Thermally Stimulated Current Study of Shallow Traps in As-Grown $TlInSe_2$ Chain Crystals

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Thermally stimulated current measurements were carried out on as-grown $TlInSe_2$ single crystals. The investigations were performed in temperatures ranging from 10 to 260 K with heating rate of 0.3 K s^{-1}. The analysis of the data revealed the hole traps levels located at 6 and 57 meV. The activation energies of the traps have been determined using various methods of analysis, and they agree with each other. The concentration (2.8×10^{13} and 3.4×10^{12} cm^{-3}) and capture cross section (4.1×10^{-28} and 2.9×10^{-26} cm^2) of the traps were estimated for peaks A and B, respectively. It was concluded that in these centers retrapping was negligible, as confirmed by the good agreement between the experimental results and the theoretical predictions of the model that assumes slow retrapping.

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1. Introduction

$TlInSe_2$ compound belongs to a class of semiconductors with TlSe-type structure [1]. $In^{3+}Se_2^{2-}$ groups form chains extending along the tetragonal c-axis of the material. These negatively charged chains are bonded together by Tl^{1+} ions. It is rather easy to cleave the crystals along c-axis into two mutually perpendicular planes. Due to its interesting characteristics, the low-dimensional $TlInSe_2$ single crystal has attracted the attention of researchers. The crystal is reported to be implantable in device production field. As for example, a heterojunction based on semiconductors with a chain crystal structure TlSe–$TlInSe_2$ was produced. This heterojunction was reported to be sensitive to the light and hard radiation [2]. Recently, a new semiconductor detector of neutron radiation, based on a $TlInSe_2$ crystal, has been studied [3].

Some of the physical properties of $TlInSe_2$ crystal have been investigated. Particularly, reports on: specific heat capacities [4], piezoelectric properties [5], optical and electrical properties [6, 7], dielectric measurements [8] and thermoelectric power [9] have been published. $TlInSe_2$ has the indirect and direct optical band gaps $E_{gi} = 1.07$ eV and $E_{gd} = 1.35$ eV at room temperature, respectively [10]. $TlInSe_2$ compound exhibits, in its electrical behavior, many nonlinear effects, such as S-type characteristics with voltage oscillations in the negative resistance region, and switching and memory effects [11].

The influence of defects on the performance of optoelectronic devices is a well-known subject. In optoelectronic devices such as LEDs or lasers, defects may introduce nonradiative recombination centers to lower the internal quantum efficiency or even render light generation impossible, depending on defect density. In the case of electronic devices, defects introduce scattering centers lowering carrier mobility, hence hindering high-frequency operation. Thus, it is very useful to get detailed information on energetic and kinetic parameters of trapping centers in semiconductors in order to obtain high-quality devices. Among the several experimental methods for determining the properties of trap centers in semiconductors, thermally stimulated current (TSC) measurements are relatively easy to perform and provide information on trap states [12–19].

The purpose of the present work is to obtain the detailed information about the trapping centers in undoped $TlInSe_2$ chain crystals by TSC measurements.

2. Experimental details

Single crystals of $TlInSe_2$ crystals were grown by the Bridgman method from the stoichiometric melt of the starting materials sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The ampoule was moved in a vertical furnace through a thermal gradient of 20 °C/cm, between the temperatures 375 and 150 °C at a rate of 6 mm/h. The resulting ingots (grey in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The chemical composition of $TlInSe_2$ crystals was determined by energy dispersive

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spectroscopic analysis using JSM-6400 Electron Microscope. The composition of the studied samples (Tl:In:Se) was found to be 25.4:25.2:49.4, respectively. The X-ray powder diffraction technique was used to identify the crystalline nature of $TlInSe_2$ compound. For this purpose, a Philips PW1740 diffractometer with a monochromatic Cu K_α radiation ($\lambda = 0.154049$ nm) at scanning speed of $0.02°2\theta$/s were used. The lattice parameters (determined from the X-ray diffraction patterns) of the tetragonal unit cell, calculated by the least squares computer program "Treor 90", were found to be $a = 0.8071$ and $c = 0.6861$ nm. These parameters were in good agreement with those reported previously [1].

The sample with dimensions of $8.0 \times 4.0 \times 1.5$ mm^3 was used for TSC measurements. Both the hot probe technique and the sign of the Hall coefficient indicated that the samples exhibit p-type conduction [11]. The sample was attached to the copper holder using silver paste. Two electrodes were made using silver paste according to sandwich geometry: one was on the front as a small droplet to allow illumination and the other one was at the back covering the whole surface of the sample to maintain electrical and thermal conductivity. Thin copper wires were used to attach to the electrodes for circuit connection. The copper holder was mounted on the cold finger of the cryostat and the back side was grounded through the sample holder.

