Studies of Junction Parameters of Sn/(p)Bi$_2$S$_3$ Schottky Junction Prepared by Vacuum Evaporation Technique

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Abstract

The forward bias current-voltage (I-V) characteristics of vacuum deposited Sn/(p)Bi$_2$S$_3$ metal semiconductor (MS) Schottky diodes have been studied at room temperature and elevated temperatures. The junctions exhibited rectifying I-V characteristics and also photovoltaic effect. Different junction-parameters such as ideality factors, band gap, short-circuit current, open circuit voltage, fill factor, efficiency etc. have been determined from I-V characteristics of the junction. The ideality factor $n$ and series resistance $R_s$ was found to decrease and zero bias barrier height $\phi_b$ found to remain more or less constant with the increase of temperature in (308-328)K range. Proper doping, annealing and hydrogenation are necessary to reduce the series resistance so as to achieve high conversion efficiency of the junction. More works are being carried out in this direction.

Key words: photovoltaic effect, ideality factors, band gap, fill factor, Schottky diodes, series resistance.

1. Introduction

Among the non-conventional renewable energy resources, solar energy is a potential source of renewable energy which is easily available all over the world. There are various methods to convert solar energy into other form. Solar cell directly converts light into electrical energy. The exploration of low cost and eco-friendly materials to fabricate solar cell have been subject of both experimental and theoretical studies in the present time. The Bi$_2$S$_3$ thin film with reported band gap (1.2-1.7) eV [1, 2, 3] and high absorption coefficient ($10^4$ to $10^5$ cm$^{-1}$) has been creating interest to the scientist for its possible use as solar cell. The optical band gap of our sample was found to be 1.45eV. Up to our knowledge no data have been reported on Schottky barrier junction of Bi$_2$S$_3$ thin films prepared by thermal evaporation method except our report [4]. However, there are few reports of junctions on Bi$_2$S$_3$ thin films prepared by chemical methods [5, 6, 7, 8, 9, 10]. The Bi$_2$S$_3$ thin films reported to be n-type in nature [11, 12, 13, 14]. The Bi$_2$S$_3$ thin films used in polymer solar cell shows acceptor type nature [5, 6]. The Cu$_3$BiS$_3$ thin films have been reported to behave as p-type semiconductor [15]. In the present work, electrical and optical properties have been studied on Sn/(p)Bi$_2$S$_3$ Schottky barrier diode prepared by evaporation method.

2. Experimental Procedure

Three thick films of Nickel (Ni), each of width 1mm and a length 25 mm were first deposited by vacuum evaporation on a chemically cleaned glass substrate (3×3cm$^2$ size). Above these Ni films, Bi$_2$S$_3$ (SIGMA ALDRICH) powder and 7.21% Indium (In) was simultaneously deposited from two different sources by thermal evaporation technique covering an area (1.5×1.5 cm$^2$). It has been observed that Bi$_2$S$_3$ highly decomposes during vacuum evaporation [16] and also found to react with some base materials. Therefore, special care is taken in depositing Bi$_2$S$_3$
thin films. The films then annealed in air inside an oven for five hours at temperature 438K. The type of carriers of these films were examined by hot probe method and found to behave as p-type. Over the composite film three tin (Sn) films each of width 1mm and length 25mm were vacuum deposited horizontally making crossed with the Nickel films. Thus 9 Sn/(p)Bi$_2$S$_3$ Schottky junction, each of equal area (1mm$^2$) were obtained on the same substrate. The Ni (work function = 5.01eV) films connected to (p)Bi$_2$S$_3$ (work function= 4.93eV ) [17] films were used as the lower electrode and Sn (work function = 4.08eV) films deposited over the (p) Bi$_2$S$_3$ was used as the upper electrode. They form Schottky contact with the (p) Bi$_2$S$_3$ films. During all depositions, substrates were kept more or less at room temperature (308 K) and pressure was maintained at 10$^{-5}$ Torr.

For measuring $I$-$V$ of the junctions, the sample was mounted on a specially designed sample holder fitted inside a vacuum chamber. Electrical and optical measurements were performed at room temperature as well as at elevated temperatures using a specially designed electronic temperature controller. To measure $I$-$V$ under illumination, the junction inside the chamber was illuminated using white light from a tungsten halogen lamp (500 W) through a glass window. The light was incident from the "Sn" side. The input intensity of the light was measured with a Lux meter (Luxmat-300ED; Research Ins ND-110028, India). The type of carrier concentration was determined by hot probe method. The capacitance of the junction was measured by 4-digit auto compute LCR-Q meter (Aplab-4910). The monochromator (Oriel 7722) fitted with a grating 1200 per cm, blazed at 35nm (Oriel 77233) was used to study the spectral response of the junctions. The input and output slits were set at 3mm. A tungsten halogen lamp was used to illuminate the entrance slit of the monochromator. Output of the monochromator was carefully allowed to fall on the junction for spectral response measurement. Thickness of all films was measured using interference technique. All electrical measurements were performed at pressure 10$^{-2}$ Torr.

