Low-Temperature Thermoluminescence Studies on $TlInS_2$ Layered Single Crystals

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Thermoluminescence characteristics of $TlInS_2$ layered single crystals grown by the Bridgman method were investigated in the low temperature range of 10–300 K. The illuminated sample with blue light ($\approx$ 470 nm) at 10 K was heated at constant heating rate. Curve fitting, initial rise and various heating rate methods were used to determine the activation energy of the trap levels. All applied methods showed good consistency about the presence of five trapping centers located at 14, 19, 350, 420, and 520 meV. Behavior of the TL curve for various heating rates was investigated. Traps distribution has also been studied. The activation energies of the distributed trapping centers were found to be increasing from 14 to 46 meV.

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1. Introduction

Semiconducting chalcogenides formulated with $TlBX_2$ (where B = Ga or In; X = S or Se) are important compounds for researchers working on the characterization of semiconductor materials. Their structural properties and potential optoelectronics applications make these materials attractive in the related technological areas [1–4]. These layered semiconductors belong to the monoclinic system with space group of $C2/c$ at room temperature. Their crystal structures consist of alternating two-dimensional layers arranged perpendicular to the [001] direction. Each successive layer makes a 90° angle with the previous layer.

Among the chalcogenides, $TlInS_2$ is a useful sample for optoelectronic applications [5, 6] due to having high photosensitivity in the visible spectral range and high birefringence with wide transparency range of 0.5–14 μm. Structural [1, 7–9], optical [10–13] and electrical [2, 10, 14] characterization of $TlInS_2$ have been studied to explore other possible technological applications. One of the factors affecting the characteristics of the semiconductors is the presence of defects and/or impurities. Therefore, determination of the properties of the trapping centers in the forbidden energy gap has much importance in the semiconductor technology. Our research group focused on this point and previously studied the photoluminescence (PL) and thermally stimulated current (TSC) properties of many ternary and quaternary chalcogenides. PL measurements on $TlInS_2$ crystals revealed two bands centered at 2.41 eV and 1.52 eV at $T = 11.5$ K [15]. Analysis on the PL spectra showed that there is a radiative transition from a shallow donor level to a deep acceptor level. We have carried out the TSC experiments on $TlInS_2$ crystals in the temperature range of 10–300 K [16–18]. In the cited papers, shallow and deep trapping centers were found at 12, 14, 400, 570, and 650 meV. Capture cross sections, attempt-to-escape frequencies and concentrations of the centers were also evaluated.

One of the methods used for the characterization of trapping centers is thermoluminescence (TL). The TL method can be summarized as follows. At a low temperature, the sample is subjected to a radiation having energy greater than the band gap energy. In this manner, charges are excited to higher delocalized bands. While returning to their initial states, some of the excited carriers are trapped in the trap levels. The trapped carriers should have enough energy to be excited to the delocalized band. In the TL measurements, the needed energy is provided by "heat". The excited charge carriers from the trap levels by increasing the temperature of the sample recombine with the opposite charge carriers. If the recombination is radiative, activation energies of trap levels can be detrmined by analyzing the temperature dependence of the number of photons emitted.

In the present paper, thermoluminescence properties of the $TlInS_2$ layered single crystals were investigated in the low temperature range of 10–300 K. The observed TL curves were analyzed to obtain properties of the trapping centers in undoped crystals.

2. Experimental details

$TlInS_2$ single crystals were grown by the Bridgman method from a stoichiometric starting melt sealed in the evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 25 cm in length) with a tip at the bottom, in our crystal growth laboratory (Middle East Technical University). 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 had no cracks and voids on the surface. The electrical conductivity

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of the intentionally undoped crystals was n-type as determined from hot probe method.

Dimensions of the sample used for TL experiments were $5 \times 3 \times 1$ mm^3. TL measurement setup was built around a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). A LakeShore Model 331 temperature controller was used to adjust the sample temperature. A light tight measurement chamber carrying the detector (a photomultiplier tube, PMT), a blue light source (≈ 470 nm) (light emitting diode, LED) and the optics was connected to the optical access port of the cryostat (quartz window). The sample was positioned on the focal plane of the optics for illumination and detection of the emitted photons. Luminescence emitted from the crystal was focused by lenses on the photomultiplier tube (Hamamatsu R928; spectral response: 185 to 900 nm) working in photon counting regime. Pulses from the photomultiplier were converted into TL pulses using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and counted by the counter of the data acquisition module (National Instruments, NI-USB 6211). A high power blue LED generating light at a peak maximum of 2.6 eV, bigger than band gap energy was used to illuminate the sample. A software program written in LabView^{TM} graphical development environment was used to control whole measurement system/devices. The sample was irradiated at 10 K for 600 s, experimentally determined time to fill the traps completely. Then, after 120 s of waiting, the sample was heated at a constant heating rate and the emitted photon counts were recorded as a function of temperature.

