Chapter 6

Electrical Properties of Bi₂S₃ and Bi₂O₃ thin films

The theoretical background of electrical and optical properties of semiconducting films has been discussed in Chapter 3. Preparation details of the Bi₂S₃ and Bi₂O₃ thin films and experimental arrangements for measuring different electrical and optical properties of the films have been presented in Chapter 4. The electrical properties such as ohmic contact to the films, electrical resistivity, energy band gap, aging effect of the films etc. and optical properties such as effect of light on resistivity, dielectric constant, reflectance, transmittance, absorbance etc. of the films have been presented in this Chapter.

6 Electrical Properties of Bi₂S₃ and Bi₂O₃ thin films

6.1 Sample preparation and measurement of electrical properties

It has been observed that both Bi₂S₃ and Bi₂O₃ samples decompose during evaporation [1-5]. Decomposition of the compounds during evaporation leads either to nonstoichiometric films or to layered films. To overcome this difficulty special care have been taken in depositing thin films and they were annealed before performing experiment. Electrical measurements were performed under vacuum condition. Preparation details, experimental arrangement and procedure to measure I-V characteristics of the samples have been presented in Chapter 4.
6.2 Ohmic contact

When semiconductor is made intimate contact with metal, two types of $I-V$ characteristics are observed: (a) linear and (b) non-linear. The intimate contacts which shows linear $I-V$ characteristics for both directions (forward and reverse) of current flow is known as ohmic contact. In practical semiconductor junction, the term ohmic contact may be used to describe any contact which allows charge carriers to move freely into and out of device and does not interfere with the operation of the device [6].

![I-V plot](image)

**Fig.44:** $I-V$ of a Ni-(p)Bi$_2$S$_3$-Ni sample of thickness 0.2991 μm and carrier concentration $12.578 \times 10^{16}$ cm$^{-3}$ (Sd for dark and Si under illumination at 2000 Lux; (b) Al-(n)Bi$_2$O$_3$-Al sample of thickness 0.6442 μm and carrier concentration $66.688 \times 10^{14}$ cm$^{-3}$ (S$_{0d}$ for dark and $S_{0i}$ under room illumination at 2000 Lux), all are at room temperature (303K).

The $I-V$ plots of a typical Ni-(p)Bi$_2$S$_3$-Ni gap type thin film and a typical Al-(n)Bi$_2$O$_3$-Al gap type thin film in dark and under illuminated condition for both forward
and reverse bias are shown in Fig.44. The $S_d$ and $S_i$ are two $I-V$ characteristics of Ni-
(p)Bi$_2$S$_3$-Ni gap type thin film taken in dark and under room illumination (2000 Lux). Both $S_i$ and $S_d$ plots show linear nature for both forward and reverse bias. The linear $I-V$
characteristics showed by the Ni-(p)Bi$_2$S$_3$-Ni sample for both forward and reverse
current in dark and under illumination confirm the good ohmic contact between
(p)Bi$_2$S$_3$ (work function 4.93eV) \cite{7} thin film and Ni (work function 5.422eV) \cite{8} metal. The contact nature of extrinsic Bi$_2$O$_3$ (work function 6.23eV) \cite{9} films with some
base metals have been examined. The $S_{0d}$ and $S_{0i}$ are two linear $I-V$ characteristics of a
typical Al-(n)Bi$_2$O$_3$-Al film in dark and under illumination both for forward and reverse
bias. The linear nature of $I-V$ characteristics confirms the ohmic contact between
(n)Bi$_2$O$_3$ films and Al (work function 4.18 eV) \cite{10} metal. The required condition for
ohmic contact between metal and semiconductor as mentioned in section 3.6.1 of
Chapter 3 is satisfied between (p)Bi$_2$S$_3$ and Ni and between (n)Bi$_2$O$_3$ and Al.

6.3 Temperature variation resistivity of annealed (p)Bi$_2$S$_3$ films

The electrical conductivity of pure and unannealed films were found to be
very poor. The Conductivity of the films were found to improve on annealing. The In
doped Bi$_2$S$_3$ films exhibited p-type nature with sufficient conductivity. The temperature
variation $I-V$ characteristic of a typical gap type annealed (p)Bi$_2$S$_3$ thin film is shown in
Fig.45. The currents of the gap type (p)Bi$_2$S$_3$ thin films were found to increase with the
increase of temperature. The resistivity of a typical annealed (p)Bi$_2$S$_3$ film has been
observed to vary from 214.636 $\Omega$.cm to 3.774 $\Omega$.cm within the temperature range 298K-
440K. Temperature dependence of dark conductivity ($\sigma$) of a typical sample deposited
at room temperature 303K has been shown in Fig.46. Similar nature of temperature
variation of conductivity ($\sigma$) have been observed for all In doped annealed (p)Bi$_2$S$_3$ films, except a slight shift in conductivity depending on concentration. Each curve of $\ln\sigma$ vs $T^{-1}$ plots (Fig.47) shows two distinct slopes, one corresponding to low temperature range (303-357)K and other above 357K. From the intrinsic region the value of band gap were calculated using relation [11]

