CHAPTER 8

Studies on (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ Heterojunctions

The optical and electrical properties of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunctions prepared by thermal evaporation method are presented in this Chapter. The preparation details and measuring technique of the junction parameters have been represented in Chapter 4. The background theories of heterojunction have been discussed in Chapter 3. Results on C-V characteristics, I-V characteristics, photovoltaic properties, photoresponse etc. of the junctions have been discussed in details. Heterojunction parameters such as ideality factor, saturation current density, built-in potential, series resistance and photovoltaic parameters such as short-circuit current, open-circuit voltage, maximum output power, fill factor, PV efficiency etc. of the junctions have been presented in this chapter.

8 Results and discussion

8.1 Current-voltage characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ in dark

It has been observed that both Bi$_2$S$_3$ and Bi$_2$O$_3$ samples decompose during evaporation. Therefore special care was taken in depositing (p)Bi$_2$S$_3$ and (n)Bi$_2$O$_3$ films. Proper annealing was done for each film before making junctions. For measurement of I-V characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions, Ni film deposited on one side with (p)Bi$_2$S$_3$ film and Al film deposited on the other side with (n)Bi$_2$O$_3$ film were used as electrodes making the structure as Ni-(p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$-Al. Both films formed good ohmic contacts with the respective semiconductors. The current-voltage characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$S$_3$ junction was found to be rectifying in nature as shown in Fig.89 for
three typical junctions. The current density equation for heterojunction is given in the equation (3.73) of Chapter 3 as

\[
J = J_o \left[ \exp\left(\frac{qV_a}{nkT}\right) \right]
\]  (8.01)

the diode ideality factor \((n)\) and the reverse saturation current \((J_o)\) of the junctions were determined from the slope and intercept of \(\ln(J)\) versus \(V\) plots. Fig.90 shows the linear

Fig.89: \(I-V\) characteristics of three typical \((p)\)Bi$_2$S$_3/ (n)\)Bi$_2$O$_3$ heterojunctions in dark for different doping concentrations (Sample no: \(S_1, S_6, S_9\)).
Fig. 90: $\ln J$ versus $V$ plots of three typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions with different doping concentrations in dark (Sample no. S$_7$, S$_8$, S$_9$).

Fig. 91: $\ln J$ versus $V$ plots of three typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunctions for different doping concentrations (Sample no. S$_7$, S$_8$, S$_9$) under illuminations.
region of lnJ versus V plots of three typical junctions for different doping concentrations in dark. From the study it has been observed that saturation current density of the junctions increase with the increase of doping concentration while ideality factor decreases. Using the same relation (8.01) the diode ideality factor and reverse saturation current density under illumination were found out from the slopes and intercepts of lnJ versus V plots in Y axis. The ideality factors for each junction under illumination was found to be lower than in dark and saturation current under illumination was found to be higher than in dark. Three typical lnJ versus V plots of (p)Bi₂S₃/(n)Bi₂O₃ junctions under illumination for different doping concentrations are shown in Fig.91. The values of ideality factor and saturation current density of the junctions for both dark and illuminated conditions are presented in Table 8.01.

Table 8.01: Junction parameters of three typical (p)Bi₂S₃/(n)Bi₂O₃ junctions in dark and under illumination conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>Sample no.</th>
<th>Doping concentration</th>
<th>Saturation current density</th>
<th>Ideality factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p)Bi₂S₃/(n)Bi₂O₃ junction</td>
<td>Dark</td>
<td>S₁</td>
<td>7.324</td>
<td>3.424</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S₂</td>
<td>59.544</td>
<td>66.688</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S₉</td>
<td>125.78</td>
<td>82.130</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>Illumination</td>
<td>S₁</td>
<td>7.324</td>
<td>3.424</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>(2000 Lux)</td>
<td>S₂</td>
<td>59.544</td>
<td>66.688</td>
<td>0.191</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S₉</td>
<td>125.78</td>
<td>82.130</td>
<td>0.223</td>
</tr>
</tbody>
</table>
8.1.2 Series resistance on $I$-$V$ characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions

The effect of series resistance ($R_s$) on $I$-$V$ characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions have been studied both in dark and under room illumination. To evaluate series resistance of the junctions the $\ln I$ versus $V$ plots were plotted for each junction. The $\ln I$ versus $V$ plots for three typical junctions in dark are shown in Fig. 92. The deviation of $\ln I$ versus $V$ plots from linearity shows the existence of series resistance in the junctions. The deviation values ($\Delta V$) at different values of $\ln I$ were found out from $\ln I$ versus $V$ plots. The $\ln I$ values were converted to $I$ values and $I$ versus $\Delta V$ plots were plotted for different junctions.

