Trapping Center Parameters in N-Implanted $Tl_2Ga_2S_3Se$ Single Crystals by Thermally Stimulated Currents Measurements

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As-grown $Tl_2Ga_2S_3Se$ crystals have been doped by ion implantation technique. The samples were bombarded at room temperature in the direction perpendicular to the layer by N ion beam of about 120 keV having dose of 1×10^{16} ions/cm^2. The effect of N implantation with annealing at 300 °C was studied by using thermally stimulated current measurements. The investigations were performed in temperatures ranging from 10 to 290 K. The experimental evidence was found for presence of one deep hole trapping center with activation energy of 392 meV. The capture cross-section was calculated as 3.9×10^{-20} cm^2. Also the concentration of the traps was estimated to be 8.0×10^{11} cm^{-3}.

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1. Introduction

The layered-structured semiconductor $Tl_2Ga_2S_3Se$ is formed from $TlGaS_2$ crystal by replacing quarter of the sulfur atoms with selenium atoms. The crystal lattice has two-dimensional layers arranged parallel to the (001) plane [1, 2]. The bonding between Tl and S (Se) atoms in $Tl_2Ga_2S_3Se$ is an interlayer type whereas the bonding between Ga and S (Se) is an intralayer type. The optical and electrical properties of $TlGaS_2$, $TlGaSe_2$, and $Tl_2Ga_2S_3Se$ crystals were studied in Refs. [3–9]. The indirect and direct band gap energies for $Tl_2Ga_2S_3Se$ crystal at room temperature were found as 2.38 and 2.62 eV, respectively. These crystals are useful for optoelectronic applications as they have high photosensitivity in the visible range of the spectra and high birefringence in conjunction with a wide transparency range of 0.5–14.0 μm [8]. In our previous studies [10, 11], we reported the results of thermally stimulated current (TSC) measurements on as-grown $Tl_2Ga_2S_3Se$ layered crystals. The investigations were performed in the temperatures ranging from 10 to 320 K with heating rates of 0.6–1.2 K s^{-1}. The analysis of the data revealed one electron and one hole trap levels located at 11 and 498 meV, respectively.

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. Among the several experimental methods for determining the properties of trap centers in semiconductors, TSC measurements are relatively easy to perform and provide detailed information on trap states [12–19].

The purpose of the present work is to obtain detailed information concerning trapping centers in N-doped $Tl_2Ga_2S_3Se$ layered crystals using the well-established technique of TSC measurements. We utilized two methods to analyze the measured TSC spectra. The activation energy, the capture cross-section and the concentration of the hole traps in N-doped $Tl_2Ga_2S_3Se$ crystals are reported.

2. Experimental details

$Tl_2Ga_2S_3Se$ polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals of $Tl_2Ga_2S_3Se$ were grown by the Bridgman method. The resulting ingot appears red in color and the freshly cleaved surfaces were mirror-like. For the implantations, the surface of sample parallel to the layers was bombarded at room temperature by nitrogen ion beam of about 120 keV having dose of 1×10^{16} ions/cm^2. The sample dimensions were 6.0×5.5 mm^2. In the TSC spectra, no peak was observed before doping and annealing of the selected sample. After doping, the annealing was performed in argon medium for the sample at temperature 300 °C for 45 min, to possibly remove the damage induced by implantation and also to activate nitrogen related doping centers. For TSC measurements, electrical contacts were made on the sample surface with silver paste according to "sandwich" geometry. In this configuration, the electrodes are placed on the front and back sides of the sample. Thin copper

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wires were attached to the electrodes for circuit connection.

The TSC measurements were performed in the temperature range from 10 to 290 K using a closed-cycle helium cryostat. The sample was mounted on the cold finger of the cryostat. Constant heating rate of 0.3 K s^{-1} was achieved by a Lake–Shore 331 temperature controller. A Keithley 228 A voltage/current source and a Keithley 6485 picoammeter were used for the TSC measurements. The temperature and current sensitivities of the system were about 10 mK and 2 pA, respectively.

At low enough temperatures, when the probability of thermal release is negligible, the carriers are photoexcited by using a light emitting diode generating light at a maximum peak of 2.6 eV. The trap filling was performed by illumination under bias voltage of $V_1 = 1$ V at the initial temperature $T_0 = 10$ K for about 10 min. Then the excitation was turned off. After an expectation time (≈ 60 s) the bias voltage of $V_2 = 100$ V was applied to the sample and temperature was increased at constant rate.

