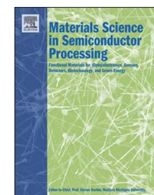
Materials Science in Semiconductor Processing 63 (2017) 72–75

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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



Study of the optical and photoelectrical properties of TlGaSeS layered single crystals

S. Delice[a,*], N.M. Gasanly[b,c]

[a] Department of Physics, Hitit University, 19030 Çorum, Turkey
[b] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
[c] Virtual International Scientific Research Centre, Baku State University, 1148 Baku, Azerbaijan

ARTICLE INFO

Keywords:
Semiconductors
Optical properties
Photoconductivity

ABSTRACT

Transmission spectra (*T*) of TlGaSeS crystals in the photon energy (*hv*) range 1.38–2.38 eV are used to determine the energy gap. The indirect band gap of 2.30 eV was established employing the photon energy dependence of the first derivative $dT/d(hv)$ and the photon energy dependence of absorption coefficient. In order to obtain information about the defect states in the energy gap of TlGaSeS crystals, photoconductivity (PC) measurements are performed in the 140–300 K range. Photoconductivity spectra in the photon energy range of 1.77–3.10 eV show two peaks related to intrinsic and extrinsic excitations. It was revealed that the first peak shifts slightly towards the low energy side with increasing temperature, whereas the second one shifts more significantly to the high energy range. It was assumed that for latter peak the deviating PC originates from the distributed energy levels in the band gap where the photoelectrons arise or where they go.

1. Introduction

Improving of optoelectronic devices gains great momentum with the optical and photoelectrical investigations of semiconductor materials. Thallium based ternary compounds have been attracted tremendous interest by researchers for decades and have been studied for different purposes serving to development of science and technology. Particularly, the ternary $TlGaS_2$ and $TlGaSe_2$ crystals have been abundantly investigated in terms of their electrical and optical properties [1–5]. In the visible region of spectrum, they exhibit high photosensitivity and possess wide transparency range varying between 0.5 and 14.0 µm [6]. The studies on $TlInS_2$ crystals which have anisotropic physical properties revealed the suitability to many applications such as X-ray, gamma and neutron detectors, visible and infrared sensitive receivers and piezoelectric photo resistors [7,8]. $TlGaSe_2$ crystals have also been inspected to investigate phase matched second harmonic generation effect [9]. The quaternary compounds being obtained from $TlGaS_2$ and $TlGaSe_2$ crystals by substituting constituent elements can also be promising for optoelectronic applications. The band gap of the quaternary $TlGaSe_xS_{(2-x)}$ (x=0.5, 1.0, 1.5) can be varied by replacing the selenium (sulfur) atoms with sulfur (selenium) atoms. This gives opportunity to obtain higher radiant efficiency at broader wavelength region. The quaternary TlGaSeS layered crystals have two-dimensional layers which are parallel to the (001) plane. Interlayer bonding occurs between Tl and S(Se) atoms and intralayer bonding is created between Ga and Se(S) atoms. Since TlGaSeS crystal exhibits remarkable physical properties, they promise for technological applications, especially in the areas that concerns with the development of photosensitive and photoresponsive devices.

The temperature-dependent electrical resistivity and Hall mobility of TlGaSeS crystal (160–350 K) were reported in Ref. [10]. The study allowed to determine the energy of acceptor centers as 230 and 450 meV. Alharbi [11] investigated the electrical conductivity and Hall effect for TlGaSeS crystals over a wide temperature range of 278–563 K. As a result of these measurements, the position of the acceptor level was evaluated to be 250 meV. The transmittance and reflectance investigations of TlGaSeS crystals in the wavelength range of 400–1100 nm have been carried out and reported in Ref. [12]. The optical indirect transitions with the band gap energy of 2.27 eV were found by means of the analysis of the absorption data at room temperature. Moreover, TlGaSeS crystals have been studied in the low temperature range of 10–180 K by the help of thermoluminescence measurements [13]. Two distinctive glow peaks were observed around peak maximum temperatures of 39 and 131 K. Applications of the curve fitting method revealed the presence of trap levels having activation energies of 16 and 97 meV.

