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Thermally stimulated currents in layered Ga_4SeS_3 semiconductor

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Thermally stimulated current (TSC) measurements are carried out on nominally undoped Ga_4SeS_3 layered semiconductor samples with the current flowing along the *c*-axis in the temperature range of 10 to 150 K. The results are analyzed according to various methods, such as curve fitting, initial rise and Chen's methods, which seem to be in good agreement with each other. Experimental evidence is found for the presence of three trapping centers in Ga_4SeS_3 with activation energies of 70, 210 and 357 meV. The calculation yielded 7.9×10^{-21}, 7.0×10^{-19} and 1.5×10^{-13} cm^2 for the capture cross section, and 1.6×10^{10}, 6.5×10^{10} and 1.2×10^{11} cm^{-3} for the concentration of the traps studied.

1 Introduction

Ternary gallium chalcogenide Ga_4SeS_3 is formed from the GaS–GaSe system and has an indirect band gap of 2.42 and 2.49 eV at T = 300 and 4.2 K, respectively [1, 2]. Ga_4SeS_3 crystals, like binary compounds GaS and GaSe, have a layered structure. Each layer has four atomic planes with the sequence S(Se)–Ga–Ga–S(Se). The interlayer bonds are van der Waals type and weak, while the intralayer bonds are covalent and strong. The physical properties of the GaS–GaSe system are of interest in view of possible optoelectronic device applications in the visible region. By varying the composition of the GaS–GaSe system, the energy gap of the complete series covers a wide range of the visible spectrum. These crystals are promising materials for the production of light emitting and optical switching devices [3, 4] and photodetectors [5]. One of the determining factors in the eventual device performance of semiconductors is the presence of impurity and defect centers in the crystal. Thus, it is very useful to get detailed information on energetic and kinetic parameters of such centers in Ga_4SeS_3 semiconductor in order to obtain high-quality devices.

There is only one paper in the literature concerning the study of thermally stimulated currents (TSC) in GaS–GaSe system in the high-temperature range 80–300 K [6]. These crystals were grown using the iodine-assisted chemical transport method. Three trap levels with activation energies of 165, 425 and 610 meV have been found in the band gap. In our previous paper [7], we presented the results of a photoluminescence (PL) investigation of Ga_4SeS_3 crystals in the 500–850 nm wavelength region and in the 10–200 K temperature range. The study resulted in the observation of two PL bands centered at 527 nm (2.353 eV) and 658 nm (1.884 eV) at T = 10 K. Two donor levels located at 43 and 64 meV are determined from the temperature dependence of PL intensity.

The purpose of the present work is to obtain further detailed information concerning deep and shallow traps in undoped Ga_4SeS_3 crystals using the well-established technique of TSC measurements. In con-

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trast with previous TSC measurements on GaS–GaSe system, we employ for the first time a wide temperature range of 10–300 K. The measurements in the temperature range below 80 K allow us to check for the possibility of shallow trap states. We report on the activation energy, the capture cross section and concentration of the traps in Ga_4SeS_3 crystals.

2 Experimental details

Ga_4SeS_3 polycrystals were synthesized from the elements with purity better than 99.999%, taken in stoichiometric proportions. Single crystals of Ga_4SeS_3 were grown by the Bridgman method. The X-ray diffraction data showed that Ga_4SeS_3 crystallizes in hexagonal unit cell with lattice parameters: a = 0.3625 and c = 1.5690 nm. Crystals suitable for measurements were obtained by easy cleavage of an ingot along the layers, which are perpendicular to the c-axis. Typical sample dimensions were 5.5 × 4.2 × 1.5 mm^3. The room-temperature conductivity, mobility and electron concentration were 9×10^{-10} $(\Omega\ cm)^{-1}$, 48 $cm^2\ V^{-1}\ s^{-1}$ and 3×10^9 cm^{-3}, respectively.

