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Optical parameters of anisotropic chain-structured $Tl_2InGaTe_4$ crystals by spectroscopic ellipsometry

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ABSTRACT

Spectroscopic ellipsometry measurements were performed on $Tl_2InGaTe_4$ single crystals in the 1.2–6.2 eV range for orientations of electric field, parallel ($\boldsymbol{E}//\boldsymbol{c}$) and perpendicular ($\boldsymbol{E}\perp\boldsymbol{c}$) to optic axis $\boldsymbol{c}$. Spectral dependence of optical parameters; real and imaginary components of the dielectric function, refractive index and extinction coefficient were obtained from the analyses of experimental data using an ambient-substrate optical model. The analysis of the absorption data calculated using the extinction coefficient showed the existence of indirect transitions in the crystal with an energy band gap of ~0.72 eV for both orientations. Interband transition (critical point) energies were revealed using second-energy derivative spectra of the dielectric function. The results showed the presence of five each interband transition structures for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E}\perp\boldsymbol{c}$ orientations.

1. Introduction

Ternary semiconducting compounds, $TlGaTe_2$ and $TlInTe_2$, have been investigated in recent years due to their interesting optical and electrical properties. These chalcogenides present nonlinear effects giving them an important position in the negative resistance, switching and memory device applications [1–3]. High thermoelectric power properties of $TlGaTe_2$ and $TlInTe_2$ take attention of researchers studying on relevant areas [4]. Theoretical and experimental studies reported the indirect band gap energies of $TlGaTe_2$ and $TlInTe_2$ compounds as 0.66 and 0.86 eV, respectively [5,6]. These chain materials being structural analogues of the binary TlSe have highly anisotropic crystal structure [7]. The lattice parameters of $TlGaTe_2$ and $TlInTe_2$ were reported from the analysis of powder diffraction data as $a = 0.84199$, $c = 0.68174$ nm and $a = 0.8478$, $c = 0.71855$ nm, respectively [8].

$Tl_2InGaTe_4$ belonging to the chain-structured semiconducting group is a structural analogue of $TlInTe_2$ ($TlGaTe_2$) in which half of the trivalent indium (gallium) atoms are replaced by gallium (indium) atoms [9]. The analysis of x-ray diffraction pattern of the $Tl_2InGaTe_4$ crystals revealed the crystal structure as tetragonal having lattice parameters of $a = 0.8453$ and $c = 0.6966$ nm [10]. The space group of the crystal was also reported in the same work as $D_{4h}{}^{18}$–$I4mcm$. In the lattice of the compound In(Ga) atoms are each surrounded by four Te atoms and form chains along the tetragonal c-axis. The band gap energy of the crystal was determined as 0.85 eV from the temperature dependence of conductivity [11].

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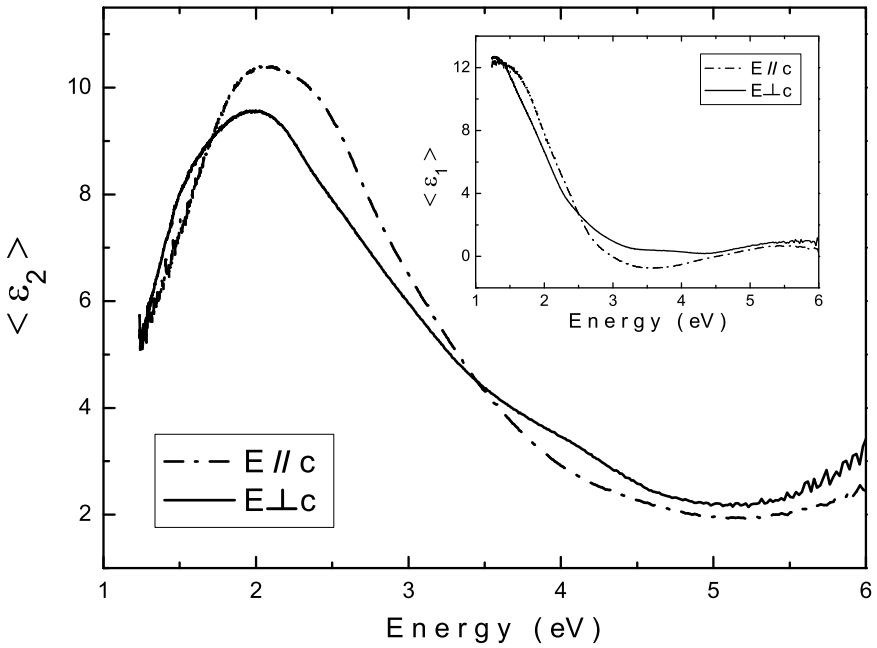

Fig. 1. Spectral dependencies of the imaginary and real (inset) parts of dielectric function for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ configurations of $Tl_2InGaTe_4$ crystals.

