Effect of doping with ‘se’ on structural, optical, electrical and thermoelectric properties of multilayers of Bi$_2$Te$_{2.7}$Se$_{0.3}$ / Sb$_2$Te$_3$ to enhance thermoelectric performance

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1. Introduction

Thermoelectrics is a promising area for the conversion of any type of waste heat into electricity and suitable for power generation. The initial applications of thermoelectric materials was in spacecraft such as in Cassini, Voyager, and New Horizons [1, 2]. But now they have many other applications, such as in microcoolers and generators, in CCD technologies, and in infrared detectors. The unique property of thermoelectric devices for conversion of environmental waste heat introduced the elegant concept of harvesting energy from body. The source of energy from a body is thermal energy, which can be utilized and converted into self-powered wearable device [3]. To make a body-wearable device, the heat exchange from hot side to cold side is limited due to large inefficient thermal resistances [4]. It should be remember that the material used for body-wearable device should have low thermal conductivity. Generally TE devices are not practically applicable, due to their low efficiency. Much research has been done in this field to increase the thermoelectric efficiency. The thermoelectric efficiency is directly dependent on a dimensionless quantity known as Figure of merit (ZT). Higher ZT values of lead to large thermoelectric efficiency. ZT directly depends on electrical conductivity and Seebeck coefficient and inversely proportional to thermal conductivity. The formula for figure of merit \( ZT = S^2\sigma T/k \), where \( S \) is Seebeck coefficient, \( \sigma \) is electrical conductivity and \( k \) is thermal conductivity and \( T \) is absolute temperature. Much research has been done to increase the value of electrical conductivity and Seebeck coefficient by selecting an appropriate material. Bi$_2$Te$_3$ is most promising thermoelectric material showing good thermoelectric properties at room temperature, which can be used for many applications. Recent research on \( n \)-type Bi$_2$Te$_3$ alloys showing high ZT using nanostructuring [5–7], nonoelusions [8], texturing [9] and point defect engineering [10]. In many researches, it was found that \( n \)-type Bi$_2$Te$_3$ compounds have been shown high value of ZT but still they are not suitable for practical applications such as harvesting body heat due to non-optimized properties at room temperature. So, high value of ZT of a material with optimizing transport property at room temperature is required. To satisfy the above requirement recent researches are focused on decreasing lattice thermal conductivity by preparing superlattice structures. Recent enhancements have been done by Venkatasubramanian by fabricating superlattice structures of Bi$_2$Te$_3$ / Sb$_2$Te$_3$ with high figure of merit 2.4. For body heat harvesting applications, high value of \( \sigma \) and \( S \) with relatively low value of \( K \) is required at room temperature. So, as it is known that bismuth telluride has been shown to possess the best thermoelectric properties at room temperature and when it is doped with Sb, Se or with some other element it becomes an efficient thermoelectric material. Doping is a very common technique for the improvement in thermoelectric properties by increasing electrical conductivity and decreasing thermal conductivity as doping increased electron-phonon scattering. It has been reported that doping of elements like C, Sn, Pb, O, S, Se can increase the thermoelectric properties of Bi$_2$Te$_3$ [11–16]. Superlattice structures are focused on either a multilayered heterojunction arrangement or by doping in one of the material to form a series of homojunctions [17]. It has been observed that appropriate amount of doping into a superlattice structure can make high performance thermoelectric module and can also develop new properties [18]. Thus, the present work is focused on the synthesis of multilayered Bi$_2$Te$_{2.7}$Se$_{0.3}$ / Sb$_2$Te$_3$ structures to fulfill the above requirement.
2. Experimental details

All the samples single layer Bi$_2$Te$_2$Se$_{0.3}$ and Sb$_2$Te$_3$ (50 nm) each, their bilayer Bi$_2$Te$_2$Se$_{0.3}$–Sb$_2$Te$_3$ (103 nm), 5 layers of thickness (510 nm) and 10 layers of total thickness (1024 nm) are fabricated on clean glass substrate by e-beam evaporation technique. The thickness of the films was measured from quartz crystal thickness monitor of vacuum coating unit. The Bi$_2$Te$_2$Se$_{0.3}$ and Sb$_2$Te$_3$ are purchased in the powder form from Sigma Company with 99.99% purity. Substrate were cleaned with acetone and dried at room temperature. All the thin films are deposited in a vacuum chamber under the pressure of $\sim 10^{-6}$ Pa with rate of evaporation for Bi$_2$Te$_2$Se$_{0.3}$ was $\sim 2\text{Å/Sec.}$ and for Sb$_2$Te$_3$ is $\sim 10\text{Å/Sec.}$ Structural properties are analyzed by XRD in Banasthali Vidyapeeth, Banasthali. The electrical properties like hall measurement, Carrier concentration, mobility, conductivity, sheet resistance and I–V measured were carried out through four probe method in MNIT, Jaipur. The optical properties were measured by LAMBDA 750 (Perkin Elmer) in MNIT, Jaipur to determine the band gap of the samples.

