PRAMANA
— journal of
physics

Vol. 86, No. 4
April 2016
pp. 893–900

Defect characterization of Ga_4Se_3S layered single crystals by thermoluminescence

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MS received 8 November 2014; revised 25 February 2015; accepted 25 February 2015
DOI: 10.1007/s12043-015-1081-x; ***e*Publication:** 17 November 2015

Abstract. Trapping centres in undoped Ga_4Se_3S single crystals grown by Bridgman method were characterized for the first time by thermoluminescence (TL) measurements carried out in the low-temperature range of 15−300 K. After illuminating the sample with blue light (∼470 nm) at 15 K, TL glow curve exhibited one peak around 74 K when measured with a heating rate of 0.4 K/s. The results of the various analysis methods were in good agreement about the presence of one trapping centre with an activation energy of 27 meV. Analysis of curve fitting method indicated that mixed order of kinetics dominates the trapping process. Heating rate dependence and distribution of the traps associated with the observed TL peak were also studied. The shift of peak maximum temperature from 74 to 113 K with increasing rate from 0.4 to 1.2 K/s was revealed. Distribution of traps was investigated using an experimental technique based on cleaning the centres giving emission at lower temperatures. Activation energies of the levels were observed to be increasing from 27 to 40 meV by rising the stopping temperature from 15 to 36 K.

Keywords. Thermoluminescence; semiconductors; defects.

PACS Nos 71.20.Nr; 71.55.−i; 78.60.Kn

1. Introduction

GaSe and GaS belonging to III–VI group of semiconducting compounds are effective materials to be used in optoelectronic devices in red and blue regions. These compounds form GaS_xSe_{1-x} mixed crystals without restrictions on the concentration of the constituent compounds ($0 \leq x \leq 1$) [1–5]. Lattices in the crystal structure of GaSe, GaS and GaS_xSe_{1-x} layered semiconductors have strong ionic–covalent intralayer and weak van der Waals interlayer interactions. By changing the composition of the constituent compounds in the mixed crystals, band-gap energy of the series covers a wide range of the visible spectrum. So, GaS_xSe_{1-x} mixed crystals can be promising candidates to be

used especially in the fabrication of long-pass filters, light emitting and optical switching devices [6] and photodetectors [7]. Previously, technical applications of the GaS_xSe_{1-x} mixed crystals have been studied. Zhang *et al* investigated the phase matching properties for second harmonic generation (SHG) in GaS_xSe_{1-x} mixed crystals at room temperature [8]. The possibility of broadband THz pulse generation in mixed crystals is reported in ref. [9]. Moreover, taking into consideration the technological applications of constituent compounds GaSe and GaS in the near-blue-light emitting device [10], SHG of CO_2 laser [11], generation of coherent infrared radiation from mid-IR to THz region [12] and light modulator [13] areas, GaS_xSe_{1-x} mixed crystals can be thought of as important candidates to be used in the relevant areas due to the wide variety of their optical parameters. Mixed crystals were also investigated from the point of fundamental research. Optical properties of GaS_xSe_{1-x} mixed crystals ($0 \leq x \leq 0.5$) grown by Bridgman method were studied using transmission and piezoreflectance measurements [1]. The analysis of the obtained spectra showed that band-gap energy increases from 1.986 eV (GaSe) to 2.37 eV ($GaS_{0.5}Se_{0.5}$). Previously, our research group reported studies on the optical and electrical characterization of Ga_4Se_3S crystals. The analysis of the room-temperature transmission and reflection measurements revealed that Ga_4Se_3S exhibits indirect transitions with a band-gap energy of 2.08 eV [14]. The dispersion and oscillator energies, static dielectric constant and static refractive index values of the crystal were also given in this paper. Analysis of the temperature-dependent band-gap energy of Ga_4Se_3S resulted in rate of change of the band-gap energy with a temperature of -9.5×10^{-4} eV K^{-1} and absolute zero value of the band-gap energy of 2.25 eV [15]. Electrical characterization experiments showed that the electrical resistivity and Hall mobility of the crystal are $7.7 \times 10^6\ \Omega$ cm and 98 $cm^2\ V^{-1}\ s^{-1}$, respectively [16].

