Low temperature absorption edge and photoluminescence study in TlIn(Se$_{1-x}$S$_x$)$_2$ layered mixed crystals

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Abstract

Transmission on TlIn(Se$_{1-x}$S$_x$)$_2$ mixed crystals ($0.25 \leq x \leq 1$) 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

TlIn$_2$ 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 TIBx$_2$, where $B = \text{In or Ga}$ and $X = \text{S or Se}$ [2]. Optical and photoelectrical properties of TlIn$_2$ 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 TlIn$_2$ and TlInSe$_2$ form a series of TlIn(Se$_{1-x}$S$_x$)$_2$ (0.25 $\leq x \leq 1$) 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 selenium (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 $\leq x \leq 1$) 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 $0.25 \leq x \leq 1$ 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.
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(Se1-xSx)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 Ti, 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(Se1-xSx)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(Se1-xSx)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(Se1-xSx)2 mixed crystals. The wavelength dependence of dT/dλ presents peaks at energies corresponding to band gap energies. The obtained energy values of TlIn(Se1-xSx)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

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Fig. 1. (a–d). Energy dispersive spectroscopic analysis of TlIn(Se1-xSx)2 mixed crystals.
with holes in the valence band. Since the studied crystals were not
transmittance spectrum. Moreover, taking into account the type of band
gap energies reported in the referenced papers, was reported previously as 2.58 eV for
value shows a good consistency with that obtained from derivative of
region 400–620 nm at T = 10 K. De-
previously reported values. The direct band gap energy of TlInS2 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

4. Conclusions
Transmission and photoluminescence measurements were performed on TlIn(Se1−xSx)2 mixed crystals (0.25 ≤ x ≤ 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


