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Temperature- and excitation-dependent photoluminescence in TlGaSeS layered crystals

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ABSTRACT

Photoluminescence (PL) spectra of TlGaSeS layered single crystals have been studied in the wavelength region of 695–1010 nm and in the temperature range of 20–56 K. Two PL bands centered at 773 (1.605 eV, A-band) and 989 nm (1.254 eV, B-band) were observed at $T = 20$ K. Variations of both bands have been investigated as a function of excitation laser intensity in the range from 4.2 to 111.4 mW cm^{-2}. These bands are attributed to recombination of charge carriers through donor–acceptor pairs located in the band gap of the crystal. Radiative transitions from deep donor levels located at 0.721 and 1.069 eV below the bottom of conduction band to shallow acceptor levels located at 0.008 and 0.011 eV above the top of the valence band are suggested to be responsible for the observed A- and B-bands in the PL spectra, respectively.

1. Introduction

The layered semiconductor TlGaSeS is formed from $TlGaSe_2$ and $TlGaS_2$ crystals by replacing half of the selenium (sulfur) atoms with sulfur (selenium) atoms. The crystal lattice has two-dimensional layers arranged parallel to the (0 0 1) plane [1,2]. The bonding between Tl and Se(S) atoms in TlGaSeS is an interlayer type whereas the bonding between Ga and Se(S) is an intralayer type. These crystals have received a great deal of attention due to their optical and electrical properties in view of the possible optoelectronic device application. Optical and photoelectrical properties of $TlGaSe_2$ and $TlGaS_2$ crystals were reported in Refs. [3–10]. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of 0.5–14 μm make these crystals useful for optoelectronic applications [10]. The optical properties of TlGaSeS layered single crystals have been investigated by measuring the transmission and reflection in the wavelength region between 400 and 1100 nm [11]. The indirect transitions with a band gap energy of 2.27 eV was established by means of the analysis of absorption data at room temperature. The rate of change of the indirect band gap with temperature, $\gamma = -3.2 \times 10^{-4}$ eV/K, was determined from the transmission measurements in the temperature range of 10–300 K. The dispersion of the refractive index was discussed in terms of the Wemple–DiDomenico single-effective-oscillator model. The oscillator energy, the dispersion energy, the oscillator strength, and the zero-frequency refractive index were determined.

One of the determining factors in the eventual device performance of semiconductors is the presence of impurity and/or defect centers in the crystal. Thus, it is very useful to get detailed information on energetic parameters of recombination centers in semiconductor in order to obtain high-quality devices. In the present paper, we report the intensity variations of the PL emission bands with temperature (20–56 K) and excitation laser intensity (4.2–111.4 mW cm^{-2}) in TlGaSeS crystals. The analysis of the data suggests that the radiative transitions originate from recombination of charge carriers from donor to acceptor states.

2. Experimental

Single crystals of TlGaSeS were grown by the Bridgman method from stoichiometric melt of starting materials sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The resulting ingots (red in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The chemical composition of TlGaSeS crystals was determined by Energy Dispersive Spectroscopic Analysis (EDSA) using JSM-6400 Electron Microscope. The composition of the studied samples (Tl:Ga:Se:S) was found to be 25.7:25.9:24.3:24.1, respectively.

The electrical conductivity of the studied sample was p-type as determined by the hot probe method. Crystals suitable for PL measurements had typical sample dimensions of 6 mm × 3 mm × 2 mm. The green line ($\lambda = 532$ nm) of a continuous

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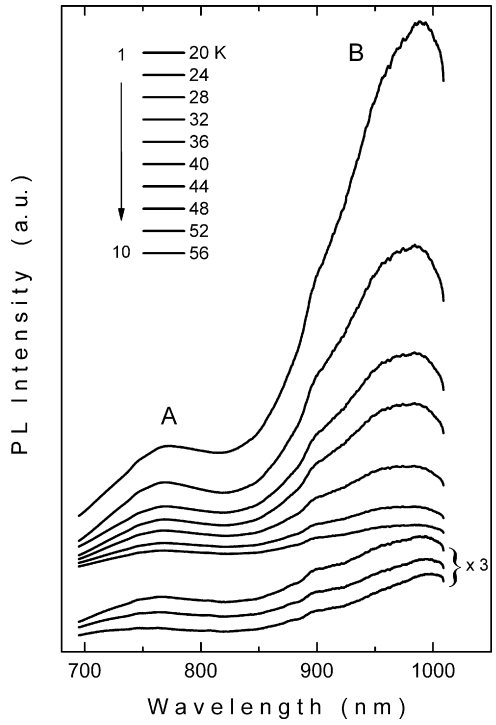

