Physica B: Physics of Condensed Matter 530 (2018) 82–85

Contents lists available at ScienceDirect

Physica B: Physics of Condensed Matter

journal homepage: www.elsevier.com/locate/physb

Low temperature absorption edge and photoluminescence study in $TlIn(Se_{1-x}S_x)_2$ layered mixed crystals

N.M. Gasanly [a,b,*]

[a] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
[b] Virtual International Scientific Research Centre, Baku State University, 1148, Baku, Azerbaijan

ARTICLE INFO

Keywords:
Semiconductors
Band gap energy
Photoluminescence
Mixed crystals

ABSTRACT

Transmission on $TlIn(Se_{1-x}S_x)_2$ mixed crystals ($0.25 \le x \le 1$) were carried out in the 400–800 nm wavelength range at $T = 10$ K. Band gap energies of the studied crystals were obtained using the derivative spectra of transmittance. The compositional dependence of direct band gap energy at $T = 10$ K revealed that as sulfur composition is increased in the mixed crystals, the direct band gap energy rises from 2.26 eV ($x = 0.25$) to 2.56 eV ($x = 1$).

Photoluminescence spectra of $TlIn(Se_{1-x}S_x)_2$ mixed crystals were studied in the wavelength region of 400–620 nm at $T = 10$ K. The observed bands were attributed to the transitions of electrons from shallow donor levels to the valence band. The shift of the PL bands to higher energies with elevating sulfur content was revealed. Moreover, the composition ratio of the mixed crystals was obtained from the energy dispersive spectroscopy measurements.

1. Introduction

$TlInS_2$ and $TlInSe_2$ crystals have received a great deal of attention due to their optical and electrical properties in view of the possible optoelectronic device applications [1]. They belong to the interesting group of ternary semiconductors with the chemical formula $TlBX_2$, where B = In or Ga and X = S or Se [2]. Optical and photoelectrical properties of $TlInS_2$ crystal were studied in Refs. [3–5]. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.5–14 l m make this crystal useful for optoelectronic applications [5]. The compounds $TlInS_2$ and $TlInSe_2$ form a series of $TlIn(Se_{1-x}S_x)_2$ ($0.25 \le x \le 1$) mixed crystals. Recently, we studied the effect of isomorphic atom substitution on the lattice parameters of $TlIn(Se_{1-x}S_x)_2$ mixed crystals [6]. A structural phase transition (monoclinic to tetragonal) due to substitution of anion (selenium for sulfur) was observed in the composition range of $x < 0.25$. In Ref. [7], the effect of isomorphic atom substitution on the refractive index and oscillator parameters of $TlIn(Se_{1-x}S_x)_2$ mixed crystals ($0.25 \le x \le 1$) have been studied at room temperature through the transmittance and reflectivity measurements in the wavelength range of 400–1100 nm. The spectral dependence of the refractive index for all compositions of studied crystals were obtained. The compositional dependence of the indirect band gap energy in $TlIn(Se_{1-x}S_x)_2$ mixed crystals was reported in Ref. [8]. It was revealed that the energy band gap decreases monotonically from 2.44 eV ($x = 1$) to 2.08 eV ($x = 0.25$). Previously, in Ref. [9], the ellipsometry measurements were carried out on $TlIn(Se_{1-x}S_x)_2$ mixed crystals in the spectral range of 1.5–6.0 eV at room temperature. The energies of interband transitions of $TlIn(Se_{1-x}S_x)_2$ mixed crystals were obtained. The variation of these transitions energies with the isomorphic anion substitution was established.

The aim of the present work is to expand the optical studies on the $TlIn(Se_{1-x}S_x)_2$ mixed crystals by performing the transmission measurements in the range of $0.25 \le x \le 1$ at $T = 10$ K. The transmittance spectra were used to obtain the band gap energy of the studied crystals. The effect of sulfur/selenide composition in the mixed crystals on the band gap energy was investigated. Moreover, PL measurements on studied crystals were performed at $T = 10$ K. The composition ratio of the elements (Tl: In: Se: S) in the mixed crystals were obtained from energy dispersive spectroscopy.

