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Trapping Center Parameters in $TlInS_2$ Layered Crystals by Thermally Stimulated Current Measurements

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Thermally stimulated current measurements are carried out on $TlInS_2$ layered single crystal with the current flowing perpendicular to the c-axis in the temperature range of 10 to 90 K. The results are analyzed according to various methods, such as curve fitting, heating rate, and initial rise methods, which seem to be in good agreement with each other. Experimental evidence is found for one trapping center in $TlInS_2$ crystal in the low-temperature region.

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1. Introduction

The III–III–VI_2 family of crystals exhibit quasi low-dimensionality in the form of layered and chain structures and has become increasingly attractive due to their interesting structural properties and potential optoelectronic applications [1]. Members of this family of crystals, designated with the chemical formula $TlBX_2$ (where B = In or Ga; X = S, Se, or Te) are known as thallium dichalcogenides. They have both layered ($TlGaS_2$, $TlGaSe_2$, $TlInS_2$) and chain ($TlInSe_2$, $TlInTe_2$, $TlGaTe_2$) structures. At room temperature, $TlInS_2$ belongs to monoclinic system with space group C_2/c. The lattice of $TlInS_2$ crystals consists of alternating two-dimensional layers parallel to the (001) plane with each successive layer turned through a right angle with respect to the preceding one [1].

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Among many $TlBX_2$-type compounds, $TlInS_2$ has been studied rather well. The forbidden gap of $TlInS_2$ was measured by both absorption and reflection spectroscopy as a function of temperature and was found to be a direct band gap with an energy of 2.58 eV at $T = 10$ K [2, 3]. A high photosensitivity in the visible range of spectra, high birefringence in conjunction with a wide transparency range of $0.5-14$ μm make this crystal useful for optoelectronic applications [4]. For possible applications in optoelectronic device in the visible range, a great deal of attention has been devoted to the study of the structural [1, 5, 6], electrical [7–9], and optical [2–4, 8, 10, 11] properties. In this regard, detailed information on the presence of the impurity and defect centers in the crystal is very useful to fabricate high-quality devices. The thermally stimulated currents (TSC) technique has been extensively used in the past to determine the thermal ionization properties of imperfection centers in semiconductors [12–14].

In our previous paper [15], we presented the temperature dependencies (11–100 K) of the photoluminescence spectra in $TlInS_2$ crystal. We observed two photoluminescence (PL) bands centered at 515 nm (2.41 eV, A-band) and 816 nm (1.52 eV, B-band) at $T = 11$ K. Analysis of the data showed that the A-band was due to radiative transitions from the moderately deep donor level located at 250 meV below the bottom of the conduction band to the shallow acceptor level located at 20 meV above the top of the valence band. There is only one paper in literature concerning the study of TSC spectra in $TlInS_2$ crystals in the high-temperature range 90–300 K [16]. A series of trap levels with energy depths ranging from 150 to 220 meV has been found in the energy gap. However, the shallow levels in $TlInS_2$ crystal in the temperature range below 90 K have not been studied.

The purpose of the present work is to obtain further detailed information concerning shallow traps in undoped $TlInS_2$ crystals using the well-established technique of TSC measurement. In contrast with previous TSC measurements on $TlInS_2$ crystals, for the first time we employ a low-temperature range of 10–90 K. The measurements in the temperature range below 90 K allow us to check the possibility of extremely shallow trap states. We used the various methods to analyze the measured TSC spectra. We report on the activation energy, the capture cross-section, and concentration of the traps in $TlInS_2$ crystal.

2. Experimental details

$TlInS_2$ polycrystals were synthesized from high purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of $TlInS_2$ were grown by the modified Bridgman method. No intentional doping of the crystals was performed. The analysis of X-ray diffraction data showed that $TlInS_2$ crystallizes in a monoclinic unit cell with lattice parameters: $a = 1.0942$, $b = 1.0484$ and $c = 1.5606$ nm, and $\beta = 100.70^\circ$. The samples were prepared by cleaving an ingot

parallel to the crystal layer, which was perpendicular to the c-axis. The typical sample dimensions are $8 \times 3 \times 0.5$ mm^3. The electrical conductivity of the studied samples was p-type as determined by the hot probe method.

To carry out TSC measurements, electrical contacts were made on the sample surface with silver paste according to gap geometry. In this configuration, the electrodes are placed at two opposite edges of the front surface of the crystal. The sample was mounted on the cold finger of the cryostat with a non-conducting g-varnish. Thin copper wires were attached to the electrodes by small droplets of silver paste.

