



## Thermally stimulated currents in *n*-InS single crystals

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### Abstract

Thermally stimulated current measurements are carried out on as-grown *n*-InS single crystals in the temperature range of 10–125 K. Experimental evidence is found for four trapping centers present in InS. They are located at 20, 35, 60 and 130 meV. The trap parameters have been determined by various methods of analysis, and they agree well with each other.

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### 1. Introduction

The family of III–VI semiconducting compounds such as GaS, GaSe, InSe, and InS has as a characteristic, the coexistence of cation–cation and cation–anion bonds. GaS, GaSe and InSe show an easy cleavage due to layered structures, but InS does not show it. InS crystallizes in an orthorhombic structure composed of the ethane-like  $S_3InInS_3$  atomic arrangement mutually linked by sharing S corners. Therefore, the crystal structure of InS can be considered as a three-dimensional network different from the layered structure of its counterparts. The structural properties of indium sulfide are fairly well established [1]. Electrical conductivity and Hall effect [2,3], optical absorption [2,4], Raman scattering and infrared reflectivity [5,6], and photoluminescence [7] investigations in InS crystals have been reported. The indirect and direct energy gaps at room temperature are located at 1.90 and 2.44 eV, respectively [2]. High photo-conductive and photoluminescence properties makes this compound a promising optoelectronic material [2,7]. The optical constants, electrical resistivity, as well as the space charge limited currents in

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InS thin films have also been reported [8]. There is only one short note in literature concerning the study of thermally stimulated currents (TSCs) in InS crystals in the high-temperature range 95–180 K [9]. Due to the lack of low-temperature measurements, one broad band with incomplete ascending part was observed in TSC spectra. Thus, no systematic investigation has been carried out about the energy levels present in the forbidden gap of InS crystals. Arising from chemical impurities and/or structural defects, they strongly influence the photoelectronic properties of the semiconductors.

The aim of the present paper is to report the results of a detailed study of TSC of nominally undoped InS single crystals in a temperature range of 10–125 K. Low-temperature experiments allow us to check for the possibility of extremely shallow trap levels. From the analysis of the experimental data, relevant trapping parameters such as activation energy, capture cross section and concentration of some centers present in the analyzed indium sulfide single crystals, have been determined.

## 2. Experimental details

Indium sulfide polycrystals were synthesized from high-purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of InS were grown by the modified Bridgman method. The analysis of X-ray diffraction data showed that they crystallize in an orthorhombic unit cell with parameters:  $a = 0.394$  nm,  $b = 0.444$  nm and  $c = 1.065$  nm. Crystals suitable for measurements were obtained by hard cleavage along (1 0 0) plane perpendicular to optical  $c$ -axis. In the TSC measurements, samples with a typical size of  $9.5$  mm  $\times$   $4.5$  mm  $\times$   $1.5$  mm were used. The electrical conductivity of the studied samples was  $n$ -type as determined by the hot-probe method.

To perform TSC measurements silver paste contacts were made on the sample surface according to gap geometry. In this configuration, the electrodes are placed at two opposite edges of the front surface of the crystal. The sample was mounted on the cold finger of a cryostat with a non-conducting g-varnish. Thin copper wires were attached to the electrodes by small droplets of silver paste.

All measurements were carried out in vacuum in a “CTI-Cryogenics M-22” closed-cycle helium system extended from 10 to 125 K with constant heating rate  $\beta = 0.08$  K/s. The traps were filled by creating carriers via band-to-band photoexcitation of the samples. The light source was a 488 nm line (2.715 eV, 100 mW) of “Spectra Physics” argon laser. The TSCs were measured by a “Keithley 619” electrometer. The TSC and temperature data were stored in a personal computer.

In a typical experiment, samples are cooled down to  $T = 10$  K and kept at this temperature for  $\sim 10$  min. Then, they are illuminated in proximity to a contact for a fixed period of time ( $t = 15$  min) at an applied bias voltage of 2 V. After the light is turned off, the photoconductivity signal is allowed to decay for 5–10 min. The samples are then heated at a constant rate from 10 to 125 K.

## 3. Results and discussion

Fig. 1 shows the TSC spectrum obtained at a heating rate of  $\beta = 0.08$  K/s. We could not measure the TSC spectra in the high-temperature region ( $T > 125$  K) due to the strong increase of dark conductivity, which is consistent with the results reported in [3]. At temperatures 29.0, 36.7, 76.0 and 88.5 K, four peaks appear after isolating the TSC peak by curve fitting technique with the first and last two overlapping each other.

