Original research article

Spectroscopic ellipsometry characterization of Ge$_{30-x}$Sb$_x$Se$_{70}$ films using combinations of multiple dispersion functions

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1. Introduction

Glasses of the Ge–Sb–Se are promising materials for the fabrication of optical fibers due to their high transparency, large band gap low dispersion, low light scattering and good mechanical properties [1,2]. The glass forming region in the Ge–Sb–Se system extends from 5 to 35 at.% germanium, 5–40 at.% antimony, the rest being selenium [1]. Therefore number of investigations has been performed on this system in order to connect the physical properties of the material with the industrialized needs [3–6]. The studies of optical constants have yielded significant information on the role of composition of various component atoms in the chalcogenide network. Previously [7], we studied the optical properties of Ge$_{30-x}$Sb$_x$Se$_{70}$ thin films, using a spectrophotometer technique (ST). In order to model ST data, we used Swanepoel's method [8,9]. Note that the Swanepoel’s method is usually used by envelop technique or in connection with Cauchy formula as a dispersion model.

\[ n(\lambda) = f_0 + \frac{f_1}{\lambda^2} + \frac{f_2}{\lambda^4} \]

where $f$'s are adjusted parameters and $\lambda$ is wavelength. It should be mentioned that the Cauchy model is an empirical relation which relates the refractive index to the wavelength with parameters that have no physical meaning. In addition,

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this model is not Kramers-Kroning (KK) consistent. It is well known that according to KK, the value of the refractive index can be calculated if the value of extinction coefficient is known.

On the other hand, a significant attention in the ellipsometric technique of thin chalcogenide glasses and films has been observed [10–16]. The main advantages of the ellipsometric methods are fast, nondestructive, very sensitive to the presence of surface layers and versatile optical method that permits precise evaluation of the thickness and the optical properties of a thin film.

In this paper, we present the optical function spectra of as-prepared Ge$_{30-x}$Sb$_x$Se$_{70}$ thin films with (x = 0, 5, 10 15 and 25). The optical properties are studied by variable angle spectroscopic ellipsometry (VASE). To fit the optical parameters of studied films, two groups of linear combination of oscillators were employed. First group consists from one Tauc–Lorentz oscillator with two or three Gaussian oscillators (TL + G). Second group one Cody–Lorentz oscillators with two or three Gaussian (CL + mG) oscillators. The parameterization of models are also presented.
2. Experimental

Bulk glasses of the Ge$_{30-x}$Sb$_{x}$Se$_{70}$ with ($x = 0, 5, 10, 15$ and $25$), system were prepared by the conventional melt-quenching technique. Thin films of the prepared compositions were deposited on corning glass at room temperature by thermal evaporation technique. Details of the bulk and films preparation process are presented elsewhere [7]. Optical measurements are done with a Woollam Variable Angle Spectroscopic Ellipsometer (VASE) system. Measurements are carried out in the visible and near-UV region of the spectrum from wavelength 245 nm to 1200 nm with step of 1.59 nm, at $55^\circ$, $65^\circ$ and $75^\circ$ angles of incidence. Data analysis was performed with the WVASE32 software [17]. In the present study only the mean squared error (MSE) is used to be an index on the difference between the experimental results and data generated using the model. The minimum value of MSE the better fitting is obtained.
3. Theory

3.1. Spectroscopic ellipsometry

The outcome of VASE can be obtained by measuring the alter of polarization states of the light upon the reflection at the surface of a sample. Polarization state data is related to reflected light intensity by the equation

$$\rho = \frac{r_p}{r_s} = \tan \psi \epsilon$$

where $r_p$ and $r_s$ represent the reflection coefficient for $p$ and $s$ waves, respectively. $\psi$ is the angle of the polarization direction, and $\Delta$ is an angle indicating eccentricity of the polarization ellipse.

A common representation of the SE data $\psi$ and $\Delta$ is a pseudodielectric function [18]

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = \varepsilon_0 \left[ \frac{1 - \rho}{1 + \rho} \right]^2 \sin^2 \Phi_a + \cos^2 \Phi_a \tan^2 \Phi_a$$
Fig. 4. (a, b) Measured (open circles) and modeled (solid curves) $\Psi$ and $\Delta$ spectra at angles of incidence from 55°, 65° and 75° for a Ge$_{15}$Sb$_{15}$Se$_{70}$ film.