The TSC measurements have been performed from 10 to 90 K using an Advanced Research Systems closed-cycle helium gas cooling cryostat. Constant

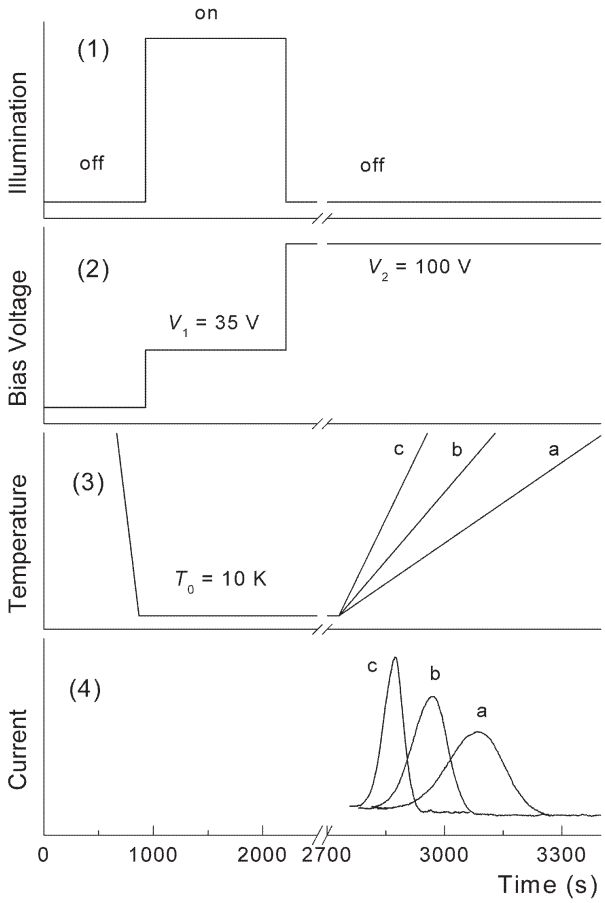

Fig. 1. Principles of TSC experiment: (1) time period of applied illumination; (2) variation of bias voltage; (3) temperature variation with time; (4) TSC signal for three linear heating rates: 0.10 (a), 0.17 (b), 0.30 K/s (c).

heating rates in the range of 0.10–0.30 K/s have been obtained by applying dc current to a 37.5 Ω NiCr heater filament wound around the sample holder. Linear increase in temperature has been achieved by a Lake Shore 331 temperature controller utilizing the temperature sensor. Keithley 228A Voltage/Current source and Keithley 6485 picoammeter are used to measure TSC. The temperature sensitivity of the system is about 10 mK and the current sensitivity of the TSC system is approximately 1 pA. The trap filling is performed by illumination under bias voltage of $V_1 = 35$ V at the initial temperature $T_0 = 10$ K for about 20 min. At low enough temperatures, when the probability of thermal release is negligible, carriers are photoexcited using a LED, generating light at a maximum peak of 2.6 eV, and trapped in the gap states. When the excitation is turned off and an expectation time ($\approx$ 5 min) has elapsed, the bias voltage of $V_2 = 100$ V is applied to the sample and the temperature is increased at a constant rate. Figure 1 illustrates the principles of TSC experiments for three different heating rates.

3. Results and discussion

3.1. Activation energy and cross-section determination

Figure 2 shows typical TSC curves for $TlInS_2$ single crystal, measured at three linear heating rates of $\beta = 0.10$, 0.17, and 0.30 K/s in the 10–70 K temperature range. The amount of thermally stimulated current gradually increases and the maximum temperatures (T_m) shift to higher temperatures as the heating rate is increased.

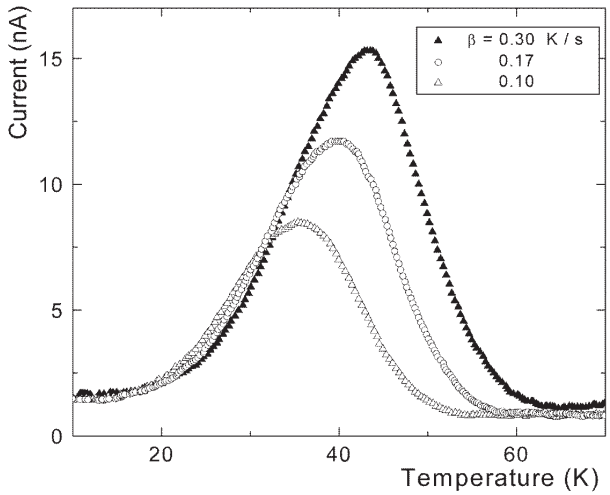

Fig. 2. Experimental TSC curves for $TlInS_2$ crystal, measured at three linear heating rates: 0.10, 0.17, and 0.30 K/s.