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{2k_BT}\right)$$

(6.1)

The band gaps so obtained at high temperature region were about 1.580eV, 1.479eV, and 1.245 eV for doping concentration 15.223x10$^{15}$/cm$^3$, 72.314x10$^{15}$/cm$^3$, and 29.267 x 10$^{16}$/cm$^3$ respectively. The corresponding activation energies obtained from the slopes at low temperature region were about 0.366eV, 0.332eV and 0.327eV. Values of some electrical parameters of three typical annealed (p)Bi$_2$S$_3$ thin films are given in Table 6.01. A change has been observed in the band gap energy and activation energy with doping concentration. Decrease in band gap energy and activation energy with increasing doping concentration indicates that there has been band tailoring due to increase in doping concentration [12]. All films studied in the present case were semitransparent. The thickness dependence of band gap energy arises due
Fig. 45: Temperature variation $I-V$ plot of a typical gap type Ni-(p)Bi$_2$S$_3$-Ni thin film of thickness 0.5961\,\mu m.

Fig. 46: $\sigma$ vs $1/T$ plot of a typical Ni-(p)Bi$_2$S$_3$-Ni gap type sample (0.3241\,\mu m).
Fig. 47: $\ln \sigma$ versus $1/T$ plots of three typical gap type Ni-(p)Bi$_2$S$_3$-Ni thin films for three different carrier concentrations.

to [13] (i) a large density of dislocation, (ii) quantum size effect, (iii) change of barrier height due to change in grain size in polycrystalline films. The thickness of the films in the present case is sufficiently large hence quantum size effect contribution is nil. Also contribution due to dislocation is small. However, grain size seems to affect the band gap energy.

The values of activation energy at low temperature region correspond to impurity conduction due to excess In. As the temperature is raised the impurity levels are exhausted and conduction becomes intrinsic in nature. The temperature was not lower enough to see the phonon assisted conduction mechanism.
Table 6.01: Values of some electrical parameters of three typical annealed (p)Bi\textsubscript{2}S\textsubscript{3} thin films.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Thickness (µm)</th>
<th>Carrier concentration (N_a) (10^{15})(cm(^{-3}))</th>
<th>Activation energy (E_a)(eV)</th>
<th>Energy gap (E_g)(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{10})</td>
<td>0.3521</td>
<td>15.223</td>
<td>0.366</td>
<td>1.380</td>
</tr>
<tr>
<td>(S_{11})</td>
<td>0.2762</td>
<td>72.314</td>
<td>0.332</td>
<td>1.279</td>
</tr>
<tr>
<td>(S_{12})</td>
<td>0.2991</td>
<td>292.676</td>
<td>0.327</td>
<td>1.343</td>
</tr>
</tbody>
</table>

6.4 Temperature variation \(I-V\) characteristics of Bi\textsubscript{2}O\textsubscript{3} films

The detail of preparation of (n)Bi\textsubscript{2}O\textsubscript{3} films have been discussed in Chapter 4. The temperature variation \(I-V\) characteristics of both annealed and as-deposited Bi\textsubscript{2}O\textsubscript{3} films have been studied. Two electrodes of Al were vacuum deposited for ohmic contact at the two ends of rectangular Bi\textsubscript{2}O\textsubscript{3} films keeping a gap of various areas such as 0.1168 cm\(^2\), 0.0614 cm\(^2\), 0.1554 cm\(^2\), 0.1632 cm\(^2\) etc. between the two electrodes. The background theory in detail is given in Chapter 3. The \(I-V\) characteristics of a typical as-deposited Bi\textsubscript{2}O\textsubscript{3} film is shown in Fig.48. Here A, B and C are three cycles of heating for \(I-V\) characteristics measurements of the same sample. Plot A shows the temperature variation \(I-V\) characteristics of the sample for the first time heating. From the plot it has been observed that current slowly decreases with the increase of temperature up to 157\(^{0}\)C, above 157\(^{0}\)C current rises up to 200\(^{0}\)C, above 200\(^{0}\)C current again decreases with the increase of temperature. The first portion of the curve may be considered to be Bi dominated which shows metallic behaviour [14]. The decrease of current with the
Increase in temperature may be due to partial oxidisation of Bi which was produced during deposition due to partial decomposition of Bi₂O₃ during evaporation [14].

