Linear and non-linear optical properties of reactive magnetron DC sputtered ZnTe thin films for opto-electronic devices

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Abstract. Zinc Telluride thin films were prepared by reactive magnetron direct current sputtering method and the temperature of the glass substrates changed from 150 to 350 °C. The band gap of ZnTe films increased from 2.32 to 2.42 eV. The normal dispersion of refractive index (n) for ZnTe films is described using the model of Wemple-Di Domenico (WDD) single-oscillator. The oscillator energy, dispersive energy and static refractive index (n0) of ZnTe films were reported. The Verdet coefficient (V) is estimated from the normal dispersion studies. The first-order (Ist) and third-order (IIIrd) non-linear optical susceptibilities (χ(1), χ(3)), refractive index (n2) of ZnTe films were calculated.

1. Introduction
ZnTe is a direct band gap semiconductor with 2.20-2.32 eV at room temperature (RT) and exhibits p-type semiconducting behaviour. It is a cheap effective material with a large absorption-coefficient value and exhibiting photovoltaic properties [1, 2]. Recently, this compound found applications in photovoltaic cells, LED, manufacturing of opto-electronic and energy efficient devices [3, 4]. ZnTe compound exhibits cubic structure with a lattice parameter (a) of 6.103 Å [5]. The detailed data on optical constants, dispersion parameters and non-linear properties of these films have less reports in the literature review. The non-linear properties had importance in integrated optical devices (switches, filter, modulators, etc). The main objective of this research study is to analyze the effect of substrate temperature on the linear and non-linear optical parameters of ZnTe thin films.

2. Experimental details
ZnTe films were prepared by using reactive magnetron DC sputtering process with the metallic targets of Zinc and Tellurium. ZnTe films were deposited at room temperature (RT) and changing the temperature of glass substrates from 150 to 350 °C. The targets used for sputtering had a dimension of 2-inch diameter and 4 mm thickness of Zinc (with purity 99.99%) and Tellurium (with purity 99.99%)
had been used in this work. The sputtering gas of argon was released into the chamber by mass flow controllers (MFC). The base pressure in the vacuum chamber was 2.4 x 10^{-6} Torr, the substrate and target is at a distance of 60 mm. After pre-sputtering with argon gas for 10-15 min, the working pressure of 3 mTorr was maintained during the deposition. The power during sputtering was set to 110 W for Zinc and 85 W for Tellurium. The thickness of the films measured by surface profilometer (Talysurf) was in the range of 320 - 360 nm. X-ray diffraction (XRD) profiles of ZnTe thin films were measured with X-ray diffractometer having radiation of CuKα. The X-ray tube is maintained with current 25 mA, voltage of 30 KV and the scan speed of 0.02(20) per sec. Optical absorption spectra of ZnTe films was measured at the wavelength of 300 - 2500 nm using UV-Vis-NIR spectrophotometer (Model: JASCO V-670, Japan).

3. Results and discussion

Figure 1(a) illustrates the absorption spectra of ZnTe films prepared at various substrate temperatures. The shifting of absorption edge towards lower energies of photon for the thermal treated layers can be due to change in the grain size. Figure 1(b) shows the extrapolation of (αhν)² versus hv of ZnTe films. The intercept corresponding to straight line on hv axis represents the band gap of ZnTe films. The optical band gap (Eg) of ZnTe films increased from 2.32 to 2.42 eV with an increment of substrate temperature. The obtained values of Eg for the films were found in good agreement with the previous reported works [6-8].

![Figure 1](image-url)

**Figure 1.** (a) Optical absorbance spectra of ZnTe films and (b) Tauc’s plot for ZnTe films prepared at various substrate temperatures.

The refractive index (n) of ZnTe films were estimated from the equations provided in our research works [9]. The change in ‘n’ of the films with wavelength (λ) is shown in Fig. 2(a), the decreasing trend in refractive index value with an increase of wavelength (λ) and saturated at longer wavelengths. Such behaviour shows ZnTe thin films were free from structural defects. At λ = 550 nm, the ‘n’ varies from 2.57 to 2.36 with an increment in substrate temperature which may be because of change in the packing density. In other words, the variation in the refractive index is due to the stoichiometric in the ZnTe films and uniformity, which makes shifts the band gap of the ZnTe films.