2. Experimental details

$TlIn(Se_{1-x}S_x)_2$ polycrystals were synthesized using elements prepared in stoichiometric proportions. Single crystals were grown by Bridgman method [10] in evacuated silica tubes in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal gradient

* Department of Physics, Middle East Technical University, 06800 Ankara, Turkey.
E-mail address: nizami@metu.edu.tr.

https://doi.org/10.1016/j.physb.2017.11.042
Received 12 July 2017; Received in revised form 2 November 2017; Accepted 12 November 2017
Available online 13 November 2017
0921-4526/

of 30 °C/cm, between the temperatures 850 and 650 °C at a rate of 0.5 mm/h. The resulting ingots (from orange to red in color) had no cracks and voids on the surface. The samples for transmission and PL measurements were taken from the middle part of the ingot. The freshly cleaved platelets (along the layer plane (001)) were mirror-like. Thicknesses of the used samples for transmission experiments were in the range of 10–15 μm. The determination of the chemical composition of $TlIn(Se_{1-x}S_x)_2$ mixed crystals was performed using the energy dispersive spectral (EDS) analysis. The experiments were performed using JSM-6400 scanning electron microscope. NORAN System6 X-ray Microanalysis System and Semafore Digitizer were basic equipments to analyze the chemical composition of the studied crystals.

All the studied samples were n-type as determined by the hot probe method. The PL was excited by the 457.9 nm (2.71 eV) line of a Spectra-Physics argon ion laser parallel to the ***c***-axis. The emission was collected in the backscattering geometry from the face of the crystal. The surface of the sample was freshly cleaved just prior to loading it onto the cold finger of a CTI-Cryogenics M-22 closed-cycle helium cryostat and the sample was cooled down to 10 K. PL spectra were dispersed with a U-1000 Jobin-Yvon double-grating spectrometer and detected by a cooled GaAs photomultiplier using standard photon counting electronics. The PL spectra have been corrected for the spectral response of the optical apparatus.

Transmission measurements were carried out in the 400–800 nm wavelength range at $T = 10$ K using Shimadzu UV 1201 model spectrophotometer with resolution of 5 nm, which consisted of a 20 W halogen lamp, a holographic grating and a silicon photodiode. Transmission measurements were performed under normal incidence of light with a polarization direction along the (001) plane.

3. Results and discussion

Fig. 1 shows the EDS spectra of the studied samples to get the chemical composition of the crystals. The EDS analyses are based on the relative counts of the detected X-rays which are emitted from the radiated sample and characteristics for every element having unique energy levels [11]. The emission energies for Tl, In, Se and S elements are (0.531, 1.875, 2.268 and 2.389), (3.286, 3.487, 3.713, 3.920, 3.729 and 3.937 keV), (1.379, 1.419, 1.434 and 1.475 keV) and (0.163, 0.164, 2.307, 2.464 and 2.470 keV), respectively [12]. As can be seen from the figure, intensity of the peak at 1.475 keV related with Se decreases as the selenium composition diminishes in the $TlIn(Se_{1-x}S_x)_2$ mixed crystals. EDS analysis showed that atomic composition of the studied crystals are well-matched with composition x increasing from 0.25 to 1 by intervals of 0.25.

Fig. 2 presents the transmission spectra of $TlIn(Se_{1-x}S_x)_2$ mixed crystals in the wavelength region of 400–800 nm at $T = 10$ K. These spectra can be used to get the absorption edge of the crystal using different analysis methods. One of these methods is derivative spectrophotometry (DS) which has been a powerful technique used in literature for three decades. DS is an attractive method used to obtain the information about peak signals in the experimental curve under the light of values revealed from the maxima and minima positions of the derivative curve [13]. In the present paper, we have used the derivative spectra of transmittance curves to determine the band gap energies. Fig. 3 shows the first derivatives of each spectrum for $TlIn(Se_{1-x}S_x)_2$ mixed crystals. The wavelength dependence of $dT/d\lambda$ presents peaks at energies corresponding to band gap energies. The obtained energy values of $TlIn(Se_{1-x}S_x)_2$ mixed crystals from each spectrum are equal 2.26, 2.36, 2.48 and 2.56 eV for compositions $x = 0.25$, 0.50, 0.75 and 1, respectively. They indicate that band gap energy shows a rising behavior with increase of sulfur composition (inset of Fig. 3). This increasing behavior of band gap energies is in agreement with reported observation which state that E_g increases with elevating concentration of the smaller anion [14]. At this point, it will be worthwhile to compare obtained energies with