2. Results and Discussion

2.1. Study of $I$-$V$ Characteristic

Nine Schottky barrier diodes (Sn/(p)Bi$_2$S$_3$) of equal area (.01cm$^2$) was fabricated on a micro slide glass substrate. All junctions show more or less same $I$-$V$ characteristics. The curves show rectifying [Fig.1(a)]. nature with very low photovoltaic effect. The current density $I$ was calculated from the well known expression [18],

$$J = J_0 \exp \left( \frac{qV}{nkT} \right) \left\{1- \exp\left(-\frac{qV}{kT}\right)\right\}$$

where $J_0$ is reverse saturation current density and is equal to

$$J_0 = A^* T^2 \exp\left(-\frac{q\Phi_B}{kT}\right)$$

The $J_0$ values were found out by extrapolating the linear portion of ln[$I$/{$1-\exp(-qV/kT)$}] vs $V$ plots (plots are not shown) to the intercept on the current axis at zero bias ($V=0$) and the ideality factor $n$ was calculated from the slope of the plot(not shown) using ,

$$n = \frac{q}{kT} \frac{dV}{dJ}$$

The $J_0$ values of the junctions at room temperature (308K) in dark and under illumination (2000Lux) were found to vary within (3-3.3) x10$^{-7}$ Acm$^{-2}$ and (6-7) x10$^{-7}$Acm$^{-2}$ respectively. The ideality factor of the junctions studied in the present case at room temperature (308K) was found to vary within (5.2- 5.7) in dark and (4-4.4) under illumination (2000Lux). The $I$-$V$ characteristic of the Sn/(p)Bi$_2$S$_3$ Schottky junction have been studied in (308-328)K [Fig. 1(b)] range to understand the detail information about conduction mechanisms or the nature of barrier formation at the MS diodes. The rectification has been observed to increase with the increase in temperature. The values $n$ and $J_0$ at different temperatures were found out from ln[$I$/{$1-\exp(-qV/kT)$}] vs $V$ plots [Fig. 2(a)] using Eq. (1) as discussed above. The value of Richardson's constant ($A^*$ ) of a typical junction was found out.
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from the intercept of $\ln[J_o/T^2]$ vs $1/T$ plots [Fig.2 (b)] on $\ln[J_o/T^2]$ axis for $1/T=0$. The value was found to be 87.35 $\text{Acm}^{-2} \text{K}^{-2}$. Using A* value the zero bias barrier height ($\phi_b$) values of the Schottky junction for different temperature have been calculated by using Eq. (2). The $J_o$, $n$ and $\phi_b$ values found out at different temperatures are shown in Table 1. It is apparent from Table 1, that, $J_o$ and $n$ values of the junction are strongly temperature dependent. The $\phi_b$ values found to remain more or less constant within (308-328)K. The value of $n$ has been observed to decrease from 5.7 to 4.3 and $J_o$ has been found to increase from $1.310^{-9}$A to $16.6 \times 10^{-9}$A with the increase of temperature in (308-328)K .

The presence of interfacial layer, image force lowering of barrier height, recombination of electron and hole in the depletion region and tunnelling effect are the main regions for ideality factor greater than unity. The high values of the ideality factor show that there is a deviation from TE theory in the current conduction mechanism. Moreover, the ideality factor varies almost linearly with $T^{-1}$ [Fig. 3(a)]. The temperature dependence of $n$ suggests that the current conduction mechanism is controlled by the thermionic field emission theory . The barrier height does not change significantly with the change of temperature from 303K to 328K.