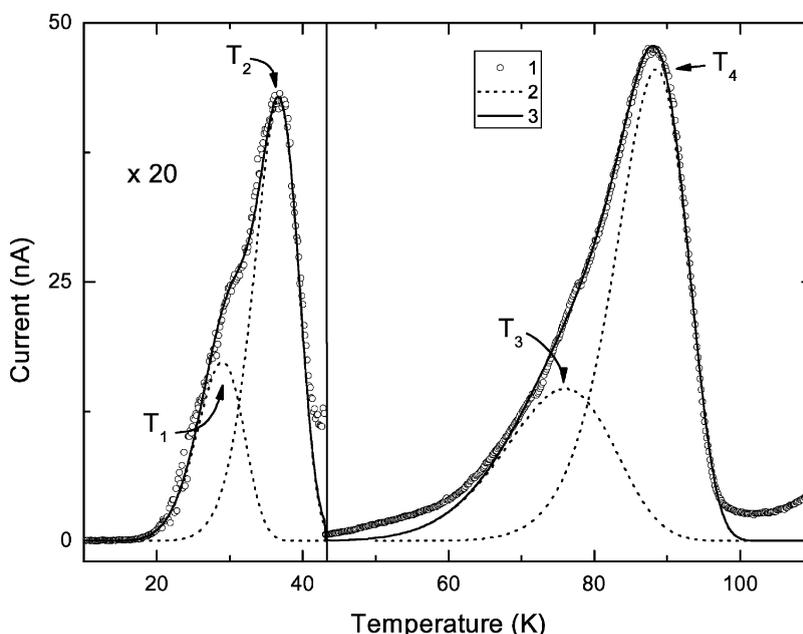


Fig. 1. Decomposition of the TSC spectrum of InS crystal into four separate peaks using conventional curve fitting method. Experimental data (1); decomposed peaks (2), using Eqs. (2) and (5); total fit to the experimental data (3) using Eq. (5). Low-temperature part of TSC spectrum is multiplied by a factor of 20.

### 3.1. Activation energy and capture cross section determination

Experimental TSC curves have been analyzed by using three different methods: curve fitting, peak shape and initial rise methods.

#### 3.1.1. Curve fitting method

Under monomolecular conditions (i.e. slow retrapping) the TSC curve of a discrete set of traps with a trapping level  $E_t$  below the conduction band is described by the equation [10]:

$$\sigma = n_t \tau \epsilon \mu v \exp \left\{ -\frac{E_t}{kT} - \int_{T_0}^T \frac{v}{\beta} \exp \left( -\frac{E_t}{kT} \right) dT \right\}. \quad (1)$$

Here,  $\sigma$  is the thermally stimulated conductivity,  $n_t$  the initial density of filled traps,  $\tau$  the lifetime of a free electron,  $\mu$  the electron mobility,  $\beta$  the heating rate,  $T_0$  the temperature from which heating begins following the filling of the traps,  $v$  the attempt-to-escape frequency of a trapped electron and  $k$  the Boltzmann's factor. If it is assumed that  $v$  is independent of  $T$  and that over the temperature span of TSC curve, the variation of  $\mu$  and  $\tau$  with  $T$  can be ignored, Eq. (1) can be rewritten approximately as:

$$\sigma = A \exp(-t - B \exp(-t) t^{-2}), \quad (2)$$

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

$$A = n_t \tau \epsilon \mu v \quad \text{and} \quad B = v E_t / \beta k. \quad (3)$$

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

$$B = \exp(t_m) \frac{t_m^3}{t_m + 2}. \quad (4)$$

In TSC spectra of InS crystals we observed four peaks,  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$ , with  $T_1$  and  $T_2$ , and  $T_3$  and  $T_4$  overlapping each other. In this paper, we analyzed all peaks simultaneously. For that purpose, the fitting function comprising the sum of all features of the TSC peak spectrum was built as:

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

where  $\sigma_i(T)$  denotes contribution of each peak alone, calculated by means of Eq. (2), and  $m$  denotes number of traps involved in the calculation. Good agreement between the experimental TSC curves and theoretical ones, computed with the assumption of slow retrapping suggests that retrapping does not occur for the traps studied (Fig. 1). Using this method four trapping centers have been determined with activation energies of 0.020, 0.035, 0.060 and 0.130 eV (Table 1).

Once the curve has been fitted and the values of  $E_t$  and  $T_m$  for each peak are determined (Table 1), Eqs. (4) and (3) were used to calculate  $B$  and the attempt-to-escape frequency  $\nu$ , respectively. Knowing the value of  $\nu$ , one can calculate the capture cross section of the traps according to the following expression:

$$S_t = \frac{\nu}{N_c \nu_{th}},$$

where  $N_c$  is the effective density of states in the conduction band and  $\nu_{th}$  is the thermal velocity of a free electron. The calculated values of  $S_t$  were found to be  $1.6 \times 10^{-23}$ ,  $2.6 \times 10^{-22}$ ,  $3.4 \times 10^{-24}$  and  $1.2 \times 10^{-20}$  cm<sup>2</sup> for peaks  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$ , respectively (Table 1). The small values of the capture cross sections justify the assumption of monomolecular kinetics.