![Graph showing temperature dependent I versus V characteristics](image)

**Fig. 48:** Temperature dependent $I$ versus $V$ characteristics of a typical as-deposited Al-(n)Bi₂O₃-Al gap type sample in dark (measured for three times A, B and C).

The oxidisation of Bi in the sample enhances the semiconducting property of the sample which causes to increase current with the increase of temperature in $(157-200)^{0}\text{C}$ range. Above $200^{0}\text{C}$ the sample looses semiconducting property and oxidisation of remaining Bi becomes prominent [14]. Plot B is the temperature variation $I$-$V$ characteristic of the same sample for second time heating (after cooling, temperature was again raised for 2\textsuperscript{nd} time). This plot shows semiconductor nature of the sample with lower conductivity than previous one up to about $200^{0}\text{C}$ and above $200^{0}\text{C}$ the sample looses semiconducting property [14]. The low current shown by curve B than curve A confirms the conversion of Bi to Bi₂O₃. Plot C is the temperature variation $I$-$V$
characteristic of the same sample for third consecutive heating (after 2nd time cooling temperature was again raised). This plot shows semiconducting nature of the sample with lower conductivity than the previous two characteristics up to 300°C. The low current in plot C than in plot B confirms the transition of the sample to more semiconducting due to oxidisation of remaining free Bi in the sample. It has been observed from A, B and C characteristics that resistivity of the Bi$_2$O$_3$ films increases in the subsequent heatings and semiconductor property of the films also increases. Increase of resistivity of Bi$_2$O$_3$ films with annealing temperature have been reported by other workers [15]. There might be phase transition during annealing which may be a cause of change the conductivity of the sample [15]. The annealed Bi$_2$O$_3$ films do not show such type of temperature variation of $I$-$V$ characteristics.

The temperature variation of $I$-$V$ characteristics of annealed (n)Bi$_2$O$_3$ samples were measured in dark and corresponding resistivites and conductivities were calculated. The temperature variation of $I$-$V$ characteristic of a typical annealed (n)Bi$_2$O$_3$ film is shown in Fig.49. The Sn doped annealed Bi$_2$O$_3$ films exhibited n-type nature with sufficient conductivity. The resistivity of a typical sample has been observed to vary from 554.35MΩ.cm to 304.51Ω.cm within the temperature range 304K-453K. Temperature dependence of dark conductivity of a typical annealed (n)Bi$_2$O$_3$ film deposited at room temperature 303K have been shown in Fig.50. Similar nature of temperature variation of conductivity were observed for all Sn doped annealed Bi$_2$O$_3$ films, except a slight shift in...
Fig. 49: Temperature variation $I-V$ plot of a typical annealed gap type Al-(n)Bi$_2$S$_3$-Al thin film.

Fig. 50: $\sigma$ versus $1/T$ plot of a typical annealed gap type Al-(n)Bi$_2$O$_3$-Al film.
conductivity depending on the doping concentration. Each curve of ln$\sigma$ vs $T^{-1}$ plots (Fig. 51) shows two distinct slopes, one corresponding to low temperature range (303-344)K and other above 344K. From the intrinsic region the value of band gap was calculated using relation (6.1). The band gap energy so obtained at high temperature region were about 2.383 eV, 2.210 eV, 2.043 eV for doping concentration $4.658 \times 10^{14}/\text{cm}^3$, $6.688 \times 10^{14}/\text{cm}^3$, $8.213 \times 10^{15}/\text{cm}^3$ respectively. The corresponding activation energies obtained from the slopes at low temperature region were about 0.392 eV, 0.453 eV and 0.309 eV. The literature survey reveals that reported data on electrical energy gap is very few. G. I. Rusu et al. found electrical energy gap of Bi$_2$O$_3$ in the range of (1.68-2.10) eV [14]. The activation energies and the electrical band gaps evaluated for three different types of annealed (n)Bi$_2$O$_3$ films have been given in Table 6.02. A change has been observed in the band gap energy and activation energy with carrier concentration. Decrease in band gap energy and activation energy with increasing
of doping concentration indicates that there has been band tailoring due to increase in doping concentration [12]. All films studied in the present case were semitransparent.

The thickness dependence of band gap energy arises due to [13]: (i) a large density of dislocation, (ii) quantum size effect, (iii) change of barrier height due to change in grain size in polycrystalline films. The thickness of the films in the present study is sufficiently large hence quantum size effect contribution is nil. Also contribution due to dislocation is small. However, grain size seems to affect the band gap.

The values of activation energy at low temperature range correspond to impurity conduction due to excess Sn. As the temperature is raised the impurity levels are
exhausted and conduction becomes intrinsic in nature. The temperature was not lower enough to see the phonon assisted conduction mechanism.