The TSC measurements were carried out in the temperature range of 10–260 K using a closed cycle helium cryostat. A Lake–Shore 331 temperature controller was utilized to provide constant heating rate of 0.3 K s^{-1}. A Keithley 228 A voltage/current source and a Keithley 6435 picoammeter were employed for TSC measurements. At low temperatures, carriers were excited by a light emitting diode, generating light at a maximum peak of 2.6 eV. The trap filling was performed by illumination under a bias voltage $V_1 = 0.1$ V for about 300 s at the initial temperature $T_0 = 10$ K. Then the excitation was turned off. After an expectation time 60 s, the bias voltage $V_2 = 1$ V was applied to the sample and the temperature was increased at a constant rate.

3. Results and discussion

When the front surface of the sample is illuminated, both types of carriers are created in this region. Only one type of carriers will be driven along the whole field zone, while the second type is collected very quickly depending on the bias voltage. Only the former can be trapped. It was revealed that if the polarity of the illuminated surface is positive, the intensity of the TSC curve was highest (inset of Fig. 1). It means that the holes are distributed in the crystal and then trapped. Therefore, the peaks appearing in the TSC spectra of $TlInSe_2$ crystal can be assigned to hole traps.

3.1. Activation energy determination

There are several methods to evaluate the trapping parameters from the experimental TSC spectra. We have used the curve fitting, initial rise and peak shape methods for the analysis of the present data.

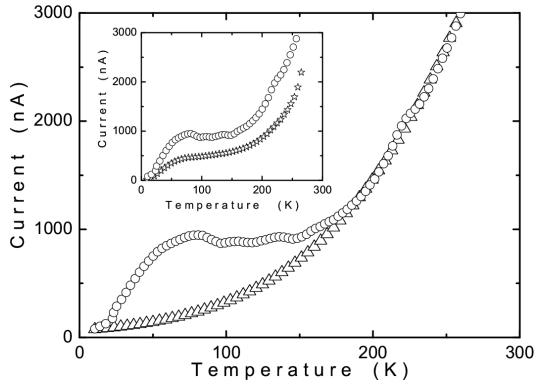

Fig. 1. Typical TSC curve (circles) of $TlInSe_2$ single crystal. The dark current (triangles) is also shown. Inset: experimental TSC curves of $TlInSe_2$ crystals under bias voltage. Circles and stars show the experimental data obtained when the polarity of illuminated surface was positive and negative, respectively.

3.1.1. Curve fitting method

Relative magnitudes of capture cross sections S_t and S_r of the trapping and recombination centers, respectively, play important roles in analysis of TSC data. For $S_t \ll S_r$ the process is monomolecular, i.e. slow retrapping occurs. The cases $S_t = S_r$ and $S_t \gg S_r$ are bimolecular and fast retrapping, respectively. We have tried all possibilities and found that the monomolecular process leads to the best results for present data. For the monomolecular conditions (i.e. slow retrapping), the TSC curve of a discrete set of traps with trapping level E_t is described by [12]:

$$I(T) = n_0 \tau e \mu \nu A \left(\frac{V_2}{L}\right) \times \exp\left(-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(-\frac{E_t}{kT}\right) \mathrm{d}T\right), \quad (1)$$

where n_0 is the initial density of filled traps, τ is the lifetime of a free carrier, μ is the carrier mobility, V_2 is the applied voltage, A and L are the area and the thickness of the sample, respectively, and T_0 is the temperature where heating begins after filling of the traps. If we assume ν to be independent of T and ignore the variation of μ and τ with T over the temperature span of the TSC curve, Eq. (1) can be rewritten as

$$I = A_0 \exp\left(-t + B \int_{t_0}^{t} \exp\left(-\tilde{t}\right) \tilde{t}^{-2} \mathrm{d}\tilde{t}\right), \quad (2)$$

where $t = E_t/kT$, and A_0 and B are constants

$$A_0 = n_0 \tau e \mu \nu \quad \text{and} \quad B = \frac{\nu E_t}{\beta k}. \quad (3)$$

If Eq. (2) is differentiated and equated to zero to find

the maximum of the curve, which occurs at $t = t_m = E_t/kT_m$, then

$$B = \exp(t_m)\, t_m^2. \tag{4}$$

In order to analyze all peaks of spectra simultaneously, the fitting function comprising the sum of all features of the TSC spectra was built as

$$I(T) = \sum_{i=1}^{m} I_i(T)\,, \tag{5}$$

where $I_i(T)$ denotes the current contribution of each peak, calculated by means of Eq. (2), and m denotes the number of trap levels involved in the calculation.