### 3.1.2. Peak shape method

In the peak shape method [11], the activation energy of trap is evaluated by using three parameters:  $\tau = T_m - T_l$ ,  $\delta = T_m - T_h$ ,  $w = T_h - T_l$ , 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

Table 1

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

| Peak  | $T_m$ (K) | $E_t$ (eV)                |                        |                          | $S_t$ (cm <sup>2</sup> ) | $N_t$ (cm <sup>-3</sup> ) |
|-------|-----------|---------------------------|------------------------|--------------------------|--------------------------|---------------------------|
|       |           | Curve fitting method [10] | Peak shape method [11] | Initial rise method [12] |                          |                           |
| $T_1$ | 29.0      | 0.020                     | 0.022                  | 0.020                    | $1.6 \times 10^{-23}$    | $9.0 \times 10^{12}$      |
| $T_2$ | 36.7      | 0.035                     | 0.037                  | 0.035                    | $2.6 \times 10^{-22}$    | $2.1 \times 10^{13}$      |
| $T_3$ | 76.0      | 0.060                     | 0.066                  | 0.060                    | $3.4 \times 10^{-24}$    | $3.6 \times 10^{14}$      |
| $T_4$ | 88.5      | 0.130                     | 0.133                  | 0.128                    | $1.2 \times 10^{-20}$    | $7.5 \times 10^{14}$      |

of the trap is then

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

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

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

Here  $\mu_g = \delta/w$ , the values of which were predicted by Chen and Kirsh [11] as 0.42 for first order and 0.52 for second order kinetics. Obtained values of  $\mu_g$  for our decomposed peaks  $T_1, T_2, T_3$  and  $T_4$  were found to be 0.46, 0.44, 0.45, and 0.43, respectively. This indicates that the retrapping process is negligible for these centers. The averaged values of calculated activation energies  $E_{\tau}, E_{\delta},$  and  $E_w$  for four peaks are reported in Table 1.

### 3.1.3. Initial rise method

Initial rise method [12], 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  $1/kT$  should yield a straight line with a slope of  $(-E_t)$ , as shown in Fig. 2. The progressive shift from the linear behavior at high

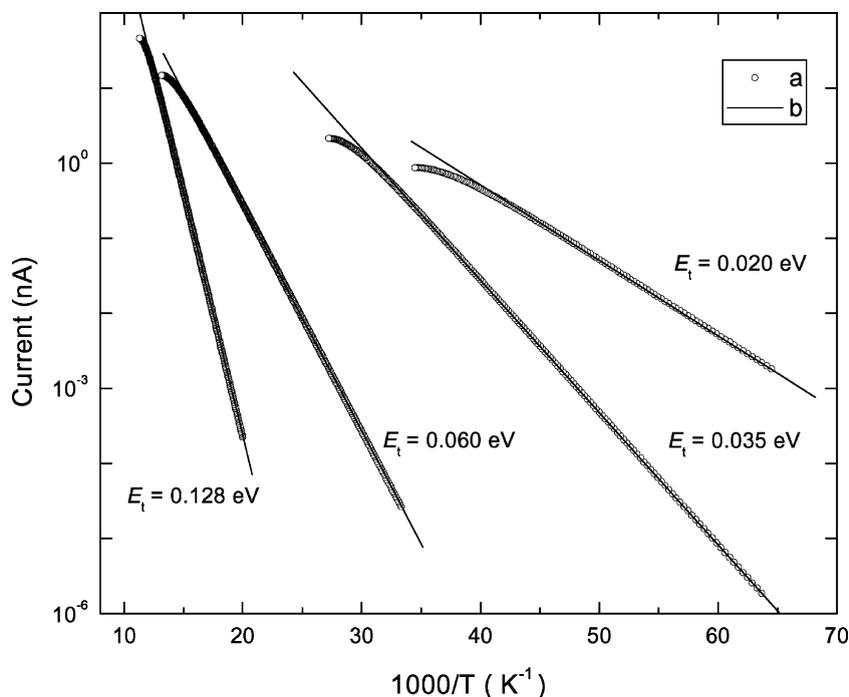


Fig. 2. TSC vs.  $1000/T$  for all four peaks in TSC spectrum of InS crystal. Experimental data (a), theoretical fits using initial rise method (b).

current is due to exceeding the critical temperature  $T_c$ , after which the exponential law is no longer valid [13]. The activation energies of the traps calculated by this procedure are found to be 0.020, 0.035, 0.060 and 0.128 eV for peaks  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$ , respectively (Table 1).

### 3.2. Trap concentration determination

The concentration of the traps was estimated using the relation [14]

$$N_t = \frac{Q}{A} LeG.$$

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, which equals to the number of electrons passing through the sample for each absorbed photon.  $N_t$  was calculated by assuming  $G = 1$ , because it was not possible to measure  $G$  under the same TSC conditions with the necessary accuracy. The values of  $N_t$  obtained for four traps are presented in Table 1.

## 4. Conclusions

Four trapping levels at 0.02, 0.04, 0.06 and 0.13 eV have been detected in as-grown  $n$ -InS single crystals by the TSC technique. These levels in undoped layered crystals may be associated with the presence of structural defects and/or unintentional impurities. The trap parameters were determined by various methods of analysis, and they agree well with each other. The retrapping process is negligible for these levels, as confirmed by the good agreement between the experimental results and the theoretical predictions of the model that assume slow retrapping.

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