Table 6.02: Values of some electrical parameters of three typical annealed (n)Bi₂O₃ films.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Thickness (μm)</th>
<th>Carrier concentration N_d (10¹⁴ cm⁻³)</th>
<th>Activation energy Eₐ (eV)</th>
<th>Energy gap E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁₆</td>
<td>0.4351</td>
<td>4.658</td>
<td>0.392</td>
<td>2.383</td>
</tr>
<tr>
<td>S₁₇</td>
<td>0.5211</td>
<td>66.688</td>
<td>0.453</td>
<td>2.210</td>
</tr>
<tr>
<td>S₁₈</td>
<td>0.4723</td>
<td>82.132</td>
<td>0.309</td>
<td>2.043</td>
</tr>
</tbody>
</table>

6.5 Aging effect on resistivity

The change in resistivity of a semiconductor film with time is known as aging effect. Aging effect on film resistivity was studied at room temperature. For this purpose the resistivity of freshly prepared and annealed films were measured at different interval of times. The films were preserved in a desiccator under vacuum condition. The variation of resistivity with time of a typical annealed (p)Bi₂S₃ film and a typical annealed (n)Bi₂O₃ film have been shown in Fig.52. The resistivity of annealed (p)Bi₂S₃ films has been observed to decrease very rapidly within the initial stage of aging and at slow rate approaching to saturation value after about 12 days. Similar case was also observed for (n)Bi₂O₃ and approaching a saturation value after about 8 days. The aging effect is connected with some slow changes within the films and in the interfacial layer with time due to a number of causes [17]. Migration of charged ions together with the corresponding charges of the films would give rise to dipoles, which would modify the
surface states [17]. The effects are more prominent in case of metal oxide semiconductors (MOS) [17].

![Graph](attachment:image.jpg)

Fig. 52: Variation of resistivity of a typical annealed $\text{Bi}_2\text{S}_3$ film (A) and of a typical annealed $(n)\text{Bi}_2\text{O}_3$ film (B) with time (days).

### 6.6. Photoconductivity

#### 6.6.1 Effect of light on $I-V$ characteristics

Theoretical background of the effect of light on $I-V$ characteristics has been discussed in Chapter 3. For measuring photoconductivity two Ni electrodes were vacuum deposited over each $(p)\text{Bi}_2\text{S}_3$ films making a suitable gap and two Al electrodes were vacuum deposited over each annealed $(n)\text{Bi}_2\text{O}_3$ film keeping a suitable gap between the electrodes (as discussed in Chapter 4). The photoconductivity of the gap type samples were measured under vacuum condition by exposing the gap type sample to different light intensities. The plots of photocurrent versus light intensities for a typical annealed $(p)\text{Bi}_2\text{S}_3$ film and a typical annealed $(n)\text{Bi}_2\text{O}_3$ film are shown in Fig 53.
and Fig.54 respectively. The annealed (p)Bi₂S₃ films show linear increase of photocurrent with the increase of illumination intensity in (750-1500)Lux as shown in figures for a typical (p)Bi₂S₃ sample. Above 1500 Lux photocurrent gradually increases and reaches saturation value beyond 2600 Lux.

The investigation on annealed (n)Bi₂O₃ films indicates linear increase in photocurrent with light intensity in (4500-8500) Lux range. Above 8500 Lux the photocurrent gradually increases and reaches saturation value beyond 10000 Lux.

Fig.53: Saturation current versus illumination intensity plot of a typical annealed gap type Ni-(p)Bi₂S₃-Ni film.
6.6.2 Photoconductive rise and decay measurement

The photoconductive rise and decay curves have been recorded with X-Y/t recorder. The measurements were carried out at room temperature and under vacuum condition. The (p)Bi₂S₃ samples were exposed to light of intensity 750 Lux, 950Lux, 1320Lux and 1530Lux and corresponding rise and decay curves have been recorded by X-Y/t recorder. Similarly, rise and decay plots of annealed (n)Bi₂O₃ films for different illumination intensities have been recorded by X-Y/t recorder. The details of measuring technique have been discussed in Chapter 4. Rise and decay of photocurrent versus time (t) plots of a typical gap type annealed (p)Bi₂S₃ film for different illumination intensities are shown in Fig.55 and the plots for a typical annealed (n)Bi₂O₃ film for four different illumination intensities are shown in Fig.56. In all cases rise and decay processes show initial fast rise and subsequently slower decay.
Rise and decay curve can be explained on the basis of creation of electrons and holes under the influence of light accompanied by their recombination. The current reaches a steady value when the rate of recombination becomes equal to the rate of generation of new carriers and concentration of carriers reaches a steady value. When light ceases to fall on the sample, the initial drop in photocurrent is controlled by recombination mechanism alone and depends on the lifetime of the majority carriers [18]. The values of $\tau_r$ and $\tau_d$ of a typical annealed (p)Bi$_2$S$_3$ film for four different illumination intensities are given in Table 6.03 and the values of $\tau_r$ and $\tau_d$ of a typical annealed (n)Bi$_2$O$_3$ films with four different illumination intensities are given in Table 6.04.

