Effect of X-ray Irradiation on Structural and Optical Properties of Topological Insulator Bismuth Telluride Nano-Structure Thin Film

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Abstract: Bismuth Telluride (Bi$_2$Te$_3$) thin films were grown onto optical flat fused quartz and chronic glass by using a thermal evaporation technique for optical and structural investigations, respectively. The prepared films were divided into three groups; the first group was as-grown films, and the second and third groups were irradiated with X-ray radiation with energies 6 and 15 MeV. The crystal structure and morphology of the grown Bi$_2$Te$_3$ thin films were identified by X-ray diffraction (XRD) and scan electron microscopy (SEM) before and after exposed to X-ray irradiation. The optical constants (Refractive index, n, and absorption index, k) of as-grown and irradiated Bi$_2$Te$_3$ thin films were estimated and calculated in the wavelength range from 200 to 2500 nm by using spectrophotometric measurements of transmittance and reflectance at normal incidence. The estimated onset optical gap $E_{onset}$ for as-grown equal to 0.35 eV and this value was found to be decreased corresponding to the increasing in X-ray radiation energy. The variation of the refractive index of normal dispersion is well described by the single oscillator model. The dielectric constant at infinite frequency ($\varepsilon_{\infty}$), the lattice dielectric constant ($\varepsilon_L$) and the ratio of free carrier concentration of the effective mass (N/m*) are calculated. Finally, the nonlinear optical parameters are calculated using some empirical relations.

Keywords: bismuth telluride; thin film; X-ray irradiation; the linear dispersion parameters; the non-linear dispersion parameters

I. Introduction

Bismuth-based tritellurides and triselenides, which are well-known thermoelectric materials because they possess the highest thermoelectric figure of merit known at room temperature [1] It have been used in thermoelectric refrigerators for the temperature control of semiconductor devices such as laser diodes or CCDs (charge coupled devices) [2], optical recording systems [3], magneto-resistance [4], and strain gauges [5]. Recently, Bi$_2$Te$_3$ was predicted to be three-dimensional (3D) topological insulator (TI); a new class of quantum matter with conductive massless Dirac fermions on the surface [6]. The 3D-TIs possess fully gapped bulk states and gapless surface states, which can be described by the Rashba spin-orbit Hamiltonian [7-9]. Bismuth Telluride thin films have been fabricated by using different techniques such as; flash thermal evaporation, sputtering, electrochemical deposition, metal-organic chemical vapor deposition and mechanically exfoliated method [10-17]. In this work, the authors aim to fabricate Bi$_2$Te$_3$ thin films by thermal evaporation technique at substrate temperature 623 K and investigate the effects of X-ray irradiation process on the structural and optical constants (Refractive index, n, and absorption index, k) and nonlinear optical properties.

The interaction of ionizing radiations (such as X-rays, gamma rays, etc.) with material, mainly, occurs by means of electronic excitation, electronic ionization, and, primarily, atomic displacement of the orbital electrons [18]. The influence of radiation on the material depends on dose rate and the parameters of the films. The degradation is more severe for the higher dose and the thinner films [19, 20]. Bi$_2$Te$_3$ thin films have been studied but much of the optical properties of Bi$_2$Te$_3$ are unknown. The exposure of solid to ionizing radiations produces changes in the microstructural properties of the material, which in turn affects the optical properties. Study of these changes is quite important, not only to understand physicochemical functions and spectroscopic properties of this material but also to increase their applicability in different fields and enable information about the induced irradiation defects and their interaction with the matter components. The main purpose of this work is to study in detail the induced changes in the topological and the morphological nanostructures of Bi$_2$Te$_3$ thin films and estimate the related optical and dispersion parameters of these films before and after exposed to X-ray radiation.

II. Experimental procedures

Bismuth Telluride Bi$_2$Te$_3$ in powder form with a purity of 99.99% was purchased from Aldrich Chem. Bi$_2$Te$_3$ thin films were grown by a vacuum thermal evaporation technique using a high vacuum coating unit (Edward, E 306 A, England), under a pressure of about 4×10$^{-7}$ Pa. Which deposited on a flat glass substrates for the structural properties and quartz substrates for the optical properties. A boat-shaped tungsten filament was
used to thermally evaporate Bi$_2$Te$_3$ in a vacuum. The films are divided into two groups. The first (as-grown) group is characterized as prepared. The second group was irradiated in air, at temperature 299.3 K and airpressure 1010.1 hPa with field size 10×10 cm at SSD 100 cm by high energy X-ray (6 MeV and 15 MeV) with a dose rate 4 Gy/min using aClinac (Dual energy Linear Accelerator DMX - Varian). The exposure time for irradiation process is constant 2.5 min and the exposed dose for 6 MeV is 10 Gy ± 0.018 and for 15 MeV 10 Gy ± 0.01; the output X-ray radiation beam calibrated using (UNIDOS E T10008-80685 Electrometer, TM30010-03870 Ionization Chamber, PTW Freiburg, Germany). The optical absorption spectra for the Bi$_2$Te$_3$ thin films of thickness 36 nm, exposed to different levels of the X-ray radiation energy, were recorded using (JASCO model V-570 UV–VIS-NIR) Spectrometer for the wavelengths in the range 200-2500 nm. These absorption spectra were analyzed to obtain the dose dependence of the optical band gap. The SEM images, for the Bi$_2$Te$_3$ thin films have been analyzed using X – ray Diffraction (model X’pert) with utilized monochromatic Cu-Kα radiation (λ=1.54056 Å). In the degrees range of $10^\circ$– $65^\circ$. In order to understand the changes in the structural and optical properties due to X-ray irradiation.

