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Trapping centers and their distribution in $Tl_2In_2Se_3S$ layered single crystals

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ABSTRACT

Thermally stimulated current (TSC) measurements have been carried out on $Tl_2In_2Se_3S$ layered single crystals in the temperature range of 10–175 K. The TSC spectra reveal the presence of two peaks (A and B). The electronic traps' distributions have been analyzed by different light illumination temperature techniques. It was revealed that the obtained traps' distribution can be described as an exponential one. The variations of one order of magnitude in the traps' density for every 30 meV (A peak) and 59 meV (B peak) were estimated. Moreover, the mean activation energy, attempt-to-escape frequency, capture cross section and concentration of the traps were determined.

1. Introduction

The compound $Tl_2In_2Se_3S$ belongs to the group of layered semiconductor families. This crystal is a structural analog of $TlInS_2$, in which three quarters of sulfur atoms are replaced by selenium atoms [1]. The crystal lattice consists of alternating two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by a 90° angle with respect to the previous layer. Interlayer bonding is formed between Tl and S(Se) atoms while the bonding between In and S(Se) atoms is an intralayer type. The fundamental structural unit of a layer is the $In_4S_6(Se_6)$ adamantane-like units linked together by bridging S(Se) atoms. The Tl atoms form nearly planar chains along the [110] and [1$\bar{1}$0] directions.

In our previous study, energy dispersive spectroscopic, X-ray powder diffraction, transmission and photoluminescence (PL) measurements were performed for $Tl_2In_2Se_3S$ crystals [2]. As a result, the compositions of the studied samples (Tl:In:Se:S) were found to be 25.7:25.9:36.2:12.2, respectively. The parameters of the monoclinic unit cell were determined as $a = 0.70674$, $b = 0.79060$ and $c = 0.56367$ nm, and $\beta = 92.56°$. From transmission and reflection measurements, the indirect band gap energy was found to be $E_{gi} = 2.08$ eV at room temperature. A broad emission band centered at 633 nm (1.96 eV) was observed in the PL spectra at $T = 25$ K. The variation of the spectra with laser excitation intensity and temperature suggested that the transitions between the donor and acceptor levels were responsible for the observed emission band. As the studied crystals were not intentionally doped, the acceptor states were thought to originate from uncontrolled impurities or point defects, created during crystal growth [2].

Ternary and quaternary layered–structured semiconductors show many peculiar properties. There is a large number of applications such as memory switching elements, emission modulators and nonlinear optical transducers in nonlinear optics and photoelectronics [3,4].

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 the 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 detailed information on trap states [5–12].

The purpose of the present work is to obtain the detailed information about the trapping centers and their distribution in undoped $Tl_2In_2Se_3S$ layered single crystals by TSC measurements.

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2. Experimental details

$Tl_2In_2Se_3S$ polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. $Tl_2In_2Se_3S$ single crystals were grown by the Bridgman method 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 30 °C cm^{-1}, between the temperatures 760 and 410 °C at a rate of 1.0 mm h^{-1}. The resulting ingots (red in color) showed good optical quality and the freshly cleaved surfaces were mirror-like. The sample with dimensions of 11.0 × 11.0 × 1.5 mm^3 was used for TSC measurements. The electrical conductivity of the studied sample was *n*-type as determined by the hot probe method. 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. The conductivity of studied crystals within the layer is about four orders of magnitude higher than that normal to the layer [13]. Therefore, the distribution of electric field lines through the sample covers almost all the volume for the current contact configuration. 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 10–175 K using a closed cycle helium cryostat. A Lake-Shore 331 temperature controller was utilized to provide constant heating rates in the range of 0.4–1.0 Ks^{-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. Generally, the trap filling was performed by illumination under a bias voltage $V_1 = 1$ V for about 1300 s at the initial temperature $T_0 = 10$ K. However, for the revealing of traps distribution, they were filled at different illumination temperatures ($T_{0i} = 10$, 20, 30, 40, 50 and 60 K). Then the excitation was turned off. After an expectation time 300 s, the bias voltage $V_2 = 100$ V was applied to the sample and the temperature was increased at a constant rate. As the dark current contribution was low in $Tl_2In_2Se_3S$, a bias voltage $V_2 = 100$ V could be applied during heating. The illumination and heating parameters of the optimum TSC conditions for $Tl_2In_2Se_3S$ crystal are shown in Fig. 1.