Fig.55: Rise and decay of photocurrent with time for a typical annealed gap type Ni-(p)Bi$_2$S$_3$-Ni thin film for four different illumination intensities at room temperature (doping concentration $29.267 \times 10^{16}$ cm$^{-3}$).
Fig.56: Rise and decay of photocurrent with time for a typical annealed gap type Al-
(n)Bi$_2$O$_3$-Al thin film for four different illumination intensities at room temperature
(carrier concentration $8.213 \times 10^{15} \text{cm}^{-3}$).

The photoconductive decay is proportional to the rate of release of electrons from
traps and takes an exponential form for single trap energy with no retrapping. In actual
practise the decay curve have been fitted most often by an expression of the form,

$$ I_t = I_o (1 + at)^{-b} $$

(6.2)

$$ = I_t e^{-bt} $$ (considering $1 + at \equiv t$ $a$ is a constant)

where $I_o$ is the initial photocurrent at $t=0$ and $I_t$ is the photocurrent after time $t$ and $b$ is
the decay constant. The plot of ln$I_t$ versus ln$t$ was plotted for decay portion (light off) of
each $I$-$V$ characteristics. For each illumination two linear regions (slopes) are obtained
for both annealed (p)Bi$_2$S$_3$ and annealed (n)Bi$_2$O$_3$ films. Two decay constants ($b_1$ and
$b_2$) have been evaluated for each film from the slopes. The value of decay constant as
determined from the slopes of ln$I_t$ versus ln$t$ curves using above relation have been
observed to increase with the increase of illumination intensities for all samples. The \( \ln I \) (\( I \)-photocurrent) versus \( \ln t \) (\( t \)-time) plots of photoconductive decay of a typical annealed (p)\( \text{Bi}_2\text{S}_3 \) film at four intensities of illumination is shown in Fig. 57 and the plots for a typical annealed (n)\( \text{Bi}_2\text{O}_3 \) film is shown in Fig. 58.

The instantaneous life time has been evaluated from the initial stage of photoconductive decay curve (not shown here) using the relation

\[
\tau = \Delta \sigma / \left[ d/dt(\Delta \sigma) \right]_{t=0}
\]

Where \( \Delta \sigma \) is the conductivity at steady state (just at \( t=0 \)). The value of life time has been found to be a function of illumination intensity. The instantaneous life time for a typical (p)\( \text{Bi}_2\text{S}_3 \) thin film and (n)\( \text{Bi}_2\text{O}_3 \) thin film for different illumination intensities are given in Table 6.03 and Table 6.04 respectively.

Fig. 57: \( \ln I \) versus \( \ln t \) plots of a typical annealed Ni-(p)\( \text{Bi}_2\text{S}_3 \)-Ni film (carrier concentration \( 29.267 \times 10^{16} \text{cm}^{-3} \)) for four different illumination intensities.
Fig. 58: InI versus lnI plots of a typical annealed gap type Al-(n)Bi$_2$O$_3$-Al film (carrier concentration 8.213 x 10$^{15}$ cm$^{-3}$) for four different illumination intensities.

Table 6.03: Photoconductive characteristic of a typical annealed (p)Bi$_2$S$_3$ film (thickness 0.4352 μm), carrier concentration 29.267 x 10$^{16}$/cm$^3$.

<table>
<thead>
<tr>
<th>Illumination intensity (Lux)</th>
<th>Rise time ($\tau_0$ (second))</th>
<th>Fall time ($\tau_0$ (Second))</th>
<th>Decay constant ($b_1$, $b_3$)</th>
<th>Life time (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>2.40</td>
<td>2.50</td>
<td>1.196, 0.550</td>
<td>0.54</td>
</tr>
<tr>
<td>950</td>
<td>2.05</td>
<td>2.30</td>
<td>1.435, 0.667</td>
<td>0.46</td>
</tr>
<tr>
<td>1320</td>
<td>1.95</td>
<td>2.10</td>
<td>1.534, 0.765</td>
<td>0.40</td>
</tr>
<tr>
<td>1530</td>
<td>1.30</td>
<td>1.90</td>
<td>1.668, 0.784</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Table 6.0 4 Photoconductive characteristic of a typical annealed (n)Bi$_2$O$_3$ film (thickness 0.4662μm), carrier concentration $8.213 \times 10^{15}/$cm$^3$.