TABLE

The activation energy (E_t), capture cross section (S_t) and concentration (N_t) of traps for two TSC peaks of $TlInSe_2$ crystal.

Peak	T_m [K]	E_t [meV]			S_t [cm^2]	N_t [cm^{-3}]
		Curve fitting method	Peak shape method	Initial rise method		
A	68.7	6	7	5	4.1×10^{-28}	2.8×10^{13}
B	134.4	57	68	56	2.9×10^{-26}	3.4×10^{12}

Figure 1 demonstrates the typical TSC curve of $TlInSe_2$ crystal when the polarity of illuminated surface was positive; the dark current (triangles) is also presented. Figure 2 shows the calculated TSC spectrum of $TlInSe_2$ crystal representing the difference between experimental TSC and dark current curves. Attempts to fit the theoretical curve to experimental data with only single peak were not successful. This fact forced us to fit the data by means of two peaks (designated A and B). As a result we have obtained a good fit for the experimental data. The activation energies for these peaks were found to be $E_{tA} = 6$ meV and $E_{tB} = 57$ meV (Table). A good agreement has been obtained between the experimental TSC data and the theoretical curve computed by assuming slow retrapping. This suggests that retrapping does not occur for the traps of $TlInSe_2$ studied in the present work.

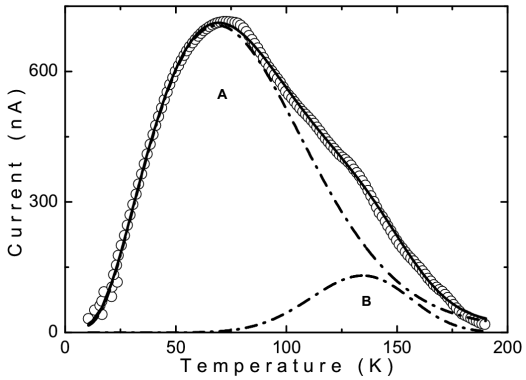

Fig. 2. TSC spectrum of $TlInSe_2$ crystal, representing the difference between experimental TSC and dark current curves, and decomposition of this spectrum into two separate peaks (A and B). Open circles are experimental data. Dashed-dotted curves represent decomposed peaks. Solid curve shows total fit to the experimental data.

3.1.2. Initial rise and peak shape methods

The initial rise method, valid for all types of recombination kinetics, is based on the assumption that the TSC is proportional to $\exp(-E_t/kT)$, when the traps begin to empty with increasing temperature [12]. Thus, a semi-logarithmic plot of the current versus $1/T$ gives a straight line with a slope of $(-E_t/k)$. The plots for TSC peaks of $TlInSe_2$ crystal are shown in Fig. 3. The progressive deviation from the linear behavior at high current for peak A is due to exceeding critical temperature, after which the exponential law is no longer valid [20]. The activation energies of the traps calculated by this procedure were found to be 5 and 56 meV (Table).

The experimental TSC curves for $TlInSe_2$ crystals have also been analyzed by using the peak shape method [21]. In this method, the activation energy can be evaluated by using parameters: $\tau = T_m - T_l$, $\delta = T_h - T_m$, $w = T_h - T_l$ and $\mu_g = \delta/w$, where T_m is the temperature corresponding to the maximum current, T_l and T_h are the low and high half-intensity temperatures, respectively. The activation energies of the traps were determined using the following expressions:

$$E_\tau = [1.51 + 3.0(\mu_g - 0.42)]\, kT_m^2/\tau - [1.58 + 4.2(\mu_g - 0.42)]\, 2kT_m\,,$$

$$E_\delta = [0.976 + 7.3(\mu_g - 0.42)]\, kT_m^2/\delta\,,$$

$$E_w = [2.52 + 10.2(\mu_g - 0.42)]\, kT_m^2/w - 2kT_m\,.$$

The averaged value of the activation energies E_τ, E_δ and E_w for the observed peaks A and B were estimated as 7 and 68 meV, respectively.

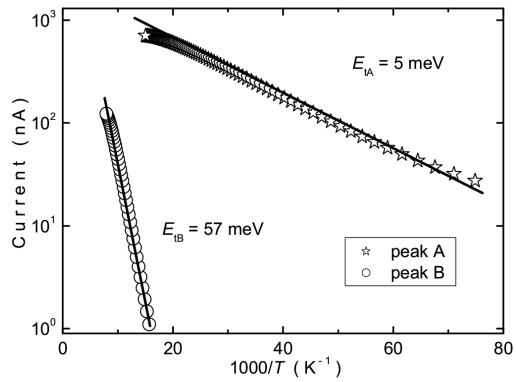

Fig. 3. Thermally stimulated current versus $1000/T$ for peaks in the TSC spectrum of $TlInSe_2$ crystals. Open circles and stars are experimental data. Solid lines are theoretical fits using initial rise method.