Electrodes were deposited by evaporating gold under high vacuum, on both crystal surfaces in a sandwich geometry. Their thickness was about 100 nm on the back side and 10 nm on the front side, the latter corresponding to higher transmittance of the incident light. The sample was mounted on the cold finger of a cryostat with conducting silver paste. The back side was grounded through the sample holder. A thin gold wire was attached to the front side electrode by small droplet of silver paste. The *I–V* characteristics were checked to be symmetric with respect to the polarity.

All measurements were carried out in vacuum in a "CTI-Cryogenics M-22" closed-cycle helium system. The traps were filled by creating carriers with band-to-band photoexcitation of the samples. The light source was a 488.0 nm line (2.541 eV, 50 mW) of a "Spectra Physics" argon laser. The thermally stimulated currents were measured by a "Keithley 619" electrometer. The TSC and temperature data were stored in a personal computer.

In a typical experiment, the samples are cooled down to T = 10 K and kept at this temperature for ~10 min. Then they are illuminated through the semitransparent front electrode for a fixed period of time (t = 25 min) under particular biasing condition and left for ~10–25 min to allow the photoconductivity signal to decay after exposure to light. The samples are then heated with a constant rate β = 0.18 K s^{-1} from 10 up to 300 K at an applied bias voltage of 100 V.

3 Results and discussion

Figure 1 shows a typical TSC curve for Ga_4SeS_3 crystal measured with heating rate of β = 0.18 K s^{-1}. We were unable to measure the TSC spectra in the high-temperature region (T > 150 K) due to strong increase of dark conductivity. At temperatures of 55.7, 116.8 and 126.2 K, three peaks appear after isolat-

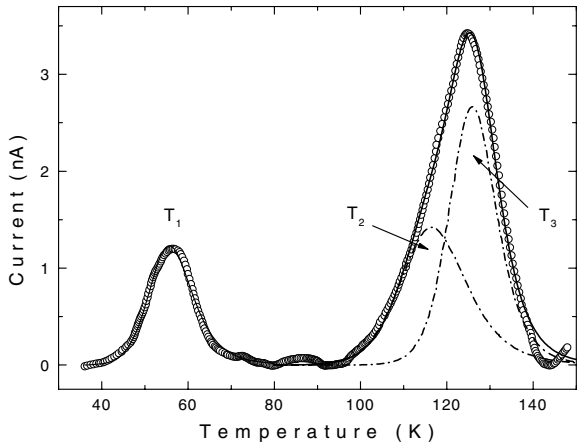

Fig. 1 Experimental TSC spectra of Ga_4SeS_3 crystal with heating rate of 0.18 Ks^{-1} and decomposition of high-temperature part of this spectrum into two separate peaks. Open circles are experimental data. Dashed curves represent decomposed peaks. Solid curve shows total fit to the experimental data.

ing the TSC peak by a curve-fitting technique, with the last two overlapping each other. Activation energies and capture cross section of the traps are determined using three different methods: curve-fitting, peak-shape and initial-rise methods.

3.1 Curve-fitting method

The theoretical form of the TSC curve corresponding to a discrete trap that empties with retrapping (second-order kinetics) is given by the following Eq. [8]:

$$\sigma = \frac{n_{t0}^2 \tau \mu e \nu \exp(-E_t/kT)}{N_t \left[1 + \frac{n_{t0}}{N_t} \frac{\nu}{\beta} \int_{T_0}^{T} \exp\left(-E_t/kT\right) dT\right]^2}. \tag{1}$$

Here, σ is the thermally stimulated conductivity, n_{t0} the initial density of filled traps, E_t the trap depth, N_t the density of traps, τ the lifetime of a free electron, μ the electron mobility, β the heating rate and T_0 the temperature from which heating begins following the filling of the traps. $\nu = N_c \upsilon_{th} S_t$ is the attempt-to-escape frequency of a trapped electron, where N_c is the effective density of states in the conduction band, υ_{th} the thermal velocity of a free electron and S_t the capture cross section of the trap.

