Effect of Fe doping on the structural, electrical and optical properties of Bi$_2$Te$_3$ thin films

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MS received 27 June 2022; accepted 10 September 2022

Abstract. In this work, the structural, morphological, electrical and optical properties of Bi$_{2-x}$Te$_3$Fe$_x$ ($x = 0, 0.3$ and $0.5$ at%) thin films were investigated. X-ray diffraction investigations revealed the formation of hexagonal Bi$_2$Te$_3$ structure for undoped and Fe-doped films. Scanning electron microscopy observations revealed an increase in the average grain size from 20.4 to 43.5 nm with increasing Fe doping ratio from 0 to 0.5 at%. A transition from N-type conduction to P-type conduction with a decrease in carrier concentration was observed after Fe doping with 0.3 at%. Energy-dispersive X-ray spectroscopy spectra confirmed the presence of Fe in the doped films. The optical absorbance (Abs), transmittance ($T$%) and reflectance ($R$%) spectra of Bi$_{2-x}$Te$_3$Fe$_x$ films were measured in the spectral range from 200 to 2500 nm. Both $T$% and $R$% were strongly affected by Fe doping. The optical bandgap decreased from 0.26 to 0.17 eV with increasing Fe ratio from 0 to 0.5 at%. Over most of the studied wavelength range, the refractive index values increased with increasing Fe doping ratio. The optical conductivity values were mainly increased with Fe doping. The examined optical and electrical properties of Bi$_{2-x}$Te$_3$Fe$_x$ ($x = 0, 0.3$ and $0.5$ at%) thin films may enable rapid material selection for designing certain applications such as optical coatings.

Keywords. Fe-doped Bi$_2$Te$_3$ thin films; structural characteristics; electrical properties; optical properties.

1. Introduction

In the recent decade, Bi$_2$Te$_3$ thin films have received much interest from various research groups all over the world due to their practical applications in technology-based devices such as high-efficiency low-cost thin-film thermoelectric generators for wireless devices [1], energy storage and electrochemical devices [2], flexible thermal sensors [3], thin film solar cells [4], anode materials in Li-ion batteries [5] and thin film Hall bar devices [6].

Doping is considered one of the most reliable procedures to change structural and transport properties of chalcogenide thin films, thereby fulfill the requirements of the recent advanced applications [7]. In particular, Bi$_2$Te$_3$ thin films have been doped by various metals for different purposes. For example; Ahmed et al [8] reported a significant conductivity enhancement by 6.5 times in favour for Sb-doped Bi$_2$Te$_3$ film compared to the undoped film, in addition to a significant improvement in thermoelectric characteristics. Harrison et al [9] reported the growth of Ho-doped Bi$_2$Te$_3$ thin films. They achieved a large saturation moment for these films, which is beneficial for incorporation into heterostructures. Srerung et al [10] studied the undoped and In-doped co-binary Cu$_{2-x}$Te and Bi$_2$Te$_3$ thin films coated on WO$_3$ electrodes for Na–S batteries. They reported values of $\sim 21$ and $19$ mAh g$^{-1}$ for the highest specific capacity of the charge and discharge cycles, respectively, with average coulombic efficiency of $\sim 96\%$. This approach enhances the performance of the Na–S batteries. Jariwala et al [11] examined the effect of Fe doping on the structural and optical properties of Bi$_2$Te$_3$ thin films. They reported that the films display high reflectance and low transmittance in the UV and visible spectral wavelength ranges.