3.2. Determination of capture cross section and concentration of the traps

Once the TSC curve was fitted and the values of E_t and T_m were determined (Table), thereafter Eqs. (4) and (3) were used to calculate B and the attempt-to-escape frequency ν, respectively. Knowing the values of $\nu = 0.004$ and 1.11 s^{-1}, the capture cross sections of traps were calculated using relation

$$S_t = \frac{\nu}{N_v v_{th}},$$

where $N_v = 2(2\pi m_h^* kT/h^2)^{3/2}$ is the effective density of states in the valence band and v_{th} is the thermal velocity of a free hole. The effective mass $m_h^* = 0.65m_0$ [22] was utilized to evaluate N_v and v_{th}. Using the latter values, the calculated values of S_t were found to be 4.1×10^{-28} and 2.9×10^{-26} cm^2 for peaks A and B, respectively (Table). It will be noted that the obtained magnitudes of capture cross sections of the traps for studied crystal are low, which suggests a strong repulsive barrier to capture the carriers [23].

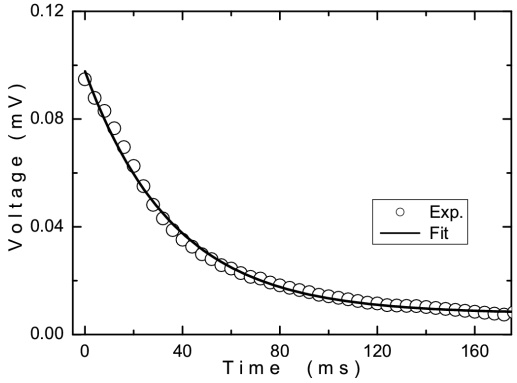

Fig. 4. A photoconductivity decay curve for $TlInSe_2$ crystal. Open circles are experimental data. Solid curve shows the theoretical fit to the experimental data.

The concentration of the traps was estimated using the relation [24]

$$N_t = \frac{Q}{ALeG}, \tag{6}$$

where Q is the amount of charge released during the TSC measurement that can be calculated from the area of the TSC peaks and G is the photoconductivity gain determined from [25]

$$G = \frac{\tau}{t_{tr}} = \frac{\tau \mu V_2}{L^2}. \tag{7}$$

Here, τ is the carrier lifetime and t_{tr} is the carrier transit time between the electrodes. The carrier lifetime can be determined from the photoconductivity decay experiments [26]. The experiments were carried out by developing the setup as follows. We formed a coplanar structure on the sample with ohmic electrodes separated by a small gap and that was illuminated by a high efficiency blue LED controlled by a digital signal generator operating square waves. The photocurrent was amplified by a fast current–voltage converter circuit. The signal was recorded by a fast digital voltmeter and transmitted to the computer. The recorded data were analyzed to determine the decay time of the photocurrent. The current decays are nearly exponential after termination of light pulse at $t = t_0$. The carrier lifetime τ is determined by the corresponding output voltage equation

$$V = V_0 + C \exp\left(-\frac{t}{\tau}\right), \tag{8}$$

where V_0 is the voltage at $t = \infty$ and C is a constant. The theoretical fit (solid line) using Eq. (8) to the experimental data for $TlInSe_2$ crystal is shown in Fig. 4. From the decay of photocurrent, carrier lifetime was obtained as $\tau = 35.3$ ms. The corresponding photoconductivity gain was found to be $G = 941$ from Eq. (7) utilizing $V_2 = 1$ V and $\mu = 600$ cm^2 V^{-1} s^{-1} [22]. The traps concentrations in $TlInSe_2$ crystal were evaluated using Eq. (6) as 2.8×10^{13} and 3.4×10^{12} cm^{-3} for peaks A and B, respectively (Table).

4. Conclusions

Two trapping centers with activation energies of 6 and 57 meV were detected in as-grown $TlInSe_2$ single crystals by TSC technique. Since the crystals studied 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 determined by various methods of analysis agree with each other. The retrapping process is negligible as confirmed by the good agreement between the experimental results and the theoretical predictions of the model that assumes slow retrapping. The capture cross sections of the traps were calculated to be 4.1×10^{-28} and 2.9×10^{-26} cm^2. Also the concentrations of the traps were estimated as 2.8×10^{13} and 3.4×10^{12} cm^{-3}.

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