Fig. 1. Temperature dependence of PL spectra from TlGaSeS crystal at excitation laser intensity $L = 111.4\,\mathrm{mW\,cm^{-2}}$. Note that for curves 8–10, intensities have been multiplied by a factor of three.

frequency-doubled YAG:Nd^{3+} 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 down to 20 K, and the temperature was controlled within an accuracy of ±0.5 K. The PL spectra of the sample in the region 695–1010 nm were analyzed using an "Oriel MS-257" grating monochromator and "Hamamatsu S7010-1008" FFT-CCD Image Sensor with single stage electric cooler. Sets of neutral density filters were used to adjust the exciting laser intensity from 4.2 to 111.4 mW cm^{-2}. PL spectra have been corrected for the spectral response of the optical apparatus. All the spectra have been analyzed by using a fitting program "Peak Fit for Win 32 Version 4".

3. Results and discussion

Fig. 1 presents the PL spectra of TlGaSeS crystals in 20–56 K temperature range at constant laser excitation intensity $L = 111.4\,\mathrm{mW\,cm^{-2}}$. All spectra have been analyzed using a fitting procedure to decompose the overlapped bands. The procedure yields the intensities and peak positions of the bands. The observed emission bands are centered at 773 nm (1.605 eV, A-band) and 989 nm (1.254 eV, B-band) at $T = 20$ K. As seen from Fig. 1, the intensities of both bands decrease with increasing temperature. As for the peak positions of the bands, they remain almost unchanged (inset of Fig. 1). In this inset we also present the temperature dependence of the energy band gap, E_g, for TlGaSeS crystals which was revealed in Ref. [11]. It is observable that this dependence is also nearly unchanged in the temperature range of 20–56 K.

The experimental data for the temperature dependence of PL bands intensities can be fitted by the following expression [12]:

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

where I_0 is a proportionality constant, E_t the thermal activation energy, k the Boltzmann constant and α is the recombination process rate parameter. Fig. 2 shows the temperature dependence of the emission band maximum intensities as a function of the reciprocal temperature in the 20–56 K range. The best fits using Eq. (1),

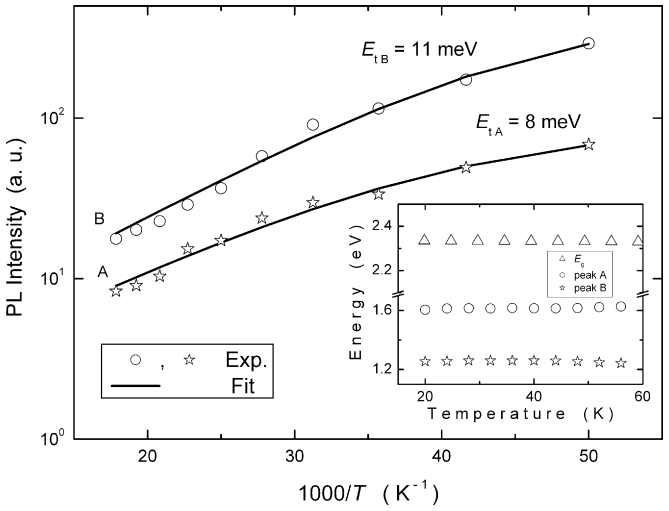

Fig. 2. Temperature dependencies of PL bands intensities for TlGaSeS crystal. Circles and stars are the experimental data. Solid curves show the theoretical fits using Eq. (1). Inset: temperature dependencies of energy band gap and emission A- and B-bands peak energies.

demonstrated by the solid curves in Fig. 2, have been achieved with parameters $I_{0A} = 92.8$, $E_{tA} = 0.008$ eV, $\alpha_A = 55.9$ and $I_{0B} = 469.7$, $E_{tB} = 0.011$ eV, $\alpha_B = 177.7$ for A- and B-bands, respectively. Since TlGaSeS crystal is p-type semiconductor, we believe that these levels are shallow acceptor levels located above the top of the valence band. These shallow levels can be considered as originating from defects, created during the growth of crystals, and/or unintentional impurities.