The aim of the present paper is to expand our studies on Ga_4Se_3S single crystal by investigating its thermoluminescence properties for the first time below room temperature to characterize the trapping centre(s) arising due to the defects which are one of the principal factors affecting the performance of optoelectronic devices such as LEDs and lasers. These technological devices may be affected by the defects introducing nonradiative recombination centres which lower the internal quantum efficiency or even render light generation impossible. In the materials used for electronic devices, defects may act as scattering centres which lower carrier mobility, hence hindering high-frequency operation. Therefore, characterization of trap centres existing due to the presence of defects in materials is important to get high-quality devices.

2. Experimental details

Ga_4Se_3S polycrystals were synthesized from high-purity elements prepared in stoichiometric proportions. Gallium (Aldrich cat. no. 263273), selenium (Aldrich cat. no. 204307) and sulphur (Fluka cat. no. 84680) were of 99.999% purity. Ga_4Se_3S single crystals were grown by Bridgman method from the stoichiometric melt of the starting materials sealed in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 25 cm in length) with the tip at the bottom. The ampoule moving vertically in a furnace at a rate of 0.5 mm h^{-1} was subjected to temperature difference varying between 650 and 1000°C through a thermal gradient of 30°C cm^{-1}. The grown ingots were easily cleaved

along the planes, which are perpendicular to the c-axis of the crystal. The freshly cleaved surfaces have good optical quality such that they seem mirror-like and there are no cracks or fractures on the surface. Therefore, there is no need of further burnishing and/or cleaning treatments. The obtained ingot of Ga_4Se_3S appeared red whereas GaSe and GaS crystals are dark red and yellow, respectively. Chemical composition of the crystals was obtained from energy-dispersive spectroscopy (EDS) measurements performed by JSM-6400 scanning electron microscope.

Thermoluminescence (TL) measurements were carried out using home-made experimental set-up which was built around a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). Lakeshore Model 331 temperature controller was used to adjust the sample temperature in the 15–300 K range. A photomultiplier tube (Hamamatsu R928; spectral response: 185–900 nm) working in photon counting regime, a blue light source (∼470 nm) and relevant optics to focus the light onto sample were connected to the optical access port of the cryostat (quartz window) by a measurement chamber. The sample was placed in the equipped cryostat and the environment was cooled to 15 K. At this temperature, the sample was illuminated for 600 s to fill the traps completely. The temperature was then increased with a constant heating rate after an expectation time (600 s) was elapsed in the dark. The emitted luminescence was directed to the photomultiplier tube. Hamamatsu Photon Counting Unit C3866 was used to convert pulses from photomultiplier tube into transistor–transistor logic (TTL) pulses, which were counted by the counter of the data acquisition module (National Instruments, NI-USB 6211). A software written in LabView^{TM} graphical development environment was used to control the whole measurement system/devices.

3. Results and discussion

Figure 1 shows the EDS spectrum of the Ga_4Se_3S crystal in the 0–10 keV energy range. Analysis of the EDS measurements revealed the atomic composition ratio of the constituent elements (Ga : Se : S) to be 50.6 : 37.2 : 12.2, respectively. The atomic weight ratios of the constituent elements in the mixed crystal show slight changes from that of initial ratios (50.0 : 37.5 : 12.5) in the growth process. In the grown crystal, some deficiency occurs in the compositions of sulphur and selenium.

Figure 2 shows the TL glow curve of Ga_4Se_3S crystal for a heating rate of 0.4 K/s. In the figure, temperature range in which the TL peak was observed is presented although measurements were carried out in the 15–300 K temperature range. TL spectra exhibit only one peak with a peak maximum temperature (T_m) of nearly 74 K. Several methods (curve fitting, initial rise and various heating rate methods) were used to determine trapping centre parameters associated with this peak.