### Table 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Saturation current density ($J_o$) ($\times 10^{-9}$A cm$^{-2}$)</th>
<th>Ideality factor ($n$)</th>
<th>Barrier height ($\phi_b$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>0.0317</td>
<td>5.3</td>
<td>0.82</td>
</tr>
<tr>
<td>313</td>
<td>0.0530</td>
<td>5.0</td>
<td>0.82</td>
</tr>
<tr>
<td>318</td>
<td>0.0880</td>
<td>4.8</td>
<td>0.82</td>
</tr>
<tr>
<td>323</td>
<td>0.1210</td>
<td>4.6</td>
<td>0.82</td>
</tr>
<tr>
<td>328</td>
<td>0.2421</td>
<td>4.3</td>
<td>0.82</td>
</tr>
</tbody>
</table>

2.2 Effect of Series Resistance

The presence of series resistance in the Sn/(p)Bi$_2$S$_3$ Schottky junction was also investigated. The series resistance was calculated for forward bias condition using $\ln I$ vs $V$ plot [Fig. 3(b)] and $\Delta V$ vs $I$ plot [Fig. 4(a)]. The result shows that the device possesses high series resistance both in dark and under illumination, the same was found to decrease with the increase of temperature. The series resistance of a typical junction under study was found to be 416 k$\Omega$ (in dark), 344 k$\Omega$ (2000 Lux) both calculated at 308 K same was found to decrease to 250 k$\Omega$ , when temperature was raised up to 328 K in dark.
2.3 Capacitance-Voltage Measurement

The capacitance of the junction was measured at room temperature and under reverse bias condition. The acceptor concentration \( N_a \) was calculated from the slope of \( C^2 \) vs \( V_r \) plot using the relation:

\[
C = \left( \frac{q^2 N_a}{2} \right)^{1/2} \left( V_{do} + V_r - \frac{kT}{q} \right)^{-1/2}
\]

A typical \( C^2 \) vs \( V \) plot at 1 kHz is shown in Fig. 4(b). Here \( V_{do} \) is the diffusion voltage at zero bias which is equal to \( V_i + kT/q \), where \( V_i \) is the negative intercept on the \( V_r \) axis and \( \varepsilon_s \) is the permittivity of (p)\( \text{Bi}_2\text{S}_3 \). The value of \( N_a \) for a typical junction was found to be \( 5.253 \times 10^{15}/\text{cm}^3 \). Barrier height obtained from the relation \( \phi_b = V_{do} + \xi \) (\( \xi \) is the energy difference between the Fermi level and the top of the valence band) was about 0.82 eV in dark. This value is also in good agreement with the value obtained from I-V characteristic in dark.
2.4 Photovoltaic effect

The junctions under study show photovoltaic effect (Fig. 5). The open circuit voltage and short circuit current of a typical junction was found to be 215 mV and $10 \times 10^{-9}$ A respectively. Different parameters of a typical Sn/(p)Bi$_2$S$_3$ junction illuminated have been calculated and showed in Table 2.

Investigation was also carried out on spectral response of the junctions (plot not shown here).

3. Conclusion

Thin films Sn/(p)Bi$_2$S$_3$ Schottky barrier junction prepared by vacuum evaporation exhibits rectifying I-V characteristic and photovoltaic effect. Junction
parameters such as the barrier height, the diode ideality factor, saturation current density and the Richardson’s constant of a vacuum deposited Sn/(p)Bi$_2$S$_3$ structure were determined from its I-V characteristics. The ideality factor greater than unity is attributed to the interfacial layers and series resistance associated with MS junction and within the semiconductor. They are found to change under illumination and with change in temperature. It has been observed that Bi$_2$S$_3$ compound highly decomposes into Bismuth and Sulphur and S/Bi ratio of the source was found to decreases with passes of time during evaporation, which hinders in preparing Bi$_2$S$_3$ thin film stoichiometric in composition. To overcome this difficulty special care is taken in evaporating Bi$_2$S$_3$ compound. Sulphur is highly reactive to any base material and sulphur produced during evaporation due to decomposition of Bi$_2$S$_3$, reacts with most of the base metals (counter electrode) forming sulphide compound which is one of the main regions of ideality factor greater than unity. However, this can be reduced by increasing the carrier concentration and also improving preparation technique. More works is progress in this direction.

References

[14] Y. Lu, J. Jia and G. Yi, Cite this DOI: 10.1039/ C2Ce06713g, www.rsc.org/crystengcomm

Table 2

Some photovoltaic parameters of a typical Sn/(p)Bi$_2$S$_3$ Schottky barrier junction at room temperature.
(Illumination intensity 2000Lux)

<table>
<thead>
<tr>
<th>Open circuit voltage (mV)</th>
<th>Short-circuit current density ($J$) ($10^{-7}$A/cm$^2$)</th>
<th>Maximum power output ($\mu$Wcm$^{-2}$)</th>
<th>Fill factor (%)</th>
<th>Efficiency (%)</th>
<th>Ideality factor $n$</th>
<th>Saturation current density ($J_s$) ($10^{-7}$Acm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>10</td>
<td>0.0832</td>
<td>38.70</td>
<td>0.231</td>
<td>8.74</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 2