<table>
<thead>
<tr>
<th>Illumination intensity (Lux)</th>
<th>Rise time $\tau_r$ (second)</th>
<th>Fall time $\tau_a$ (Second)</th>
<th>Decay constant $b_1$</th>
<th>Decay constant $b_2$</th>
<th>Life time (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4630</td>
<td>3.00</td>
<td>3.97</td>
<td>0.831</td>
<td>0.305</td>
<td>0.845</td>
</tr>
<tr>
<td>5550</td>
<td>1.16</td>
<td>3.35</td>
<td>0.945</td>
<td>0.341</td>
<td>0.724</td>
</tr>
<tr>
<td>7580</td>
<td>0.99</td>
<td>2.54</td>
<td>1.000</td>
<td>0.367</td>
<td>0.483</td>
</tr>
<tr>
<td>8450</td>
<td>0.97</td>
<td>2.11</td>
<td>1.003</td>
<td>0.425</td>
<td>0.369</td>
</tr>
</tbody>
</table>

6.7 Optical parameters of (p)Bi$_2$S$_3$ thin films

The optical parameters of annealed (p)Bi$_2$S$_3$ thin films and annealed (n)Bi$_2$O$_3$ thin films were measured using UV-visible spectrophotometers equipped with an integrating sphere. The main optical parameters studied are transmittance, reflectance, absorbance, refractive index, extinction co-efficient etc. The details of experimental procedure have been discussed in Chapter 4 and theories of optical properties of the films have been discussed in Chapter 3.

The transmittance ($T$) and absorbance ($A$) spectra of a typical annealed Bi$_2$S$_3$ film are shown in Fig.59. The transmittance spectrum shows a gradual increase from 600nm up to 900nm. The absorbance spectrum shows that absorbance is higher at higher energy value of the spectrum and remains steady up to 550nm and decreases sharply beyond this wavelength. The absorption coefficient was calculated from the transmittance values of two films having different thickness using relation (3.24) in Chapter 3. Since the (p)Bi$_2$S$_3$ is a direct band gap semiconductor, its band gap was found out from $(a hv)^2$ versus $hv$ plot using relation (3.17). A typical $(a hv)^2$ versus $hv$
plot of (p)Bi$_2$S$_3$ is shown in Fig.60. The optical band gap found out in this process is in the range of (1.3eV-1.7eV) and agree with the values (1.5 eV, 1.56 eV, 1.68 eV) obtained by other workers [19, 20, 21].

![Transmittance and absorbance spectra of a typical annealed (p)Bi$_2$S$_3$ film of thickness 0.4356µm.](image1)

Fig.59: Transmittance and absorbance spectra of a typical annealed (p)Bi$_2$S$_3$ film of thickness 0.4356µm.

![A $(\alpha \nu)^2$ versus $\nu$ plot of annealed (p)Bi$_2$S$_3$ film](image2)

Fig.60: A $(\alpha \nu)^2$ versus $\nu$ plot of annealed (p)Bi$_2$S$_3$ film
The transmittance spectra of annealed (p)Bi$_2$S$_3$ films interference pattern was not observed up to 900nm, so the refractive index of the films could not be found out using relation (3.26) of Chapter 3. Therefore to find out the refractive index relation (3.28) [21] was used. Using reflectance R and extinction coefficient (k) the refractive index (n) was determined. The reflectance spectrum of a typical annealed Bi$_2$S$_3$ thin film is shown in Fig.61. The values k was found out from absorption constant (a) values using relation $\alpha = 4\pi k$. From the knowledge of n and k values the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric constant of annealed (p)Bi$_2$S$_3$ have been found out using relation (3.30) and (3.31) of Chapter 3. The absorption coefficients (a), extinction co-efficient (k), refractive index (n), dielectric constant [real ($\varepsilon'$) and imaginary ($\varepsilon''$) part] etc. of (p)Bi$_2$S$_3$ film have been shown in Table 6.05.
### Table 6.05: Values of some optical parameters of annealed (p)Bi$_2$S$_3$ film.

