Low temperature thermally stimulated current measurements in N-implanted TlGaSeS layered single crystals

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ABSTRACT

As-grown TlGaSeS crystals have been implanted by a ion implantation technique. The samples were bombarded at room temperature in the direction perpendicular to the layer by nitrogen ion beam of about 120 keV having dose of 1 × 10^{16} ions/cm^2. The effect of N implantation and annealing at 300 °C was studied by using thermally stimulated current measurements. The measurements were performed in temperatures ranging from 10 K to 250 K. The experimental evidences were found for the presence of one shallow electron trapping center and one deep hole trapping center with activation energies of 6 meV and 796 meV, respectively. The capture cross-sections (3.0 × 10^{-24} cm^2 and 2.3 × 10^{-15} cm^2) and concentrations (5.6 × 10^{11} cm^{-3} and 2.1 × 10^{13} cm^{-3}) were determined for the electron and hole trapping centers, respectively.

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1. Introduction

The layered semiconducting crystal TlGaSeS is formed from TlGaSe_2 and TlGaS_2 crystals by replacing half of the selenium (sulfur) atoms with sulfur (selenium) atoms. The crystal lattice has two-dimensional layers arranged parallel to the (001) plane [1,2]. The bonding between Tl and Se(S) atoms in TlGaSeS is an interlayer type whereas the bonding between Ga and Se(S) is an intralayer type (Fig. 1). The optical and the electrical properties of TlGaSe_2, TlGaS_2 and TlGaSeS crystals were studied in Refs. [3–11]. The indirect and direct band gap energies for TlGaSeS crystal were found as 2.27 and 2.58 eV at room temperature [8]. 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 [9]. Recently, the results of the thermally stimulated current (TSC) measurements in as-grown TlGaSeS crystals were reported in Refs. [10,11].

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 non-radiative 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]. In TSC experiments, traps are filled by band-to-band excitation of carriers at low temperatures using a suitable light source. If the trapped charge carriers are thermally released to the conduction (valence) band upon heating, they give rise to a transient increase in the conductivity of the sample. A TSC curve for a single trap depth has the form of a slightly asymmetric curve with a fairly sharp maximum at a temperature, which is
determined by the trap depth, the capture cross-section of the trap and the heating rate.

The purpose of the present work is to obtain detailed information concerning trapping centers in N-implanted TlGaSeS layered crystals using the well-established technique of TSC measurements. We utilized the various methods to analyze the measured TSC spectra. The activation energies, the attempt-to-escape frequency, capture cross-sections and concentrations of the shallow electron and deep hole traps in N-implanted TlGaSeS crystals are reported.

2. Experimental details

TlGaSeS polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals of TlGaSeS 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 a dose of 1 \times 10^{16} \text{ions/cm}^2. The sample dimensions were 9.5 mm \times 6 mm. TSC peaks were not observed before implantation and annealing. After implantation, the annealing was performed in argon atmosphere for the sample at temperature 300°C for 45 min, to possibly remove the damage induced by implantation and also to activate nitrogen related implanted 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 wires were attached to the electrodes for circuit connection.

The TSC measurements were performed in the temperature range from 10 K to 250 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 \( V_1 = 1 \text{ V} \) at the initial temperature \( T_0 = 10 \text{ K} \) for about 10 min. Then the excitation was turned-off. After the relaxation time ( \( \approx 60 \text{ s} \) ) the bias voltage of \( V_2 \) was applied to the sample and temperature was increased at constant rate. In N-implanted TlGaSeS the dark current contribution is low, therefore the voltage of \( V_2 = 100 \text{ V} \) can be applied during heating.

Determination of the photoconductivity gain for a sample under the specified experimental conditions is a particular problem. The carrier lifetime was determined employing the photoconductivity decay technique \([20]\). These experiments were carried out by developing the set-up as follows. We formed ohmic contacts on both sides of the sample according to sandwich geometry and that was illuminated by a high efficiency blue LED controlled by a digital signal generator operating square waves. The photocurrent was amplified by a fast current–voltage converter circuit. The signal was recorded by a fast digital voltmeter and transmitted to the computer. The recorded data were analyzed to determine the decay time of the photocurrent.

3. Results and discussion

When the front surface of the sample is illuminated, both types of carriers are created in this region. Only one type of carrier 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. It was revealed that the different TSC peaks are observable for both illuminated surfaces. It means that the electron and hole are distributed in the crystal and then trapped. Therefore, the peaks appearing in the TSC spectra of N-implanted TlGaSeS crystal can be assigned to electron traps for negative polarity of illuminated surface and hole traps for positive polarity of illuminated surface (Fig. 2).

There are several methods to evaluate the trapping parameters from the experimental TSC spectra. We have used the curve fitting, initial rise and peak shape methods for the analysis of the present data.

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. We have tried all possibilities and found that the monomolecular process leads to the best results for present data. For the monomolecular conditions (i.e. slow retrapping), the TSC curve of a discrete set of traps with trapping level \( E_t \) is described by \([12]\)

\[
l(t) = n_0 \tau \mu A \left( \frac{V_2}{L} \right) \exp \left\{ -\frac{E_t}{kT} - \int_{T_0}^{T} \beta \exp \left( \frac{-E_t}{kT} \right) dT \right\}
\]

Fig. 1. Projection of the structure in the TlGaSeS crystal as seen from ac-plane. The ones (1) show the interlayer bonding between Tl and Se(S) atoms; the twos (2) show the intralayer bonding between Ga and Se(S) atoms. From I to V indicate different planes of atoms.
Attempt-to-escape frequency, \( \nu \), is the heating rate, \( \beta \), is the applied voltage, \( A \) and \( L \) are the area and the length of the sample, respectively, and \( T_0 \) is the temperature where heating begins after filling of the traps.