Recently, doping Bi$_2$Te$_3$ crystals and/or Bi$_2$Te$_3$ based alloys with Fe has been frequently carried out for both scientific examinations and technological applications [12–14]. Jo et al [12] examined the effect of Fe doping on Bi$_2$Te$_3$ crystals. They found a significant spin polarization for Fe-doped Bi$_2$Te$_3$ crystals, which could be useful for spintronic applications. Arévalo-López et al [13] studied Fe-doped Bi$_2$Te$_3$ crystals. The X-ray photoelectron spectroscopy results and X-ray diffraction (XRD) confirmed the fact that Fe is introduced into the Bi$_2$Te$_3$ crystal structure as Fe$^{+3}$, this inferred the Fe substitution rather than intercalation in Bi$_2$Te$_3$. Wang et al [14] used a combination of XRD, Hall-coefficient studies and magnetization to pave a simple way for probing into the location of impurity atoms.
in Bi₂Te₃ single crystals. They found that the large magnetoresistance may stem from the surface magnetism, even in the presence of Fe impurities.

Due to a small number of researches conducted on Fe-doped Bi₂Te₃ thin films, and as the perfect use of Bi₂Te₃ thin films in technological applications, such as terahertz detectors, optical fibres and optical coatings, requires full knowledge of the optical properties of these films over a wide range of wavelengths [15–17], it was necessary to conduct this work. Besides, the morphological, structural, electrical and the optical properties of Bi₂Te₃ thin films are linked together and are influenced strongly by Fe doping. Thus in this work the morphological, structural, electrical and the optical properties of Bi₂Te₃ thin films were examined.

2. Experimental

Bi, Te and Fe granules were purchased from Sigma-Aldrich, with 9.999 % purity, and used to prepare the desired ingots. Then, the desired Bi₂₋ₓTe₃Feₓ (x = 0, 0.3 and 0.5 at%) ingots were prepared using the melting technique at 1000°C and used as a source materials. After that, the thin films were prepared from the ingots onto well cleaned Si(100) and glass substrates utilizing Edwards AUTO 306 thermal evaporation coating unit. The base pressure of the coating was 5 × 10⁻⁶ torr and it decreased a pressure of 4 × 10⁻⁵ torr during evaporation of the films. The current applied during thin films preparation was 4.5 A. The evaporation rate of the films was ≈ 0.35 nm s⁻¹. The thickness (d) of the films was adjusted to be to be ≈ 55 nm using film thickness monitor (model SQM-160 INFICON).

The crystal structure of the films were examined utilizing XRD. The equipment was Bruker D8 ADVANCE diffractometer, which utilizes Cu-Kα₁ radiation (λ = 1.54056 Å). The surface morphology of the films were examined using scanning electron microscope (SEM). The quantitative elemental composition ratios of the films were estimated using energy-dispersive X-ray spectroscopy unit, which is attached to SEM (model 200JSMIT). The Hall effect measurements were carried out utilizing a system from MMR technologies Inc. at room temperature. The optical reflectance (R), transmittance (T) and absorbance (Abs) measurements of the films were done using Jasco 570 double beam spectrophotometer. The measurements were done at normal incidence in the wavelength range from 200 to 2500 nm.

3. Results and discussions

Figure 1 shows XRD patterns for Bi₂₋ₓTe₃Feₓ (x = 0, 0.3 and 0.5 at%) thin films. All the crystalline peaks of the undoped film (figure 1a) are indexed to Bi₂Te₃ with hexagonal structure. The structure is highly orientated around (1 0 11) plane. With Fe doping the peaks intensity, orientation changed strongly (figure 1b and c). The preferred orientation changed to (101) plane. No obvious peak shifts and no other crystalline phases related to Fe or Fe compounds are observed. This may have attributed to that Fe ions may substitute Bi ions in the hexagonal lattice or Fe may segregate to non-crystalline parts in grain boundaries [18,19].