The aim of the present work is to investigate the optical parameters of $Tl_2InGaTe_4$ crystals by ellipsometry measurements. Previously, temperature dependence of dielectric functions and critical points of $TlGaTe_2$ were studied using ellipsometry experiments [12]. As a result of analysis of measurements performed for configurations of electric field perpendicular and parallel to the *c*-axis, four each critical point and their rates of change with temperature were reported. In the studies regarding the band structure calculations of $TlInTe_2$ using pseudopotential method, spectral dependencies of real and imaginary parts of the complex permittivity were determined for the polarizations of parallel and perpendicular to the optic axis [6]. Spectral dependencies of real and imaginary components of the dielectric function of $TlInTe_2$ were also plotted and compared using the theoretical pseudopotential method and experimental ellipsometry measurements [5]. Moreover, the critical points in the dielectric function spectra of the $TlInTe_2$ crystals were also reported using the second-energy derivative spectra of the dielectric function [13]. In the present paper, the spectral dependencies of the components of the complex dielectric function, refractive index and extinction coefficient of $Tl_2InGaTe_4$ are presented in the range of 1.2–6.2 eV at room temperature. Furthermore, the interband transition (critical point) energies were obtained from the analyses of second-energy derivative of the dielectric function spectra.

2. Experimental details

$Tl_2InGaTe_4$ single crystals were grown by the Bridgman method from a stoichiometric melt of the starting materials sealed in evacuated (10^{-5} Torr) silica tubes. The resulting ingots (grey-black color) were easily cleaved along planes paralel to the c-axis of the crystal. The ellipsometry measurements on $Tl_2InGaTe_4$ single crystals were accomplished at room temperature in the 1.2–6.2 eV spectral range with 0.01 eV increments using SOPRA GES-5E rotating-polarizer ellipsometer. The angle of incidence of the light beam was 70°. The typical thicknesses of the used samples was around 0.8 mm. The used samples in the experiments were taken from the middle part of the ingots. As the freshly cleaved platelets were mirror-like, no further polishing and cleaning treatments were applied on the used crystals. Since optical axis $\boldsymbol{c}$ lies along the chains in the natural cleavage plane, it allows to obtain all data of the dielectric function using only one crystal surface ($\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$).

3. Results and discussion

Ellipsometry is a non-destructive optical characterization technique using the experimental parameters of ψ and Δ to find the optical constants of the studied samples. The polarization parameters ψ and Δ symbolize the amplitude ratio and phase shift of the parallel and perpendicular components of light reflected from the surface of the sample after linearly polarized light beam irradiated onto the sample. The aim of the present work is to get the spectral dependencies of components of dielectric function, refractive index and extinction coefficient and to reveal the interband transition structures and their corresponding critical point (CP) energies in $Tl_2InGaTe_4$ single crystals. The used theoretical approaches to obtain mentioned optical constants were given in details in Refs. [14,15].