This paper reports the results of the study on the optical properties of TlGaSeS layered single crystals in the photon energy range of 1.38–

* Corresponding author.
E-mail address: serdardelice@hitit.edu.tr (S. Delice).

http://dx.doi.org/10.1016/j.mssp.2017.02.005
Received 23 August 2016; Received in revised form 21 January 2017; Accepted 5 February 2017
1369-8001/ © 2017 Elsevier Ltd. All rights reserved.

2.38 eV. Furthermore, the photoelectrical properties are investigated in the temperature range of 140–300 K and the photon energy range of 1.77–3.10 eV. The results were used to elucidate the distribution of localized energy levels in the band gap of TlGaSeS crystals.

2. Experimental details

Growth process of TlGaSeS single crystals were achieved by using the Bridgman technique after synthesizing the polycrystals of TlGaSeS that were obtained from high-purity elements (at least 99.999%) provided in stoichiometric proportions. The employed silica tubes having a tip at the bottom were evacuated down to 10^{-5} Torr. The thermal gradient in a vertical furnace was 30 °C per cm. The ampule was managed to move with a rate of 1.0 mm/h between the temperatures 900 and 480 °C. The ingots (red in color) possessed mirror-like surfaces and showed good optical quality. Energy dispersive spectroscopy (EDS) measurements for TlGaSeS crystals were performed to determine the atomic composition by employing a JSM-6400 scanning electron microscope.

Transmission measurements of TlGaSeS crystals were performed in the 1.38–2.38 eV photon energy region by using a “Shimadzu" UV-1201 spectrophotometer, which consisted of a 20 W halogen lamp, a holographic grating, and a silicon photodiode. The resolution of the spectrophotometer was 5 nm. The transmission measurements were done under normal incidence of light with a polarization direction along the (001) plane, which is perpendicular to the *c*-axis of the crystal. In most cases, the thickness of the sample was about 80 μm for the room-temperature transmission measurements.

Photoconductivity measurements were performed through the homemade experimental setup developed around closed-cycle helium gas cooling cryostat at low temperatures. The indium strip coatings were made on the opposite edge of the sample surface. Electrical contacts were achieved by attaching the conductive wires to these strips using silver paste. The distance between contacts was approximately 5 mm. The photocurrent was measured along the layer, while incident light was perpendicular to the layer. The following required conditions were prepared for the sample for PC measurements, the pressure of environment was decreased about to 10^{-3} Torr and the temperature of the sample was diminished to measurement values ranging from 140 to 300 K using a temperature controller (Lake-Shore 331). Then, the sample was exposed to a light, which energy was bigger than the band gap ($h\nu > E_g$), for 10 min before the PC measurements performed at various temperatures to fill the possible defect levels in the band gap and so as to increase the magnitude of PC due to extrinsic transition. 100 W QTH (Quartz Tungsten-Halogen) monochromator illuminator (Newport Oriel Apex 70613NS), employed as a source of light, was coupled to Oriel 1/8 m Cornerstone monochromator scanning in the photon energy ranges of 1.77–3.10 eV. The light of the monochromator was directed to the sample by means of lens. Keeping the temperature constant at an intended value, the currents due to the light excitation at varying wavelength under the 80 V, supplied with a voltage/current source (Keithley 228A), were recorded on the computer utilizing a picoammeter (Keithley 6485). We choose such a high value of voltage since the PC spectra at low temperatures are more observable and comparable under this bias voltage. The dark current was also measured at 80 V before recording the current obtained with light excitation at each scanning photon energy. Ohmicity of the crystal is conserved up to 80 V which means no space charge limited current is observed up to that voltage value. This gives us flexibility to study under 80 V. After obtaining the data for the current thanks to light excitation and dark current, the photocurrent corresponding to scanning photon energy was obtained by the subtraction of those of two currents. The normalization of the measured photocurrent with the light intensity related to photon energy was taken into account for the PC spectra. The whole experimental setup was governed by software written in Labwiev (National Instruments) graphical development environment.