The grain sizes (G) of the films are calculated using Scherrer equation:

\[ G = \frac{k\lambda}{\beta\cos(\theta_c)} \]

where \( k = 0.94 \) is the Scherrer constant, \( \beta \) the full-width at half-maximum of the Gauss fit and \( \lambda \) the wavelength of the XRD radiations. The calculated values are listed in table 1. The grain size values increase with Fe doping. Similar increase in grain size with increase in doping has been reported previously for Ag-doped ZnO [20] and can be explained as follows. Fe may work as an amphoteric dopant [20] and may occupy both interstitial and lattice sites. But, because of the difference in ionic radius between Bi (1.09 Å), Te (0.97 Å) and Fe (0.645 Å) [21] ions, the segregation...
of Fe at the proximity of the grain boundaries of Bi\textsubscript{2}Te\textsubscript{3} is favourable, which may prefer the growth of larger grain-sized crystallites accompanied with an increase in the intensities of the diffraction peaks.

The dislocation density ($\delta$) is calculated utilizing the equation proposed by Williamson and Smallman [22] of the form $\delta = \phi / G^2$, where $\phi$ is a factor. When the factor $\phi$ is equal to unity, it gives minimum dislocation density, i.e.,

$$\delta = \frac{1}{G^2}$$  \hspace{1cm} (2)

The number of grains per unit area (N) is evaluated utilizing the equation [23]:

$$N = \frac{d}{G}$$  \hspace{1cm} (3)

where $d$ is the film thickness.

The lattice micro-strain ($\varepsilon$) induced broadening from crystal imperfections and distortion is calculated from the given equation [24]:

$$\varepsilon = \frac{\beta}{4\tan(\theta_c)}$$  \hspace{1cm} (4)

The obtained values for $\delta$, $N$, and $\varepsilon$ are listed in table 1. The $\delta$, $N$ and $\varepsilon$ values decrease with increase in Fe doping due to the crystal structure improvement and to the lattice defects reduction around the grain boundaries as well as to reduction of the stacking faults [25].

The lattice parameters ($a$ and $c$) are evaluated from the equation:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (5)

and are written in table 1. The calculated values are found to be close to those reported in [11].

The quantitative elemental percentage ratios of the Fe-doped and undoped films were evaluated using energy-dispersive X-ray spectroscopy. Figure 2 presents the energy-dispersive X-ray spectroscopy spectra of Bi\textsubscript{2-}$x$Te\textsubscript{3}Fe\textsubscript{x} ($x = 0, 0.3$ and $0.5$ at%) thin films. Fe, Bi, Te and Si peaks are presented. The Si peak is stemmed from the Si substrate. The obtained ratios are listed in table 1. The spectra confirm the presence of Fe in the doped films. However, the effective Fe doping is lower than that of the intended.

The SEM images taken for Bi\textsubscript{2-}$x$Te\textsubscript{3}Fe\textsubscript{x} thin films are presented in figure 3. The undoped Bi\textsubscript{2}Te\textsubscript{3} thin film (figure 3a) has uniform, closely packed spherical grains that are well distributed over the examined area. The average sizes of the grains are ranged from 20.4 to 32.7 nm. The surface morphology of the Fe-doped Bi\textsubscript{2}Te\textsubscript{3} thin films exhibits different morphologies of the surface grains that depend on Fe ratio (figure 3b and c). The degree of crystallinity enhances with Fe doping, which is in good agreement with the XRD results. The average grain sizes for $x = 0.3$ at% and

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G$ (nm)</th>
<th>$\delta$ ($10^{14}$ lines m$^{-2}$)</th>
<th>$\varepsilon$ (%)</th>
<th>$N$ ($10^{15}$ m$^{-2}$)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$\text{Chemical composition (at%)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi\textsubscript{2}Te\textsubscript{3}</td>
<td>17.4</td>
<td>33.03</td>
<td>0.359</td>
<td>10.44</td>
<td>4.257</td>
<td>29.953</td>
<td>7.036</td>
<td>44.90 55.10 —</td>
</tr>
<tr>
<td>Bi\textsubscript{1.7}Te\textsubscript{3}Fe\textsubscript{0.3}</td>
<td>37.4</td>
<td>7.14</td>
<td>0.245</td>
<td>1.05</td>
<td>4.396</td>
<td>30.454</td>
<td>6.928</td>
<td>48.52 50.87 0.61</td>
</tr>
<tr>
<td>Bi\textsubscript{1.5}Te\textsubscript{3}Fe\textsubscript{0.5}</td>
<td>40.7</td>
<td>6.04</td>
<td>0.216</td>
<td>0.82</td>
<td>4.396</td>
<td>30.454</td>
<td>6.928</td>
<td>44.51 54.62 0.87</td>
</tr>
</tbody>
</table>

