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Defect characterization in neodymium doped thallium indium disulfide crystals by thermoluminescence measurements

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ABSTRACT

Characteristics of defect centers in neodymium doped $TlInS_2$ single crystals have been investigated in virtue of thermoluminescence measurements carried out at low temperatures (10–300 K) with various heating rates between 0.4 and 1.2 K s^{-1}. One glow peak was detected with peak maximum temperature of 26 K at a rate of 0.4 K s^{-1}. The observed glow peak was analyzed using three points and heating rate methods. The analysis results revealed the presence of one trap level with activation energy of 14 meV. Three points method showed that mixed order of kinetic dominates the trapping level. Shift of peak maximum temperature to higher values and decrease in TL intensity were observed as the heating rate was increased progressively. Distribution of traps was demonstrated using an experimental method based on illumination temperature varying between 10 and 14 K.

1. Introduction

Ternary compounds of semiconductor materials have strong potential and offer remarkable opportunities for the applications in optoelectronic technology thanks to structural, optical and electronic properties [1–4]. $TlInS_2$ is one of the ternary semiconductor compounds with layered structure. Many researchers have investigated the structural, optical and electrical properties of $TlInS_2$ crystals to explore the suitability of the material to the requirements of devices produced in micro- and optoelectronic technology [1,2,5–9]. Recently, thermally stimulated current (TSC) studies on $TlInS_2$ crystals have been reported [10,11]. Existence of shallow and deep trap levels with activation energies of 12, 14 meV [10] and 400, 570, 650 meV [11] were revealed, respectively. Moreover, photoluminescence (PL) investigation of undoped $TlInS_2$ crystal was accomplished in the Ref. [12]. Analysis of observed PL spectra affirmed one deep donor energy level centered at 250 meV and one shallow acceptor level with an energy of 20 meV. Optical and electrical properties of $TlInS_2$ single crystals were also explored by virtue of photoconductivity, dark electrical resistivity, and Hall measurements in temperature regions of 110–350 K, 100–400 K, and 170–400 K, respectively [13]. Lately, we have carried out thermoluminescence (TL) measurements in the temperature range of 10–300 K for the purpose of appointing the trapping levels in $TlInS_2$ crystals [14]. Five peaks were revealed with activation energies 14, 19, 350, 420, and 520 meV in the undoped crystal.

In addition to studies on undoped $TlInS_2$ crystals, researchers have also paid great attention to doped $TlInS_2$ crystals in order for observation of the effects of the doped elements on the optical and electrical properties of the crystal [15,16]. Odrinskii et al. [16] reported the activation energies of deep trap levels in undoped and lanthanum-doped $TlInS_2$ crystal by utilizing the photo-induced current transient spectroscopy (PICTS) technique. PICTS spectra measured at low temperatures depicted successive peaks in the temperature ranges of 93–110 K, 115–135 K, 191–240 K and 240–300 K related to trap levels in undoped crystals with activation energies of 160, 180, 300 and 430 meV, respectively. The same technique revealed the presence of five trap levels in lanthanum-doped $TlInS_2$ crystals corresponding to the peaks observed in the temperature ranges of 98–115 K, 115–135 K, 145–181 K, 190–229 K and 270–320 K with activation energies of 200, 250, 300, 290 and 570 meV [16]. As compared PICTS spectra of undoped and La doped $TlInS_2$ crystals, it was clearly seen that the peak observed in the range of 145–181 K in $TlInS_2$:La crystal were not detected in the undoped crystal. Therefore, the authors attributed this peak to the existence of defect level originating from La dopant. The remaining four trap levels obtained in $TlInS_2$:La crystal were thought as arising from native defects which were already determined in undoped crystal. Moreover, doping with La atom caused to decrease in the intensity of PICTS spectra prominently so that the

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peaks observed in 98–115 K and 115–135 K were nearly absent in the PICTS spectra of $TlInS_2$:La crystal [16].

TL is typically used experimental technique to investigate the characteristics of the energy states occurring in the band gap of the semiconductors and insulators owing to the presence of defects. In the present paper, analysis results of TL measurements performed for $TlInS_2$:Nd single crystal in the temperature range of 10–300 K were reported. Trapping center parameters were revealed using a few methods known from TL theory in the literature.

2. Experimental details

$TlInS_2$ polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. Stoichiometric melt of $TlInS_2$ was doped with Nd of 99.999% purity at 1 at%. A quartz tube which has a tip at the bottom was employed to enclose and to keep the raw materials under 10^{-5} Torr. Bridgman method was used for growing of the single crystal. Vertical furnace that has temperature variation of 30 °C per cm was adjusted to move the prepared material at a rate of 0.5 mm h^{-1} between the temperatures 1000 and 650 °C. The surface of the resulting ingots was quite smooth and had no cracks. The ingot was cleaved to small pieces convenient for measurements using a razor blade perpendicular to the ***c***-axis of the crystal. p-type electrical conductivity was determined for the studied sample by hot-probe method.