In order to calculate the optical constants, the absorption coefficient, $\alpha$, the absorption index, $k$, and the refractive index, $n$, of the films at different wavelengths, we can use the following equations [21,22]:

$$\alpha = \frac{1}{d} \ln \left(1 - \frac{R^2}{4} + \frac{(1-R)^2}{4} - R^2 \right)^{1/2} \quad (1)$$

$$k = \frac{1 + R}{1 - R} \quad (2)$$

$$n = \frac{1 + k}{1 - k} + \frac{4k}{(1-k)^2} \quad (3)$$

Where $\alpha$ is the absorption coefficient and $d$ is the film thickness.

III. Results and discussion

3.1 X-ray diffraction analysis

Figure 1 show the spectrum of X-ray powder diffraction for Bi$_2$Te$_3$ in powder form were taken in a 20 range from $10^\circ$ to $65^\circ$. The pattern has many diffraction peaks with different intensities indicating that the powder of Bi$_2$Te$_3$ has a polycrystalline nature. The highest preferred orientation is found along the (0 1 5) plane. The unit cell parameters of Bi$_2$Te$_3$ in powder form were determined and the parameters found to be $a = 4.381$ Å and $c = 30.437$ Å. All the diffraction peaks in the patterns of all the powder products correspond to the peaks of rhombohedral Bi$_2$Te$_3$ (JCPDS no. 08-0021) with space group: R3m (166). The cell parameters in JCPDs no. 08-0021, $a = 4.384$ Å and $c = 30.45$ Å. Therefore, the obtained powder product is rhombohedral Bi$_2$Te$_3$.

![Fig. 1. X-ray diffraction spectra of Bi$_2$Te$_3$ powder](image)

Table 1 shows the values of Miller indices, (h k l), for highest-diffraction peak together with the interplanar spacing, $(d_{hkl})$, and our check cell is in agreement with [23-27]. Fig. 2(a) shows the XRD pattern of thermally evaporated Bi$_2$Te$_3$ thin films of thickness 27 nm grown at substrate temperature 298K. Fig. 2(b) shows the XRD pattern of thermally evaporated Bi$_2$Te$_3$ thin films of thickness 36 nm grown at substrate temperature 623 K. The diffraction pattern exhibits a broad peak around $20 = 27^\circ$, indicating that the evaporated Bi$_2$Te$_3$ film is amorphous. Fig. 2(c,d) shows the XRD pattern of irradiated films. The absence of sharp diffraction peaks and the presence of humps emphasize amorphous nature.

<table>
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<th>2θ (degree) measured</th>
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Table 1. The diffraction spacing, d measured, the Miller indices (h k l), and the relative intensity, I/I$_0$, for Bi$_2$Te$_3$ in the powder form

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3.2 Topological and morphological characterizations

The surface topography and grain shape growth for as-grown and irradiated Bi$_2$Te$_3$ thin films are investigated by scanning electron microscopy (SEM) as shown in Figure 3. The topograph (a) for as-grown Bi$_2$Te$_3$ thin films at substrate temperature 298 K shows clearly almost uniform distribution of granular shape Nano crystallite particles. The topograph (b) for as-grown Bi$_2$Te$_3$ thin films at substrate temperature 623 K shows visibly almost uniform distribution of granular shape Nano crystallite particles. The topograph (c) shows the surface morphology of the -irradiated film with high energy X-ray (6 MeV) where the particles are observed with higher aggregation and pores appear compared with that of the as-deposited film. The topograph (d) shows the surface morphology of the -irradiated film with high energy X-ray (15 MeV), which shows more pores, in other words, the X-ray radiation can modify the surface topographies of Bi$_2$Te$_3$ thin films by controlling the aggregate densification and porous properties of Bi$_2$Te$_3$ thin films[28].

