EFFECT OF BI ADDITIVE ON OPTICAL AND ELECTRICAL PROPERTIES OF QUATERNARY CHALCOGENIDE In$_3$Te$_7$Bi$_x$Se$_{90-x}$ THIN FILMS

S. S. ASHRAF$^a$, M. ZULFEQUAR$^b$

$^a$School of Engineering Sciences and Technology Jamia Hamdard , New Delhi - 62, India
$^b$Department of Physics Jamia Millia Islamia, New Delhi - 25, India

Glassy alloy of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) are prepared by melt-quenching technique. Thin films are deposited by the thermal evaporation technique on glass substrates under a pressure of 10$^{-6}$ torr. The structural analyses of these films were carried out by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Scattering (EDS). X-ray diffraction (XRD) of thin films was carried out to analyze the amorphous or polycrystalline behavior of the thin films. EDS analysis shows the presence of the compositional elements in the thin films. SEM shows the surface morphology of the thin films and development of grains. Optical studies were carried out by the Ultra violet-visible (UV-Vis) Spectroscopy in the range of 190-1100 nm. The analysis of optical absorption spectra shows indirect optical band gap. The optical band gap decreases with increasing Bismuth concentration from 1.38 eV to 1.02 eV. The DC conductivity was carried out in specially designed metallic sample holder with vacuum 10$^{-4}$ Torr. The DC conductivity of thin films of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ increases and the corresponding activation energy decreases with increasing of bismuth content which may be due to shift in Fermi level.

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1. Introduction

Chalcogenide glasses are widely used due to its property of exhibit phase change under the influence of light, heat, pressure etc. Se based chalcogenide glasses are many applications in solid state electronic devices, memory devices etc. Since pure selenium is fragile and have short life time; therefore elements from group II-VI are added to make it more robust. These chalcogenide glasses are non-linear, low phonon energy and transparent in IR region which make it useful for optical switching [1-3]. Se-Te alloys have greater hardness, higher photosensitivity and smaller aging effects [4-7]. Optical band gap ($E_g$), extinction coefficient (k) and refractive index (n) are important parameters to study the amorphous semiconducting thin film. Thin films of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ are found to exhibit the change in refractive index under the influence of UV-Vis light which makes that material to use in optical memory devices [8]. Ternary assets deliver an opportunity of altering and improving natural and physical liberty, for example band gap of InTeBi (1.68 eV) is lesser as compared to ZnSe (2.82 eV) which makes it appropriate for the tender in solar cells [9]. Due to this reason numerous researchers take interest to study of InTeBi alloy following electrical properties, structural, optical properties. Ensuing this way it may be conceivable to form novel materials with chemical and structure freedom, which has substantial care in the arena of device applications. The structure of the material and optical parameters in an amorphous semiconductor may be widely different consequence of an impurity added into material [10]. Although in crystalline semiconductors a suitable impurity is continually to deliver a new donor or acceptor states, which is not vital in amorphous semiconductor [11]. An impurity may just change the mobility of the charge carries or might familiarize structural modification in its place of if a localized impurity level in the forbidden gap exists with or without alteration of the localized states in the prohibited gap in amorphous semiconductors [12].

$^*$ Corresponding author: shahabash@gmail.com
Research of the optical properties is responsible to the result of impurities between the conduction band and valance band of the materials is a subject of excessive attention, because the results of such studies provide ways to control effectively the optical properties of amorphous semiconductors. In amorphous semiconducting thin films the greatest noteworthy constraints are the optical band gap, refractive index and extinction coefficient. To determine its optical constants, optical conduct is used of a material. On behalf of reflectance and transmittance pleasant measurements films are perfect samples. Thus, a precise observation of the optical constants is enormously significant. In the present case we studied the In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) thin films. These prepared materials have been found to exhibit the change in refractive index under the influence of light. Optical band gap (E$_g$), extinction coefficient (k) and refractive index (n) are important parameters to study the amorphous semiconducting thin film. Chalcogenide thin films are found to exhibit the changes in refractive index under the influence of UV-Vis light which make those materials to use in memory devices. The optical band gaps decrease with the increase of Bi content, this may be due to increase in grain size and increase in the density of defect states [13]. The conduction at higher temperature (300-400 K) takes place due to thermally assisted tunneling of electrons at the localized states near conduction band edge [14].

