Radiative Donor–Acceptor Pair Recombination in $Tl_2Ga_2Se_3S$ Layered Single Crystals

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The emission band spectra of $Tl_2Ga_2Se_3S$ layered crystals have been studied in the temperature range of 10–50 K and in the wavelength region of 540–700 nm. A broad photoluminescence band centered at 626 nm (1.98 eV) was observed at $T = 10$ K. Variation of emission band has been studied as a function of excitation laser intensity in the 0.4–51.5 mW cm^{-2} range. The analysis of the spectra reveals that the peak energy position changes with laser excitation intensity (blue shift). This behavior of the emission band is in agreement with the idea of separation inhomogeneity of donor–acceptor pairs. Radiative transitions from the moderately deep donor level $E_{\rm d} = 270$ meV to the shallow acceptor level $E_{\rm a} = 10$ meV were suggested to be responsible for the observed photoluminescence band.

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1. Introduction

A wide variety of binary and ternary layered semiconductors attract much interest due to possible optoelectronic applications from ultraviolet to the infrared [1, 2]. For the most part, optoelectronic properties of these materials are dominated by defects of various types and the interactions between them. Photoluminescence (PL) spectroscopy is a very suitable and widely used technique to study the defect structures of semiconductors.

Ternary and quaternary layered-structured semiconductors show many peculiar properties. There are large number of applications as memory switching elements, emission modulators and nonlinear optical transducers in nonlinear optics and optoelectronics [2, 3]. The quaternary compound $Tl_2Ga_2Se_3S$ is a structural analog of $TlGaSe_2$ [1] in which one quarter of selenium atoms are replaced by sulfur atoms. The lattice structure of this crystal is composed of two-dimensional alternating layers arranged parallel to the (001) plane; each layer is followed by another layer rotated by a 90° angle with respect to previous one. Tl and Se(S) atoms are bonded to form interlayer bonds whereas Ga and Se(S) atoms are bonded to form intralayer bonds.

The optical and electrical properties of $TlGaS_2$, $TlGaSe_2$, TlGaSeS and $Tl_2Ga_2S_3Se$ crystals were studied in Refs. [4–12]. These crystals are useful for optoelectronic applications as they have high photosensitivity in the visible range of the spectra and wide transparency range of 0.5–14.0 μm [10]. In our previous study, $Tl_2Ga_2Se_3S$ single crystals have been investigated in the temperature range of 10–260 K using thermally stimulated current (TSC) technique [13]. Experimental evidence was obtained for three trapping centers with activation energies of 12, 76 and 177 meV. Analysis of experimental TSC curves, registered at different light illumination temperatures, revealed the exponential distribution of traps. Recently, we studied the optical properties of $Tl_2Ga_2Se_3S$ crystals through transmission and reflection measurements in the photon energy range of 1.13–2.82 eV and in the temperature range of 10–300 K. As a result, the band gap energy $E_{\rm g} = 2.24$ eV ($T = 10$ K) and the rate of its variation with temperature $\gamma = -4.6 \times 10^{-4}$ eV/K were obtained [14].

In the present paper, we report the results of PL investigation of $Tl_2Ga_2Se_3S$ crystals in temperature range of 10–50 K and wide laser excitation intensity range of 0.4–51.5 mW cm^{-2}. The dependences of peak energy and intensity of emission band on temperature and laser excitation intensity variations were studied in detail. Analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states.

2. Experimental details

$Tl_2Ga_2Se_3S$ semiconductor polycrystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. The melting point of the $Tl_2Ga_2Se_3S$ crystal was determined as 835 °C. The single crystals were grown by the Bridgman method in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 15 cm in length) with a tip at the bottom. We utilized three-zone furnace; each zone about 15 cm in length. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1} at a rate of 1.0 mm h^{-1}. The resulting ingots (orange in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The chemical composition of $Tl_2Ga_2Se_3S$ crystals was determined by energy dispersive spectroscopic analysis (EDSA) us-

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ing a JSM-6400 electron microscope. The atomic composition of the studied samples (Tl:Ga:Se:S) was found to be 25.8:26.0:36.0:12.2, respectively [14]. Moreover, EDSA indicated that silicon impurities were present in $Tl_2Ga_2Se_3S$ crystals. The analysis of X-ray diffraction data showed that $Tl_2Ga_2Se_3S$ crystallizes in a monoclinic unit cell with lattice parameters: $a = 0.62040$, $b = 0.79710$ and $c = 0.81547$ nm and $\beta = 101.2°$ [14].