If it is assumed that ν is independent of T and that over the temperature span of the TSC curve, the variation of μ and τ with T can be ignored and that $n_{t0} = N_t$, which means that all the traps are filled, then Eq. (1) can be rewritten as [9]

$$\sigma = \frac{A \exp\left(-t\right)}{[1 + B \exp\left(-t\right) t^{-2}]^2}, \tag{2}$$

where $t = E_t/kT$, and A and B are constants: $A = n_{t0} \tau e \mu \nu$ and $B = \nu E_t/\beta k$.

If Eq. (2) is differentiated and equated to zero to find the maximum of the curve, which occurs when $t = t_m = E_t/kT_m$, then

$$B = \exp(t_m) \frac{t_m^3}{(t_m + 4)}. \tag{3}$$

Moreover, it is possible to calculate the capture cross section S_t with the following expression:

$$S_t = \frac{\beta E_t^2}{\left(E_t + 4\, kT_m\right) N_c \upsilon_{th} k T_m^2} \exp\left(\frac{E_t}{kT_m}\right). \tag{4}$$

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

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

where $\sigma_i(T)$ denotes the conductivity contribution of each peak, calculated by means of Eq. (2), and m denotes the number of traps involved in the calculation.

Good agreement between the experimental TSC curve and the theoretical one, computed with the assumption of second-order kinetics suggests that retrapping does occur for the trapping centers studied (Fig. 1).

The procedure described above allowed us to obtain E_t and T_m for each peak directly from the fit. As a result, we have determined three trapping centers with activation energies of 70, 210 and 357 meV (Table 1). Then using Eq. (4) and $\nu = B\beta k/E_t$ we calculated the capture cross section and attempt-to-escape frequency, respectively, for peaks T_1, T_2 and T_3 (Table 1).

Table 1 The activation energy (E_t), capture cross section (S_t), attempt-to-escape frequency (ν) and concentration (N_t) of traps for three TSC peaks of Ga_4SeS_3 crystal.

peak	T_m (K)	E_t (meV)			S_t (cm^2)	ν (s^{-1})	N_t (cm^{-3})
		curve-fitting method	peak-shape method	initial-rise method			
T_1	55.7	70	77	67	7.9×10^{-21}	8.0×10^{4}	1.6×10^{10}
T_2	116.8	210	207	205	7.0×10^{-19}	3.1×10^{5}	6.5×10^{10}
T_3	126.2	357	343	352	1.5×10^{-13}	7.6×10^{12}	1.2×10^{11}

3.2 Peak-shape method

In the peak-shape method [8], the activation energy of trap is evaluated by using three parameters: $\tau = T_m - T_l$, $\delta = T_h - T_m$, $w = T_h - T_l$, 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 energy of the trap is then

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

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

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

Here $\mu_g = \delta/w$, the values of which were predicted by Chen and Kirsh [8] as 0.42 for first-order and 0.52 for second-order kinetics. The determined values of μ_g parameter for peaks T_1, T_2 and T_3 were found to be 0.53, 0.52, and 0.51, respectively. Therefore, the observed TSC peaks should be related to second-order kinetics. The averaged values of calculated activation energies E_τ, E_δ, and E_w for three peaks are reported in Table 1.

3.3 Initial-rise method

The initial-rise method [8], valid for all types of recombination kinetics, is based on the assumption that, when the traps begin to empty as the temperature is increased, the intensity of TSC is proportional to exp ($-E_t/kT$). Thus, a plot of the logarithm of the current intensity against $1/T$ should yield a straight line with a slope of ($-E_t/k$), as shown in Fig. 2. The progressive shift from the linear behavior at high current is due to exceeding the critical temperature T_c, after which the exponential law is no longer valid [10]. The activation energies of the traps calculated by this procedure are found to be 67, 205 and 352 meV for peaks T_1, T_2 and T_3, respectively (Table 1).