<table>
<thead>
<tr>
<th>$\lambda$(nm)</th>
<th>n</th>
<th>$\alpha$($10^{-4}$cm$^{-1}$)</th>
<th>k</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>2.377</td>
<td>17.669</td>
<td>91.08</td>
<td>4.823</td>
<td>3.331</td>
</tr>
<tr>
<td>675</td>
<td>2.455</td>
<td>15.217</td>
<td>81.74</td>
<td>5.359</td>
<td>4.013</td>
</tr>
<tr>
<td>700</td>
<td>2.552</td>
<td>12.739</td>
<td>70.96</td>
<td>6.009</td>
<td>3.622</td>
</tr>
<tr>
<td>725</td>
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<td>49.87</td>
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<td>38.82</td>
<td>8.605</td>
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### 6.8 Optical parameters of annealed (n)Bi$_2$O$_3$ thin films

The transmittance and absorption spectra of annealed (n)Bi$_2$O$_3$ films have been taken by UV-visible spectrometer (Carry-300). The transmittance and absorption spectra of a typical annealed (n)Bi$_2$O$_3$ thin film is shown in Fig. 6.2. The transmittance spectra show that the transmittance gradually increases from 400nm up to 440nm, above 440nm it remains steady state up to 800nm byond which it again increases. The reverse characteristics was observed in ease of absorption spectra of annealed (n)Bi$_2$O$_3$ films. The absorption spectra show that it absorbs light in the higher energy region up to 440nm, above this all light is transmitted by the films. The absorption coefficient in the interference free region was calculated from transmittance values of two films having different thicknesses using relation (3.24) in Chapter 3. Since the (n)Bi$_2$O$_3$ is a direct
band gap semiconductor, its band gap was found out from \((ahv)^2\) versus \(hv\) plot using relation (3.17). A typical plot of \((ahv)^2\) versus \(hv\) is shown in Fig. 63.

![Transmittance spectra and absorption spectra of a typical annealed (n)Bi$_2$O$_3$ film of thickness 0.4723μm.](image)

Fig. 62: Transmittance spectra and absorption spectra of a typical annealed (n)Bi$_2$O$_3$ film of thickness 0.4723μm.

The optical energy gap of annealed (n)Bi$_2$O$_3$ films was found to be in the range of (2.49-2.78) eV, similar result have been reported in the literature [22, 23, 24]. The extinction coefficient was evaluated from \(\alpha\) using relation (3.25) of Chapter 3. The refractive index of the (n)Bi$_2$O$_3$ films was evaluated from relation (3.26) of Chapter 3 for all transmittance minima (Fig. 62) in the interference zone. Then a graph of \(n\) versus \(1/\lambda^2\) was plotted (not shown here). Extrapolating the plot to the interference free region and using relation (3.27) of Chapter 3 the \(n\) values were evaluated for interference free region. The real and imaginary part of dielectric constants were found out from \(n\) and \(k\) values using relations (3.30) and (3.31) of Chapter 3. The values of \(\alpha\), \(n\), \(k\), \(\varepsilon'\) and \(\varepsilon''\)
evaluated for the (n)Bi$_2$O$_3$ film are shown in Table 6.06. The n versus $\lambda$ plot of (p)Bi$_2$S$_3$ film is shown in Fig.64.

Fig.63: (a) A $(\alpha h\nu)^2$ versus $h\nu$ plot of annealed (n)Bi$_2$O$_3$ film.

Fig.64: n versus $\lambda$ plot of annealed (n)Bi$_2$O$_3$ film.
Table 6.06: Values of some optical parameters of a typical annealed (n)Bi$_2$O$_3$ film.

<table>
<thead>
<tr>
<th>$\lambda$(nm)</th>
<th>$n$</th>
<th>$\alpha$(10$^4$cm$^{-1}$)</th>
<th>$k$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
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<tr>
<td>425</td>
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<td>5.307</td>
<td>0.179</td>
<td>5.44</td>
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<td>2.25</td>
<td>3.584</td>
<td>0.128</td>
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<tr>
<td>475</td>
<td>2.17</td>
<td>2.933</td>
<td>0.110</td>
<td>4.691</td>
<td>0.744</td>
</tr>
<tr>
<td>500</td>
<td>2.11</td>
<td>2.728</td>
<td>0.108</td>
<td>4.44</td>
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<tr>
<td>525</td>
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<td>2.175</td>
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<td>1.385</td>
<td>0.060</td>
<td>3.992</td>
<td>0.421</td>
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<tr>
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<td>1.143</td>
<td>0.051</td>
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<td>0.400</td>
</tr>
<tr>
<td>650</td>
<td>1.76</td>
<td>1.013</td>
<td>0.042</td>
<td>3.643</td>
<td>0.309</td>
</tr>
</tbody>
</table>