Crystals suitable for PL measurements had typical sample dimensions of $6 \times 4 \times 1$ mm^3. The electrical conductivity of the studied samples was p-type as determined by the hot probe method. A 325 nm line of He–Cd laser was used as the excitation light source. PL experiments were carried out by collecting the light from the laser-illuminated face of the sample in a direction close to the normal of the layer. A "CTI-Cryogenics M-22" closed-cycle helium cryostat was used to cool the sample from room temperature to 10 K. The temperature was controlled within an accuracy of ± 0.5 K. The surface of the sample was freshly cleaved just before loading it onto the cold finger of the cryostat. The PL spectra of the sample in the region 540–700 nm were analyzed using "Oriel MS-257" grating monochromator and "Hamamatsu S7010-1008" FFT-CCD Image Sensor with single stage electric cooler. A set of neutral density filters was used to adjust the exciting laser intensity from 0.4 to 51.5 mW cm^{-2}. The registered PL spectra have been corrected for the spectral response of the optical apparatus.

3. Results and discussion

The dependence of the PL spectra on temperature provides a very important understanding of the nature and analysis of luminescence spectra. Figure 1 shows the PL spectra of $Tl_2Ga_2Se_3S$ single crystals measured in the wavelength region 540–700 nm and in the 10–50 K temperature range at a constant excitation laser intensity $L = 51.5$ mW cm^{-2}. We observed a broad emission band centered at 626 nm (1.98 eV) at $T = 10$ K. The emission band displays an asymmetrical Gaussian line shape with the full-width at half maximum of 0.27 eV. These features are typical of emission bands due to donor–acceptor pair transitions observed in ternary compounds [15]. We note that both the PL intensity and the PL peak energy change as a function of increasing sample temperature.

Figure 2 presents the shift of the peak energy position towards lower energies with increasing temperature. Here, we also show the temperature dependence of the band gap energy obtained in Ref. [14]. Since the temperature coefficient of the band gap energy of the $Tl_2Ga_2Se_3S$ crystals is negative ($\gamma = -4.6 \times 10^{-4}$ eV/K [14]), the peak energy due to the donor–acceptor transition should decrease with band gap energy as the temperature increases [16]. The observed shift of the peak energy position towards lower energies satisfies the temperature dependence expected for the transitions involving donor and acceptor levels bound with respective band edges.

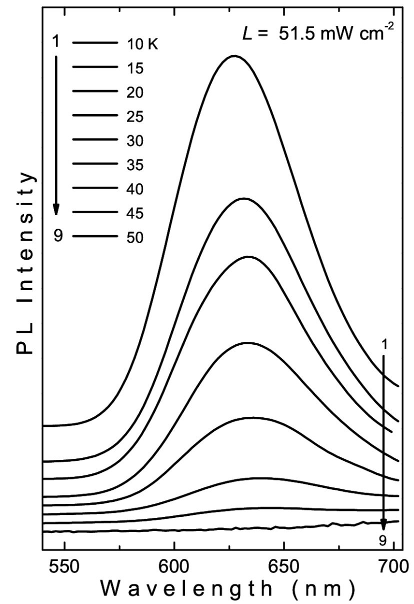

Fig. 1. Temperature dependence of PL spectra from $Tl_2Ga_2Se_3S$ crystal at excitation laser intensity $L = 51.5$ mW cm^{-2}.