Fig. 2. X-ray diffraction spectra of (a) as-grown thin film at substrate temperature 298 K and (b) as-grown thin film at substrate temperature 623 K and (c) irradiated Bi2Te3 thin films with high energy X-ray (6 MeV) and (d) irradiated Bi2Te3 thin films with high energy X-ray (15 MeV).

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3.3. Optical characterizations

3.3.1 Transmission and reflection spectra

Fig. 4 (a,b) shows Spectral distribution of T (λ) and R (λ) of as-grown and irradiated Bi$_2$Te$_3$ thin films. The spectral distribution shows two abrupt changes at the first of UV region (λ=260 nm) and the first of IR region (λ=810 nm) which represent an optical switch behavior at λ=260 and λ=810. All-optical switching mechanism based on the optical control of resonance energy transfer (RET) between particles When RET occurs spontaneously, following the absorption of light, it usually represents the principal process for the intermolecular translation of electronic energy, from the sites of initial optical excitation [29]. However, under suitable conditions such processes of energy transfer can be activated or deactivated by (non-resonant) optical stimulation. From the Figure it is evident that the optical spectral distribution is sensitive to the radiation influence. Reflectance intensity decrease at UV region; wavelength range from 190 to 260 nm and IR region; wavelength range from 810 to 2500 nm.

3.3.2 Optical dispersion characteristics

Real part of the indices, n(hν), and imaginary part, k(hν), of refraction for as-grown and irradiated Bi$_2$Te$_3$ thin films calculated from eq (2) and (3) showed in Fig 5 and 6 as a function of photon energy. The values of the real part of the indices of refraction exhibits an anomalous dispersion in the range λ <850 nm, which can be explained according to the multi-oscillator model [30]. The refractive index for all films exhibits a normal dispersion in the range λ >1000 nm, which can be understood by using the single oscillator model [31,32]. The results for the real part, n, show one peak at 815 nm in the first of IR. The intensity of this peak is descending, i.e., decrease with increasing the energy of X-ray radiation. At longer wavelength (hν→0) the calculated value of the refractive index decreases by an amount Δn=0.31 and 0.54 after irradiation process for 6 MeV and 15 MeV, respectively. The decrease in the refractive index values is attributed to the decrease of mass.
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Optical absorption analysis has widely proven to be an important and efficient tool in exploring and interpreting the various phenomena of electronic structures and processes in the materials subjected to radiation [34–25].

![Graph of n(hν) vs. hν](image1)

**Fig. 5.** The spectral dependence of the real part of refractive index, \( n(h\nu) \), for the as grown and irradiated Bi\(_2\)Te\(_3\) thin films.

![Graph of k vs. hν](image2)

**Fig. 6.** The dependence of the extinction coefficient (k) versus photon energy as a function of irradiation dose.

Fig. 7 shows the variation of the absorption coefficient (\( \alpha \)) of as-grown and irradiated Bi\(_2\)Te\(_3\) thin films with thickness 36 nm, as a function of photon energy, (h\nu). It is evident that the optical absorption spectral distribution is sensitive to X-ray radiation; a considerable shift in the absorption was observed. The absorption increase for X-ray-irradiated Bi\(_2\)Te\(_3\)film. At lower optical frequencies, Wemple and DiDomenico [37,38] introduced two parameters based on the single effective oscillatormodel; \( E_o \) to describe the dispersion of the refractive index and the single oscillator energy \( E_o \) to give quantitative information on the overall band structure of the material"average gap"[39]. The refractive index is expressed in terms of these parameters as in references[37,38]:

\[
(n^2 - 1)^{-1} = \frac{E_o}{E_d} + \frac{1}{E_o E_d} (h\nu)^2
\]

Fig. 8 shows the plot of \( (n^2 - 1)^{-1} \) against (h\nu)\(^2\) for as-grown and irradiated Bi\(_2\)Te\(_3\) thin films. \( E_o \) and \( E_d \) can be obtained from the slope and intercept of the fitted straight lines of the experimental points. The infinite
wavelength dielectric constant ($\varepsilon_\infty$) can be deduced from extrapolation the linear part of the optical dispersion at zero photon energy n (0). The results for as-grown and irradiated Bi$_2$Te$_3$ thin films are calculated in Table 2.