3. Results and discussion. Structural properties

3.1. X-Ray Diffraction (XRD)

The Xrd pattern of multilayers of Bi$_2$Te$_2$Se$_{0.3}$/Sb$_2$Te$_3$ of different thicknesses from $\sim$(50–1000 nm) has been shown in Fig. 1. The main peaks observed in single layer Bi$_2$Te$_2$Se$_{0.3}$ are at 23.46°, 28.28° and 41.05°. There is no peak observed in Sb$_2$Te$_3$ which confirms its non-crystalline or amorphous nature. As thicknesses of the samples increases more number of peaks is generated at angles 50.44°, 64.86° and 66.20°, which cannot be observed in single layer Bi$_2$Te$_2$Se$_{0.3}$. The intensity of the peaks is increased, which confirms that crystallinity of the thin films increases as number of alternate layer increases. The Xrd patterns of the multilayer structure of Bi$_2$Te$_2$Se$_{0.3}$/Sb$_2$Te$_3$ are well matched with Xrd pattern in paper of [19].

![XRD pattern of multilayers of Bi$_2$Te$_2$Se$_{0.3}$/Sb$_2$Te$_3$.](image)

**Fig. 1.** XRD pattern of multilayers of Bi$_2$Te$_2$Se$_{0.3}$/Sb$_2$Te$_3$ at room temperature

3.1.1. Grain Size. The grain size of the samples of different thicknesses can be calculated using Scherer’s formula:

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$
The calculated structural parameters Full width at half maxima (FWHM), Grain size (D), microstrain (ε), and dislocation density (δ) for alternate layers of Bi$_2$Te$_{2.7}$Se$_{0.3}$/Sb$_2$Te$_3$ of various thicknesses ranging from (50–1000 nm) for (0 1 5) orientation have been shown in Table 1.

**TABLE 1.** The calculated structural parameters, Full width at half maxima (FWHM), Grain size (D), microstrain (ε), and dislocation density (δ) for alternate layers of Bi$_2$Te$_{2.7}$Se$_{0.3}$/Sb$_2$Te$_3$ for (0 1 5) orientation

<table>
<thead>
<tr>
<th>Samples</th>
<th>FWHM ($\beta^0$)</th>
<th>Grain Size(D) (nm)</th>
<th>Strain ($\varepsilon \cdot 10^{-4}$) (lines$^{-2}$m$^{-4}$)</th>
<th>Dislocation density ($\delta \cdot 10^{13}$) (lines/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>2$Te$</em>{2.7}$Se$_{0.3}$ (50 nm)</td>
<td>0.2172</td>
<td>37.76</td>
<td>9.18</td>
<td>70.13</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$ (53 nm)</td>
<td>0.492</td>
<td>16.29</td>
<td>21.26</td>
<td>376.84</td>
</tr>
<tr>
<td>Bilayer (103 nm)</td>
<td>0.1855</td>
<td>44.28</td>
<td>7.84</td>
<td>51.00</td>
</tr>
<tr>
<td>5 layers (510 nm)</td>
<td>0.2052</td>
<td>39.94</td>
<td>8.67</td>
<td>62.68</td>
</tr>
<tr>
<td>10 layers (1024 nm)</td>
<td>0.2879</td>
<td>28.47</td>
<td>12.17</td>
<td>123.37</td>
</tr>
</tbody>
</table>

Where D is the grain size, $k$ is the shape factor (0.94), $\lambda$ is the wave length of X-ray source (1.5406 Å), $\theta$ is the Bragg’s angle and $\beta$ is full width at half maxima.

**3.1.2 Microstrain.** The microstrain ($\varepsilon$) is developed in thin films is the root mean square of variations in lattice parameters. It can be calculated from the relation:

$$\varepsilon = \frac{\beta \cos \theta}{4}$$ (2)

**3.1.3 Dislocation density.** Dislocation in Xrd is an imperfection in crystal which occurs due to misregistry of lattice in one part with another part of the lattice [17]. The dislocation density ($\delta$) is the length of dislocation lines per unit volume of crystal and it can be determined by the relation:

$$\delta = \frac{1}{D^2}$$ (3)

**3.2 Scanning Electron Microscopy (SEM)**

The SEM images of single layer of Bi$_2$Te$_{2.7}$Se$_{0.3}$ and Sb$_2$Te$_3$ are shown in Fig. 2. The average grain size from SEM analysis for Bi$_2$Te$_{2.7}$Se$_{0.3}$ and Sb$_2$Te$_3$ sample is ~44 nm and 20 nm. It was observed that crystallinity and grain size increase from single layer Bi$_2$Te$_{2.7}$Se$_{0.3}$ to bilayer. These results are in good agreement with XRD results.
4. Electrical properties