TL intensity (I_{TL}) is related to heating rate (β), activation energy (E_t) and temperature (T) by the expressions [17]

$$I_{TL} = n_0 \nu \exp\left\{-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta} \exp\left(\frac{-E_t}{kT}\right) dT\right\}, \quad \text{for first-order kinetics} \quad (1)$$

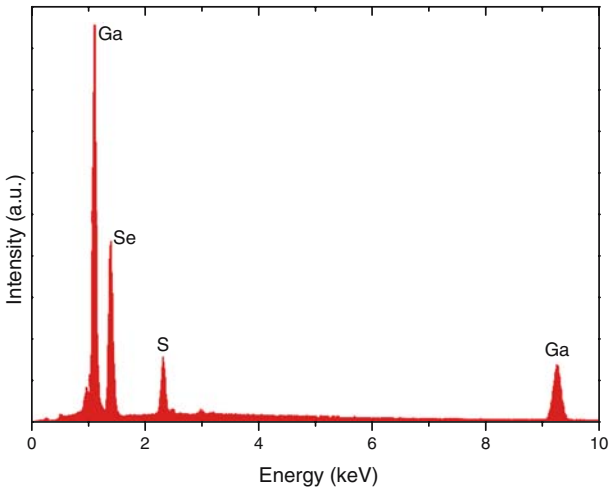

Figure 1. Energy-dispersive spectrum of Ga_4Se_3S crystal.

$$I_{\mathrm{TL}} = n_0 \nu \exp\left(-\frac{E_{\mathrm{t}}}{kT}\right)\left[1 + (b-1)\,\frac{\nu}{\beta} \times \int_{T_0}^{T} \exp\left(-E_{\mathrm{t}}/kT\right) \mathrm{d}T\right]^{b/(b-1)}, \quad \text{for non first-order kinetics,} \tag{2}$$

where n_0 is the initial concentration of trapped charge carriers, ν is the attempt-to-escape frequency, T_0 is the initial temperature of the heating process and b is the order of kinetics. b is equal to 2 for second-order of kinetics and is between 1 and 2 for

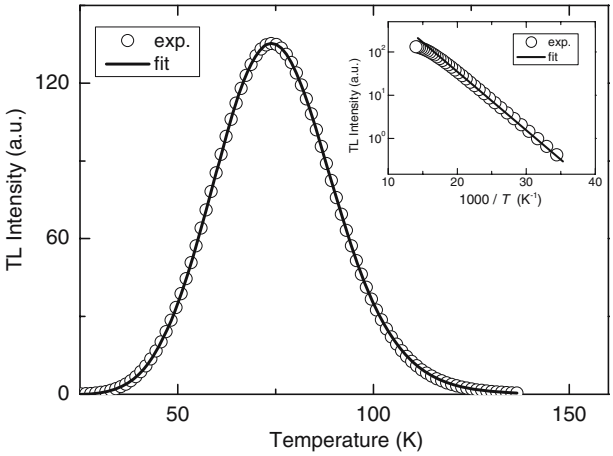

Figure 2. Experimental TL glow curve (open circles) of Ga_4Se_3S crystal with a heating rate of 0.4 K/s. Solid curve shows the fit to the experimental data. Inset: TL intensity vs. $1000/T$. The circles represent the experimental data and the line represents the theoretical fit using the initial rise method.

mixed order of kinetics. Curve fitting method is based on the fitting of the experimental TL curve using OriginPro 8 software according to eqs (1) and (2) depending on the dominant mechanism in the TL process. Analysis done using both equations gave successful results for mixed order of kinetics with parameter $b = 1.2$. Solid line in figure 2 shows the fit to the experimental data giving activation energy of the trap centre as 27 meV.

At this point, it may be informative to compare the present result of thermoluminescence concerning the activation energy of defect level with that of thermally stimulated current measurements on Ga_4Se_3S crystals. Analysis of the thermally stimulated current measurements (10–100 K) on the crystal revealed the existence of one trapping centre at 23 meV [18]. Taking into account the possible errors, these energies can be associated with the same trapping centre which may exist due to the defects created during the crystal growth process.

Initial rise method is one of the main analysis methods to determine the activation energy of a trap level [17]. The usability of this method for the trapping processes related to the first and second order of kinetics gives an effective position among other methods used for the analysis of TL glow curves. Integrals in eqs (1) and (2) are very small when the charge carriers begin excitation from the trap level. This part corresponds to the region of the peak up to ∼10% of its maximum intensity. TL intensity in this region is proportional to $\exp(-E_t/kT)$. Therefore, the plot of $\ln(I_{TL})$ vs. $1/T$ gives a straight line with a slope of $(-E_t/k)$. Inset of figure 2 shows the relevant plot (open circles) and its linear fit (solid line). The activation energy was found to be 26 meV from the slope. The agreement between the results of the initial rise and curve fitting methods is an indication of the accuracy of the activation energy.