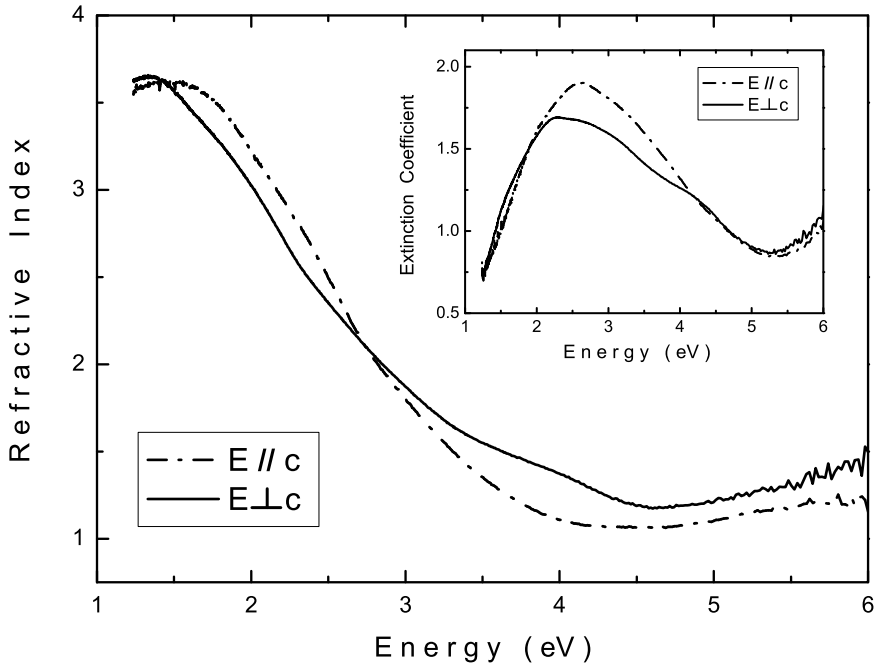

Fig. 2. Spectral dependencies of the refractive index and extinction coefficient (inset) of $Tl_2InGaTe_4$ crystals for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ configurations.

Fig. 1 and its inset show the spectral dependencies of imaginary and real components of dielectric function of $Tl_2InGaTe_4$ single crystal, respectively, for both orientations of $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ of the electric field ($\boldsymbol{E}$) vector of the incident light with respect to optical axis ($\boldsymbol{c}$). Anisotropic behavior of the crystal in respect to dielectric function can be observed from the figure. The ε_2 spectra of both configuration exhibits peaks and shoulders at some energy values which can be attributed to the critical point energy of corresponding interband transition structure. It can also be seen that peak(s) observed in $\boldsymbol{E} \perp \boldsymbol{c}$ configuration are shifted to lower energy values. Moreover, ε_2 spectra of $\boldsymbol{E} \perp \boldsymbol{c}$ configuration present an unclear peak around 4.0 eV which is not observed for $\boldsymbol{E}//\boldsymbol{c}$ configuration.

Fig. 2 and its inset presents the spectra of refractive index and extinction coefficient, respectively, calculated using the real and imaginary components of dielectric function. The anisotropic behavior of the crystal can also be seen from the figure. The comparison of refractive index of $Tl_2InGaTe_4$ with constituent compounds $TlGaTe_2$ and $TlInTe_2$ would be valuable at this point. Unfortunately, there is no any reported data about the refractive index of constituent compounds. However, refractive indices of $TlGaTe_2$ and $TlInTe_2$ can be calculated from the spectra of real and imaginary components of dielectric function given in Refs. [12,13]. The refractive index of $TlGaTe_2$ and $TlInTe_2$ were calculated around 4.1 and 3.9 for $\boldsymbol{E}//\boldsymbol{c}$ and 3.8 for $\boldsymbol{E} \perp \boldsymbol{c}$ configurations for both crystals, respectively, for photon energy of 1.5 eV. For the same energy, $Tl_2InGaTe_4$ crystal has refractive index value of ~3.6 for both configurations.

The extinction coefficient is related to the absorption coefficient (α) by the expression $\alpha = 4\pi k/\lambda$ [16]. Photon energy ($h\nu$) dependency of the absorption coefficient can be used to get the band gap energy (E_g) via the relation [16]

$$(\alpha h\nu) = A(h\nu - E_g)^P$$

where A is a constant depending on transition probability and p is an index which is equal to 2 and 1/2 for indirect and direct transitions, respectively. Analysis of the experimental data revealed that $(\alpha h\nu)$ and $(h\nu - E_g)$ relation gives a good coherence for $p = 2$ corresponding to indirect band gap transitions (see Fig. 3). The indirect band gap energies (E_{gi}) were found from intersection point of fitted line with photon energy axis for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ configuration as 0.72 and 0.70 eV. Previously reported studies revealed the band gap energy of the constituent crystals $TlInTe_2$ and $TlGaTe_2$ as 0.66 [5] and 0.86 eV [6], respectively. The obtained band gap energy of the $Tl_2InGaTe_4$ single crystals from the analysis of the ellipsometric data indicate a meaningful value when the band gap energies of the constituent compounds were took into account.

The spectral dependencies of the components of the dielectric function can also be utilized to find the energies (critical point energy) of the interband transitions. For this purpose, second derivative spectra of the real and imaginary parts of the dielectric function were plotted and fitted according to theoretical expressions [15]. Before starting to fit the experimental data, each graph was smoothed and then fitting process was accomplished for both configurations in the spectral regions which do not give any deviation on the spectra. Fig. 4 presents the associated spectra and their fits to find the CP energies. The fitting studies revealed five each interband transition structures having energies of 2.40, 2.52, 2.98, 3.65 and 4.43 eV for $\boldsymbol{E}//\boldsymbol{c}$ and 2.18, 2.52, 2.74, 3.08 and 4.09 eV for $\boldsymbol{E} \perp \boldsymbol{c}$ configuration. The anisotropic behavior of the $Tl_2InGaTe_4$ single crystal is seen more clearly from the difference of CP energies. When the CP energies of the crystals for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ configuration

