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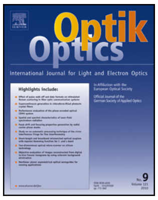

Optical and photoelectrical properties of TlInSSe layered single crystals

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ABSTRACT

Optical and electrical properties of TlInSSe layered single crystals have been studied by means of transmission, reflection and photoconductivity measurements. Transmission and reflection experiments have been carried out from 540 to 1000 nm at room temperature. Derivative analysis was applied to both transmission and reflection spectra and indirect band gap energy was found as 2.06 eV. Photoconductivity measurements have been performed in the temperature range from 245 to 300 K and in the voltage range from 10 to 80 V. From the temperature-dependent photoconductivity measurements, the observed single peak shifted to higher wavelengths with increase of temperature. The increase of photoconductivity with temperature is due to the increase in the mobility of photocarriers that can be explained by Bube model. From $\lambda_{1/2}$ method, room temperature indirect band gap of the crystal was also found as 2.06 eV. From voltage-dependent photoconductivity measurements, the peak maximum increased linearly with increase of voltage because of increase of the mobility of charge carriers. Dark current-voltage characteristic of TlInSSe crystal showed the ohmic behavior that means space charge limited current did not exist in the crystal. From the photocurrent with different illumination intensity analysis, the supralinear photoconductivity associated with the two center model was found.

1. Introduction

Semiconductor materials are used for solid state devices such as diodes, transistors, LEDs, lasers, voltage regulators. For this reason, scientists paid attention to thallium chalcogenides for possible application in device technology [1–4]. Our research group focused on TlInSSe crystals that belong to thallium chalcogenides. The atomic composition of the TlInSSe crystal (Tl: In: Se: S) was found to be 25.7: 25.9: 24.3: 24.1 using energy dispersive spectroscopic analysis, respectively [5]. The lattice parameters of the crystal that has monoclinic unit cell were established by means of X-ray diffraction measurements [5]. The photoluminescence experiments were conducted in the temperature range of 10–65 K [6]. A single emission band corresponding to donor-acceptor pair recombination was observed at 2.122 eV at 10 K. In the emission band, blue shifts with decreasing temperature and increasing laser intensity were noticed. The photoluminescence occurred as a result of transitions between donor level at 0.023 eV and acceptor level at 0.243 eV. The TlInSSe crystal was also studied by using thermally stimulated current measurements to determine activation energy, attempt-to-escape frequency, capture cross

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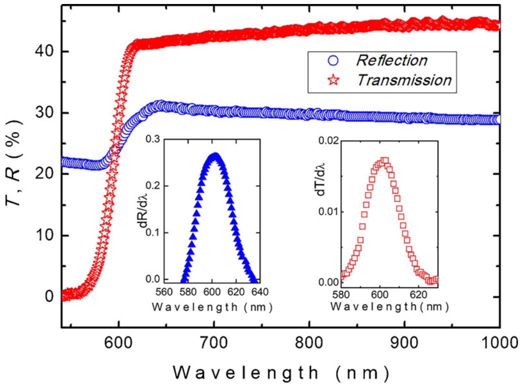

Fig. 1. Stars and circles represent transmission (T) and reflection (R) spectra, respectively. Insets: Triangles and squares show derivative curves of reflection and transmission spectra, respectively.

section and concentration of the traps [7]. From the analysis of the absorption data, indirect and direct band gap energies were calculated as 2.05 and 2.21 eV at room temperature, respectively. The absorption edge shifted toward higher energies as the temperature decreased from room temperature to 10 K [5]. The extinction coefficient, the refractive index and the dielectric function of TlInSSe crystals were also established as a result of spectroscopic ellipsometry measurements [8].

Although there were many valuable works on this compound, no information has been established on the temperature, voltage and illumination intensity dependencies of photocurrent. Moreover, none of work compared the band gap energy of the TlInSSe single crystal using derivative method of both transmission and reflection measurements and $\lambda_{1/2}$ method of the photoconductivity measurements.

The aim of this work is to report and analyze the room temperature band gap of TlInSSe crystal using transmission, reflection and photoconductivity measurements and variation of band gap with temperature from temperature dependent photoconductivity measurements. In addition, our aim is to get information about nature of recombination centers from different illumination intensity of photocurrent of TlInSSe crystal.

