated the importance of the preparation method, such as the source of evaporation, on different properties of vacuum deposited films in general and bismuth oxide films in particular. Not only the A and B films differed in electrical properties but also to some extent structurally. C-films i.e. those oxidized in air also differed considerably, structurally and electrically, from both A and B films (Goswami & Ojha, 1973).

The variations of $R_H$ and $\mu$ (of Fig. 6.4) with the thickness was similar to those observed for films of other materials. It may however be noted that $R_H$ and $\varphi$ were slightly larger in magnitude for B-films than those for the A-films deposited from a silica boat. These differences may be attributed to the variation, though small, of the composition of the oxides of bismuth-deposits depending on the container as reported by Sillen (1936). This was also confirmed by the electron diffraction studies which showed a considerable intensity-variation in different reflections of A and B films (cf Figs. 6.13 and 6.14).

The variation of $R_H$, $\varphi$, and $\mu$ with temperature, both for A and B-films, was similar. $R_H$ and $\varphi$ were almost constant at low temperature since the thermal energy to ionize donor centres was very low ($\approx 10^{-3}$ eV). However as the temperature increased thermal ionization energy increased thus raising the carrier concentration (cf Fig. 6.7) and reducing $R_H$. 

(D) DISCUSSION
This behaviour corresponds to that of a typical n-type semiconductor.

The mobility for these films, except for very low temperatures where it was more or less constant, followed the relation \( \mu \propto T^{-x} \) where \( x < 1 \) for all the film thicknesses (cf Figs. 6.9 and 6.10). Thus the mobility relation did not correspond to the scattering caused by lattice vibrations where \( x \) would have been \( 3/2 \), instead of 1 as observed in the present case. This appears to be due to the predominance of impurities and defects presumably grain boundaries, disorder, imperfection of crystallites, presence of other species such as BiO in the thermally deposited A and B-films. The lowering of the magnitude of power index from \( 3/2 \) has already been reported to be due to the increase in the impurity concentration (Debye & Conwell, 1954). However it is difficult to assign any definite scattering mechanism in the present case of the deposited films because of the uncertainty in the composition and structure of these films.

It was also observed during the vacuum treatments of C-films that the activation energy increased from 1.30 eV to 2.60 eV conforming to A-films (cf curve 2 and 3 of Fig. 6.18) and simultaneously the appearance of the films also became greyish. These changes occurring during the vacuum treatment appear to be due to the thermal dissociation of \( \text{Bi}_2\text{O}_3 \) to lower oxides. During a recent study of the gradual oxidation of bismuth films to \( \text{Bi}_2\text{O}_3 \) and effect of vacuum treatment on
the oxidized films it was found by Gadgil and Goswami (to be published) that BiO, blackish in colour, was an intermediate product during both the oxidation and the vacuum treatment processes. They have also established the structure of the suboxide (Gadgil and Goswami, 1970). Our present results along with the observations made by Gadgil and Goswami clearly suggest the presence of the intermediate suboxide (BiO) phase both during the thermal evaporation of Bi$_2$O$_3$ or the vacuum dissociation of the compound. The blackish nature of A and B as well as C(ii) films and their low resistivity also lend support to the presence of small amount of BiO in these films.

Thermoelectric power increased with the increasing temperature, reached a peak at about 400°K and then decreased with the further rise of temperature (cf Fig. 6.11). This behaviour can be accounted for by considering the films to consist of mixed charge carriers. Since the effective $a$ is determined by the mobility and the carrier concentration of electrons as well as holes present in these deposits, its decrease in the high temperature region, no doubt, suggests that the contribution of holes was becoming more predominant.