3. Results and discussion

3.1. Crystal characterization

Structural characterizations of the $TlInS_2$ samples were performed by using "Rigaku miniflex" X-ray powder diffractometer (Cu K_α radiation, $\lambda = 0.154049$ nm) operated at a scan speed of $0.02°$/s. The diffraction data were analyzed with a least-squares computer program, "TREOR 90", to obtain the lattice parameters of the monoclinic unit cell as $a = 1.0942$, $b = 1.0484$, $c = 1.5606$ nm and $\beta = 100.70°$. These results were well correlated with those reported in Ref. [8].

Chemical composition of the single crystal $TlInS_2$ sample was determined by using energy dispersive spectroscopy experiments. The measurements were performed using JSM-6400 scanning electron microscope in 0–9 keV energy range. The atomic composition ratio of constituent elements (Tl : In : S) in the crystal was found out as 25.6 : 25.2 : 49.2, respectively.

3.2. Thermoluminescence measurements

The TL measurements were carried out in the temperature range of 10–300 K at heating rate of 0.6 K/s. Figure 1 shows glow curve in 10–60 K and 150–250 K ranges at which TL peaks arise. We have applied curve fitting, initial rise, and various heating rate methods to determine the activation energies of the trapping center(s) associated with the observed glow curve.

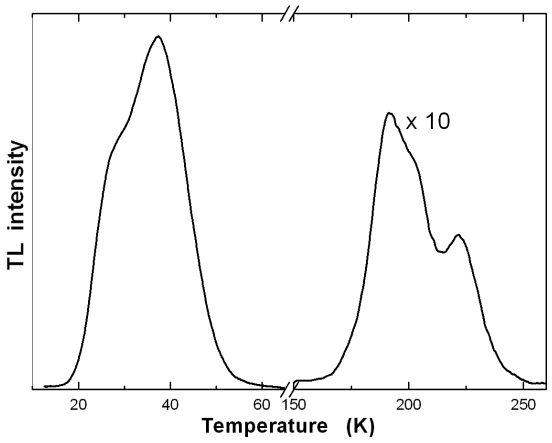

Fig. 1. Experimental TL curve of $TlInS_2$ crystal with heating rate of $\beta = 0.6$ K/s.

3.2.1. Determination of activation energy

Curve fitting method is based on approximation of the TL glow curve by analytical expression giving the temperature dependence of the TL intensity using a software program. For slow retrapping case, TL intensity is given by [19, 20],

$$I_{\mathrm{TL}} = n_0 \nu \exp\left(-\frac{E_{\mathrm{t}}}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp(-E_{\mathrm{t}}/kT)\,\mathrm{d}T\right). \quad (1)$$

Here, n_0 is initial trap concentration, ν is attempt-to-escape frequency, β is heating rate and E_{t} is activation energy of the trapping centers. The details of the curve fitting analysis were reported in our previous study [21]. The TL curves in the low and high temperature ranges were fitted for the existence of two and three peaks, respectively. A successful fitting was obtained for slow retrapping case consistent with the related theoretical approach. Figure 2a and b shows experimental TL curves of $TlInS_2$ crystal in the low and high temperature ranges, respectively. We have performed the curve fitting on these curves separately as the temperature ranges of the observed TL curves do not overlap. Activation energies of the trapping centers (A to E) were found as 14, 19, 350, 420, and 520 meV (Table). Attempt-to-escape frequencies of the trapping centers were calculated by using activation energy and peak temperatures [21]. Then capture cross-section (S_{t}) of the trap can be calculated by using the expression

$$S_{\mathrm{t}} = \frac{\nu}{N_{\mathrm{c}} \upsilon_{\mathrm{th}}},$$

where $N_{\mathrm{c}} = 2(2\pi m_{\mathrm{e}}^* kT/h^2)^{3/2}$ is the effective density of states in the conduction band and υ_{c} is thermal velocity of free electrons. The capture cross sections of the trap levels was calculated using the effective mass $m_{\mathrm{e}}^* = 0.14 m_0$ reported for $TlInS_2$ [14] (see Table).