Fig. 93 $I$ versus $\Delta V$ plots of three typical junctions. The series resistance of the junctions were evaluated from $I$ versus $\Delta V$ plots using relation ($\Delta V=I R_s$). The series resistance of the junctions evaluated in dark were in (5.702-6.703)KΩ.

To evaluate the series resistance of the junctions under illumination $\ln I$ versus $V$ plots for different junctions under illumination were plotted. Fig. 84 shows three $\ln I$ versus $V$ plots of three typical junctions with different doping concentrations. For each plot, $\Delta V$ values corresponding to different $\ln I$ values were measured. The $I$ versus $\Delta V$ plots of different junctions was plotted. The series resistance of the junctions under illumination were determined from $J$ versus $\Delta V$ plots using relation ($\Delta V=I R_s$). Fig. 94 shows three $I$ versus $\Delta V$ of three typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions with different doping concentrations under illumination.
Fig. 92: $\ln I$ versus $V$ plot of three typical (p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$ heterojunctions (Sample no, S7, S8 and S9) for different doping concentrations in dark.

Fig. 93: $I$ versus $\Delta V$ plots of three typical (p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$ junctions in dark for different carrier concentrations (Sample no. S7, S8, S9).
The series resistances of the junctions measured under illumination were found to be less than those measured in dark. The series resistances measured of three typical junctions in dark and under illumination are presented in Table 8.02.

Table 8.02: Series resistance of three typical (p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$ heterojunctions in dark and under illumination (2000Lux) for different doping concentrations (Sample no S$_7$, S$_8$, S$_9$)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Doping concentration</th>
<th>Series resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_d(10^{15} \text{cm}^{-3})$</td>
<td>$N_d(10^{14} \text{cm}^{-3})$</td>
</tr>
<tr>
<td>(p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$</td>
<td>S$_7$</td>
<td>7.324</td>
</tr>
<tr>
<td>S$_8$</td>
<td>59.544</td>
<td>66.688</td>
</tr>
<tr>
<td>S$_9$</td>
<td>125.780</td>
<td>82.130</td>
</tr>
</tbody>
</table>

Fig.94: ln$I$ versus $V$ plot of three typical (p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$ heterojunctions (Sample no, S$_7$, S$_8$, and S$_9$) for different doping concentrations under illumination.
8.1.3 Effect of temperature on $I$-$V$ characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions

Temperature variation $I$-$V$ characteristics of (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junctions have been studied in the temperature range of (298-330)K. The current as well as rectification of the junctions increases with the increase of temperature. The $I$-$V$ characteristics of a typical junction at different temperatures are shown in Fig.96. Fig.97 shows temperature variation $\ln J$ versus $V$ plots of a typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junction. The temperature variation $\ln J$ versus $V$ plots were plotted for different junctions. The ideality factor and reverse saturation current of the junctions were evaluated from the slopes and intercepts of $\ln J$ versus $V$ plots $\ln J$ at at different temperature. The temperature variation of ideality factor and saturation current density evaluated for a typical junction are tabulated in Table 8.03. The ideality factors was found to decrease with the increase of...
temperature and saturation current density was found to increase. The ideality factor was found to vary from 4.5 to 3.4 within the temperature range of (298-330)K.

Fig.96: Temperature variation $I$-$V$ characteristics of a typical (p)Bi$_2$S$_3$/ (n)Bi$_2$S$_3$ heterojunction in dark (Sample no. S9).

Fig.97: Temperature variation ln$I$-$V$ characteristics of a typical (p)Bi$_2$S$_3$/ (n)Bi$_2$O$_3$ heterojunction in dark (Sample no. S9).
Table 8.03: Variation of some parameters of a typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunction with temperature for electrode area $A=1\times10^{-2}\text{cm}^2$ (Sample no. $S_9$).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature (K)</th>
<th>Saturation current density ($10^{-4}\text{A.cm}^{-2}$)</th>
<th>Ideality factor (n)</th>
<th>Built-in potential $\varphi_{bi}$ (V)</th>
<th>Built-in potential $E^2$ (V)</th>
<th>Series resistance (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_9$</td>
<td>298</td>
<td>0.143</td>
<td>4.5</td>
<td>0.53</td>
<td>0.52</td>
<td>6.83</td>
</tr>
<tr>
<td></td>
<td>306</td>
<td>0.256</td>
<td>4.3</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>314</td>
<td>0.428</td>
<td>4.0</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>322</td>
<td>0.706</td>
<td>3.7</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>1.285</td>
<td>3.4</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 98: $\ln(J_o/T)$ versus $1/T$ plot of a typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunction (Sample no. $S_9$).
From the estimated value of $J_0$ for different temperature, $\ln(J_0/T)$ versus $1/T$ graph is plotted for the junction. Fig. 98 shows $\ln(J_0/T)$ versus $1/T$ plot of a typical junction. From the figure it is seen that the plot is a straight line, which indicates that the current transport is controlled by thermionic emission process and follows the relation (3.70). From the slope of the plot the built-in potential $V_{bi}$ of the junction was estimated. The built-in potential of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ junction measured from current-voltage characteristic is given in Table 8.03. The built-in potential of the junction has been found to be independent of temperature.