In this present work authors aim to study the optical constants and electrical properties of the In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) thin films. The properties mostly depend on the preparation and deposition technique. In the present paper, the authors aim to study the structural and optical properties of InTeBiSe$_3$ thin films prepared by melt-quenching technique which makes it likely to usage these type of materials to best not lone the magnitude nevertheless to the stage of illumination and significant in holographic optical data storage.

2. Experimental

Chalcogenide glass alloys In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) were prepared from high purity constituent elements (99.999%) in stoichiometric ratio by using melt quench technique. The constituent elements were sealed in quartz ampoules under a vacuum of 10$^{-3}$ Torr. The ampoule was kept inside a furnace at 900°C for 12 hrs so that all elements were melted. The temperature was raised at the rate of 2°C/min. During the heating process, the ampoule was shaken continuously so as to make it homogeneous. Quenching was done in ice water and the ingots were taken out by breaking the ampoule. Thermal evaporation technique used to deposit the films on clean glass substrate at a pressure of 10$^{-8}$ torr. The films prepared are kept at deposition chamber for almost 24 hours so that metastable thermodynamic equilibrium is maintained.

The X-ray diffraction (XRD) patterns of the thin films of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) give the important information about the nature and structure of the samples. Thin films’ surface topography and composition have been studied by SEM image and EDS respectively. The optical measurement was carried out by using UV/Vis spectrophotometer (Model: Camspec M550 double beam) in spectral wavelength range 190–1100 nm. For electrical measurements the deposited film on glass substrate has length ~1.5 cm, electrode gaps ~0.4-1.2 mm and thickness ~400 nm. A DC voltage of 1.5 V was applied across the sample and the resulting current measured by a Keithley electrometer (6514). The DC conductivity was carried out in specially designed metallic sample holder with vacuum 10$^{-5}$ Torr. The temperature of the film was controlled by mounting a heater inside the sample holder and measured by calibrated copper-constantan thermocouple near film.

3. Results and discussion

XRD analysis of thin film was carried out by A RegakuUltima IV X-ray Diffractometre. The radiation source Cu Kα with λ = 1.54 Å, diffraction angle in the range of 5° to 90° with scan speed of 2°/min and a chart speed of 1 cm/min were maintained [15]. The XRD pattern of graph is shown in Fig 1. The XRD diffractograms show that the Bi-rich samples (x > 10%) have some extent crystallization peaks due to the presence of other phase of the material in Bi-rich samples. Amorphous nature of the In$_3$Te$_7$Bi$_x$Se$_{90-x}$ glass alloys decreases with increase of Bi.
concentration. Surface morphology of the thin film was analysed by Scanning Electron Micrograph (SEM) apparatus JEOL (Model JSM 6380). SEM image of thin film is shown in Fig 2. SEM image shows the growth of nuclei. The grains size decreases with the increase in Bi content. This may be due to reduction in disorderliness and hence decrease in density of defect states [13].The dissociation energy for Se-In, Se-Se, Se-Te, Bi-Bi, Bi-Se ,Bi-Te and Bi-In are 257.5 KJ/mol, 239.3 KJ/mol, 259.8 KJ/mol, 200.4 KJ/mol ,280.3 KJ/mol,232.3 KJ /mol and 2018.0 KJ/mol respectively [16-17].Bismuth has greater affinity for selenium than tellurium. This shows that Bi-Se bonds require more energy to be dissociated which makes it robust.