Where $\Phi_a$ angle of incidence and $\varepsilon_a$ is the ambient dielectric function which equal unity. Note that the complex refractive index $N = n + ik$ relate to dielectric function via the following relations

$$\varepsilon = N^2$$

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

where $n$ is refractive index (real part) and $k$ extinction coefficient imaginary part. In this technique the optical constants of investigated films can be obtained by fitting the measured $\psi$ and $\Delta$ data using a proper dispersion model relating the dielectric functions over the considered wavelengths.
Fig. 5. (a, b) Measured (open circles) and modeled (solid curves) $\Psi$ and $\Delta$ spectra at angles of incidence from 55°, 65° and 75° for a Ge$_5$Sb$_{25}$Se$_{70}$ film.

3.2. Model dielectric function of amorphous semiconductors

The first dispersion model is known as the Tauc–Lorentz oscillator model developed by Jellison and Modine [19,20] to explain optical functions in both the interband absorption and the transparent regions. Thus it was used extensively to parameterized the optical functions of amorphous semiconductors. This dispersion model is based on analytical calculations of combining the Tauc band edge with the classical Lorentz broadening function to simulate the joint density-of-states (JDOS). Following the TL formalism, the imaginary part of dielectric as function in photon energy ($E$) is given as

$$\varepsilon_{2\text{TL}}(E) = \frac{(E - E_g)^2}{E^2} \frac{AE_0CE}{(E^2 - E_0^2)^2 + C^2E^2}, \quad E > E_g$$  \hspace{1cm} (7)$$

$$\varepsilon_{2\text{TL}}(E) = 0, \quad E \leq E_g$$  \hspace{1cm} (8)
Fig. 6. (a) Real and (b) Imaginary parts of pseudo-dielectric function $\varepsilon$ obtained from $\psi$ and $\Delta$ acquired for $a$-Ge$_{30-x}$Sb$_x$Se$_{70}$alloys.

Where $A$, $E_D$, $E_g$, $C$ are Lorentz oscillator Amplitude, peak transition energy optical band gap energy, and oscillator width, respectively. The real part of dielectric function $\varepsilon_1$ is calculated by the Kramers–Kronig integration formula

$$\varepsilon_{1TL}(E) = \varepsilon_1(\infty) + \frac{2P}{\pi} \int_{E_g}^{\infty} \frac{\varepsilon_2(\xi)}{\xi^2 - E^2} \, d\xi,$$

(9)

The second dispersion model signifies the CL model developed by Ferlauto et al. [21] was used to illustrate optical functions in both the interband absorption and the transparent regions. It is analogous to TL in the way that it defines the optical band gap and the Lorentz absorption peak. However, it act unlikely in the absorption onset part and the Urbach absorption term is also included.

$$\varepsilon_{2CL}(E) = \frac{E_1}{E} \exp \left( \frac{E - E_t}{E_u} \right), \quad 0 < E \leq E_t$$

(10)

$$\varepsilon_{2CL}(E) = \frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2 E^2} \left( \frac{A E_0 C E}{E^2 - E_0^2} \right)^2 + C^2 E^2,$$

(11)

where $E_t$, is a transition energy between the Urbach tail and band-to-band transitions, $E_u$ represents the extent of broadening and $E_p$ a transition energy that separates the absorption onset behavior from the Lorentzian behavior. The real part $\varepsilon_1(E)$ expression is identified as usual from a KK integration formula

$$\varepsilon_{1CL}(E) = \varepsilon_1(\infty) + l_U(E) + l_L(E)$$

(12)

$$\varepsilon_{1CL}(E) = \varepsilon_1(\infty) + \frac{2E_1 P}{\pi} \int_0^{E_t} \frac{\exp \left( \frac{E'(E - E_t)}{E_u} \right)}{E'^2 - E^2} \, dE' + \frac{2P}{\pi} \int_{E_t}^{\infty} \frac{E G(E') L(E')}{E^2 - E'^2} \, dE'$$

(13)
Fig. 7. Compositional dependence of CL oscillator parameters of the Ge$_{30-x}$Sb$_x$Se$_{70}$ thin films. (a) amplitude $A$ and broadening parameter $C$, (b) resonance energy $E_0$ and transition energy $E_T$.

where $P$ denotes the principal values of the integrals. $I_U(E)$ and $I_L(E)$ in Eq. (12) denote the Urbach tail and Lorentz oscillator integrals appearing as the second and third terms in Eq. (13), respectively.