Heating rate dependence of the observed TL peak was investigated for rates between 0.4 and 1.2 K/s (see figure 3). Generally, the variation of heating rate influences the

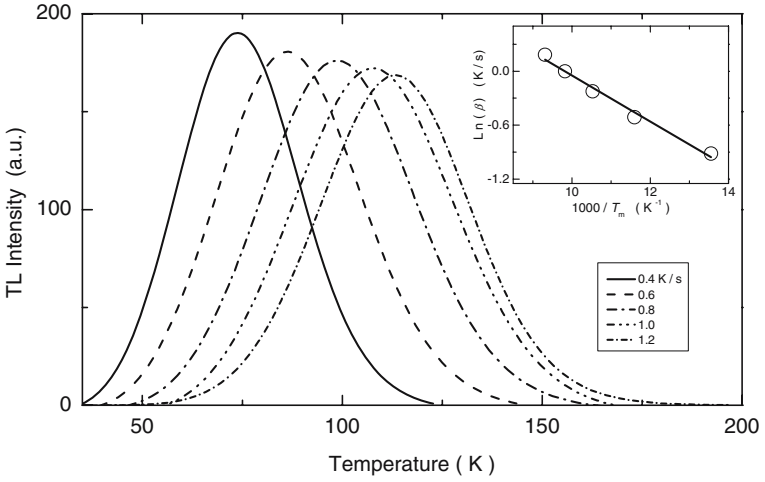

Figure 3. Experimental TL curves of Ga_4Se_3S crystal with various heating rates. Inset: The plot of $\ln(\beta)$ vs. $1000/T_m$. Circles and solid line represent the experimental data and the linear fit, respectively.

shape and the peak maximum temperature of the TL curve. If the trap concentration which is proportional to excitation time in TL experiment is not changed, T_m shifts to higher values, peak maximum intensity decreases and peak broadens. As can be seen from figure 4 presenting the variation of T_m, full-width half-maximum (FWHM) and intensity with heating rate, theoretical evidences are satisfied in our experimental data. Heating rate dependent T_m values also give an opportunity to evaluate the activation energy by taking into consideration the relation [17]

$$\beta = (\nu k/E_t)\, T_m^2\, \exp(-E_t/kT_m)\,. \tag{3}$$

In this equation, exponential term is the dominant T_m-dependent factor rather than the T_m^2 term. Therefore, the plot of $\ln(\beta)$ vs. $1/T_m$ results in a line with a slope of $-E_t/k$. In the TL experiments, one of the important points is the existence of the temperature lag effect which arises due to the temperature gradient between temperatures of the sample and the heater element that controls the temperature of the environment in which the sample is placed. This effect causes higher deflections especially for higher heating rates. Kitis and Tuyn reported a method to minimize this deflection [19]. In this method, experimental T_m values are corrected by using the expression

$$T_{mj} = T_{mi} - c \ln\left(\frac{\beta_i}{\beta_j}\right), \tag{4}$$

where c is a constant calculated using the two lower heating rates in the TL experiments. Temperature lag effect is thought to be negligible for lower heating rates. The constant c was found to be 31.1 using T_m values of 0.4 and 0.6 K/s heating rate data. The above-mentioned plot to find the activation energy was drawn with the new T_m values under the light of eq. (4) as shown in inset of figure 3 and E_t was found to be 23 meV from the above-mentioned slope.