The optical dispersion study of refractive index(n) for ZnTe thin films has been determined from the model related to single oscillator reported by Wemple and DiDomenico (WDD). From this model the oscillator energy (Eo) and dispersion energy (Ed) are determined and the refractive index (n) of ZnTe films were determined from the Wemple-DiDomenico relationship [10]

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

(1)
From the plot of \((n^2 - 1)^{-1} - 1\) versus \((h\nu)^2\) and a straight-line fit is shown in Fig. 2(b), the single oscillator (SO) parameters \(E_o\) and \(E_d\) are found from the slope of \((E_o E_d)^{-1}\) and intercept \((E_d/E_o)\). The values of \(E_o\) and \(E_d\) are shown in Table 1, these values were decreased with the increase of substrate temperature because of ordered structure and reconnection of molecular and atomic liaisons. The plot of \((n^2 - 1)^{-1}\) against \((h\nu)^2\) can be used to find the \(n_o\) from the equation
\[
(n_o^2 - 1)^{-1} = 1 + \left(\frac{E_d}{E_o}\right)^{1/2}
\]
(2)

Extrapolate the WDD relation to the zero value of \(h\nu\). The estimated values of \(n_o\) for ZnTe films were reported in Table 1. The optical moments \(M_{-1}\) and \(M_{-3}\) were determined using the equations [11]
\[
E_o^2 = \frac{M_{-1}}{M_{-3}}
\]
(3)
\[
E_d^2 = \frac{M_{-3}}{M_{-3}}
\]
(4)

These optical moments measure the average bond strength and the dielectric response of the material. The optical moments \(M_{-1}\) and \(M_{-3}\) of ZnTe thin films were found from the estimated values of \(E_o\) and \(E_d\) are reported in Table 1.

\[\text{Figure 2. (a) Refractive index (n) of ZnTe films with the variation of wavelength (b) Variation of (n^2-1)^{-1} vs (h\nu)^2 for ZnTe films.}\]

The optical properties of ZnTe films can be understood by optical dispersion (OD) parameters. Figure 3(a)-(c) shows the dispersive refractive index, group velocity \((U_g)\) and phase velocity \((V_p)\) of ZnTe films with the wavelength. The group velocity, \(U_g\) is determined from the relation [12]
\[
U_g = \frac{d\omega}{dk} = \frac{c}{\left[ n - \lambda \left( \frac{dn}{d\lambda} \right) \right]}
\]
(5)
where \(c\) = light velocity in the presence of vacuum, \(k\) = wave number, and \(\omega\) = angular frequency. The wavelength dependence of the group and phase velocity for ZnTe films is shown in Fig. 3(b) and 3(c). The results show that the group and phase velocity for ZnTe thin films improves with an increment in the wavelength.

Refractive index is related to Verdet coefficient (V) with the following relation [13]
where \( \mu_0 \) is the vacuum permeability, \( r = 0.28 \) (magneto-optical anomaly factor) for the substances with the covalent bond characteristics and nearer to one for ionic type bonding, \( e = \) electron charge, \( m = \) electron mass, \( c = \) light velocity and \( dn/d\lambda \) is the optical dispersion of the material. The wavelength dependence of Verdet co-efficient for ZnTe films prepared by varying substrate temperatures are illustrated in Fig. 3(d). It is observed the positive (+) and negative (-) values of Verdet coefficient which depends on the negative values of \( E_g \).

\[
V(\lambda) = \mu_0 r \left( \frac{e}{2mc} \right) \lambda \left( \frac{dn}{d\lambda} \right)
\]

(6)

The complex dielectric constant provides the information on electronic structure of the material and helps in the design of highly efficient opto-electronic devices. The dependent of ‘\( n \)’ on the real and imaginary dielectric constants \( (\varepsilon_1 \text{ and } \varepsilon_2) \) are explained by the Spitzer-Fan model is [14]:

\[
\varepsilon_1 = n^2 - k^2 = \varepsilon_{\infty} - \left[ \frac{e^2}{\pi c^2} \right] \frac{N}{m^*} \lambda^2
\]

(7)

\[
\varepsilon_2 = 2nk = \left[ \frac{e^2 \omega_p^2}{8\pi c^3 \tau} \right] \lambda^2
\]