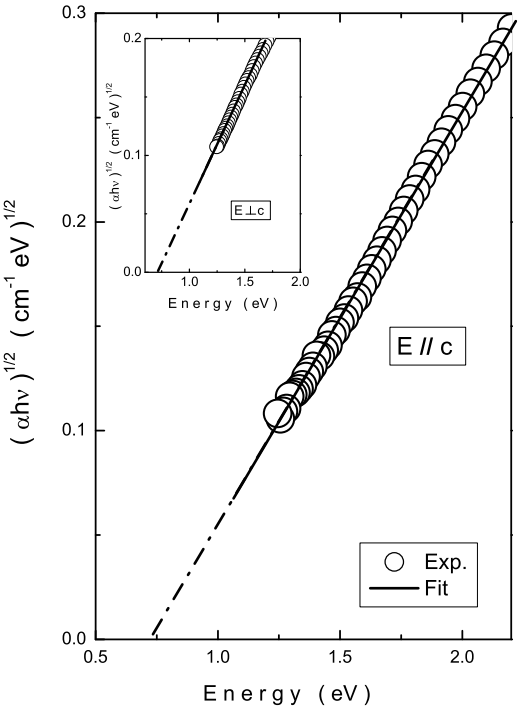

Fig. 3. The dependence of $(\alpha h\nu)^{1/2}$ on photon energy for $\boldsymbol{E}//\boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ (inset) configurations of $Tl_2InGaTe_4$ crystals.

Table 1
The comparison of critical point energies of $Tl_2InGaTe_4$ and its constituents $TlInTe_2$ and $TlGaTe_2$ for $E \perp c$ configuration.

E_{cp} (eV) for $E \perp c$		
$TlInTe_2$ [13]	$Tl_2InGaTe_4$ (This work)	$TlGaTe_2$ [12]
2.15	2.20	2.33
2.40	2.52	–
2.60	2.74	2.92
2.83	3.08	–
–	–	3.75
–	4.09	4.28

are compared, the similar shift to lower energy value observed in the spectra for $\boldsymbol{E} \perp \boldsymbol{c}$ configuration is also shown as energy decrease (except $E_{cp} = 2.51$ eV) in the interband transition. In the literature there is a similar ellipsometry study reported on the investigation of dielectric function and interband transitions on $TlGaTe_2$ and $TlInTe_2$ crystals [12,13]. At this point, it will be valuable to compare and associate CP energies of the present work on $Tl_2InGaTe_4$ and reported work on $TlGaTe_2$ and $TlInTe_2$ crystals. Table 1 presents the CP energies obtained from the analysis of second-energy derivative spectra of the dielectric function for $\boldsymbol{E} \perp \boldsymbol{c}$. The energies given in the table were associated to each other taking into account the increase of band gap energy. Since the analyses in Ref. [13] were performed up to energy value of 3 eV for $TlInTe_2$, higher CP energies of $Tl_2InGaTe_4$ and $TlGaTe_2$ crystals were only related between these two crystals. In the common energy range of these studies, CP energies show a consistent increase with the increase of band gap energy. The increasing behavior of CP energies is also in agreement with observations in the literature that CP energies increase with increasing concentration of the smaller cation or anion [17]. Any association between the CP energies of $TlInTe_2$, $TlGaTe_2$ and $Tl_2InGaTe_4$ crystals was not given for $\boldsymbol{E}//\boldsymbol{c}$ configuration. Especially, the narrowness of the common energy range of above mentioned studies makes it difficult to associate of the revealed CP energies of these crystals.

4. Conclusions

Spectral dependencies of optical parameters of the $Tl_2InGaTe_4$ single crystals were reported in the present study using spectroscopic ellipsometry experiments carried out in the 1.2-6.2 eV range. Measurements were performed for parallel and perpendicular configurations of electric field with respect to optical axis to see the anisotropic behavior of the crystal. Absorption spectra plotted by means of extinction coefficient spectra were analyzed to find the band gap energy. Analyses for both configuration resulted in indirect band gap energy of ~0.72 eV. Critical point energies were also found from the fit of second-energy derivative spectra of the dielectric function under the light of theoretical expressions. Five each critical