The third dispersion model is known as Gaussian oscillator proposed by Meneses [22] for amorphous and glassy films. In these materials, atoms randomly distributed. Therefore, each absorption band consists of numerous harmonic oscillators whose resonant frequencies have a normal distribution. Therefore the absorption band has a Gaussian character

$$
\varepsilon_{2G}(E) = A \exp \left[ - \left( \frac{E - E_0}{f.Br} \right)^2 \right] + A \exp \left[ - \left( \frac{E + E_0}{f.Br} \right)^2 \right]
$$

(14)
Fig. 8. Variations of refractive index \((n)\) with wavelength \((\lambda)\) for Ge_{30-x}Sb\(_x\) Se\(_{70}\) thin films.

Fig. 9. The calculated absorption coefficient according to combination CL group as a function of photon energy for a-Ge_{30-x}Sb\(_x\) Se\(_{70}\) films.
Fig. 10. Optical band gap dependence of Sb-content for the current work and those published for Ge_{30-x}Sb_x Se_{70} films. See Ref. [7,28–30]. Note that the solid curves are guide to eyes.

\[
\varepsilon_1(E) = \frac{2P}{\pi} \int_0^\infty \xi \varepsilon_2 \left( \xi^2 - E^2 \right)^{-1} d\xi,
\]

(15)

Here, \(A\) is the absorption amplitude, \(B_r\) is the broadening and \(E_0\) is the oscillator energy. The parameter \(f\) is a scaling constant (\(f = 6\))

4. Results and discussion

Figs. 1–5 represent the experimental data (open circles) of ellipsometer parameters \(\Psi\) and \(\Delta\) for sample contain \(x = 0, 5, 10, 15\) and 25. The data indicate approximately complete absorption in the spectral range below 435, 455, 471, 500 and 550 nm for sample contain \(x = 0, 5, 10, 15\) and 25, respectively. Transmission starts at wavelengths above the mentioned wavelengths where in this region normal oscillation in the \(\Psi\) and \(\Delta\) curves takes place.

The comparison of The VASE experimental and modeled pseudodielectric functions were analyzed using three layers system roughness/the amorphous chalcogenide thin film/glassy substrate. The dielectric function of the rough layer is calculated using the Bruggeman effective medium approximation [23]. Fig. 6(a and b) show the experimental real and imaginary parts \(\varepsilon_2\) of dielectric function spectra represented solid curves of an as-deposited Ge_{30-x}Sb_x Se_{70} with \((x = 0, 5, 10, 15\) and 25) films, respectively. It is clear from these figures that the \(\varepsilon_2\) spectrum is characterized by several divergent wide peaks, such nature is hard to fit by one oscillator model. Thus it seems to be reasonable to describe the dielectric function of the present system by linear combination of many mathematical dispersion functions.

The linear combination of oscillators functions used here contain the Tauc–Lorentz function with Gaussian – shaped functions or Cody-Lorentz function with Gaussian – shaped functions. A linear combination of different oscillators can be expressed as follows.

\[
\varepsilon_2 = TL \left( A, C, E_0, E_g \right) + \sum_{1}^{m} G(A, Br, E)
\]

(17)

Or

\[
\varepsilon_2 = CL \left( A, C, E_0E_g \right) + \sum_{1}^{m} G(A, Br, E)
\]

(18)
where $N$ is the number of ($\Psi$, $\Delta$) pairs, $M$ is the number of fitted parameters in the model and $\sigma$ are standard deviations of the experimental data points. The superscripts mod and exp indicate model-generated and experimental data, respectively.

In this study, the fitting of imaginary part of dielectric constant was performed using eqs 17 and 18. First we use one TL (one CL) combined with one Gaussian ($m = 1$). Then we increased Gaussian oscillators numbers $m = 2$ and $3$ with keeping TL (CL) at one oscillator. Until we obtain minimum the mean square error (MSE) function. It should be mentioned that the CL and TL are used to fit the fundamental band gap region, whereas Gaussian (G) – shaped functions were used to model molecular higher energies in the ultraviolet or lattice vibrations in the infrared.

The best fit values of the dispersion parameters of these films corresponding to the CL and TL group are summarized in Tables 1 and 2, respectively. Both the thicknesses of the Films and thicknesses of the surface roughness are the similar for the CL and TL group models. The values of MSE reported in Table 1 for all investigated samples are reasonably and low than its corresponding in Table 2; this may indicate on the better fitting can be obtained using CL group which is probably more appropriate rather than TL group. It should be mentioned that the ability of the Cody–Lorentz model to fit dielectric constants of amorphous semiconductors enhanced than TL comes from CL model has weak exponential absorption below.