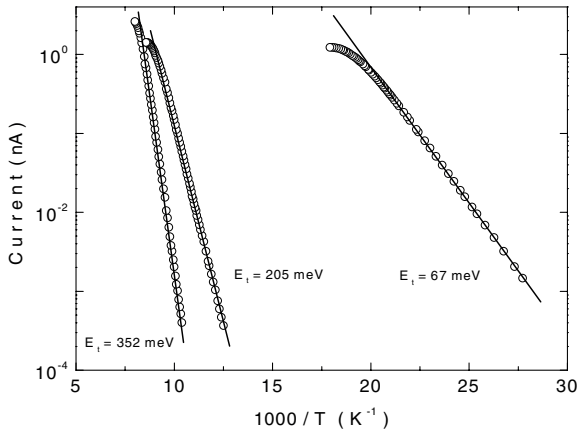

Fig. 2 TSC vs. 1000/T for all three peaks in TSC spectrum of Ga_4SeS_3 crystal. Open circles and solid lines represent experimental data and theoretical fits using initial-rise method, respectively.

At this point, it may be informative to compare these results with our previous observations on Ga_4SeS_3 crystals using PL spectroscopy, which yielded two levels at 43 and 64 meV [7]. These levels were obtained from the temperature dependence of the PL intensity. From the present results of TSC, we observe three trap levels at 70, 210 and 357 meV. It is clear that the PL level observed at 43 meV is not observed in the TSC experiments and the levels at 210 and 357 meV obtained from TSC measurements are not observed in the PL experiments. The only energy levels that are close in energy, are located at 64 meV (PL) and 70 meV (TSC). Taking into account the errors in determining the values of energy levels (about 5%) with either of the two methods (PL and TSC), we may possibly assign the obtained energies of 64 and 70 meV to the same level. We suppose that this level is partially compensated, allowing for both PL emission and thermally stimulated current.

In the previous study mentioned above, three trap levels with activation energies of 165, 425 and 610 meV have been found in the band gap of crystals grown using the iodine-assisted chemical transport method [6]. There, the two traps with lowest energies were assigned to the presence of iodine, incorporated during crystal growth, while the last one was associated with vacancies of S or Se. Considering that our samples were grown using the modified Bridgman method with no intentional doping, it is not surprising that we did not observe the levels at 165 and 425 meV, as in [6]. Furthermore, the level with an energy of 610 meV was beyond the temperature limit of our detection range.

3.4 Trap-concentration determination

The concentration of the traps was estimated using the relation [11]

$$N_t = \frac{Q}{ALeG}.$$

Here, Q is the quantity of charge released during a TSC experiment and can be calculated from the area under the TSC peaks; A and L are the area and the thickness of the sample, respectively; e is the electronic charge and G is the photoconductivity gain. The latter parameter was evaluated from the ratio

$$G = \frac{\tau}{t_r} = \frac{\tau \mu V}{L^2},$$

where τ is the electron lifetime, t_r is the electron transit time between the electrodes, V is the applied voltage and μ is the electron mobility. Electron lifetimes measured from the decay of photocurrent were equal 5.0×10^{-3}, 2.0×10^{-3} and 1.6×10^{-3} s for the peaks T_1, T_2 and T_3, respectively. The corresponding values of G were found to be 1070, 430 and 340, respectively. The values of N_t obtained for three traps are presented in Table 1.

4 Conclusions

Three trapping levels at 70, 210 and 357 meV have been detected in as-grown n-Ga_4SeS_3 layered crystals by the TSC technique. These levels in undoped layered crystals may be associated with the presence of stacking faults and/or unintentional impurities. The activation energies of the peaks, evaluated by the curve-fitting method, and also calculated using the initial-rise and Chen's methods from the isolated peaks, are in agreement with each other, within the accuracy of the method used. The retrapping process is accomplished for these levels, as confirmed by the good agreement between the experimental results and the theoretical predictions of the second-order kinetics model. The capture cross section of the traps were calculated to be 7.9×10^{-21}, 7.0×10^{-19} and 1.5×10^{-13} cm^2. The concentrations of the traps were evaluated as 1.6×10^{10}, 6.5×10^{10} and 1.2×10^{11} cm^{-3}.

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