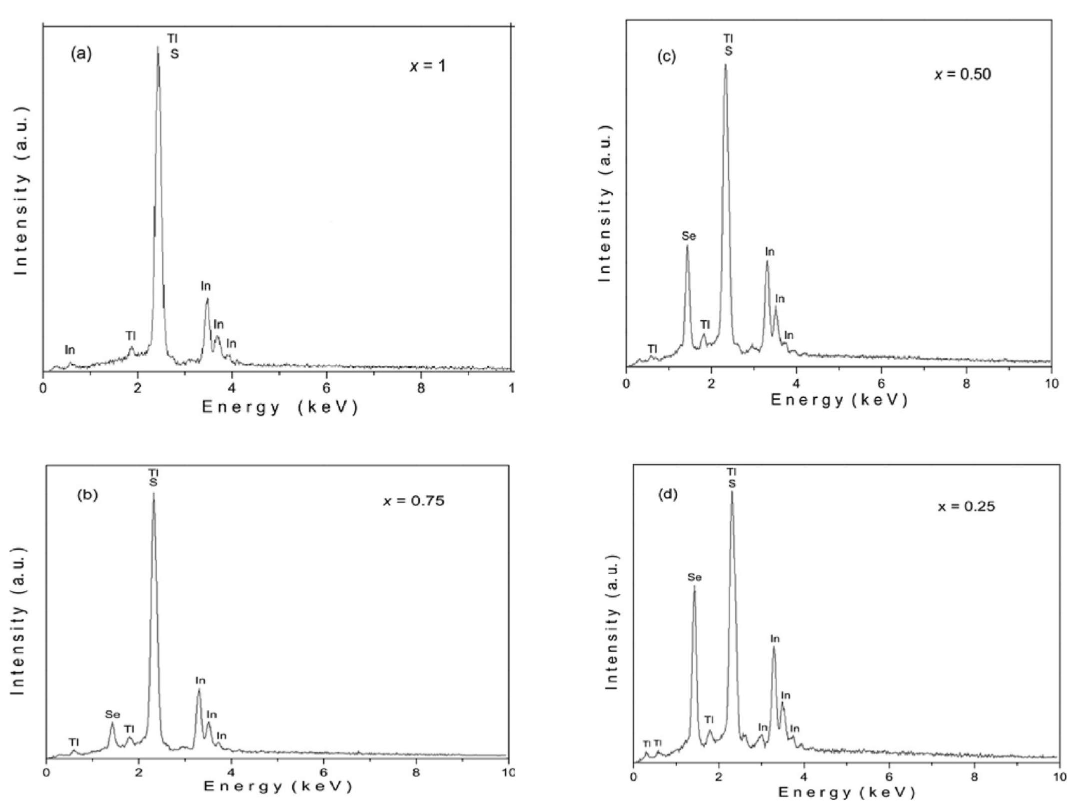

Fig. 1. (a–d). Energy dispersive spectroscopic analysis of $TlIn(Se_{1-x}S_x)_2$ mixed crystals.

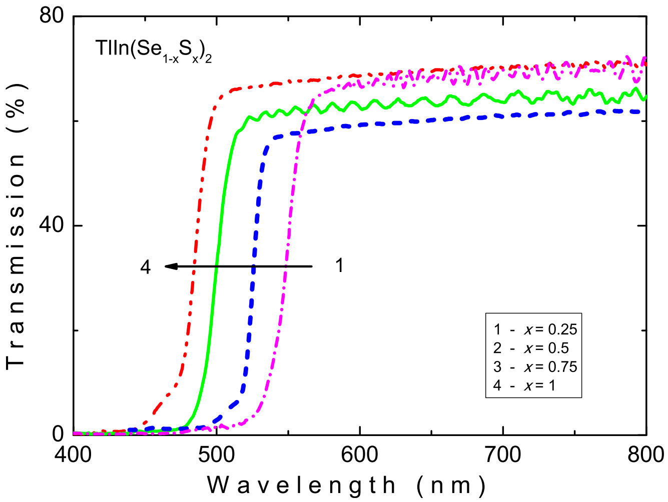

Fig. 2. Transmission spectra of $TlIn(Se_{1-x}S_x)_2$ mixed crystals in the wavelength region 400–800 nm at $T = 10$ K.