TL measurement was performed at low temperatures using a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). Temperature of the environment was managed with a temperature controller (LakeShore Model 331). Illumination and detection processes were carried out with the help of a compactly constructed light-tight chamber comprising a blue light source (~470 nm), a photomultiplier (PM) tube, and the optic elements (mirror and lenses) by connecting to the optical access port of the cryostat (quartz window). The illumination of the sample was realized at 10 K during 600 sec, which is sufficient for saturation of trap level, by directing the light source to the sample in the cryostat via mirror and lenses which were also controlled to detect the luminescence emitted from the sample by PM tube (Hamamatsu R928; spectral response: 185–900 nm). A fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) was employed to convert pulses generated by PM tube into TTL (transistor-transistor logic) pulses. The TTL pulses were counted by the counter of a data acquisition module (National Instruments, NI-USB 6211). Whole measurement system was governed by software written in LabView™ graphical development environment.

3. Results and discussions

Thermoluminescence glow peak recorded for neodymium doped $TlInS_2$ crystals at a heating rate of 0.4 K s^{-1} was shown in the Fig. 1. Due to the lack of TL peak in temperature range detected between 60 and 300 K, merely low side of the TL spectra was represented in the figure. One glow peak correlated to one trapping center in the crystal was observed with peak maximum temperature (T_m) of 26 K. As can be seen from the figure, the shape of the TL peak seems nearly symmetric as the ascending and descending part were compared. This is a powerful indication for the non-first order behavior of the TL peak. In order to calculate the thermal activation energy of the trap and to comprehend the exhibited order of kinetics, three points method improved by Rasheedy [17] was applied to TL peak. This method suggests choosing

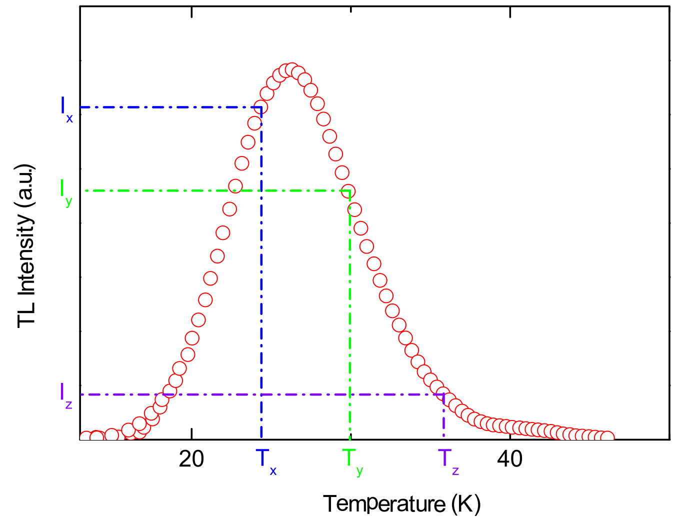

Fig. 1. Experimental TL glow peak observed with heating rate of 0.4 K s^{-1}. The dash-dotted lines are only guides for the eyes.

three arbitrary points on the experimental TL curve to determine the trap parameters. Clearly, assuming the area under the glow curve is proportional to released charge carriers from the trap level, one can obtain the E_t by using the area under the curve remaining between the selected point and final point of the TL peak by utilizing one of the following two equations [17]

$$E_t = \left\{ \ln(y) - b ln(A_x/A_y) \right\} \frac{kT_xT_y}{T_x - T_y}, \quad (1)$$

$$E_t = \left\{ \ln(z) - b ln(A_x/A_z) \right\} \frac{kT_xT_z}{T_x - T_z}, \quad (2)$$

where

$$b = \frac{T_y(T_x - T_z) ln(y) - T_z(T_x - T_y) ln(z)}{T_y(T_x - T_z) \ln\left[\frac{A_x}{A_y}\right] - T_z(T_x - T_y) ln\left[\frac{A_x}{A_z}\right]}. \quad (3)$$

In the Eqs. (1) and (2), A_x, A_y, and A_z are the areas under the curves which are rest of the TL peak after masking the initial part of the peak up to arbitrarily selected temperature points T_x, T_y, and T_z, respectively. y and z are determined as $y=I_x/I_y$ and $z=I_x/I_z$, where I_x, I_y, and I_z are the TL intensities corresponding to T_x, T_y, and T_z (see Fig. 1). b is the order of kinetics. We chose one point from the ascending tail and two points from the descending tail of the TL peak for implementation of the three points method. Thus, the activation energy and order of kinetics were found as E_t=14 meV and b=1.4. Also, the result indicated that the trap levels were dominated by general-order kinetics.

Influence of various heating rates (β) on TL glow curve(s) is one of the remarkable phenomena for investigation of TL properties of trapping states in luminescent materials. In the present work, linear heating rate response of the trap level existing in $TlInS_2$:Nd crystal was studied. Fig. 2 illustrates the TL glow curves achieved through heating the sample with various rates (0.4–1.2 K s^{-1}) in the temperature range of 15–60 K. Shift of T_m value to higher temperatures and decrease in TL intensity with increasing heating rates can be seen from the Fig. 2. Explicit variation of T_m values with increasing heating rate was explained by Anishia et al. in their TL study [18]. Many authors of published papers interpreted the reason of diminishing TL intensity with raising heating rate by ascribing to thermal quenching [19–21]. In addition, full-width-