Trap distribution study was also accomplished using an experimental technique based on thermally cleaning the centres giving emission at lower temperatures and obtaining TL

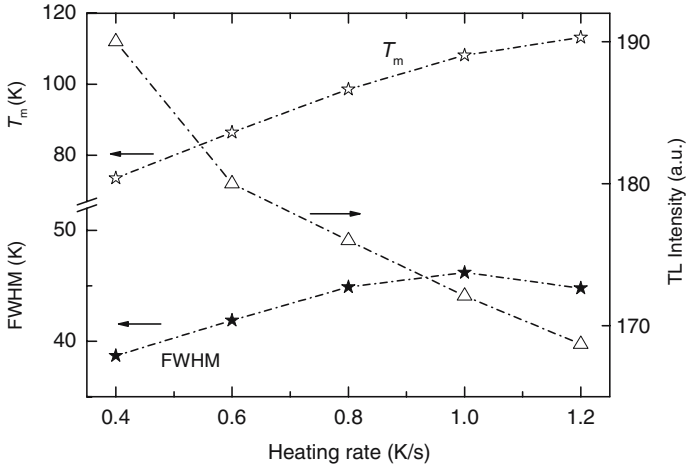

Figure 4. Dependence of peak maximum temperature, FWHM and TL intensity on heating rate.

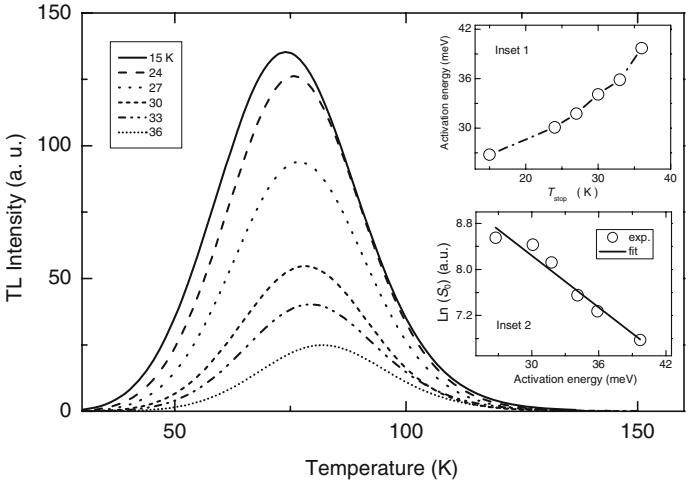

Figure 5. The glow curves of Ga_4Se_3S crystals at different T_{stop} temperatures at a heating rate of $\beta = 0.4$ K/s. Inset 1: The dependence of activation energies on T_{stop} values. Inset 2: $\ln(S_0)$ vs. activation energy.

peak associated with the remaining centres in the distribution [20,21]. In this technique $(T_m(E_t) - T_{stop})$, sample was illuminated at low temperature ($T_0 = 15$ K) and heated at a constant rate ($\beta = 0.4$ K/s) up to a stopping temperature (T_{stop}). At this time, trapping centres giving emission below T_{stop} temperature were fully or partially emptied. Then the sample was cooled to T_0 and TL experiments were carried out in the temperature range of 15–300 K without additional illumination. The obtained curve is associated only with the remaining deeper centres. Figure 5 presents the TL curves obtained for the values of T_{stop} between 15 and 36 K. The activation energies of the centres corresponding to these curves were calculated using the curve fitting method. Activation energies increase from 27 to 40 meV as T_{stop} is increased from 15 to 36 K (see inset 1 of figure 5). The TL curves obtained in figure 5 can also be analysed to get information about the energy parameter (α) characterizing the trap distribution. The details of the analysis of the trap distribution is given in ref. [18]. Inset 2 of figure 5 shows $\ln(S_0)$ plotted as a function of energy E_t, where S_0 is the area under the TL glow curve. The linearly fitted plot gives a slope $\alpha = 0.151$ meV^{-1}corresponding to 15 meV/decade, an order of magnitude variation in the trap density for every 15 meV.

4. Conclusion

Ga_4Se_3S undoped crystals were studied by thermoluminescence technique to reveal the trapping centre(s). One peak centred nearly at 74 K was observed in the TL spectra. Thermal activation energy of the trap centre associated with this peak was found to be 27 meV. Heating rate dependency of the TL intensity of the observed peak was assigned to the thermal quenching effect. Moreover, distribution of the traps was accomplished by varying T_{stop} between 15 and 36 K. The corresponding activation energies of the revealed centres in the distribution were found to be increasing from 27 to 40 meV.

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