Figure 2. Energy-dispersive X-ray spectroscopy spectra of Bi\textsubscript{2-}$x$Te\textsubscript{3}Fe\textsubscript{x} ($x = 0, 0.3$ and $0.5$ at%) thin films.
In order to study the effect of Fe doping on the electrical properties of Bi$_2$Te$_3$ thin films and the Hall effect measurements were carried out. The Hall effect results are listed in table 2. The carrier concentration of undoped Bi$_2$Te$_3$ film is $7.02 \times 10^{20}$ cm$^{-3}$ with N-type conduction. This value is in agreement with the previously reported values $6.7 \times 10^{20}$ cm$^{-3}$ and $6.0 \times 10^{20}$ cm$^{-3}$ for Bi$_2$Te$_3$ thin films prepared by thermal evaporation [26] and RF magnetron sputtering [27], respectively. The carrier concentration decreases to $1.09 \times 10^{20}$ cm$^{-3}$ after Fe doping with $x = 0.3$ and the type of the carrier changes to P-type. For Fe doping ratio of $x = 0.5$, the carrier concentration increased to $2.45 \times 10^{20}$ cm$^{-3}$ with maintaining the P-type conduction. It is worth mentioning that the transition in conduction type has been previously reported for thermally evaporated Mn-doped Bi$_2$Te$_3$ thin films [26] and Fe-doped Bi$_2$Te$_3$ single crystals [12]. Although the mobility increases with the Fe doping of $x = 0.3$, the resistivity increases by more than one order of magnitude. However, both of the mobility and resistivity decrease with further increase in Fe doping. Jo et al [12] reported that replacing the trivalent Bi ions by the divalent Fe ions in Bi$_2$Te$_3$ creates hole donors, which decreases the $n$-type carrier density and thereby change the P-type at $x = 0.3$, where the resistivity abruptly increases.

The optical absorbance (Abs), transmittance ($T$) and reflectance ($R$) for Bi$_{2-x}$Te$_3$Fe$_x$ thin films are presented in figure 4 as a function of wavelength. Over whole ultraviolet and visible spectral ranges, the transmittance has almost zero values while the absorbance and reflectance have higher values. The transmittance and reflectance values are relatively high in the near-infrared range, but the absorbance values are low over this range. Overall, the transmittance decreases with Fe doping while the reflectance increases. This behaviour is usually encountered in metal-doped semiconductors [7,28,29]. The grain sizes were enhanced with Fe doping. The enhancement in grain sizes suggest an improved crystallinity with reduced grain boundaries. Therefore, the scattering due to grain boundaries is decreased, which leads to an increase in reflectance.

The absorption coefficient ($\alpha$) was calculated utilizing film transmittance ($T$), reflectance ($R$) and thickness ($d$) from the equation:

$$\alpha = \frac{1}{d} \left( \frac{1 - R}{T} \right)$$

The optical bandgap ($E_g$) was evaluated from Tauc equation by assuming indirect allowed transition:

$$(zhv) = \beta (hv - E_g)^2$$

where $\beta$ is a constant, $\nu$ is the frequency and $h$ is Plank’s constant. Plotting $(zhv)^{1/2}$ vs. $hv$ and extrapolating the linear part to intercept with $hv$ axis, the optical bandgap can be determined as shown in figure 5. The estimated optical bandgap values are 0.26, 0.20 and 0.17 eV, for undoped and Fe-doped with $x = 0.3$ and 0.5, respectively. Thus doping with Fe increases the defect states density and modifies the structural properties, thereby reduces the optical bandgap [7]. The optical bandgap value obtained for undoped Bi$_2$Te$_3$ are among the values summarized previously in [26,30].