There are several methods in the literature to evaluate the trapping parameters from the experimental TSC spectra. We have used the curve fitting, heating rate, and initial rise methods.

3.1.1. Curve fitting method

Under monomolecular conditions (i.e. slow retrapping) the TSC curve of a discrete set of traps with a trapping level E_t below the conduction band is described by the equation [17]:

$$\sigma = n_\mathrm{t}\tau e\mu\nu \exp\left[-\frac{E_\mathrm{t}}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta}\exp\left(-\frac{E_\mathrm{t}}{kT}\right)\mathrm{d}T\right]. \tag{1}$$

Here, σ is the thermally stimulated conductivity, n_t is the initial density of filled traps, τ is the lifetime of a free electron, μ is the electron mobility, β is the heating rate, and T_0 is the temperature at which heating begins after filling the traps, ν is the attempt-to-escape frequency of a trapped electron, k is the Boltzmann constant. If we assume ν to be independent of T and ignore the variation of μ and τ with T over the temperature span of TSC curve, Eq. (1) can be rewritten as [18]:

$$\sigma = A\exp[-t - B\exp(-t)t^{-2}], \tag{2}$$

where $t = E_\mathrm{t}/kT$, and A and B are constants

$$A = n_\mathrm{t}\tau e\mu\nu \qquad \text{and} \qquad B = \frac{\nu E_\mathrm{t}}{\beta k}. \tag{3}$$

If Eq. (2) is differentiated and equated to zero to find the maximum of the curve, which occurs at $t = t_\mathrm{m} = E_\mathrm{t}/kT_\mathrm{m}$, then

$$B = \exp(t_\mathrm{m})\frac{t_\mathrm{m}^3}{t_\mathrm{m}+2}. \tag{4}$$

Good agreement has been obtained between the experimental TSC curve and theoretical one, computed with the assumption of slow retrapping (Fig. 3). This suggests that retrapping does not occur for the traps of $TlInS_2$ studied in the present work. As a result, we have determined trapping center in $TlInS_2$ crystal with activation energy of 12 meV (Table).

TABLE

Activation energy (E_t), capture cross-section (S_t) and concentration (N_t) of traps for TSC peak of $TlInS_2$ crystal.

T_m [K]	E_t [meV]			S_t [cm^2]	N_t [cm^{-3}]
	Curve fitting method [17]	Heating rate method [19]	Initial rise method [20]		
35.2	12	12	11	9.2×10^{-26}	1.7×10^{14}

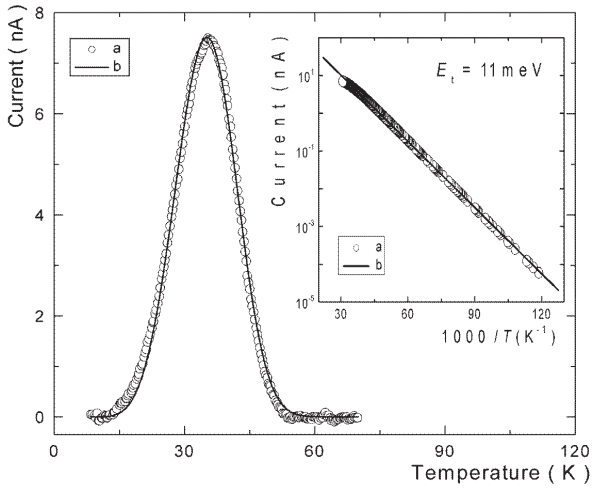

Fig. 3. Experimental TSC spectrum of $TlInS_2$ crystal obtained with heating rate of 0.10 K/s. *a* — experimental data; *b* — theoretical fit to the experimental data. Inset: the plot of current vs. $1000/T$ for initial rise part of TSC peak. *a* — experimental data; *b* — theoretical fit using initial rise method.

Once the curves have been fitted and the values of E_t and T_m for peak are determined (Table), Eqs. (4) and (3) were used to calculate B and the attempt--to-escape frequency ν, respectively. Knowing the value of ν, one can calculate the capture cross-section of the traps according to the following expression:

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

where N_c is the effective density of states in the conduction band and ν_th is the thermal velocity of a free electron. The calculated value of S_t was found to be 9.2×10^{-26} cm^2 (Table). The small value of the capture cross-section justifies the assumption of monomolecular kinetics.