For sake of simplicity, we will denote on Eqs. (17) and (18) as TL group and CL group, respectively.

In order to select an appropriate models for parameterization of optical functions. We first compare between the linear combination – generated curves and experimental data. The ultimate models accuracy depends first on whether it matches details of the experimental data curve. The goodness of the linear combination of optical model is lowest value of the root means squared error (RMSE) [20]

$$X = \frac{1}{2N - M} \sum_{i=1}^{N} \left[ \left( \frac{\Psi_i^{\text{mod}} - \Psi_i^{\exp}}{\sigma_{\Psi_i}} \right)^2 + \left( \frac{\Delta_i^{\text{mod}} - \Delta_i^{\exp}}{\sigma_{\Delta_i}} \right)^2 \right]$$

(19)
the band gap and a modified joint density-of-states. The subsequent fitting of previous oscillators to dielectric functions leads to fits ellipsometry parameters (Ψ and Δ) in Figs. 1–5. From these figures one can see that there is a relatively close agreement between both experimental data and the theoretical results of CL group (solid curves) for all Ge_{30−x}Sb_{x}Se_{70} films.

In what follows we will explain the using linear combination of several oscillator models instead of single oscillator, to fit dielectric function data of chalcogenide Ge-Sb-Se over the measured spectral range. First, we will consider that the use of single oscillator as TL or CL models. The TL or CL oscillators were used to produce the dielectric function due to the electronic transitions at the photon energy \(E\) between the valence and conduction bands. Efforts have been paid to apply these models on SE measurements of group IV thin films. These films include amorphous silicon (a-Si [24], (a-C) [25], (a-Ge) [26] and their incorporated with hydrogen [21,27,28]. Conventionally, it well known that in Ge or Si, the s and p states combine to form the sp^3 hybrid orbital. This orbital splits into bonding (\(\sigma\)) and antibonding (\(\sigma^*\)) states. In solids, the \(\sigma\) and \(\sigma^*\) levels spread out to form the valence and conduction bands, respectively. When light interact with these materials, light shows rather complicated behavior due to absorption of light. This absorption of light may cause electronic transitions from valence to the conduction bands. Thus a single oscillator model has been shown to be very useful in interpreting the SE results [21,29].

On the other hand, amorphous chalcogenides (e.g. S and Se), in contrast to amorphous Si and Ge. Six valence electrons are in a chalcogen atom. It has been proposed by Kastner [30] that the valence bands of chalcogenide atom can be separated into three sets: (i) the s band, occupied by two s electrons, and having the lowest energy, (ii) the lower p band arising from the bonding states and occupied by the two P electrons sharing in the bonding (\(\sigma\)); and (iii) the upper p band consisting of the nonbonding or lone-pair (LP) states. In the chalcogenide substances the LP band be positioned in the energy region between the \(\sigma\) and \(\sigma^*\) bands. Thus the origin of first peak in the \(e_2\) spectrum has been ascribed to electronic transitions from the LP states of the selenium atoms to the s-like antibonding lower conduction band and the second peak to the transitions between p bonding valence states and the s antibonding conduction band states [31,32]. Therefore its convenient to us combination of several oscillators.

Next, let us study the effect of Sb content on the CL oscillator parameters of the Ge_{30−x}Sb_{x}Se_{70} thin films. The compositional dependencies of Lorentz oscillator amplitude (\(A\)) and broadening parameter (\(C\)) are shown in Fig. 7(a). One can observe in this figure an increase of 230% of the Lorentz oscillator amplitude with increasing Sb concentration from 0 to 25%. However, decrease in the broadening parameter \(C\) by 177% can observed, which related to the distribution and variation in bond angles, lengths, and chemical disorder. On the other, the physical meaning of \(C\) according to quantum mechanical model describes reciprocal the average lifetime (\(\tau\)) of excited carriers between valence and conduction bands [33,34] (\(C = \tau^{-1}\)). as a result, by increasing Sb content decrease in the half-width of a \(e_2\) peak can be noted which becomes narrower and the lifetime of carriers in the excited state increases. The compositional dependence of resonance energy \(E_0\) and transition energy \(E_P\) are shown in Fig. 7(b). \(E_0\) appears to decrease at low concentration of Sb then becomes almost constant. While \(E_P\) increases at low concentration of Sb then becomes almost constant. Not that \(E_0\) separates between the absorption band gap onset from the Lorentzian regimes.