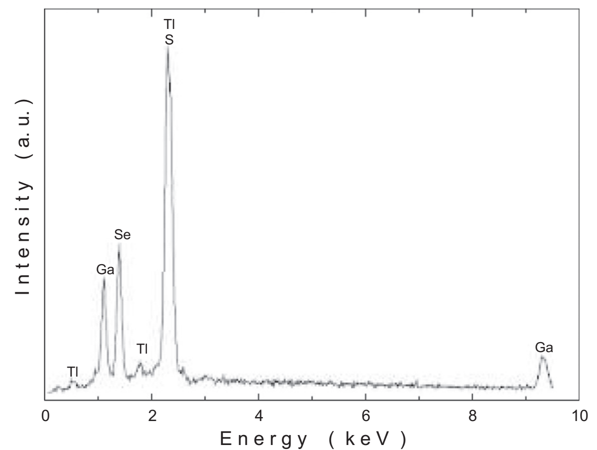


Fig. 1. Energy dispersive spectroscopic analysis of TlGaSeS crystal.

3. Results and discussion

Energy dispersive spectroscopic analysis was accomplished and the chemical composition of the each constituting elements of TlGaSeS crystal was estimated as 25.7:25.9:24.3:24.1 for Tl:Ga:Se:S, respectively, as shown in Fig. 1. Analysis of the XRD experiments was also achieved to determine the structural parameters. DICVOL 04 least-squares computer program was utilized for the purpose of calculating the lattice parameters and Miller indices (*hkl*). X-ray diffraction pattern of TlGaSeS crystal was indicated in Fig. 2. The monoclinic unit cell with found lattice parameters of a=0.7588, b=0.7645, c=0.8714 nm and β=111.85° were determined. The Miller indices were demonstrated on the diffraction peaks. The sharpness of the diffraction peaks revealed that the well crystallinity of the sample was achieved.

Transmission spectra can be used to get the absorption edge of the crystal under the light of different analysis methods. One of these methods, derivative spectrophotometry [14], has been a powerful technique used in literature for three decades, to obtain the qualitative and quantitative information from the maxima and minima positions of the derivative curve. Dependence of the transmission (T) of TlGaSeS single crystals in the photon energy ($h\nu$) range 1.38–2.34 eV at room temperature is shown in Fig. 3. Inset 1 of Fig. 3 presents the photon energy dependence of the first derivative $dT/d(h\nu)$ which reveals the peak at 2.30 eV, corresponding to the indirect band gap energy. This value is in good agreement with the E_{gi}=2.27 eV, obtained from extrapolating the fitted line of the dependence $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$, where α is absorption coefficient (inset 2 of Fig. 3).

The high photosensitivity of TlGaSeS crystals made it possible to study dc-PC spectra in a wide range of the photon energy. Fig. 4

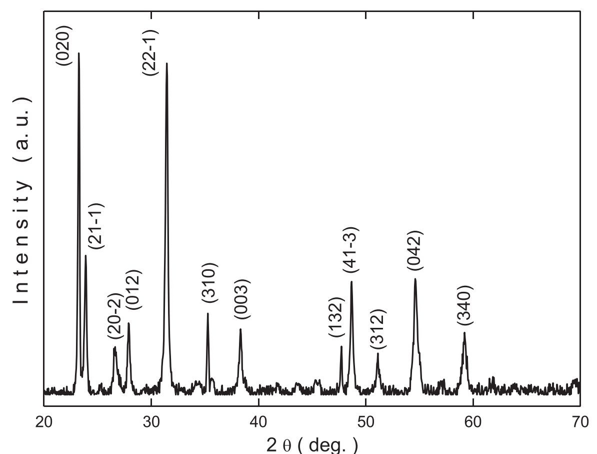


Fig. 2. X-ray powder diffraction pattern of TlGaSeS.