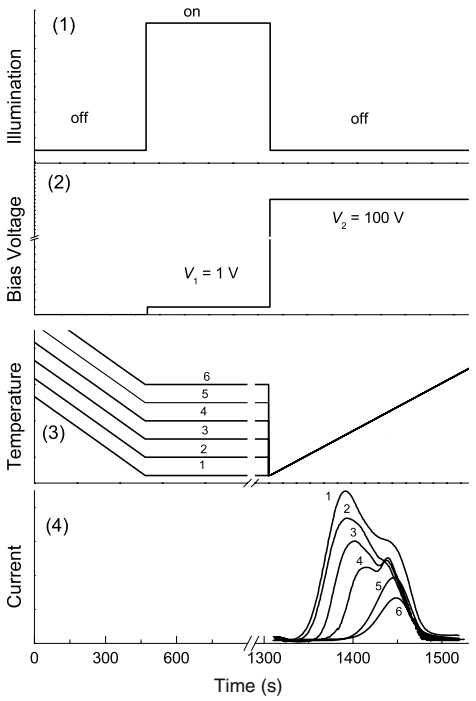

Fig. 1. Principles of the TSC experiment for $Tl_2In_2Se_3S$ crystals; (1) time period of applied illumination; (2) variation of bias voltage; (3) temperature variation with time for six different light illumination; (4) TSC spectra for six different light illumination temperatures: 10 (1), 20 (2), 30 (3), 40 (4), 50 (5) and 60 K (6).

3. Results and discussion

Relative magnitudes of capture cross sections S_t and S_r of the trapping and recombination centers, respectively, play important roles for 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. For slow retrapping process, electrons thermally excited from traps have greater probability of recombining with holes than being retrapped. In this case, the initial density of filled traps has no effect on both the shape and peaks positions of the TSC curves. Fig. 2 shows the TSC spectra of $Tl_2In_2Se_3S$ crystal registered for different illumination time (50–2700 s) at a constant heating rate of $\beta = 0.8$ K s^{-1}. The plot of the maximum values of TSC (I_{max}) versus illumination time is presented in the inset of Fig. 2. To vary the initial density of filled traps, the illumination time altered and it was observed that there was no change for both the shapes and the peaks positions of A and B peaks in TSC curves. It suggests that the traps may be considered under monomolecular condition. Since the increasing the illumination time from 1300 to 2700 s did not lead to the change for the shapes and the positions of A and B peaks in TSC curves, to decrease the duration of experiment as well as to economize helium gas we carried out the TSC measurements using the illumination time 1300 s.

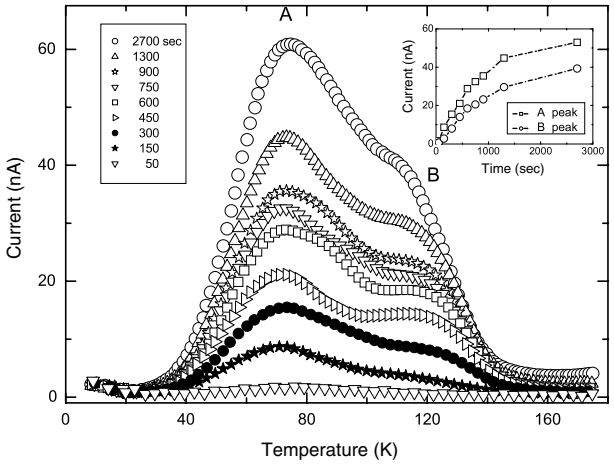

Fig. 2. TSC spectra of the $Tl_2In_2Se_3S$ crystals for various illumination times at a constant rate $\beta = 0.8$ K s^{-1}. Inset: Maximum thermally stimulated currents of A and B peaks as a function of time. The dash-dotted lines are only guides for the eye.

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. Inset of Fig. 3 shows the TSC spectra of $Tl_2In_2Se_3S$ for two biasing polarities at a constant rate of $\beta = 0.8$ K s^{-1} in the temperature range of 10–160 K. If the polarity of the illuminated surface is negative, the intensity of the peaks are highest. It means that the electrons are distributed in the crystal and then trapped. Therefore, the peaks appearing in the TSC spectra of $Tl_2In_2Se_3S$ crystal can be assigned to electron traps.