![XRD pattern of In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15) thin film.](image1.png)

**Fig.1.** XRD pattern of In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15) thin film.

![SEM images of In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15) thin films.](image2.png)

**Fig. 2.** SEM images of In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15) thin films.

The elemental composition of as-prepared In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15) thin films are checked by using the Energy Dispersive X-ray (EDX) spectroscopy. Fig.3. shows the typical EDX patterns of as-prepared thin films of In_{3}Te_{7}Bi_{x}Se_{90-x} (x = 0, 5, 10, 15). This image confirms the presence of constituent’s elements In, Te, Bi and Se. The calculated wt% values show Se (77.47%), Te (19.40%) and In (2.62%) for In_{3}Te_{7}Se_{90}, Se (62.49%), Te (24.49%),In (8.31%) and
Bi (4.61%) for In₃Te₇BiₓSe₉₀₋ₓ. Similarly the wt% values of other compositions agree well with experimentally taken wt% values. Intense peaks for Se found in the spectra of all samples are due to its high concentration as compared to other constituent such as In, Te and B.

Fig. 3. Energy Dispersive X-ray Spectroscopy (EDS) of In₃Te₇BiₓSe₉₀₋ₓ (x = 0, 5, 10, 15) thin films.

3.1 Optical Properties

The UV-Vis absorption spectra of In₃Te₇BiₓSe₉₀₋ₓ (x = 0, 5, 10, 15) thin films has been recorded in the wavelength range of 190-1100 nm by UV-Vis Spectrophotometre Model Comspec M550. The absorption coefficient (α) has been determined directly from the absorbance against wavelength curves using the relation [18-23]

\[
\alpha = \frac{\text{optical density (OD)}}{\text{thickness of the film}}
\] (1)

It has been observed that absorption coefficient increases with increase of photon energy for all samples of In₃Te₇BiₓSe₉₀₋ₓ as shown in Fig 4. Energy of the band tail also called Urbach’s energy and optical band gap has been measured using Urbach’s Rule [24] and Tauc relation [25] respectively. Urbach’s energy (width of the band tail due to localized states in amorphous semiconductor) can be calculated as

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)
\] (2)

where, \(\alpha_0\) is constant and \(E_u\) is called Urbach energy.

The Tauc relation between absorption coefficient (α) and optical band gap (E_g) is given as

\[
a h\nu = A (h\nu - E_g)^n
\] (3)

where A is a constant called band tailing parameter and \(E_g\) is called optical band gap. The index ‘n’ is associated with the type of transition which has values \(\frac{1}{2}, 2\) for direct and indirect transitions respectively [16-18]. In present thin films of In₃Te₇BiₓSe₉₀₋ₓ (x = 0, 5, 10, 15) obey indirect transition rule i.e. n = 2 and it has been shown in Fig 5. The intercept of the graph gives the optical band gap. The optical parameters of In₃Te₇BiₓSe₉₀₋ₓ (x = 0, 5, 10, 15) thin film at a wavelength of 700 nm are given in Table 1.
Fig. 4. Absorption coefficients versus photon energy in thin films of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ ($x = 0, 5, 10, 15$).

Fig. 5. Plot of $(\alpha h\nu)^{1/2}$ against photon energy $h\nu$ (eV) in thin films of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ ($x = 0, 5, 10, 15$).

Table 1. Optical parameters of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ ($x = 0, 5, 10, 15$) thin films at a wavelength of 700 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_g$ (eV)</th>
<th>$\alpha \times 10^4$ (cm$^{-1}$)</th>
<th>$k$</th>
<th>$n$</th>
<th>$E_u$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_3$Te$<em>7$Se$</em>{90}$</td>
<td>1.38</td>
<td>3.46</td>
<td>0.283</td>
<td>4.13</td>
<td>0.58</td>
</tr>
<tr>
<td>In$_3$Te$_7$Bi$<em>5$Se$</em>{85}$</td>
<td>1.21</td>
<td>2.93</td>
<td>0.194</td>
<td>3.65</td>
<td>0.59</td>
</tr>
<tr>
<td>In$<em>3$Te$<em>7$Bi$</em>{10}$Se$</em>{80}$</td>
<td>1.12</td>
<td>2.12</td>
<td>0.163</td>
<td>3.28</td>
<td>0.61</td>
</tr>
<tr>
<td>In$<em>3$Te$<em>7$Bi$</em>{15}$Se$</em>{75}$</td>
<td>1.02</td>
<td>1.62</td>
<td>0.092</td>
<td>3.02</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The value of optical band gap ($E_g$) has been calculated by taking the intercept on the X-axis. Calculated values for all samples of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ are given in Table 1. It is evident from the table that the value of optical band gap ($E_g$) decreases with increasing bismuth content. This may be due to decrease in grain size, reduction in disorderliness and decrease in density of defect states which results in increase of tailing bands [26-36]. The decrease in the optical band gap can be discussed on the basis of density of states model proposed by Mott and Davis [37]. Since chalcogenide thin films contain high concentration of unsaturated bonds or defects, therefore these defects are responsible for the presence of localized states in the amorphous semiconductor.