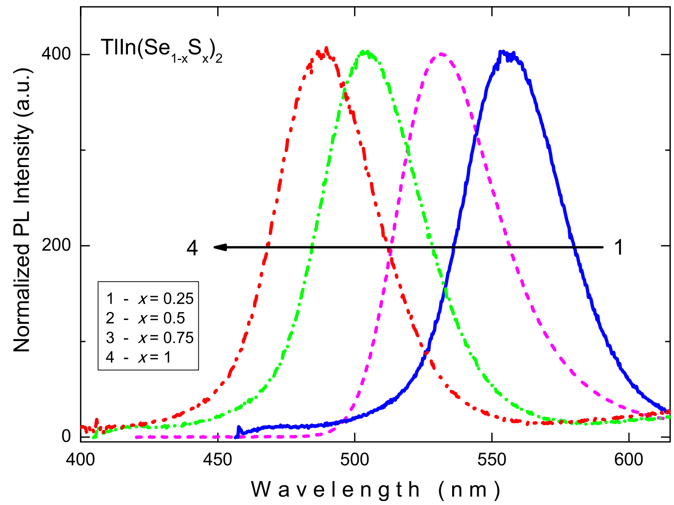

Fig. 4. Photoluminescence spectra of $TlIn(Se_{1-x}S_x)_2$ mixed crystals in the wavelength region 400–620 nm at $T = 10$ K.

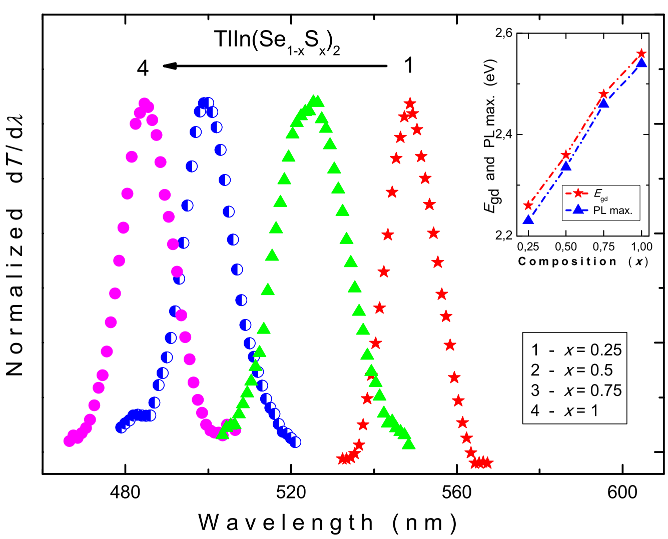

Fig. 3. The first derivatives $dT/d\lambda$ of transmission spectra for $TlIn(Se_{1-x}S_x)_2$ mixed crystals at $T = 10$ K. Inset: The dependency of direct band gap energy and photoluminescence peak energies on the composition of $TlIn(Se_{1-x}S_x)_2$ mixed crystals at $T = 10$ K.

previously reported values. The direct band gap energy of $TlInS_2$ crystals was reported previously as 2.58 eV for $T = 10$ K [15,16]. Reported energy value shows a good consistency with that obtained from derivative of transmittance spectrum. Moreover, taking into account the type of band gap energies reported in the referenced papers, E_g value obtained from our analyses can be strongly associated with direct transition structures.

The photoluminescence spectra provide a very good understanding about the nature of luminescence processes. In this study, PL spectra of $TlIn(Se_{1-x}S_x)_2$ layered mixed crystals were studied in the wavelength region 400–620 nm at $T = 10$ K and at constant excitation density of 9 W/cm^2 (Fig. 4). The observed emission bands centered at 2.23, 2.34, 2.46 and 2.54 eV have asymmetrical Gaussian line shape with low- and high-energy side half-widths of 92 and 82, 100 and 85, 112 and 100, and 118 and 107 meV for compositions of $x = 0.25$, 0.50, 0.75 and 1, respectively. Inset of Fig. 3 illustrates the shift of the PL peak energy to higher energies with increasing sulfur content. The revealed bands in PL spectra were provisionally attributed to the recombination of electrons captured during the illumination of the sample by the donor states ($E_d \approx 20$ meV) with holes in the valence band. Since the studied crystals were not intentionally doped, these centers are thought to originate from anion vacancies caused by nonstoichiometry and/or stacking faults, quite possible to exist in layered $TlIn(Se_{1-x}S_x)_2$ due to the weakness of the van der Waals forces between the layers [17].