3.1.2. Heating rate method

The relation of the heating rate with peak temperature is expressed as [19]:

$$\beta = \nu \left(\frac{E_\mathrm{t}}{kT_\mathrm{m}}\right)^{-2} \exp\left(-\frac{E_\mathrm{t}}{kT_\mathrm{m}}\right).$$

If we assume the T dependence of ν as $\nu \propto T^a$, then

$$\frac{1}{\beta} = C\frac{E_\mathrm{t}^2}{k^2}\left(\frac{1}{T_\mathrm{m}}\right)^{2+a} \exp\left(\frac{E_\mathrm{t}}{kT_\mathrm{m}}\right), \tag{5}$$

where C is a constant.

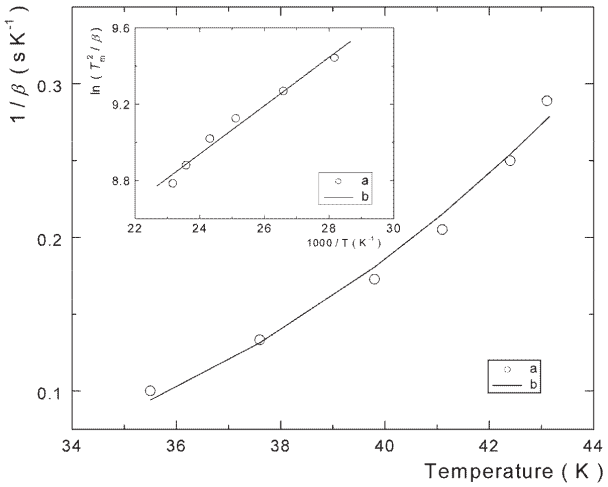

Fig. 4. $1/\beta$ vs. T for six linear heating rates. a — experimental data; b — theoretical fit using Eq. (5). Inset: $\ln(T_{\mathrm{m}}^2/\beta)$ vs. $1000/T$ for six different heating rates. a — experimental data; b — theoretical fit to the experimental data.

If various heating rates are employed and T_{m} are determined as a function of β, it is possible to derive the parameters a and E_{t} from the theoretical fit using Eq. (5) to the experimental data of $1/\beta$ vs. T_{m} (Fig. 4). The results of fitting show that satisfactory fit is obtained with $E_{\mathrm{t}} = 12$ meV and $a = 0$, i.e., ν has no T dependence. The latter result allows us to obtain the energy value of E_{t} from the plot of $\ln(T_{\mathrm{m}}^2/\beta)$ vs. $1/T$ (see inset of Fig. 4). This plot gives a straight line consistent with a trap depth of 12 meV.

3.1.3. Initial rise method

Initial rise method [20], valid for all types of recombination kinetics, is based on the assumption that, when the traps are emptied with increase in temperature, the TSC is proportional to $\exp(-E_{\mathrm{t}}/kT)$. Thus, a plot of the logarithm of the current versus $1/T$ should yield a straight line with a slope of $(-E_{\mathrm{t}}/k)$, as shown in inset of Fig. 3. The activation energy of the traps calculated by this procedure is found to be 11 meV (Table).

3.2. Trap concentration determination

The concentration of the traps was estimated using the relation [21]:

$$N_{\mathrm{t}} = \frac{Q}{SLeG}.$$

Here, Q is the quantity of charge released during a TSC experiment and can be calculated from the area under the TSC peaks; S and L are the area and the thickness of the sample, respectively; e is the electronic charge and G is the

photoconductivity gain, which equals to the number of electrons passing through the sample for each absorbed photon. N_t was calculated by assuming $G = 1$, because it was not possible to measure G under the same TSC conditions with the necessary accuracy. The value of N_t obtained for traps is presented in Table.

4. Conclusions

A trapping level at 12 meV has been detected in as-grown $TlInS_2$ layered single crystals by the TSC technique. Since the $TlInS_2$ crystals are not intentionally doped, the observed levels are thought to originate from defects created during the growth of crystals and/or unintentional impurities. The trap parameters were determined by various methods of analysis, and they agree well with each other. The retrapping process is negligible for this level, as confirmed by the good agreement between the experimental results and the theoretical predictions of the model that assumes slow retrapping. The capture cross-section of the traps is calculated to be 9.2×10^{-26} cm^2. Also the concentration of the traps is estimated to be 1.7×10^{14} cm^{-3}.

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