Figure 6a and b presents the change in the refractive index ($n$) and extinction coefficient ($k$) for Bi$_{2-x}$Te$_3$Fe$_x$ thin
films as a function of wavelength. Over most of the studied wavelength range, the refractive index values increase with increasing Fe doping. This increase in $n$ values can be attributed to the enhancement in polarizability associated with Fe atoms \[7\]. Also, the extinction coefficient values increase with Fe doping due to the increase in surface defects by Fe doping, which produces localized states, therefore increase the light absorption. For all films, the values of extinction coefficient increase with wavelength to reach maximum in the shorter wavelength then they decrease at longer wavelengths, which can be ascribed to the absorption at the fundamental edge of these materials \[22\].

The optical conductivity ($\sigma_{\text{opt}}$) is an important parameter for the practical applications, which measures the electrical conductivity in the alternating field. $\sigma_{\text{opt}}$ is calculated from

$$\sigma_{\text{opt}} = \frac{\alpha n c}{4\pi},$$

where $c$ is the light velocity. The optical conductivity of Bi$_{2-x}$Te$_3$Fe$_x$ thin films as a function of incident photon energy is shown in figure 7. The optical conductivity firstly increases steeply with photon energy to certain higher values, then it increases slowly. This increase in optical conductivity values with photon energy is attributed to the photo-excitation of orbital electrons and the charge transfer excitation \[31\]. The optical conductivity values are mainly increased with increasing Fe doping ratio. This increase in optical conductivity has been encountered for other metal-doped chalcogenide systems \[32\].

4. Conclusions

Bi$_{2-x}$Te$_3$Fe$_x$ ($x = 0$, 0.3 and 0.5 at\%) alloys were prepared by the melt quenching method and the thin films were prepared by thermal evaporation. XRD revealed the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (Ω cm)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$n$ (cm$^{-3}$)</th>
<th>Carrier type</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>4.89×10$^{-3}$</td>
<td>1.82</td>
<td>7.02×10$^{20}$</td>
<td>Electron</td>
<td>0.26</td>
</tr>
<tr>
<td>Bi$_{1.7}$Te$<em>3$Fe$</em>{0.3}$</td>
<td>1.53×10$^{-2}$</td>
<td>3.73</td>
<td>1.094×10$^{20}$</td>
<td>Hole</td>
<td>0.20</td>
</tr>
<tr>
<td>Bi$_{1.5}$Te$<em>3$Fe$</em>{0.5}$</td>
<td>1.25×10$^{-2}$</td>
<td>2.04</td>
<td>2.45×10$^{20}$</td>
<td>Hole</td>
<td>0.17</td>
</tr>
</tbody>
</table>
polycrystalline nature of all the prepared films with a hexagonal structure. The average grain sizes increased with Fe doping. A transition from N-type conduction to P-type conduction with a decrease in carrier concentration was observed after Fe doping with 0.3 at%. For Fe doping ratio of \( x = 0.5 \), the carrier concentration increased again with maintaining the P-type conduction. The transmittance decreased whereas the reflectance, refractive index, extinction coefficient and the optical conductivity increased with Fe doping. The \( E_g \) values decreased from 0.26 to 0.17 eV with increasing Fe ratio from 0 to 0.5 at%.

Acknowledgements

This study was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

References


Figure 6. Refractive index (\( n \)) and extinction coefficient (\( k \)) for Bi\(_{2-x}\)Te\(_3\)Fe\(_x\) (\( x = 0, 0.3 \) and 0.5 at%) thin films as a function of wavelength.

Figure 7. The optical conductivity of Bi\(_{2-x}\)Te\(_3\)Fe\(_x\) (\( x = 0, 0.3 \) and 0.5 at%) thin films as a function of incident photon energy.
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