As we mentioned above, the intensity of the emission band decreases with respect to increasing temperature. A thermal quenching of the band is observed above $T = 35$ K. The experimental data for the temperature dependence of the PL band intensity can be fitted by the following expression [17]:

$$I(T) = \frac{I_0}{1 + \alpha \exp(-E_t/kT)}, \quad (1)$$

where I_0 is a proportionality constant, E_t is the thermal activation energy, k is the Boltzmann constant, and α is the recombination process rate parameter. Inset of Fig. 2 shows the temperature dependence of the band intensity as a function of the reciprocal temperature in the 10–50 K range. The best fit using Eq. (1), demonstrated by the solid curve in inset of Fig. 2, has been achieved with parameters $I_0 = 1.3 \times 10^4$, $E_t = 10$ meV, $\alpha = 87$. Since the $Tl_2Ga_2Se_3S$ crystal is a p-type semiconductor, we consider that the revealed level is the acceptor level ($E_a = 10$ meV) located above the top of the valence band. This shallow acceptor level in undoped $Tl_2Ga_2Se_3S$, belonging to the A^3B^6 family, may be associated (as in the case of GaSe crystals having layered structure [18]) with the presence of defects and/or stacking faults, which are due to the weak interlayer bonding in the studied crystals. Moreover, this level may be considered as originating from uncontrolled Si impurities introduced into $Tl_2Ga_2Se_3S$ during the crystal growth process in ungraphatized ampoules [14].

In elucidating the nature of observed luminescence from $Tl_2Ga_2Se_3S$ crystal, laser excitation intensity dependence of the PL spectra is an important consideration. Figure 3 presents the PL spectra for 14 different

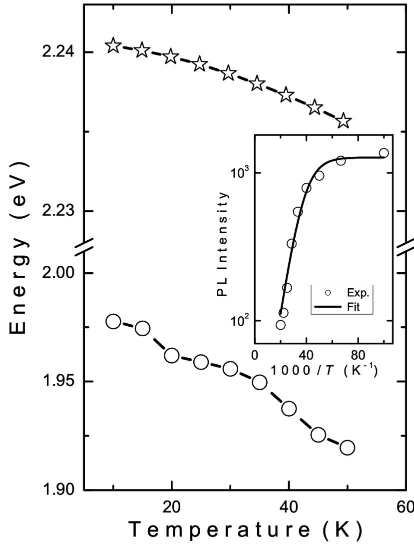

Fig. 2. Temperature dependences of the band gap energy (stars) and emission band peak energy (circles) for $Tl_2Ga_2Se_3S$ crystal. The data for energy band gap are taken from Ref. [14]. The dashed curves are only guides for the eye. Inset: temperature dependence of PL intensity at emission band maximum. Solid curve shows the theoretical fit using Eq. (1).

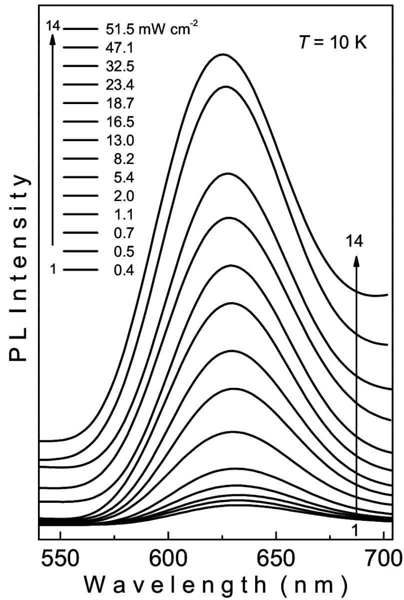

Fig. 3. Excitation laser intensity dependence of PL spectra of $Tl_2Ga_2Se_3S$ crystal at $T = 10$ K.