3. Results and discussion

Figure 1 demonstrates the typical TSC curve of N-doped $Tl_2Ga_2S_3Se$ crystal, the dark current (triangles) is also presented. Inset of Fig. 1 shows the calculated TSC spectrum representing the difference between experimental TSC and dark current curves. TSC measurements carried out on the N-doped $Tl_2Ga_2S_3Se$ crystals in the temperature range of 10–290 K showed that there is one peak in the TSC curve starting to exist nearly at 175 K and ending nearly at 290 K (inset of Fig. 1). Therefore, the figures related to TSC measurements in this study were plotted in the 175–290 K temperature range. To change the initial density of traps, the TSC spectra of $Tl_2Ga_2S_3Se$ crystal were recorded for different illumination times (0–600 s) at constant heating rate of $\beta = 0.3$ K s^{-1}. The shape of the TSC spectra and $T_{\max}$ values remained almost invariable for different values of illumination time. This result indicates that the observed trap may be considered under the monomolecular (slow retrapping) conditions. It was established that traps are filled completely after nearly 600 s. Therefore, the illumination time for TSC experiments was taken as 600 s. Moreover, it was revealed that if the polarity of the illuminated sample surface is positive, the intensity of the TSC curve was highest. It means that the holes are distributed in the crystal and then trapped. Therefore, the peak appearing in the TSC spectra of N-doped $Tl_2Ga_2S_3Se$ crystal can be assigned to hole traps.

The theoretical form of the TSC curve of a discrete set of traps with trapping level E_t is described under the monomolecular conditions (i.e., slow retrapping) by the equation [20]:

$$I(T) = C \exp\left(-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(-\frac{E_t}{kT}\right) dT\right), \quad (1)$$

where C is a constant which depends on the experimental conditions and properties of the crystal, ν is the attempt-to-escape frequency, k is the Boltzmann constant, β is the heating rate and T_0 is the temperature at which heating begins after filling of the traps. When the curve fit method [21] was used to analyze the experimental data under the theoretical approach of slow retrapping process, data were fitted successfully with one peak (solid curve in inset of Fig. 1) having the activation energy of $E_t = 392$ meV. The capture cross-section ($S_t = 3.9 \times 10^{-20}$ cm^2) and attempt-to-escape frequency ($\nu = 1.9 \times 10^6$ s^{-1}) of the observed trap were calculated according to the expressions presented in Ref. [21] and using the value of E_t and peak temperature ($T_m = 247.5$ K) determined from the curve fit analysis. For these evaluations the effective mass of holes was taken as $m*_h = 0.4m0_0$ [22].

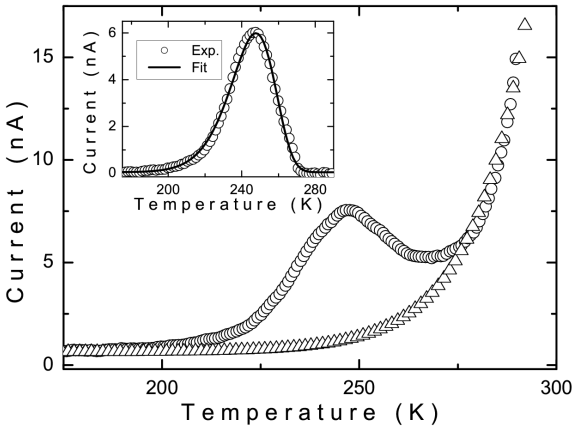

Fig. 1. Typical TSC curve (circles) of N-doped $Tl_2Ga_2S_3Se$ crystal. The dark current (triangles) is also shown. Inset: TSC spectrum of N-doped $Tl_2Ga_2S_3Se$ crystal, representing the difference between experimental TSC and dark current curves. Open circles are experimental data. Solid curve shows the fit to the experimental data.

The derivative of the natural logarithm of the thermally stimulated current (Eq. (1)), under the assumption of that v is independent of T, is obtained as

$$\frac{d(\ln I)}{dT} = \frac{E_t}{kT^2} - \frac{\nu_t}{\beta} \exp\left(-\frac{E_t}{kT}\right). \quad (2)$$

Since the current is maximal at $T = T_m$, Eq. (2) yields

$$\frac{E_t}{kT_m^2} = \frac{\nu_t}{\beta} \exp\left(-\frac{E_t}{kT_m}\right). \quad (3)$$

Using Eq. (3), the second derivative of the $\ln(I)$ can be written at the peak maximum temperature as

$$\left[\frac{d^2(\ln I)}{dT^2}\right]_m = -\frac{E_t}{kT_m^3}\left(2 + \frac{E_t}{kT_m}\right) = \alpha_m. \quad (4)$$

Activation energy of the observed trap can be calculated from the slope of the tangent (α_m) at $T = T_m$ of the first derivative of the TSC curve. When the graph of the first derivative of the current is plotted (Fig. 2), it was revealed that the derivative is equal to zero at $T_m = 247.5$ K with a tangential slope of $\alpha_m = -6.2 \times 10^{-3}$.