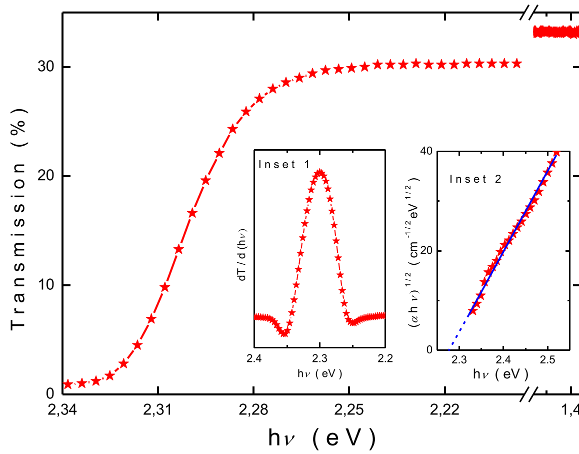


Fig. 3. Transmission spectrum of TlGaSeS crystal. Inset 1 presents the derivative spectrum of transmission spectrum $dT/d(h\nu)$. Inset 2 shows the dependence of $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$.

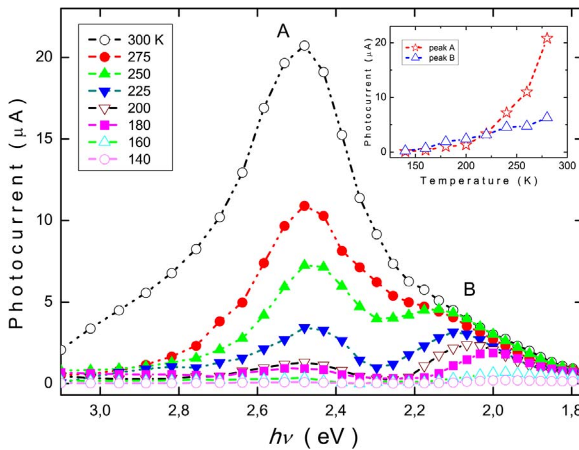


Fig. 4. Photocurrent spectra of TlGaSeS crystal in the temperature range of 140–300 K at bias voltage V=80 V. Inset shows the variations of photocurrent with temperature for peaks A and B.

presents the spectral distribution of dc-PC for TlGaSeS single crystals in the temperature range 140–300 K and in the wavelength range 400–700 nm. All the spectra are characterized by an increasing edge corresponding to the onset of optical absorption. Above absorption edge ($h\nu$≈2.30 eV), with the increase of photon energy photocurrent diminishes due to absorption becoming more and more intense, thus causing photo generation of charge carriers closer to the surface, where defect recombination is more probable. There are two peaks of the dc-PC in the studied temperature range. Because the band gap of the TlGaSeS crystals is 2.30 eV at room temperature, the first peak (A) at 2.32 eV is related to an intrinsic (indirect band–band) transition. The second peak (B) was registered at 2.21 eV, which could be attributed to an extrinsic transition due to the ionization of deep impurities.

It is evident from Fig. 4, that the first peak shifts slightly (about 0.08 eV) towards low photon energy side with increasing temperature from 140 to 300 K, whereas the second one shifts more significantly (about 0.27 eV) to high energy range of the spectra. It is assumed that for peak B the deviating PC originates from the distributed energy levels in the band gap where the photoelectrons arise or where they go. It should be noted that the previous studies of thermoluminescence, electrical conductivity and Hall effect in p-type TlGaSeS crystals have revealed the shallow defect levels with activation energies of 16 and 97 meV [13] and three deep defect levels with energies of 230, 250 and 450 meV [10,11].