2. Experimental details

TlInSSe crystals were grown by Bridgman method. The constituent elements of stoichiometric proportions were fused into the silica tubes with a tip at the bottom. The elements with 99.999% purity were used. The tube was moved with a speed of 1 mm/h from 900 to 480 °C, so the temperature gradient was 30 °C/cm. After the process, very bright and red in color ingots were occurred.

Transmission and reflection experiments were conducted in the wavelength region from 540 to 1100 nm at room temperature by using a “Shimadzu” UV-1201 model spectrophotometer with 20 W halogen lamp, silicon photodiode and holographic grating. For the transmission experiments first the empty holder was used as reference after that the sample was attached to the holder. The light coming from monochromator directed towards the normal of sample surface. The light had polarization to the (001) plane which is perpendicular to the *c*-axis of the crystal. For the reflection experiments first the gold mirror was used as reference after that sample was attached to the holder. The light had an angle of incidence 5°. For both transmission and reflection measurements, the resolution was 5 nm.

For photoconductivity measurements, contacts were made on the samples according to the sandwich geometry. A copper wire was stuck to the front face of the sample by using very small piece of silver paste for wide surface illumination as much as possible. All back face was covered by silver paste and attached to the copper holder to allow electrical conductivity of the sample. Sandwich geometry was used for the studied sample since the conductivity of samples along the layer is greater than that the normal to the layer about four orders of magnitude [2]. For this reason, electric field applies all volume of the sample for current contact configuration. The copper holder was affixed to the cold finger of the cryostat and the back side was grounded through the sample holder. The pressure was diminished to 10^{-3} Torr and temperature was decreased from room temperature to 245 K utilizing closed-cycle helium gas cooling cryostat. Temperature was adjusted by a temperature controller which is a Lake-Shore 331. Voltage was applied to the sample by a Keithley 228A voltage source and current was measured by a Keithley 6485 picoammeter. A Newport Oriel Apex 70613NS Quartz Tungsten-Halogen lamp with 100 W power was used as a light source for an Oriel l/8 m Cornerstone monochromator. The incident light from monochromator focused to the sample surface by using lenses. The wavelength varied from 540 nm to 1000 nm with 5 nm steps keeping the voltage constant at 80 V. For each wavelength first dark conductivity was measured and then light conductivity was recorded. Subtracting the dark conductivity from light conductivity, the photoresponse was obtained at a certain voltage and temperature. The same scanning was repeated with varying temperatures from 245 K to room temperature at 80 V and with varying voltages from 10 to 80 V at room temperature. For the photocurrent measurements with different illumination intensities, the illumination intensity of the lamp was changed from 19 to 115 mW/cm^2 with varying the current of the lamp

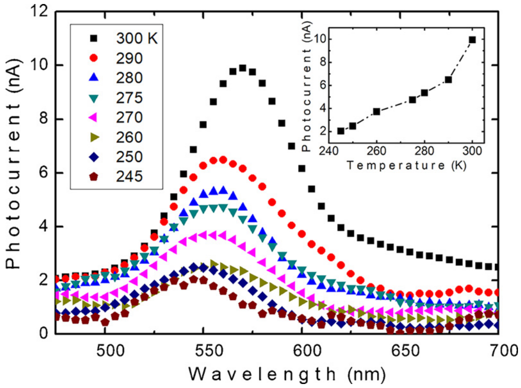

Fig. 2. Photoresponse spectra of TlInSSe crystal at various temperatures from 245 to 300 K. Inset: The variation of maximum photocurrent values with temperature. Dashed line is only guide for eye.

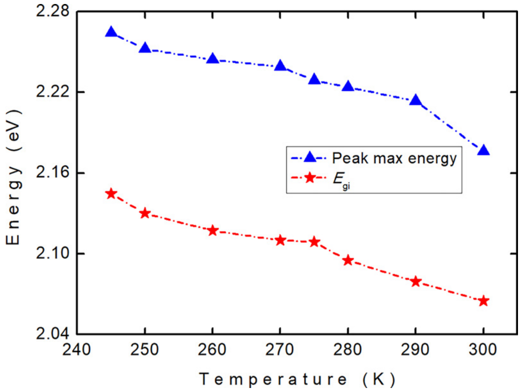

Fig. 3. The variation of peak maximum energies and band gap energies with temperature. Triangles and stars show peak maximum and band gap energies, respectively. Dashed lines are only guides for eye.

from 50 to 90 mA with 10 mA steps at room temperature. For all these measurements the computer software written in National Instruments Labview was used.