TABLE

The activation energy (E_t), capture cross-section (S_t) and attempt-to-escape frequency (v) of revealed traps of the $TlInS_2$ crystal.

Peak	T_m [K]	E_t [meV]				S_t [cm^2]	v [s^{-1}]
		Curve fitting method	Initial rise method	Heating rate method	After thermal celaning		
A	26.4	19	18	–	–	1.7×10^{-21}	550
B	37.1	14	13	12	15	5.9×10^{-24}	3.6
C	189.3	520	510	–	–	4.6×10^{-13}	7.5×10^{12}
D	199.3	420	410	–	–	1.8×10^{-16}	3.3×10^{9}
E	220.6	350	350	–	–	1.8×10^{-19}	3.9×10^{6}

We have also applied the initial rise method effective for all types of kinetics. In this method, the initial part of the TL peak is proportional to $\exp(-E_t/kT)$ when the trapped carriers are excited to the non-localized states [19]. When the initial portion of the curve was analyzed, $\ln(I_{TL})$ vs. $1/T$ graph gives a straight line with a slope of $(-E_t/k)$. Insets of Fig. 2a and b represent the corresponding plots of the experimental data (open circles) and their linear fits (solid lines). Activation energies of the traps were found as 13, 18, 350, 410, and 510 meV (Table). These results show a good consistency with those obtained from curve fitting method. Since the studied crystals were not intentionally doped, these trapping centers are thought to originate from anion vacancies caused by nonstoichiometry and/or stacking faults, quite possible to exist in layered $TlInS_2$ due to the weakness of the van der Waals forces between the layers [22].

Our studies on the TL curve were expanded by applying the thermal cleaning, various heating rates, and different stopping temperatures methods. Each of these methods has characteristic purposes. However, the intensities of the high-temperature TL peaks are very low, not suitable to apply these techniques. Below, we present the results and analysis of these measurements for intensive low-temperature peaks in TL glow curve.

Thermal cleaning technique is helpful in separating overlapping peaks. For this purpose, the excited sample at low temperature ($T = 10$ K) is heated up to a temperature enough to excite all the carriers from the trap level corresponding to lower peak maximum temperature (T_m). Then the sample is cooled to initial temperature and TL curve is measured in whole temperature range (10–300 K) by heating the sample without additional illumination. The TL curve obtained by this way carries only the characteristics of the peak having higher T_m. We have applied thermal cleaning method to separate peak B from peak A. Figure 3 shows observed TL curves before (circles) and after (stars) thermal cleaning. The activation energy of the remaining TL curve after thermal cleaning was found as 15 meV using curve fitting method (see inset of Fig. 3). This value is nearly equal to that of peak B obtained from curve fitting method mentioned above. Therefore, we can say that TL curve obtained after thermal cleaning corresponds to peak B.

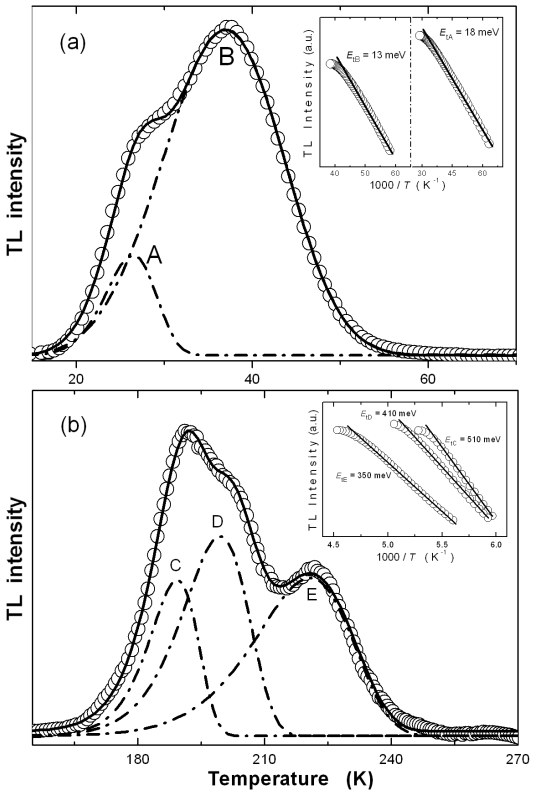

Fig. 2. Experimental TL curve of $TlInS_2$ crystal and decomposition of this curve into (a) two separate peaks in the low and (b) three separate peaks in the high temperature ranges. Open circles are experimental data and dashed curves represent decomposed peaks. Solid curve shows total fit to the experimental data. Insets: TL intensity vs. $1000/T$ for observed peaks. Open circles are experimental data and solid lines are the fitted straight lines.