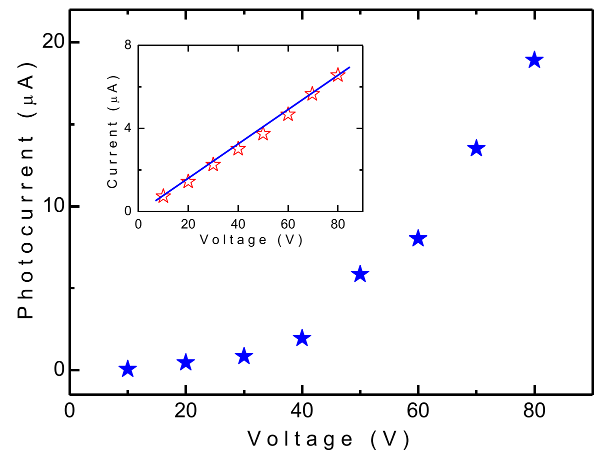


Fig. 5. Photocurrent in TlGaSeS crystals at various bias voltages at T=300 K for peak A. Inset: Current-voltages variation for TlGaSeS crystals at T=300 K.

Inset of Fig. 4 shows that the values of photocurrent grow with increase in temperature range 140–300 K for peaks A and B up to nearly 21 μA and 6 μA, respectively. The spectral distribution of PC of TlGaSeS crystal at different bias voltages was also measured and the structure of the spectrum is found to remain constant but the magnitude of the PC increases with the increase of bias voltages. As seen in Fig. 5, the magnitude of PC rises slowly at low voltages and more rapidly at higher voltages. The increase of the mobility of the photogenerated carriers with voltages may be responsible for the increment in the PC. The current-voltage characteristics of the sample were studied as shown in inset of Fig. 5. There is no space charge limited current since the crystal demonstrates ohmicity up to 80 V.

The energy gap, E_g, was determined by so called “the $\lambda_{1/2}$ method” [15–17]. According to this method, E_g is evaluated by utilizing from the point on the spectral curve where the photocurrent value falls to half maximum. Applying “the $\lambda_{1/2}$ method”, the energy gap E_g of TlGaSeS crystal could be calculated at every temperature as presented in Fig. 6, which shows that the value of the band gap energy decreases as temperature increases. Actually, it falls of about 0.08 eV as the temperature is increased from 140 to 300 K. The temperature coefficient of E_{gi} (dE_{gi}/dT) was calculated from the straight-line portion; it was found to be -5.7×10^{-4} eV/K.

The energy of peak B at T=300 K (2.21 eV) may be assigned to the transitions from defect level of 110 meV to the indirect conduction band, while the energy of peak B at T=140 K (1.94 eV) may be attributed tentatively to the transitions from defect level of 460 meV to the indirect conduction band (Fig. 6). Indeed, these values of energy

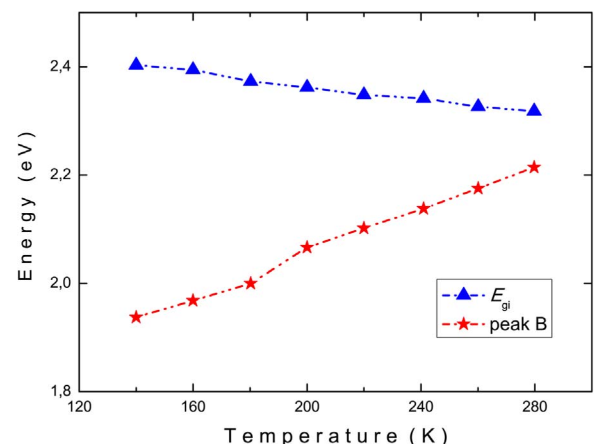


Fig. 6. The indirect band gap energy E_{gi} and energy of peak B versus temperature plotted from PC results for TlGaSeS crystal in the temperature range of 140–300 K.

levels 110 and 460 meV are in satisfactory agreement with those (97 and 450 meV) reported in Refs. [10,13] from thermoluminescence and electrical conductivity experiments, respectively.