excitation laser intensities at $T = 10$ K. From analysis of the spectra, we obtained the information about the peak energy position and intensity for emission band at different laser excitation intensities. Our analysis reveals that the peak energy position (E_p) changes with laser excitation intensity (blue shift). This behavior of the emission band is characteristic for DAP recombination and is due to the separation inhomogeneity (close and distant spaced) of donor–acceptor pairs for which increasing laser excitation intensity leads to blue shift of the band by exciting more pairs that are closely spaced [16, 17, 19]. A careful inspection of the data shows that the emission band maximum slightly shifts towards higher energies ($\Delta E_p = 10$ meV) with increasing excitation laser intensities from 0.4 to 51.5 mW cm^{-2} (i.e., about 5 meV per decade of exciting radiation intensity). The magnitude of the observed blue shift is fairly well correlated with that of $TlGaSe_2$ crystal (6 meV/decade) [20].

At low excitation laser intensities only a small fraction of the donor and acceptor levels trap carriers. This leads to recombination from distant pairs only. At high enough excitation laser intensities all donors and acceptors are excited, which leads to a contribution from closer pairs as well. The energy of the emitted photon during a donor–acceptor pair transition has a positive contribution from a Coulombic interaction between ionized impurities. This contribution increases as the separation between the pairs decreases [16]. Furthermore, radiative transition probabilities for different pair separations are different and decrease exponentially as a function of the pair distance [16]. Distant pair recombination (contributing to the low-energy part of a donor–acceptor pair emission band) saturates at high excitation laser intensities; whereas close pairs have larger transition probability and can accommodate more carriers. We, therefore, observe a shift of the emission band peak energy to higher energy as the excitation laser intensity increases.

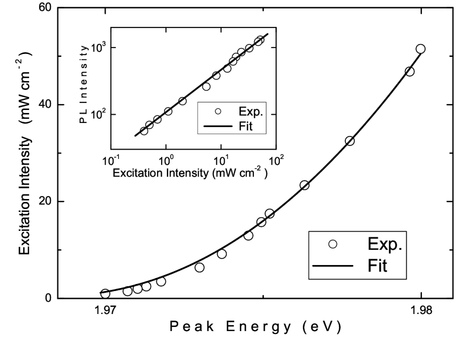

Fig. 4. Excitation laser intensity versus emission band peak energy at $T = 10$ K. The solid curve represents the theoretical fit using Eq. (2). Inset: dependence of PL intensity at the emission band maximum versus excitation laser intensity at $T = 10$ K. The solid line shows the theoretical fit using Eq. (3).

The dependence of the emission band peak energy (E_p) at $T = 10$ K as a function of excitation laser intensity (L) is given in Fig. 4. The experimental data in Fig. 4 are then fitted by the following expression:

$$L(E_p) = L_0 \frac{(E_p - E_\infty)^3}{(E_B + E_\infty - 2E_p)} \exp\left(-\frac{2(E_B - E_\infty)}{E_p - E_\infty}\right), \quad (2)$$

where L_0 is a proportionality constant, E_B is the emit-

ted photon energy of a close donor–acceptor pair separated by a shallow impurity Bohr radius (R_B), and E_∞ is the emitted photon energy of an infinitely distant donor–acceptor pair [21]. From a nonlinear least square fit to the experimental data, the photon energy values for an infinitely distant donor–acceptor pair and a close donor–acceptor pair separated by R_B are found to be $E_\infty = 1.96$ eV and $E_B = 2.00$ eV, respectively. These limiting photon energy values are in good agreement with the band gap energy ($E_g = 2.24$ eV [14]) and the observed values of the peak energy position (i.e., $E_\infty < 1.97 \text{ eV} < E_p < 1.98 \text{ eV} < E_B < E_g$) at $T = 10$ K.