Fig. 99: $C^2$ versus $V$ plot of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ heterojunction in dark (Sample no. S9).
8.1.4 Built-in potential of (p)Bi$_2$S$_3$/nBi$_2$O$_3$ junctions

The $C^2$ vs $V_r$ plots at frequency 1KHz for a typical (p)Bi$_2$S$_3$/nBi$_2$O$_3$ junction has been shown in Fig.99. The built-in potential $V_{bi}$ of the junctions were calculated from the intercept ($V_i$) of $C^2$ vs $V_r$ plots using the relation (3.43). The built-in potential obtained for a typical junction is given in Table 8.03.

![Graph](image-url)  
**Fig.100:** Photovoltaic characteristic of three typical (p)Bi$_2$S$_3$/nBi$_2$O$_3$ junctions having different doping concentrations (Sample no S7, S8, S9).
Fig. 101: Photovoltaic effect of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ heterojunction for different illumination intensities (Sample no. S9).

Fig. 102: ln($J_\infty$) vs. $V_{oc}$ plot for a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ junction (Sample no. S9).
8.1.5 Photovoltaic effect

The (p)Bi₂S₃/(n)Bi₂O₃ junctions were studied for their photovoltaic performance under various light intensities. The I-V curve (in fourth quadrant) under illumination reveals the photovoltaic effect of the junctions. The open-circuit voltage (\(V_{oc}\)) was obtained from the intercept on the voltage axis and short-circuit current (\(J_{sc}\)) was obtained from the intercept on the current axis of the J-V plot under illumination. The J-V characteristics of three typical (p)Bi₂S₃/(n)Bi₂O₃ junctions under same illumination intensity are shown in Fig.100. The values of maximum power output, fill factor and efficiency have been calculated by using relation (3.79), (3.80) and (3.81) respectively as given in Chapter 3. Present investigation on photovoltaic J-V characteristics of the junctions with variation of doping concentration shows that short-circuit current, open-circuit voltage, fill factor and efficiency of the junction increases with the increase of doping concentration. The ideality factor decreases with the increase of doping concentration. The open-circuit voltage, short-circuit current, fill factor and efficiency of three typical (p)Bi₂S₃/(n)Bi₂O₃ junctions under illumination (6400lux) are given in Table 8.04.

8.1.6 Diode parameters under illumination:

To measure the diode ideality factor \(n\) and reverse saturation current \(J_o\) for the junction under illumination, relation (3.77)

\[
J_{sc} = J_o \left[ \exp \left( \frac{qV_{oc}}{nkT} \right) - 1 \right]
\]  

(8.1)
was used. For this purpose, $J_{sc}$ and $V_{oc}$ of the junctions were measured at three different levels of illumination. Fig. 101 shows $J-V$ plots of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ junction for three different illumination intensities. Then ln$J_{sc}$ versus $V_{oc}$ plot of the junction was plotted and from the slope and intercept of the plot in ln$J$ axis diode ideality factor ($n$) and reverse saturation current density ($J_0$) under illumination were calculated. The ln$J_{sc}$ versus $V_{oc}$ plot of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ junction is shown in Fig. 102. Some diode parameters of a typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ heterojunction under illumination have been given in Table 8.04. Comparing the values of diode parameters in dark (from Table 8.01) and under illumination (Table 8.04) for the same junction the diode ideality factor is observed to decrease under illumination, while the saturation current density $J_0$ is found to increase under illumination. It has been observed from the present study that diode ideality factor of the junction decreases with the increase of doping concentration.

Table 8.04: Some photovoltaic parameters of three typical (p)Bi$_2$S$_3$/Bi$_2$O$_3$ junction at room temperature and for same illumination intensity (6400Lux).