The temperature dependence of the band gap energy for a semiconductor can be expressed in two main parts [18]:

$$\frac{dE_g}{dT} = \left(\frac{dE_g}{dT}\right)_{\text{lat. exp.}} + \left(\frac{dE_g}{dT}\right)_{\text{el.}-\text{ph.}}. \quad (1)$$

The first term results from the variation of the band gap due to the thermal expansion of the crystal. It may be either positive or negative in sign depending on the specific properties of the electron states of the band extrema and the relative ordering of levels [19]. The second term arises from electron-phonon interaction and is always negative in sign for all semiconductors. Consequently, the whole dependence of the band gap of the material on temperature may be either negative or positive depending on the term that contributes more. The temperature coefficient of indirect band gap of TlGaSeS crystal was obtained to have negative sign ($dE_{gi}/dT = -5.7\times10^{-4}$ eV/K), which suggest that the electron-phonon interaction term is larger than the lattice expansion contribution.

4. Conclusion

Optical and photoelectrical properties of TlGaSeS crystals grown by Bridgman method were investigated. In the optical studies, the indirect energy gap was determined to be 2.30 eV. The spectral distribution of photocurrent of TlGaSeS in the range of photon energy between 1.77 and 3.10 eV possesses two maxima at 2.48 and 2.14 eV related to intrinsic and extrinsic excitations, respectively. The temperature dependence of photocurrent investigated in the temperature range from 140 to 300 K shows that the first maximum shifts slightly towards the low energy side with increasing temperature, while the second one shifts more significantly to the high energy range. It was supposed that for latter maximum the photocurrent variation originates from the distributed energy levels in the band gap where the photoelectrons arise.

References

[1] Y. Shim, W. Okada, K. Wakita, N. Mamedov, J. Appl. Phys. 102 (2007) 083537.
[2] J.A. Kalomiros, N. Kalkan, M. Hanias, A. Anagnostopoulos, K. Kambas, Solid State Commun. 96 (1995) 601.
[3] I.M. Ashraf, M.M. Abdel-Rahman, A.M. Badr, J. Phys. D: Appl. Phys. 36 (2003) 109.
[4] A. Kato, M. Nishigaki, N. Mamedov, M. Yamazaki, S. Abdullaeva, E. Kerimova, H. Uchiki, S. Iida, J. Phys. Chem. Solids 64 (2003) 1713.
[5] M.M. El Nahass, M.M. Sallam, S.A. Rahman, E.M. Ibrahim, Solid State Sci. 8 (2008) 488.
[6] K.R. Allakhverdiev, Solid State Commun. 111 (1999) 253.
[7] S.N. Mustafaeva, E.M. Kerimova, N.Z. Gasanov, Phys. Solid State 40 (1998) 561.
[8] S.N. Mustafaeva, A.I. Hasanov, Power Eng. Probl. 1 (2005) 101.
[9] M. Yu, Seyidov, R.A. Suleymanov, F. Salehli, Phys. Lett. A 376 (2012) 643.
[10] A.F. Qasrawi, N.M. Gasanly, J. Appl. Phys. 113 (2013) 023712.
[11] S.R. Alharbi, Chin. Phys. B 22 (2013) 058105.
[12] I. Guler, N.M. Gasanly, J. Korean Phys. Soc. 51 (2007) 2031.
[13] S. Delice, N.M. Gasanly, Mod. Phys. Lett. B 16 (2014) 1450133.
[14] C.B. Ojeda, F.S. Rojas, Microchem. J. 106 (2013) 1.
[15] R.H. Bube, Photoelectronic Properties of Semiconductors, Cambridge University Press, Cambridge, 1992.
[16] I.M. Ashraf, J. Phys. Chem. B 108 (2004) 10765.
[17] I.M. Ashraf, A. Elshaikh, A.M. Badr, Phys. Stat. Solidi (b) 241 (2004) 885.
[18] I.J. Pankove, Optical Processes in Semiconductors, Prentice-Hall, New Jersey, 1971.
[19] M. Hanias, A. Anagnostopoulos, K. Kambas, J. Spyridelis, Phys. B 160 (1989) 154.