The laser excitation intensity dependence of PL spectra also provides valuable information about the recombination mechanism responsible for the observed luminescence. Fig. 3 presents the PL

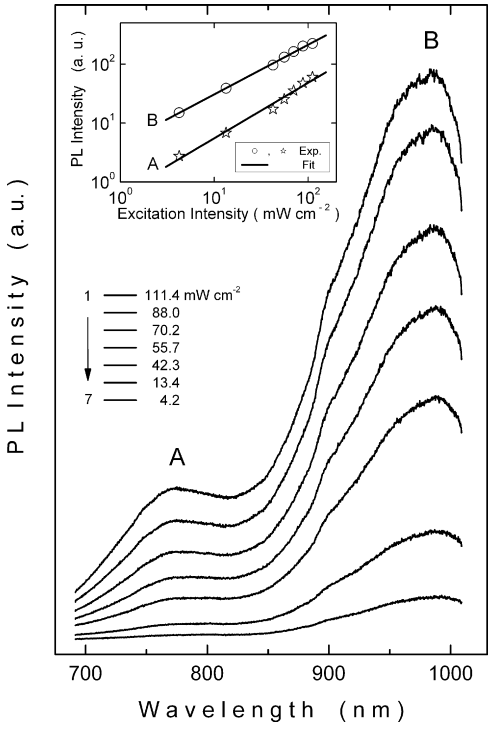

Fig. 3. PL spectra of TlGaSeS crystal as a function of excitation laser intensity at $T = 20$ K. Inset: dependence of PL intensities at the emission maximums versus excitation laser intensity for A- and B-bands at $T = 20$ K. The solid lines show the theoretical fits using Eq. (2).

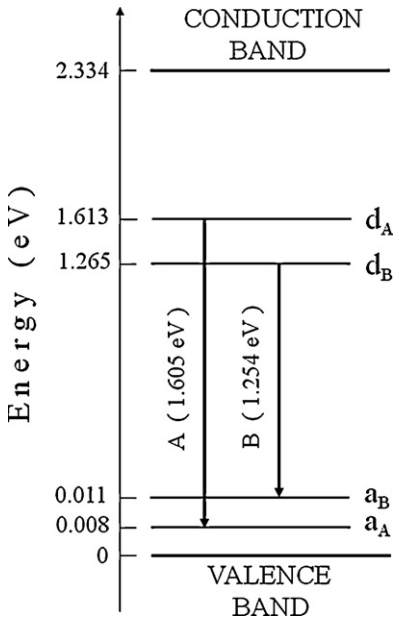

Fig. 4. Proposed energy-level diagram of TlGaSeS crystal at $T = 20$ K.

spectra for 7 different laser intensities at $T = 20$ K. From analysis of the spectra, we obtained the information about the peak energy position and intensity for emission bands at different laser excitation intensities. Our analysis reveals that the peak energy positions of A- and B-bands do not shift with increasing laser excitation intensity. In contrast with inhomogenously distributed donor–acceptor pairs where increasing laser intensity excites more pairs that are closely spaced leading to blue shift of the peak energy of the observed bands [13], this result suggests that the donor–acceptor pairs are located at only closely spaced sites and are distributed homogenously.

In PL spectra of TlGaSeS crystal, the increase in the peak intensities of both bands with increase in the laser excitation intensity was observed. The logarithmic plots of PL intensities versus laser excitation intensity are given in inset of Fig. 3. Experimental data can be fitted by a simple power law of the form

$$I \propto L^{\gamma'} \tag{2}$$

where I corresponds to the PL intensity, L corresponds to excitation laser intensity and γ is a dimensionless constant. We find that PL intensity at the emission band maximum increases sublinearally with increase of excitation laser intensity with the values of $\gamma = 0.94$ and 0.84 corresponding to A- and B-bands, respectively. It is well known that for excitation laser photon energy exceeding the band gap energy E_g, the exponent γ is generally $1 < \gamma < 2$ for free and bound exciton emission, whereas $0 < \gamma \leq 1$ is typical for free-to-bound and donor–acceptor pair recombination [14,15].

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 TlGaSeS crystal $T = 20$ K (Fig. 4). In the proposed scheme, shallow acceptor levels a_A and a_B are located at $E_{aA} = 0.008$ eV and $E_{aB} = 0.011$ eV above the top of the valence band, respectively. Here, it is necessary to recall the general expression for emission energy of donor–acceptor pair as [13]

$$h\nu = E_g - E_a - E_d, \tag{3}$$

where E_g is the band gap energy of TlGaSeS crystal, E_a and E_d are the acceptor and donor level energies, respectively. A simple calculation with Eq. (3) for A- and B-bands emissions by using the values of $E_g = 2.334$ eV [11], $h\nu_A = 1.605$ eV ($h\nu_B = 1.254$ eV) and $E_{aA} = 0.008$ eV ($E_{aB} = 0.011$ eV) gives us the energies of the deep donor levels E_{dA} and E_{dB} as 1.613 and 1.265 eV, respectively (Fig. 4). Taking into account the above considerations, the observed emission A- and B-bands in the PL spectra have been attributed to the radiative transitions from the donor level d_A to the acceptor level a_A and from the donor level d_B to the acceptor level a_B, respectively.