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Short-circuit current density $J_{sc}$ ($10^{-4}$Acm$^{-2}$)</th>
<th>Open-circuit voltage (mV)</th>
<th>Maximum power output (mW)</th>
<th>Fill factor</th>
<th>Efficiency</th>
<th>Ideality factor</th>
<th>Saturation current density $J_0$ ($10^{-4}$Acm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_7$</td>
<td>1.033</td>
<td>83</td>
<td>3.2</td>
<td>0.37</td>
<td>0.055</td>
<td>4.02</td>
<td>0.12</td>
</tr>
<tr>
<td>S$_8$</td>
<td>1.055</td>
<td>88</td>
<td>3.4</td>
<td>0.36</td>
<td>0.058</td>
<td>3.96</td>
<td>0.24</td>
</tr>
<tr>
<td>S$_9$</td>
<td>1.075</td>
<td>95</td>
<td>3.6</td>
<td>0.35</td>
<td>0.062</td>
<td>3.82</td>
<td>0.31</td>
</tr>
</tbody>
</table>
The spectral response of the (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junction was studied in the wavelength range 400-950nm using a monochromator. Fig. 103 shows the short-circuit current spectral response of a typical (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ junction. The maximum short-circuit current was obtained corresponding to the wavelength about 733nm which is well within the visible region. The value of the band edge calculated from the height peak was found to be about 1.7eV (733nm) which implies that the absorption is mostly within Bi$_2$S$_3$ layer of the structure.
Discussions

Both Bi$_2$O$_3$ and Bi$_2$S$_3$ samples have been observed to dissociate during vacuum evaporation.

As a result as-deposited films of Bi$_2$O$_3$ and Bi$_2$S$_3$ produced by thermal evaporation of Bi$_2$O$_3$ and Bi$_2$S$_3$ respectively were found to be nonstoichiometric in composition. Therefore special care was taken in depositing thin films. Proper annealing was done of each film before junction fabrication. It has been observed that as-deposited Bi$_2$O$_3$ films do not show semiconductor nature. This might be due to presence of free Bi, produced due to decomposition of Bi$_2$O$_3$ sample during evaporation. The annealed Bi$_2$O$_3$ films show semiconductor nature due to oxidization of free Bi during annealing, so only annealed films were used in the fabrication of junctions. The Bi$_2$S$_3$ sample, was observed to decompose during evaporation. Sulfur reaches first the substrate and forms sulfur film over the substrate. If deposition is continued Bi film forms over the sulfur film. So, special care was taken in depositing the Bi$_2$S$_3$ compound.

The (p)Bi$_2$S$_3$/(n)Bi$_2$O$_3$ heterojunctions have been prepared by thermal evaporation method and some junction parameters and photovoltaic parameters of the junctions have been studied. All the prepared junctions were found to exhibit rectifying behaviour with soft reverse current. Non saturating reverse current implies that the barrier height is lowered with reverse bias voltage [1]. The diode parameters of the junction have been measured from the current voltage characteristics of the junctions. The diode parameters of the junctions with the variation of doping concentration have been studied. The diode ideality factor of all junctions was found to be greater than unity. The presence of interfacial layer, image force lowering of built-in potential,
recombination of electron and holes in the depletion regions and tunnelling are the main reasons [2] for ideality factor to be greater than unity. The saturation current density and the ideality factor of the junction are found to increase with the increase of doping concentrations.

The effect of series resistance on $I-V$ characteristics of the junctions has been studied both in dark and under illuminated condition. All the junctions show high series resistance (6.162-7.187)KΩ which decreases under illumination and also with the increase of doping concentration.

The barrier height or built-in potential of the junctions were calculated from $J-V$ and $C-V$ study. The values of built-in potential of the junctions calculated from $C-V$ measurements were found to be less than those found from $I-V$ measurement. This may be due to the presence of interfacial layer in junction.

All junctions show very low photovoltaic effect with very low conversion efficiency. The study of photovoltaic effect on the junctions with variation of doping concentration shows that short-circuit current, open-circuit voltage, fill factor and conversion efficiency of the junctions increase with the increase of doping concentration for same illumination intensity.

The low values of short-circuit current for all junctions are due to higher value of diode ideality factor. In the polycrystalline films, the grain boundary potential may effect the series resistance and open-circuit voltage of solar cell [2]. recombination of photogenerated carriers takes place at grain boundaries and hence the short-circuit current is reduced [3,4]. The recombination of photogenerated carriers at the interface
states and low barrier height are also responsible for the low photovoltaic performance of the junctions [5]. The high defect density in thermally evaporated Bi$_2$S$_3$ and Bi$_2$O$_3$ layers also affect the photovoltaic performance of the devices. Also the counter electrodes of the prepared devices were not so thin enough to allow the whole light to penetrate through it, a part of the incident spectrum is reflected and a part is transmitted through the counter electrode, does the incident also not match with the band gap of the semiconductors used for junctions. All these factors reduce the photovoltaic efficiency of the junctions.
References