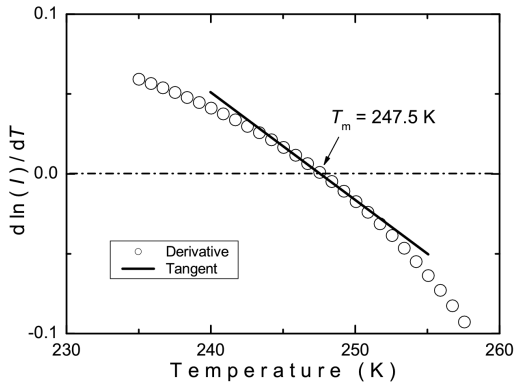

Fig. 2. Derivative of the thermally stimulated current of N-doped $Tl_2Ga_2S_3Se$ crystal. Open circles are experimental data and the line is the tangent at $T_m = 247.5$ K.

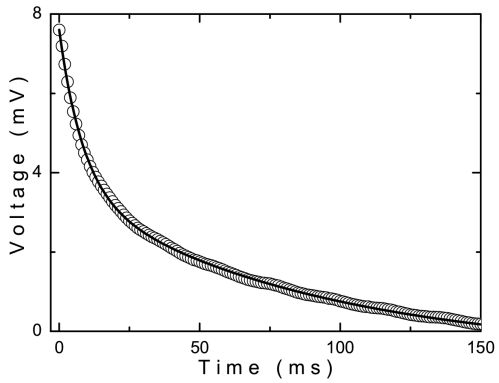

Fig. 3. A photoconductivity decay curve for N-doped $Tl_2Ga_2S_3Se$ crystal. Open circles are experimental data. Solid curve shows the theoretical fit to the experimental data.

The activation energy of the trap corresponding to this α_m value is found from Eq. (4) as $E_t = 395$ meV.

The concentration of the traps was estimated using the relation [23]:

$$N_t = \frac{Q}{ALeG}, \tag{5}$$

where Q is the amount of charge released during the TSC measurement, that can be calculated from the area of the TSC peak, e is the electronic charge, G is the photoconductivity gain, A and L are the area and length of the sample, respectively. The photoconductivity gain G was calculated from the expression [24]:

$$G = \frac{\tau}{t_{tr}} = \frac{\tau \mu V_3}{L^2}, \tag{6}$$

where τ is the carrier lifetime, t_{tr} is the carrier transit time between the electrodes, V_3 is the applied voltage and μ is the carrier mobility. We used the photoconductivity decay experiments to obtain the carrier lifetime and then to calculate the photoconductivity gain G. The photocurrent decay is nearly exponential after termination of light pulse at $t = t_0$. The carrier lifetime τ was determined from the corresponding output voltage expressed as [25]:

$$V = V_0 + D \exp\left(-\frac{t}{\tau}\right), \tag{7}$$

where V_0 is the voltage at $t = \infty$ and D is a constant. Figure 3 shows the theoretical fit to the experimental data using Eq. (7) for N-doped $Tl_2Ga_2S_3Se$ crystal. The carrier lifetime was obtained as 21 ms from the decay of the photocurrent. The corresponding photoconductivity gain was found to be 197 from Eq. (6), using $V_3 = 1$ V and $\mu = 60$ cm^2/(V s) [22]. Then, the value of concentration obtained for traps is evaluated as $N_t = 8.0 \times 10^{11}$ cm^{-3}.

4. Conclusions

TSC measurements on the N-doped $Tl_2Ga_2S_3Se$ crystal revealed that there exists one hole trapping center at 392 meV energy level. Since TSC peak was not seen in the spectra before doping and annealing, the observed level is thought to originate from N centers, created by doping and annealing processes. 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-section of the trap is calculated to be 3.9×10^{-20} cm^2. Also the concentration of the trap is estimated to be 8.0×10^{11} cm^{-3}.

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