In PL spectra of $Tl_2Ga_2Se_3S$ crystal, the increase in the peak intensities of emission band with increase in the laser excitation intensity was also observed. To follow more thoroughly the behavior of emission band, we plotted in logarithmic scale the PL emission band maximum intensity versus excitation laser intensity (inset of Fig. 4). The behavior of band with respect to excitation laser intensity is clearly demonstrated by this graph. For the analysis, the experimental data for emission band in the spectra were fitted by the power law of the form

$$I \propto L^n, \tag{3}$$

where I is the PL intensity at the emission band maximum, L is the excitation laser intensity and n is a dimensionless exponent. It was found that the PL emission band maximum intensity increases sublinearly (i.e., $n = 0.64$) with respect to the excitation intensity (inset of Fig. 4). For an excitation laser photon with an energy exceeding the band gap energy E_g, the coefficient n is generally $1 < n < 2$ for the free- and bound-exciton emission, and $n \le 1$ for free-to-bound and donor–acceptor pair recombinations [22, 23]. Thus, the obtained value of $n = 0.64$ confirms our assignment of the observed emission band in $Tl_2Ga_2Se_3S$ spectra to donor–acceptor pair recombination.

The analysis of the PL spectra as a function of temperature and excitation laser intensity allows one to obtain a possible scheme for the states located in the forbidden energy gap of the $Tl_2Ga_2Se_3S$ crystal. In the proposed scheme, shallow acceptor level is located at 10 meV above the top of the valence band. On the basis of general expression for the emission energy of donor–acceptor pair [16] and taking into account E_g and E_∞, the sum of the activation energies of the donor (E_d) and acceptor (E_a) levels, involved in the emission band, has been estimated as being

$$E_d + E_a = E_g - E_\infty = 2.24 \text{ eV} - 1.96 \text{ eV} = 0.28 \text{ eV}.$$

Considering that the acceptor level is located at 10 meV above the top of the valence band, this result suggests that the donor level involved in the emission band is located at 270 meV below the bottom of the conduction band. Taking into account the above considerations, the observed emission band in the PL spectra has been attributed to the radiative transitions from the donor level to the acceptor level. The moderately deep donor level in p-type $Tl_2Ga_2Se_3S$ layered crystal can be associated with Se vacancies, which are frequently encountered in resembling materials, due to the non-stoichiometry of chalcogenide atoms in the lattice. Similar transitions involving deep donor levels have also been revealed for other ternary layered crystals [20, 24].

At this point, it is worthwhile to compare present results with those obtained in our previous observations on $Tl_2Ga_2Se_3S$ crystals using TSC measurements in the temperature range of 10–260 K, which yielded the trap levels with activation energies of 12, 76 and 177 meV [13]. From the present results using PL spectroscopy, we observed acceptor level of 10 meV. It is clear that the trap levels observed at 76 and 177 meV are not observed in the PL experiments. The only energy levels, which are close in energy, are located at 10 meV (PL) and 12 meV (TSC). Taking into account the errors in determining the values of energy levels (about 5%) with either of two methods (PL and TSC), we may possibly assign the obtained energies of 10 and 12 meV to the same level. We suppose that this level is partially compensated, allowing for both PL emission and thermally stimulated current.

4. Conclusions

We measured low temperature (10–50 K) PL spectra of $Tl_2Ga_2Se_3S$ single crystals grown by the Bridgman method. At $T = 10$ K, a broad PL band centered at 626 nm (1.98 eV) was observed. It was revealed that the intensity of the emission band decreases with increasing temperature. This behavior was accounted for introducing a shallow acceptor level $E_a = 10$ meV and a moderately deep donor level $E_d = 270$ meV in the forbidden energy gap of the $Tl_2Ga_2Se_3S$ crystal. Also, the intensity of the emission band maximum increases sublinearly with respect to the excitation laser intensity and confirms our assignment that the observed emission band in $Tl_2Ga_2Se_3S$ is due to donor–acceptor pair recombination. Moreover, the analysis of the PL spectra reveals that the peak energy position changes with laser excitation intensity (blue shift). This behavior of the emission band is in agreement with the idea of separation inhomogeneity of donor–acceptor pairs. As the studied crystals were not intentionally doped, the acceptor and donor states are thought to originate, respectively, from defects and/or stacking faults, and from Se vacancies due to non-stoichiometry, created during crystal growth.

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