4.1. I–V Measurements

Figure 3 shown the I–V behavior of multilayers of Bi$_2$Te$_{2.7}$Se$_{0.3}$ / Sb$_2$Te$_3$ at room temperature. The current is flowing through the samples in milliamper range. The graph shows that slope of the curves increase with thicknesses which determine the conductivity of the sample. It is also been observed that single layer Bi$_2$Te$_{2.7}$Se$_{0.3}$ and Sb$_2$Te$_3$ show almost linear behavior but a nonlinear behavior is observed as thickness increases up to 5 layers. The semiconducting behavior of the curves increases with thickness which shows that decreasing conductivity.

![I–V curves of multilayers of Bi$_2$Te$_{2.7}$Se$_{0.3}$ / Sb$_2$Te$_3$ at room temperature.](image)

**TABLE 2.** Represents Electrical properties of multilayers of Bi$_2$Te$_{2.7}$Se$_{0.3}$ / Sb$_2$Te$_3$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bulk conc. ($10^{21}$)</th>
<th>Sheet resistance ($10^3$ Ω)</th>
<th>Conductivity ($10^2$ Ω·cm)$^{-1}$</th>
<th>Hall coefficient, R$_{H}$ ($10^{-3}$ cm$^3$/C)</th>
<th>Mobility, $\mu$ (cm$^2$/V·sec.)</th>
<th>Magneto resistance ($10^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>2$Te$</em>{2.7}$Se$_{0.3}$</td>
<td>1.38</td>
<td>0.815</td>
<td>2.43</td>
<td>4.58</td>
<td>1.10</td>
<td>0.56</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$</td>
<td>2.64</td>
<td>1.00</td>
<td>1.87</td>
<td>2.35</td>
<td>4.58</td>
<td>16100</td>
</tr>
<tr>
<td>Bilayer</td>
<td>0.67</td>
<td>0.984</td>
<td>0.99</td>
<td>9.23</td>
<td>1.58</td>
<td>1.11</td>
</tr>
<tr>
<td>5 layers</td>
<td>0.13</td>
<td>0.207</td>
<td>0.95</td>
<td>3.42</td>
<td>4.30</td>
<td>1.93</td>
</tr>
<tr>
<td>10 layers</td>
<td>0.12</td>
<td>0.152</td>
<td>0.64</td>
<td>2.53</td>
<td>5.77</td>
<td>0.50</td>
</tr>
</tbody>
</table>

In order to examine the electronic transport properties, Bulk carrier concentration ($n$), mobility ($\mu$) and Hall coefficient (R$_{H}$) were measured at room temperature. The sign of Hall coefficient was positive for all the samples. It shows that main electrical charge carriers are hole and showing $p$-type semiconducting behavior. The maximum value of hall coefficient 9.23 ($10^{-3}$ cm$^3$/C) is found for bilayer sample but decreases as thickness of the sample was further
increases. A high value of carrier concentration of \((10^{21})\) is achieved for all the samples and decrease with thickness. Mobility increases as the number of alternate layers increases. Maximum mobility \(5.77\) (cm\(^2/V\)-sec.) and minimum carrier concentration \(0.12 \cdot 10^{21}\) is found to be for 10-layered sample.

Magneto resistance is also an important parameter to study in the field of thermoelectricity which is the tendency of material to change its electrical resistance on the application of an external magnetic field. In multilayer system tunnel junctions are formed that’s why the term giant magnetoresistance (GMR) is used. A high GMR is achieved for single layered \(\text{Sb}_2\text{Te}_3\) which shows that maximum change in resistance is observed for \(\text{Sb}_2\text{Te}_3\) on the application external magnetic field.

5. Optical properties

In optical properties, absorbance spectra of all the samples with different thickness were recorded using UV-VIS-NIR double beam spectrometer in the range of \((200–1100)\) nm. Fig. 4 show the optical absorption spectra of single layer \(\text{Bi}_2\text{Te}_2.7\text{Se}_{0.3}\), \(\text{Sb}_2\text{Te}_3\) and Bilayer sample. It is obvious that absorption increases with thickness. But, as the thickness increases to 5 or 10 layers, the absorbance pattern was not clearly observed. Because as thickness of the sample is large, the absorbance is greater and only some part of the light will be transmitted through the sample. It is clearly observed from the graph that low absorbance is found in 300–350 nm region which lies in visible region. For all the three samples maximum absorbance was found only at one position which confirms the uniformity of the sample.

\[ \alpha = \frac{2.303}{d} \log_{10} \frac{1}{T} \]  

(4)

where \(T\) is transmittance and \(d\) is the thickness of the film.