(8)

where \( \varepsilon_{\infty} \) = dielectric constant with high frequency, \( e = \) electronic charge, \( c = \) light speed in vacuum, \( N/m^* = \) ratio of optical carrier concentration to the effective mass of electron, \( \omega_p = \) plasma frequency and \( \tau = \) optical relaxation time. The plot of real dielectric constant \( (\varepsilon_1) \) versus \( \lambda^2 \) for zinc telluride films prepared at various substrate temperatures are illustrated in Fig. 4(a). It is noticed the linear dependent of \( \varepsilon_1 \) on \( \lambda^2 \) with higher wavelengths, the \( \varepsilon_2 \) and \( N/m^* \) values were obtained from extrapolating \( \lambda^2 \) to zero and the slope. Figure 4(b) shows the change in imaginary dielectric constant \( (\varepsilon_2) \) with \( \lambda^2 \) for ZnTe films, the \( \varepsilon_2 \) is lower than the value of \( \varepsilon_1 \) which indicates the light energy loss is minimum. The variation of \( \varepsilon_1 \)
and \( \varepsilon_2 \) with the substrate temperature is attributed due to the defects such as stresses, voids, inhomogeneity, discontinuities, grain boundaries etc. The decrease in \( \varepsilon_1 \) and \( \varepsilon_2 \) for ZnTe films with a variation of substrate temperature (ST) from 150 to 350 °C is because of loss of energy which occurs due to the absorption of energy by free carriers present in the medium.

The plasma frequency \( (\omega_p) \) is estimated from the relation

\[
\omega_p^2 = \left[ \frac{4\pi N e^2}{\varepsilon_\infty m^*} \right]
\]

From the \( \omega_p \), the relaxation time \( \tau \) is determined and noted in Table 1. By the observation of both \( \varepsilon_\infty \) and \( N/m^* \) values increased with the increase of ST from 150 to 350 °C.

The non-linear refractive index \( (n_2) \) of the films is derived from Tichy and Ticha relation [15, 16]. From the Miller’s generalized rule, the static refractive indices \( (n_o) \) of ZnTe films were deduced from Wemple-DiDomenico model

\[
n_2 = \left[ \frac{12\pi \chi^{(3)}}{n_o} \right]
\]

where \( \chi^{(3)} \) is the IIId non-linear susceptibility, which is given as

\[
\chi^{(3)} = A \left( \chi^{(1)} \right)^4
\]

where

\[
\chi^{(1)} = \left[ \frac{E}{4\pi E_o} \right]
\]

where \( A \) is \( 1.7 \times 10^{-10} \) esu, \( \chi^{(3)} \) is given by the relation

\[
\chi^{(3)} = \left[ \frac{A}{4\pi} \right] (n_o^2 - 1)^4
\]

The values of \( n_2, \chi^{(1)}, \) and \( \chi^{(3)} \) are given in Table 4. It is noticed that these values decreased with an increment in the substrate temperature from 150 to 350 °C. Thus, ZnTe films is suitable to change refractive index and oscillator energy parameters by varying substrate temperature. Therefore, the ZnTe films were found in designing nonlinear optical device applications/optoelectronic devices.
Conclusions

ZnTe films were grown from magnetron DC sputtering by changing substrate temperature from 150 to 350 °C. The dispersive study of ZnTe films were analysed by the Wemple-Di Domenico single-oscillator (SO) model. It was examined that the decrease of oscillator energy $E_o$ and dispersion energy $E_d$ with an increment in substrate temperature. The Verdet coefficient for the ZnTe films was deduced from the refractive index that exhibits a negative range depending on optical band gap. In addition, non-linear properties such as $\chi^{(3)}$ and $n_2$ are also reported. We conclude that ZnTe films will be useful for futuristic optical devices and opto-electronic devices.

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Table 1 Optical dispersion and non-linear optical properties of ZnTe films.

| Parameter | $E_o$ (eV) | $E_d$ (eV) | $M_1$ | $M_3$ (eV^2) | $n_o$ (eV^2) | $\varepsilon_{0}$ | N/m* (10^4 cm^3 g^-1) | $\omega_p$ (10^14 Hz) | $\tau$ (10^13 s) | $\chi^{(1)}$ (10^13 esu) | $\chi^{(3)}$ (10^13 esu) | $n_2$ (10^-12 esu) |
|-----------|------------|-----------|-------|-------------|--------------|----------------|----------------------|-----------------|---------------|----------------|----------------|-------------|
|          | RT 2.32    | 2.01      | 5.51  | 0.67        | 1.93         | 3.37           | 0.988                | 1.02            | 0.97          | 0.22          | 3.88          | 2.32        |
|          | 150°C 2.34 | 2.08      | 4.62  | 0.51        | 1.79         | 3.22           | 0.985                | 0.97            | 1.03          | 0.17          | 1.66          | 2.34        |
|          | 250°C 2.40 | 2.19      | 3.79  | 0.36        | 1.65         | 2.73           | 0.992                | 0.92            | 1.08          | 0.14          | 0.61          | 2.40        |
|          | 350°C 2.42 | 2.21      | 3.05  | 0.33        | 1.56         | 2.46           | 1.04                 | 0.87            | 1.15          | 0.11          | 0.31          | 2.42        |