3. Results and discussion

There are some techniques to get information about absorption edge of the crystal using the transmission and reflection spectra. One of these methods is derivative spectroscopy. This technique is used to get both qualitative and quantitative information from maximum and minimum positions of derivative curves [9]. Fig. 1 shows transmission and reflection spectra from 540 to 1000 nm. From the first derivative of the transmission and reflection spectra with respect to wavelength, derivative curves shown in inset of Fig. 1 were obtained. The maximum positions of both derivative curves show the same wavelength value as 601 nm which corresponds to indirect band gap energy as 2.06 eV. This energy value is in very good agreement with the indirect band gap energy that is 2.05 eV which is given in Ref. [5].

Photosensitivity of TlInSSe crystal allowed us to perform the photoconductivity measurements. Fig. 2 shows photoconductivity of TlInSSe single crystals in the temperature range of 245–300 K and in the wavelength range of 475–700 nm at 80 V. Only one peak was observed in photoconductivity spectra. The observed peak maximum values shifted towards higher wavelengths with temperature. The increase in photoconductivity with temperature can be associated with the increase in the mobility of photocarriers that explained by Bube model [10]. In this model, Fermi energy level moves to the middle of the band gap while the temperature increases and the lifetime of carriers is to increase because occupation of recombination centers decreases. Thus, photoconductivity increases with the increase of temperature. The increase is clearly seen in inset of Fig. 2.

Band gap energy values were obtained from the half of maximum photocurrent values in long wavelength region which is called as "$\lambda_{1/2}$ method" [11,12]. Band gap energies with varying temperatures from 245 to 300 K were shown in Fig. 3. Band gap energies decrease from 2.15 to 2.06 eV while the temperature increases from 245 to 300 K. From the room temperature photoconductivity analysis, we found indirect band gap energy as 2.06 eV. This value is the same with the energy value calculated using derivative method from transmission and reflection measurements. Fig. 3 also shows the peak maximum energy variations with temperature. As seen in Fig. 3, band gap energies and peak maximum energies have almost the

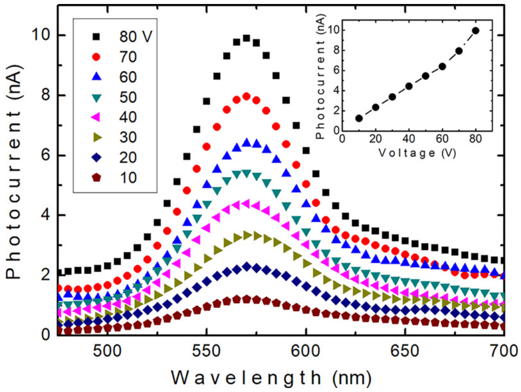

Fig. 4. Photoresponse of TlInSSe crystal with different voltages from 10 to 80 V. Inset: The variation of maximum peak photocurrents with voltages. The line is only guide for eye.

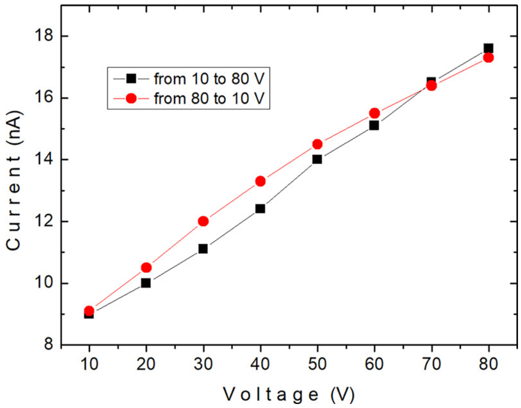

Fig. 5. Dark current values of TlInSSe crystal with different voltages at room temperature. Circles and squares are the data for voltages decreased from 80 to 10 V and increased from 10 to 80 V, respectively. The lines are guides for eye.

same behavior with temperature. Both of them decrease with the increase of temperature. The change of indirect band gap with temperature, dE_{gi}/dT, was calculated as $-1.3 \times 10^{---3}$ eV/K from the straight line portion using Fig. 3. In the below equation, if second term corresponding to electron phonon interaction is greater than the first term corresponding to lattice expansion, dE_{gi}/dT becomes negative [13]. In our study, dE_{gi}/dT is negative, as we mentioned above, so the contribution of electron phonon interaction is greater than that of the lattice expansion.