3.2. DC Conductivity

The DC conductivity of the In$_3$Te$_7$Bi$_x$Se$_{90-x}$ ($x = 0, 5, 10, 15$) thin films of thickness 400 nm was studied in the temperature range of 300 K-390 K using two probe method. The DC conductivity can be expressed by Arrhenius relation [37-41] as follows:

$$\sigma_{dc} = \sigma_0 \exp (\Delta E/KT)$$ (4)
where $\Delta E$ is called activation energy, $K$ is Boltzmann constant and $\sigma_0$ is pre-exponential factor.

Fig. 6 shows the temperature dependent DC conductivity of thermally evaporated thin films. It is clear from the Fig. 13 that graph between 1000/T (K⁻¹) versus $\ln \sigma_{dc}$ gives straight line due to thermally activated process for dc conduction and its slope gives activation energy. The calculated values of conductivity ($\sigma_{dc}$), activation energy ($\Delta E$) and $\sigma_0$ are given in Table 2. The conductivity increases with the increase in Bi content. It is suggested from the Table 2 that the conduction is due to thermally assisted tunneling of charge carriers in the localized states in band tails [42-46].

![Graph showing conductivity and activation energy](image)

**Table 2.** Electrical parameters in In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) thin films at a temperature of 310 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{dc}$ (Ω⁻¹cm⁻¹)</th>
<th>$\sigma_0$ (Ω⁻¹cm⁻¹)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_3$Te$<em>7$Se$</em>{90}$</td>
<td>$3.7 \times 10^{-9}$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>0.37</td>
</tr>
<tr>
<td>In$_3$Te$_7$Bi$<em>5$Se$</em>{85}$</td>
<td>$2.1 \times 10^{-7}$</td>
<td>$4.2 \times 10^{-5}$</td>
<td>0.21</td>
</tr>
<tr>
<td>In$<em>3$Te$<em>7$Bi$</em>{10}$Se$</em>{80}$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>$2.8 \times 10^{-4}$</td>
<td>0.16</td>
</tr>
<tr>
<td>In$<em>3$Te$<em>7$Bi$</em>{15}$Se$</em>{75}$</td>
<td>$2.6 \times 10^{-4}$</td>
<td>$2.1 \times 10^{-2}$</td>
<td>0.12</td>
</tr>
</tbody>
</table>
4. Conclusion

Alloys of In$_3$Te$_2$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10 and 15) have been deposited on ultraclean glass substrate by thermal evaporation technique at room temperature and under the pressure of 10$^{-4}$ torr. XRD pattern confirms the amorphous nature of thin films. EDS analysis shows the presence of constituent elements in the thin films. SEM image tells surface morphology of the thin films. The optical band gap ($E_g$) decreases with increasing Bismuth concentration. This may be due to decrease in grain size, increasing disorderliness and increase in density of defect states which results in increase of tailing bands. The optical absorption measurements shows indirect band transition which decreases with increase in bismuth concentration. The value of optical constants extinction coefficient (k) and refractive index (n) changes significantly with incident photon energy as well as with increasing bismuth concentration. The DC conductivity increases and the corresponding activation energy decreases which may be due to increase in the density of localized states.

References