The refractive index in the semiconductor is a measure of its transparency to incident spectral radiation. Thus it is convenient to depict the relation between the refractive index and wavelength. The optical functions (refractive indices) obtained by The Cody–Lorentz model analysis of VASE data for amorphous present data are shown in Fig. 8. The refractive index, \(n\), in this study varies smoothly in the range of 240–1200 nm, with the maximum occurring at about 475 nm. When we compare the present results of \(n\) with our previous work results (Fig. 3) we found that the \(n\)-values, in both Figs, increase with increasing Sb content. At long wavelength where normal dispersion occurs, both figures express correctly optical functions in the non–absorbing region of the chalcogenide films. However, at short wavelength, the previous work data predict the trend of \(n\) goes to unlimited values.

The absorption coefficient (\(\alpha\)) of the examined Ge_{30−x}Sb_{x}Se_{70} films is determined from the well-known relation, \(\alpha = 4\pi k/\lambda\) where \(k\) is the value of the extinction coefficient at a given wavelength. The spectral behavior of the absorption coefficient as a function of photon energy for different compositions Ge_{30−x}Sb_{x}Se_{70} thin films with \((x = 0, 5, 10, 15\) and 25\) thin films is illustrated in Fig. 9. We can noticed that the increases of Sb-content accompanied by a move towards low energies. This shift designated that the absorption edge should decrease with increasing the Sb content. The absorption coefficient of amorphous semiconductors is known to change rapidly for photon energies near to their band gap.

Fig. 10 represents the dependence of \(E_g\) on at.% Sb for the present work together with data published for different chemical compositions of Ge-Sb-Se chalcogenide semiconductor. The closed and open circles represents the present data calculated according to combination of CL-group and TL-group, respectively. One can observe in Fig. 10 a decrease of 174% and 151% of the \(E_g\) estimated by CL-group and TL-group, respectively with increasing Sb concentration from 0 to 25%. Other symbols in fig. @@@ represent the previous work data (abdell-Wahab et al. [7], data published by Nikolic et al. [35] (Ge_{28}Sb_{x}Se_{72−x} (0 ≤ x ≤ 20)) and Fayek and El-Sayed [36] (Ge_{28}Sb_{x}Sb_{72} with 0 ≤ x ≤ 28)). Fig. 9 showed a decrease of \(E_g\) with the increase of Sb-content. In the present case this decreases followed by increases beyond x = 10.

Conversely, Sharma et al. [37] found that the addition of Sb to Ge-Se glasses increase both the activation energy of crystallization (\(E_c\)) as well as the activation energy of glass transition (\(E_g\)) up to certain content of Sb then followed by decreasing value of \(E_c\) and \(E_g\). They explained such behavior as the glasses have higher tendency towards crystallization when the amount of Sb is high.
It should be mentioned that the variation of $E_b$ with Sb content was discussed in the previous work in the framework of mean bond energy and the distribution of different bond types via Manca [38,39] relation

$$E = b \left( \sum_j c_j E_{bj} + a \right)$$

(20)

where $a$, $b$ are adjusted parameters, $c_j$ is a relative fraction of the $j$-type bonds in the given composition and $E_{bj}$ is the bond energy of the $j$-type bond. To calculate $c_j$, two approaches have been introduced. The first is chemically ordered model (COM), where formation of hetero-polar bonds is preferred than that of homo-polar bonds. The second is random covalent network model (RCNM) supposes that all possible bonds exist. The calculated values of $E_b$ of the present system according to COM are greater than RCNM when $b$ and $a$ in Eq. (20) be the same in both calculations. Based on our previous calculation and Sharma et al. investigation we can phenomenologically assume that at low Sb content the bonds arranged according to RCNM and at higher Sb content, the bonds follows the COM.

5. Conclusion

The optical constants and the thicknesses of the thermal evaporation Ge$_{30-x}$Sb$_x$Se$_{70}$ with ($x$ = 0, 5, 10, 15 and 25) thin films were simultaneously determined from the curve fitting of the ellipsometric data. For the analysis of ellipsometric data, two group of linear combination consist from two TL with one Gaussian and from two CL with one Gaussian oscillators were used. The CL group gives appropriate fit to present data.

References