The electronic transition between valence band and conduction band can also be calculated from absorption coefficient using:

\[ \alpha = A(h\nu - E_g)^P \]  

(5)

where \(A\) is constant, \(E_g\) is the optical band gap, \(h\nu\) is incident photon energy and \(P\) has discrete values like \(\frac{1}{2}\), \(\frac{3}{2}\), \(\frac{4}{2}\), etc., depending upon the transition. For direct and allowed transition \(P = \frac{1}{2}\), in direct but forbidden case \(P = \frac{3}{2}\), and for indirect and allowed transition \(P = 2\) and for forbidden case it will be 2 or more. The band gap is determined by extrapolation on \(x\)-axis in curve between \((\alpha h\nu)^2\) and \(h\nu\). The optical band gap has been determined for different thickness shown in Fig. 5. It has been shown that band gap increases with thickness up to the bilayer and then decreases for 5-layered sample. The graphs show the direct and allowed transitions. These values of band gaps \(E_g\) for \(\text{Bi}_2\text{Te}_2.7\text{Se}_{0.3}\), \(\text{Sb}_2\text{Te}_3\), Bilayer and layers are 1.34, 1.72, 1.56, 1.22 eV. The variation in band gaps is due to variation
in grain size and dislocation density. As dislocation density is high resulting in high band gap of a semiconductor because presence the separation distance of dislocations are greater than interatomic distance [21]. The results are in good agreement with the results of XRD shown in Table 2.

![Graphs of Bi$_{2}$Te$_{2.7}$Se$_{0.3}$–Sb$_{2}$Te$_{3}$ thin films](image)

**FIG. 5.** Band gaps of Bi$_{2}$Te$_{2.7}$Se$_{0.3}$–Sb$_{2}$Te$_{3}$ thin films

### 5.1. Thermoelectric Properties

<table>
<thead>
<tr>
<th>Sample details</th>
<th>Seebeck coefficient S (µV/K)</th>
<th>Resistivity ρ (µΩ·m)</th>
<th>Power factor (10$^{-3}$ W/m·K$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{2}$Te$</em>{2.7}$Se$_{0.3}$</td>
<td>-87</td>
<td>41.15</td>
<td>0.183</td>
</tr>
<tr>
<td>Sb$<em>{2}$Te$</em>{3}$</td>
<td>210</td>
<td>53.4</td>
<td>0.825</td>
</tr>
<tr>
<td>Bilayer</td>
<td>238</td>
<td>101.0</td>
<td>0.560</td>
</tr>
<tr>
<td>5 layers</td>
<td>167</td>
<td>105.2</td>
<td>0.265</td>
</tr>
<tr>
<td>10 layers</td>
<td>123</td>
<td>156.2</td>
<td>0.096</td>
</tr>
</tbody>
</table>

In thermoelectric measurements, Seebeck coefficients of the samples were measured at room temperature. The Seebeck coefficient, resistivity and power factor of the samples are shown in Table 3. The negative value of Seebeck
coefficient for single layer $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ shows $n$-type charge carrier and positive values for other samples show $p$-type charge carriers. The results have been shown that maximum Seebeck coefficient is achieved for bilayer sample but Power factor is maximum for $\text{Sb}_2\text{Te}_3$. The variations in Seebeck coefficient and power factor are shown in Fig. 6.

![Fig. 6. Seebeck coefficient and power factor of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$–$\text{Sb}_2\text{Te}_3$ thin films](image)

### 6. Conclusion

The multilayered thin films of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ / $\text{Sb}_2\text{Te}_3$ variable thickness from (50–1000) nm were deposited on glass substrate at room temperature by using e-beam evaporation technique. The effect of thickness on structural, electrical and optical properties was studied. XRD studies indicates that the single layer $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ thin film showed polycrystalline nature with preferred orientation along (0 1 5) plane, whereas the single layer $\text{Sb}_2\text{Te}_3$ show non crystalline or amorphous nature. Also, as the number of layers increases, the intensity of the planes also increases, which shows that crystallinity increases with thickness. The grain size also increases from single layer to bilayer, but after that, it decreases as the number of layers further increases. SEM analysis shows that single layer $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Sb}_2\text{Te}_3$ have average grain size around 44 nm and 20 nm respectively. Results of I–V curve shows that slope increases with thickness and in electrical properties conductivity and charge carrier concentration decreases, whereas mobility increases with thickness. The optical properties show that absorption of all the samples were near visible region and optical transition was found to be direct and allowed. The energy band gap varies with thickness and lies between (1.34–1.72) eV. The maximum band gap was found for $\text{Sb}_2\text{Te}_3$. In thermoelectric measurements, the maximum Seebeck was found for Bilayer sample, but the power factor was maximum for single layer $\text{Sb}_2\text{Te}_3$.

### References


Effect of doping with ‘se’ on structural, optical, electrical and thermoelectric properties of multilayers...

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