The relationship between the lattice dielectric constant ($\varepsilon_L$) and refractive index, n, is given by [32]:

$$n^2 = \varepsilon_L - \left(\frac{\varepsilon^2}{4\pi \varepsilon_0 c^2}\right) \frac{N}{m^*} \lambda^2(6)$$

Where $\varepsilon_L$ is the high frequency dielectric constant, $e$ is the elementary charge, $\varepsilon_0$ is the permittivity of free space and (N/m*) is the ratio of free carrier concentration to the free carrier effective mass. Fig. 9 shows the linear relation between $n^2$ and $\lambda^2$ for the as-grown and irradiated Bi$_2$Te$_3$ thin films. Extrapolating the linear parts to zero wavelengths indicated the value 11.22 for $\varepsilon_L$ of the as-grown film, and the values 12.95 and 17.12 for $\varepsilon_L$ of the X-ray irradiated Bi$_2$Te$_3$ thin films by energies 6 MeV and 15 MeV, respectively. The ratio of free carrier concentration could be calculated from the slope of these linear parts, where the ratio (N/m*) was considered to be $4.24 \times 10^{44}$ Kg$^{-1}$ m$^{-1}$ for the as-grown and $4.54 \times 10^{44}$ Kg$^{-1}$ m$^{-1}$, $4.75 \times 10^{44}$ Kg$^{-1}$ m$^{-2}$ for X-ray
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irradiated Bi₂Te₃ thin films by energies 6 MeV and 15 MeV, respectively. The disagreement between ε₇ and ε₈ may be due to the differences in free carrier contribution [40].

![Graph](image)

Fig. 9. n² versus square of the wavelength (λ²) as a function of irradiation dose.

3.3.3 Energy gap determination

The band structure and the existence of an energy gap are believed to be dependent upon the arrangement of nearest atomic neighbors and the existence of local or short-range order. Mott was the first who proposed the concept of short-range order in amorphous solids [41]. The types of transition and the value of optical energy gap can be demonstrated by Bardeen et al. [42] as

\[ a h v = \alpha_0 (h v - E_g)^\gamma \]  

where \( a \) is a constant, and equals 0.37 ± 0.04 eV for covalently bonded crystalline and amorphous chalcogenides, \( N_c \) is the coordination number of the cation that is the nearest neighbor to the anion, \( N_e \) is the effective number of valence electrons per anion and \( Z_a \) is the formal chemical valence of the anion (here \( Z_a = 2 \) for Bi₂Te₃), \( N_e \) has the value equal to 9.3. The obtained value of coordination number from Eq. (8) listed in Table.2.

Various theoretical models were proposed by various researchers for the estimation of the third order susceptibility, \( \chi^{(3)} \) and nonlinear refractive index, \( n_2 \) [47]. Ticha et al. have combined Miller generalized rule and static refractive index (estimated by WDD single-oscillator model) [48-51]. According to that model,
the following relations were used for the estimation of the third order susceptibility, $\chi^{(3)}$, and non-linear refractive index ($n_2$):

$$\chi^{(3)} = A \frac{n_2^2}{4\pi} (n_2^2 - 1)^4$$

(9)

Where $A = 1.7 \times 10^{-10}$, $\chi^{(3)}$ is measured in esu and $n_2$ is the static refractive index.

$$n_2 = (12\pi \frac{\chi^{(3)}}{n_0})$$

(10)

Irradiation dose dependent third-order susceptibility and non-linear refractive index are tabulated in Table 3.

Table 3. Irradiation dose dependent third-order susceptibility and non-linear refractive index

<table>
<thead>
<tr>
<th>X-ray Energy</th>
<th>$\chi^{(3)}$ x 10^{-9} (esu)</th>
<th>$n_2$ x 10^{-6} (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>0.94</td>
<td>0.75</td>
</tr>
<tr>
<td>6 MeV</td>
<td>1.71</td>
<td>1.26</td>
</tr>
<tr>
<td>15 MeV</td>
<td>6.11</td>
<td>3.87</td>
</tr>
</tbody>
</table>

IV. Summary and conclusions

The main conclusions can be summarized as follows. The analysis of XRD of Bi$_2$Te$_3$ proved that the received powder material form polycrystalline patterns with hexagonal structure and the as-grown Bi$_2$Te$_3$ thin films have amorphous structure. X-ray irradiation affected the measured values of transmission, reflectance and absorption spectra. In the spectral range 200–2500 nm the refractive index showed anomalous dispersion in the wavelength range of (λ< 1000 nm) while in the wavelength more than 1000 nm, it is found that the refractive index dispersion data obeyed the single oscillator model. The advantage of using the single oscillator equation for the fit of the experimental data is that, it provides an indirect rather than direct band gap. The X-ray irradiation has an effect on the excitonic and impurities levels, this may due to the change in the microstructure of the film. The type of electronic transition responsible for optical properties is an indirect allowed transition. On the other hand, the analysis examines the change in the refractive index of the as-deposited and irradiated films. It is found that the refractive index dispersion data obeyed the single oscillator model. An interpretation of single oscillator parameters and Drude and free carriers absorption have been described for the analysis of refractive index dispersion before and after irradiation.

References


References


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