3.2.2. Heating rate dependence of TL glow curve

The heating rate dependence of the TL curve was investigated for rates between 0.2 and 1.0 K/s (Fig. 4a and b). According to Chen and McKeever [19], increase

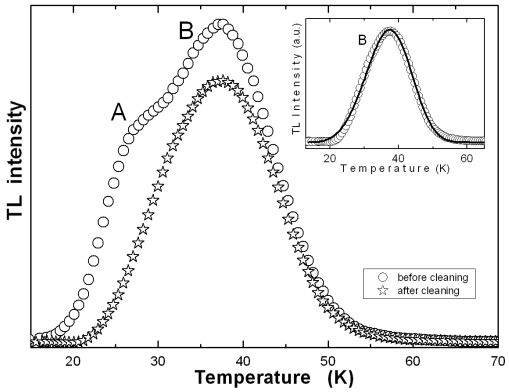

Fig. 3. Experimental TL glow curves before (circles) and after (stars) thermal cleaning for a heating rate of 0.6 K/s. Inset: experimental TL curve (circles) after thermal cleaning and its fit (solid line) according to curve fitting method.

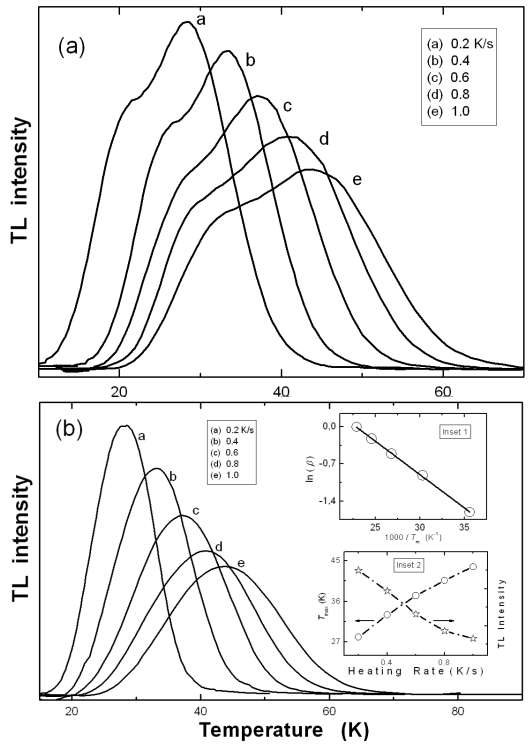

Fig. 4. Experimental TL curves of $TlInS_2$ crystal with different heating rates (a) before thermal cleaning and (b) after thermal cleaning. Inset 1: $\ln(\beta)$ versus $1000/T_m$ for various heating rates. Open circles are experimental data and solid line shows the theoretical fit to the experimental data. Inset 2: the variation of peak maximum temperature (circles) and TL maximum intensity (stars) with heating rate.

of the heating rate results in a shift of T_m to higher temperatures and also a decrease of peak intensity. The shift of T_m with increase of β was empirically explained by Anishia et al. [23] in their study on lithium magnesium borate (LMB) phosphors. At a heating rate of β_1, phosphors spend a long time at a temperature T_1. So, an amount of thermal release of electrons at T_1 could take place. At a higher heating rate of β_2, phosphors spend shorter time at the same temperature T_1. Consequently, there occurs a decrease in the number of thermally released electrons. A higher temperature T_2 is needed to release the same number of electrons for heating rate β_2. This way, the TL glow curve shifts to higher temperatures for higher heating rates. The observed TL glow curves at various heating rates obey this rule as seen from Fig. 4a. Increase of heating rate also resulted with decrease of TL peak intensity and increase of peak width. In literature, there are several methods to determine the activation energy from the heating rate dependence of T_m. In the thermally stimulated phenomena, heating rate is given as [19]:

$$\beta = (\nu k/E_t)T_m^2 \exp(-E_t/kT_m). \quad (2)$$

In this equation T_m dependence of the exponential term is the dominant factor rather than the T_m^2. Consequently, the linear fit of the plot of $\ln(\beta)$ versus $1/T_m$ results with a slope of $-E_t/k$. The overlapped peaks do not allow applying heating rate method to determine the T_m value. Therefore, we have applied this method on peak B after thermal cleaning peak A. Figure 4b and insets show the heating rate dependence of the peak B and the mentioned plot (open circles) and its linear fit (solid line). The activation energy was obtained from the slope of the linear fit as 12 meV. Inset 2 of Fig. 4b shows the variation of the T_m and peak intensity with heating rate.

3.2.3. Traps distribution

The results presented above were obtained by assuming a discrete, single energy for the trap center associated with a localized level. However, in highly defective semiconductors, trap depths may exhibit a distribution in the forbidden energy gap. For the purpose of understanding and revealing the distribution of traps, we have applied an experimental technique based on thermal cleaning of the centers corresponding to lower T_m values and obtaining TL glow curve associated with remaining centers [19, 24]. This technique ($T_m(E_a) - T_{stop}$) was applied as follows. The sample was illuminated at low temperature ($T_0 = 10$ K) and heated at a constant heating rate ($\beta = 0.6$ K/s) up to a temperature (T_{stop}) which provides cleaning of peaks with lower T_m value. Then the sample was cooled to an initial low temperature and TL measurements were carried out in the whole temperature range without additional illumination. Since the levels associated with lower T_m value were emptied, the obtained new TL curve carries the characteristics of remaining deeper energy levels.

Figure 5 shows the TL curves obtained after applying the mentioned technique for different T_{stop} values between 10 and 33 K. As seen from the figure, peak A is entirely cleaned thermally when the temperature was stopped at 21 K. As T_{stop} is increased, peak maximum temperatures shift to higher values. All curves given in the figure were fitted using curve fitting method to reveal the traps distribution. The inset of Fig. 5 shows the

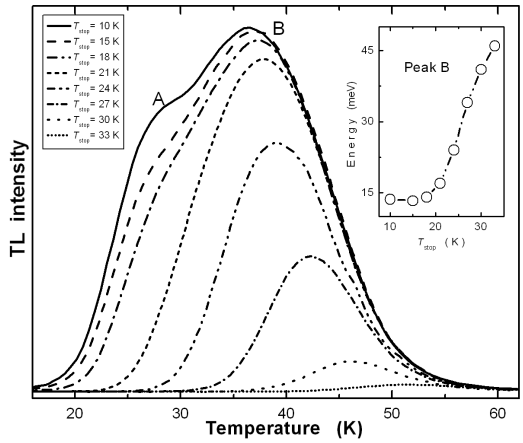

Fig. 5. The glow curves of $TlInS_2$ crystals after different T_{stop} temperatures at heating rate of $\beta = 0.6$ K/s. Inset: the variation of activation energies on T_{stop} values for peak B.

dependence of the activation energies of the distributed traps associated with peak B on stopping temperatures in the range of 10–33 K. The increase of activation energy from 14 to 46 meV is an evidence of the existence of traps distribution in the forbidden energy gap.

4. Conclusion

Thermoluminescence characteristics of $TlInS_2$ have been investigated in the low temperature range of 10–300 K. TL peaks were observed in the low (10–60 K) and high (160–260 K) temperature regions. Curve fitting, initial rise and various heating rate methods were applied to determine the activation energies of the associated trapping centers. All methods resulted with consistent energy values of 14, 19, 350, 420, and 520 meV. Capture cross-sections and attempt-to-escape frequencies of the traps were also found from the results of the curve fitting method. The analyses of the experimental results agree well with the theoretical approach of the slow retrapping case. Moreover, heating rate dependence of TL peak temperature and intensity was investigated in the range of 0.2–1.0 K/s. Heating rate method was also utilized to calculate the activation energy of the related traps. Distribution of the traps has been revealed using an experimental technique ($T_m(E_a)$–T_{stop} method) based on thermal cleaning. The activation energy was found to increase from 14 to 46 meV, an evidence for the existence of traps distribution in the forbidden energy gap.

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