$$\frac{dE_g}{dT} = \left(\frac{dE_g}{dT}\right)_{L-ex} + \left(\frac{dE_g}{dT}\right)_{e-p}$$

The photoconductivity experiments have also been conducted at different bias voltages from 10 to 80 V as shown in Fig. 4. The photocurrent values at maximum peak positions increased with increase of bias voltage as a result of the increase of mobility of photogenerated charge carriers but peak maximum positions remained same. The maximum photoconductivity values increased almost linearly with increase of bias voltage as shown in the inset of Fig. 4.

Fig. 5 shows the dark current-voltage study of TlInSSe crystal at room temperature. The dark current values were recorded while the voltage was decreasing from 80 to 10 V and increasing from 10 to 80 V. For both current-voltage measurements, they showed more or less same variation. The current increased with the increase of bias voltage almost linearly that means space charge limited current did not exist because the studied sample shows ohmicity until 80 V. From the linear fit to current-voltage curves the resistance of the studied sample was calculated as $8 \times 10^9\ \Omega$.

The variation of photocurrent (I_{ph}) with different illumination intensities (ϕ) of 19, 34,55, 81, 113 mW/cm^2 was also studied to obtain information about nature of recombination centers. Fig. 6 shows the ln I_{ph} versus ln ϕ plot of TlInSSe crystal at room temperature. The relation between $I_{\ ph}$ and ϕ can be defined as; $I_{\ ph} \propto \phi^{\ n}$, where n is a power exponent that is a function of recombination mechanism of non-equilibrium carriers [14]. From the linear fit to the ln I_{ph} versus ln ϕ graph, n was found as 1.17. $n > 1$ indicates existence of supralinear photoconductivity correlated with the two center model. According to this model, the life time of free carriers is increasing with increasing illumination intensity so the material becomes more photosensitive with increasing illumination intensity [10].

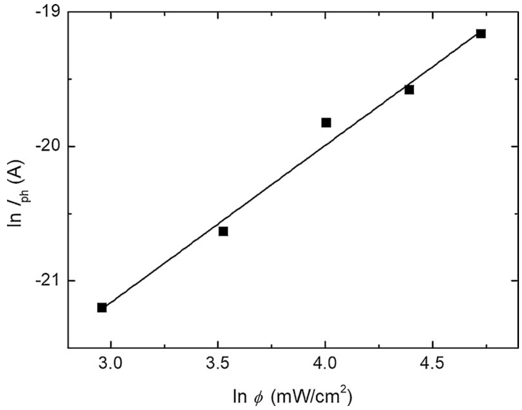

Fig. 6. The variation of photocurrent (I_{ph}) with illumination intensity (ϕ) for TlInSSe at room temperature. The straight line is fit to the experimental data.

4. Conclusions

Optical and photoelectrical properties of TlInSSe layered crystal were analyzed by means of transmission, reflection and photoconductivity measurements. Applying derivative method to room temperature transmission and reflection spectra, indirect band gap of crystal was calculated as 2.06 eV. From the photoconductivity measurements performed in the temperature range of 245–300 K, the red shift in maximum photocurrent values with increase of temperature was observed. This shift was explained utilizing Bube model. The $\lambda_{1/2}$ method was applied to temperature-dependent photoconductivity spectra to calculate the indirect band gap energies E_{gi}. The rate of change dE_{gi}/dT was determined as $-1.3 \times 10^{---3}$ eV/K. The negative value of temperature coefficient means that the contribution of electron-phonon interaction is larger than that of the lattice expansion. From room temperature photoconductivity spectrum, the indirect band gap energy was found as 2.06 eV which is in good agreement with the energy value obtained from derivative analysis. Furthermore, dark conductivity measured with different applied voltages in the range of 10–80 V showed ohmic behavior, and the resistance of crystal was calculated as $8.0 \times 10^9\ \Omega$. From the photocurrent measured with different illumination intensities, the existence of supralinear photoconductivity associated with the two center model was established. The increase of photocurrent with elevating illumination light intensity makes TlInSSe crystal useful for technological applications as photodetectors.

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