In view of the layered structure of TlGaSeS crystals, we cannot exclude the possibility of glide of layers during the growth of single crystals. Clearly, such a glide may create deep defect levels in high concentrations, as found in layer compounds [16,17]. The energy of such levels corresponds approximately to the middle of the band gap. Therefore, we assume that the deep donor levels with activation energies of 0.721 and 1.069 eV represent defects associated with the layered structure of crystals studied. Shallow acceptor levels may also be assigned to the structure defects, but this does not exclude the possibility that they may represent unintentional impurities.

At this point, it may be informative to compare present PL results with the ones obtained from our previous thermally stimulated current (TSC) studies on TlGaSeS, which resulted in the existence of trap level at 12 meV [18]. The results of present PL study suggested the presence of two recombination levels with energies 8 and 11 meV. It is obvious that the energy level at 8 meV was not observed in TSC experiments. The energy levels that are close in energy, are located at 11 meV (PL) and 12 meV (TSC). Taking into account the errors in determining the values of energy levels (about 5%) with either of the two methods (PL and TSC), we may possibly assign the obtained energies of 11 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

The PL spectra of TlGaSeS crystals were studied as a function of temperature and excitation laser intensity. Two broad emission bands centered at 773 (1.605 eV, A-band) and 989 nm (1.254 eV, B-band) were observed at $T = 20$ K. The variation of the spectra with laser excitation intensity and temperature suggest that the transitions between the donor and acceptor levels can be responsible for the observed emission bands. Also, the intensities of the emission bands increase sublinearly with respect to the excitation laser intensity and confirm our assignment that the observed emission bands in TlGaSeS are due to donor–acceptor pair recombination. As the studied crystals were not intentionally doped, the donor and acceptor states are thought to originate from defects, created during crystal growth, and/or from uncontrolled impurities.

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References

[1] A.M. Panich, J. Phys. Condens. Matter 20 (2008) 293202.
[2] K.A. Yee, A. Albright, J. Am. Chem. Soc. 113 (1991) 6474.
[3] Y. Shim, W. Okada, K. Wakita, N. Mamedov, J. Appl. Phys. 102 (2007), 083537.
[4] M. Hanias, A. Anagnostopoulos, K. Kambas, J. Spiridelis, Mater. Res. Bull. 27 (1992) 25.
[5] I.M. Ashraf, M.M. Abdel-Rahman, A.M. Badr, J. Phys. D. Appl. Phys. 36 (2003) 109.
[6] A. Kato, M. Nishigaki, N. Mamedov, M. Yamazaki, S. Abdullaeva, E. Kerimova, H. Uchiki, S. Iida, J. Phys. Chem. Sol. 64 (2003) 1713.
[7] M.M. El Nahass, M.M. Sallam, S.A. Rahman, E.M. Ibrahim, Solid State Sci. 8 (2008) 488.
[8] V. Grivickas, V. Bikbajevas, P. Grivickas, Phys. Stat. Sol. (b) 243 (2006) R31.
[9] B. Gurbulak, S. Duman, Phys. Scr. 77 (2008), 025702.
[10] K.R. Allakhverdiev, Solid State Commun. 111 (1999) 253.
[11] I. Guler, N.M. Gasanly, J. Korean Phys. Soc. 51 (2007) 2031.

[12] J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, New Jersey, 1971.
[13] P.Y. Yu, M. Cardona, Fundamentals of Semiconductors, Springer, Berlin, 1995.
[14] E. Zacks, A. Halperin, Phys. Rev. B 6 (1972) 3072.
[15] A. Bauknecht, S. Siebentritt, J. Albert, M.Ch. Lux-Steiner, J. Appl. Phys. 89 (2001) 4391.
[16] A.M. Akhmedov, A.E. Bakhyshov, A.A. Lebedev, M.A. Yakobson, Sov. Phys. Semicond. 12 (1978) 299.
[17] A.E. Bakhyshov, B.A. Natig, B. Safuat, S.R. Samedov, Sh.M. Abbasov, Sov. Phys. Semicond. 24 (1990) 828.
[18] T. Yildirim, N.M. Gasanly, Curr. Appl. Phys. 9 (2009) 1278.