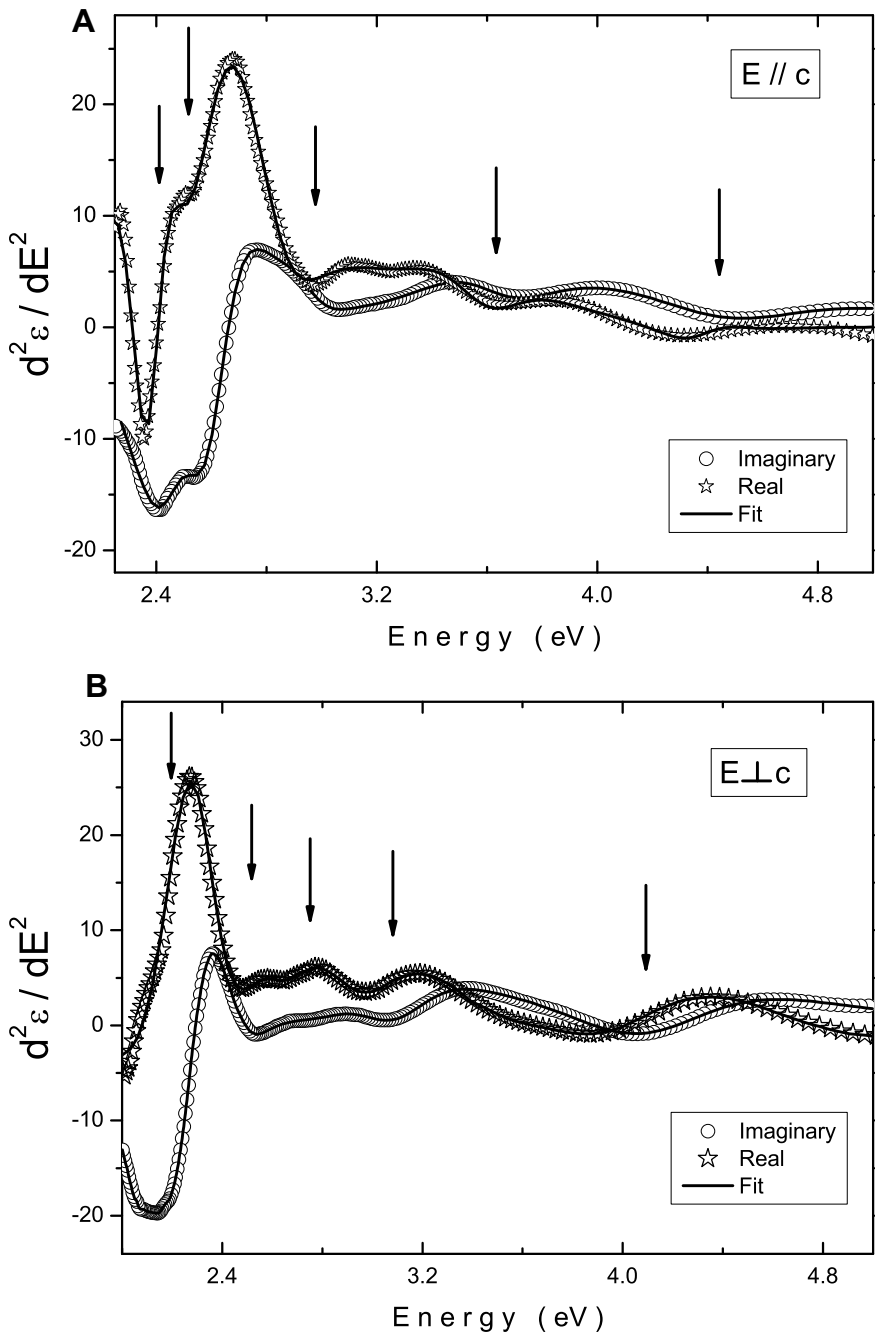

Fig. 4. Second-energy derivative spectra of the dielectric function for $Tl_2InGaTe_4$ crystals for (a) $\boldsymbol{E}//\boldsymbol{c}$ and (b) $\boldsymbol{E} \perp \boldsymbol{c}$ configuration. Open circles and stars represent the second-energy derivative spectra of the real and imaginary parts of the dielectric function, respectively. The solid curves show the fit to the experimental data. For clarity only one-third of the circles and triangles are shown. The arrows represent the positions of the critical point energies.

points were revealed for both configuration. In the critical point energies and spectra of optical parameters, a shift to lower energy values was observed for $\boldsymbol{E} \perp \boldsymbol{c}$ configuration compared to $\boldsymbol{E}//\boldsymbol{c}$ configuration.

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