Figs. 3 and 4 show the experimental TSC spectra of the N-implanted TlGaSeS crystal for the heating rate of 0.3 K s\(^{-1}\). From curve fit using Eq. (1) (solid line) we determine the activation energies of 6 meV and 796 meV for negative and positive polarity of illuminated surfaces, respectively. A good agreement has been obtained between the experimental TSC data and the theoretical curve computed by assuming slow retrapping. This suggests that retrapping does not occur for the traps of N-implanted TlGaSeS, studied in the present work.

Initial rise method was also applied for analyzing the revealed peaks. The effectiveness of this method comes due to its usability to calculate the activation energies of traps without considering type of recombination kinetics. According to this method, initial part of the TSC curve shows the same behavior in both slow and fast retrapping process. TSC is proportional to \( \exp(-E/kT) \) when the trapped charge carriers are excited by the help of increasing temperature [21]. In this way, the activation energies of revealed traps can be evaluated from the logarithmic plots of current as a function of \( 1/T \) (see insets of Figs. 3 and 4) giving a straight line with a slope of \( (-E/k) \). The activation energies of the electron and hole traps were calculated as 7 meV and 798 meV, respectively. These values are in good agreement with the values obtained from the curve fitting method.

The experimental TSC curves for N-implanted TlGaSeS crystals have also been analyzed by using the peak shape method [21]. In this method, the activation energy can be evaluated by using parameters: \( \tau = T_m - T_b \), \( \delta = T_b - T_m \), \( w = T_n - T_l \), and \( \mu_B = \delta/w \), where \( T_m \) is the temperature corresponding to the maximum current, \( T_l \) and \( T_b \) are the low and high half-intensity temperatures, respectively. The activation energy of the traps is determined using the following expressions:

\[
E_i = \left\{ \frac{[1.51 + 3.0(\mu_B - 0.42)]kT_m^2}{\tau} \right\} - [1.58 + 4.2(\mu_B - 0.42)]2kT_{\text{max}}. \]
\[
E_\delta = \left\{ \frac{0.976 + 7.3(\mu_B - 0.42)]kT_{\text{max}}^2}{\delta} \right\} - 2kT_{\text{max}}. \]
\[
E_w = \left\{ \frac{[2.52 + 10.2(\mu_B - 0.42)]kT_{\text{max}}^2}{w} \right\} - 2kT_{\text{max}}. \]

The averaged value of the activation energies \( E_i \), \( E_\delta \) and \( E_w \) for the observed peaks were estimated as 9 meV for electron traps and 827 meV for hole traps.

Attempt-to-escape frequency (\( \nu \)) and capture cross section (\( S_{\text{c}} \)) of the revealed traps can be determined using the values \( E_i \) and peak maximum temperatures (\( T_{\text{max}} = 20 \) K and \( T_{\text{max}} = 234 \) K), obtained from the curve fit analysis, by
the expressions [22]

\[ \nu = \frac{\beta E_t}{kT_m^2} \exp\left(\frac{E_t}{kT_m}\right) \quad \text{and} \quad S_t = \frac{\nu}{N_{cv}v_{th}} \]  

(3)

where \( N_{cv} \) is the effective density of states in the conduction (valence) band and \( v_{th} \) is the thermal velocity of a free electron (hole). As a result, we found the values of \( \nu \) (1.1 and \( 3.0 \times 10^{11} \) s\(^{-1} \)) and \( S_t \) (3.0 \( \times 10^{-24} \) cm\(^2\) and 2.3 \( \times 10^{-15} \) cm\(^2\)) for the electron and hole trapping centers, respectively.

The concentrations of the traps were estimated using the relation [18,23]

\[ N_t = \frac{Q}{\text{ALeG}_I} \]  

(4)

where \( G \) is the photoconductivity gain, \( e \) is the electronic charge and \( Q \) is the amount of charge released during the TSC measurement, that can be calculated from the area of the TSC peak. The photoconductivity gain \( G \) is evaluated from the following expression [24]

\[ G = \frac{C}{V_0 + C \exp\left(-\frac{t}{\tau}\right)} \]  

(5)

where \( t \) is the voltage at \( t = \infty \) and \( C \) is a constant.

Figs. 5 and 6 show the theoretical fit (solid lines) to the experimental data. Solid curve shows the theoretical fit to the experimental data.

for the negative and positive polarity of illuminated surfaces, respectively.

4. Conclusions

The electron and hole trapping centers with activation energies of 6 meV and 796 meV, respectively, were detected in N-implanted TlGaSeS single crystals. Since TSC peaks were not seen before implantation and annealing, the observed levels are thought to originate from N defects, created by implantation and annealing processes. The trap parameters determined by various methods of analysis agree with each other. 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-sections were calculated to be 3.0 \( \times 10^{-24} \) cm\(^2\) and 2.3 \( \times 10^{-15} \) cm\(^2\) for the electron and hole trapping centers, respectively. Also the concentrations of the traps were estimated as 5.6 \( \times 10^{11} \) cm\(^{-3}\) and 2.1 \( \times 10^{13} \) cm\(^{-3}\), respectively.

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