6.9 Comparative study

The optical parameters such as absorption co-efficient, refractive index, extinction co-efficient, real and imaginary parts of dielectric constant were studied from transmission and absorbance spectra of vacuum deposited annealed (p)Bi$_2$S$_3$ films and annealed (n)Bi$_2$O$_3$ films. The absorbance spectra of annealed (p)Bi$_2$S$_3$ films show maximum steady absorbance up to 550 nm and gradually decreases up to 900nm. Transmittance spectra of the films show that transmittance starts from about 650nm and reaches maximum value at 900nm. The absorption co-efficients evaluated on annealed (p)Bi$_2$S$_3$ were found to be high (of the order of 10$^4$cm$^{-1}$). These reveal that annealed (p)Bi$_2$S$_3$ is a good absorbing material in the visible region and seems to be a promising material for using as an absorbing material in the fabrication of optoelectronic devices.
and photovoltaic cells. The study of the absorbing spectra of annealed (n)Bi$_2$O$_3$ films shows that the films absorb light of wavelength lower than 440 nm and transmit light of wavelength higher than 440 nm, which is clear from the transmittance spectra of annealed (n)Bi$_2$O$_3$ films. The films are highly transparent (maximum transmittance 80% at 500nm) with low absorption coefficient. Comparison at 500nm shows that refractive index $n$ as well as imaginary dielectric constant $\varepsilon''$ of annealed (p)Bi$_2$S$_3$ film are higher than those of annealed (n)Bi$_2$O$_3$ film. These properties of annealed (n)Bi$_2$O$_3$ films show the viability of the films to be used as window layer in the fabrication of heterojunction solar cells. In all cases the refractive indices of annealed (n)Bi$_2$O$_3$ films were found to decrease towards the higher wavelength indicating that films posses good transmission properties towards higher wavelengths. This indicates that (n)Bi$_2$O$_3$ can act as an efficient semiconductor as well as window layer in junction devices.

Summary

In the present study it has been observed that both Bi$_2$S$_3$ and Bi$_2$O$_3$ decomposed during evaporation and therefore stoichiometry is not retained in the deposited films. Therefore special care is required in depositing thin films. Moreover, as-deposited films are not suitable to be used in device formation. Only, proper annealed films show suitable $I-V$ and photoconductive characteristics and can be used in device preparation. The result of resistivity measurement at different temperatures, photoconductive rise and decay, effect of light on resistivity, aging effect on resistivity, ohmic contact between sample films and metals, some optical constants
such as absorption coefficient, refractive index, complex dielectric constants, optical band gaps measured from transmittance and absorbance have been discussed in details.

The as-deposited Bi$_2$S$_3$ films were found to pose very high resistivity in dark as well as under illuminated condition. The compounds were doped with appropriate doping materials. The resistivity of annealed (p)Bi$_2$S$_3$ and annealed (n)Bi$_2$O$_3$ films were found to be 3.76x10$^2$Ω cm and 44.64x10$^4$Ω cm at room temperature corresponding to doping concentration 72.341x10$^{15}$ cm$^{-3}$ and 8.213x10$^{15}$ cm$^{-3}$ respectively. It is evident that ln$\sigma$ vs $T^{-1}$ plots shows two distinct slops one corresponding to low temperature range and the other at higher temperature range from which activation energies and energy band gaps were calculated. These values were found to be varying with their doping concentrations. Aging effect on the films was studied at room temperature. The resistivity of annealed (p)Bi$_2$S$_3$ and annealed (n)Bi$_2$O$_3$ films has been observed to increase in the initial stage of aging and approaches a steady value after about twelve days and eight days respectively.

A study on the effect of illumination on $I-V$ characteristics of all films have been carried out. It has been found that both resistivity and photocurrent are functions of illumination. Studies indicates a gradual increase of photocurrent with light intensity in annealed (p)Bi$_2$S$_3$ films and annealed (n)Bi$_2$O$_3$ films and reaches a steady state value above 2600 Lux and 10000 Lux respectively. The instantaneous life time has been also observed to be a function of illumination.

In all cases, the absorbance has its maximum value at higher energy and decreases towards the lower energy. It has been observed from the absorption spectra that annealed (p)Bi$_2$S$_3$ film has a high absorption coefficient which is required for a good conversion efficiency.
Annealed (n)Bi$_2$O$_3$ films show high transmittance in their transmittance from 500nm to 800nm which indicates the viability of the material to be used as window layers in junction devices. The refractive index $n$ as well as imaginary part of dielectric constant $e''$ of annealed (n)Bi$_2$O$_3$ film are found to be usually smaller than those of annealed (p)Bi$_2$S$_3$ films. This indicates that (n)Bi$_2$O$_3$ is an efficient semiconductor for using as window layer.

The optical band gap of annealed (p)Bi$_2$S$_3$ films and annealed (n)Bi$_2$O$_3$ films were determined from $(h\nu \alpha)^2$ versus $h\nu$ plots and were found in the range of (1.3-1.7)eV and (2.49-2.78)eV respectively. In all cases band gap energy found from optical absorption coefficient has been observed to be slightly greater than the energy gap obtained from temperature dependence of conductivity.
References


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