4. Conclusions

Transmission and photoluminescence measurements were performed on $TlIn(Se_{1-x}S_x)_2$ mixed crystals ($0.25 \le x \le 1$) grown by Bridgman method in the 400–800 and 400–620 nm wavelength regions, respectively, for compositions of $x = 0.25$, 0.5, 0.75 and 1.0 at $T = 10$ K. Derivative analyses of transmittance of the mixed crystals showed that band gap energy increases from 2.26 eV ($x = 0.25$) to 2.56 eV ($x = 1$) as selenium is replaced by sulfur. The observed bands in PL spectra provisionally were assigned to the recombination of electrons from shallow donor levels with the holes in the valence band. The shift of the PL bands to higher energies with increasing sulfur content was revealed. Moreover, the composition ratio of the mixed crystals was determined utilizing the energy dispersive spectroscopy measurements.

References

[1] A.M. Panich, Electronic properties and phase transitions in low-dimensional semiconductors, J. Phys. Condens. Matter 20 (2008) 293202–293242.
[2] K.A. Yee, A. Albright, Bonding and structure of $TlGaSe_2$, J. Am. Chem. Soc. 113 (1991) 6474–6478.
[3] M. Hanias, A. Anagnostopoulos, K. Kambas, J. Spyridelis, Electrical and optical properties of as-grown $TlInS_2$, $TlGaSe_2$ and $TlGaS_2$ single crystals, Mater. Res. Bull. 27 (1992) 25–38.
[4] S.R. Samedov, O. Baykan, A. Gulubayov, Energy spectra of the local states in the forbidden gap of monoclinic TlInS2xSe2(1-x) crystals, Int. J. Infrared Millim. Waves 25 (2004) 735–747.
[5] K.R. Allakhverdiev, Two-photon absorption in layered TlGaSe2, TlInS2, TlGaS2 and GaSe crystals, Solid State Commun. 111 (1999) 253–257.
[6] N.M. Gasanly, Influence of isomorphic atom substitution on lattice anisotropy of thallium dichalcogenide layered mixed crystals, Acta Phys. Pol. A 110 (2006) 471–477.
[7] N.M. Gasanly, Effect of isomorphic atom substitution on the refractive index and oscillator parameters of $TlInS_{2x}Se_{2(1-x)}$ ($0.25 \le x \le 1$) layered mixed crystals, Cryst. Res. Technol. 45 (2010) 1141–1144.
[8] N.M. Gasanly, Effect of temperature and isomorphic atom substitution on optical absorption edge of $TlInS_{2x}Se_{2(1-x)}$ mixed crystals ($0.25 \le x \le 1$), Cryst. Res. Technol. 45 (2010) 525–528.
[9] I. Guler, Optical analysis of $TlInS_{2x}Se_{2(1-x)}$ mixed crystals, J. Appl. Phys. 115 (2014), 033517.
[10] J.C. Brice, Crystal Growth Processes, Thomson Science and Professional, 1987. Philadelphia.
[11] J.J. Friel, X-Ray and Image Analysis in Electron Microscopy, Princeton Gamma-Tech, Princeton, 2003.

[12] J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, J. Michael, Scanning Electron Microscopy and X-Ray Microanalysis, Springer Science, LLC, New York, 2007.

[13] C.B. Ojeda, F.S. Rojas, Recent applications in derivative ultraviolet/visible absorption spectrophotometry: 2009-2011, Microchem. J. 106 (2013) 1–16.

[14] S.G. Choi, Y.D. Kim, S.D. Yoo, D.E. Aspnes, D.H. Woo, S.H. Kim, Optical properties of AlxGa1-xP ($0 \leq x \leq 0.52$) alloys, J. Appl. Phys. 87 (2000) 1287–1290.

[15] J.A. Kalomiros, A.N. Anagnostopoulos, Excitonic and other interband transitions in $TlInS_2$ single crystals, Phys. Rev. B 50 (1994) 7488–7494.

[16] G.I. Abutalybov, A.A. Aliev, L.S. Larionkina, I.K. Neimanzade, E.Y. Salaev, Reflection spectra of TlInS2 single crystals, Sov. Phys. Solid State 26 (1984) 511–513.

[17] V. Capozzi, Kinetics of radiative recombination in GaSe and influence of Cu doping on the luminescence spectra, Phys. Rev. B 28 (1983) 4620–4627.