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Thermoluminescence in gallium sulfide crystals: an unusual heating rate dependence

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Trap centres in gallium sulfide single crystals have been investigated by thermoluminescence measurements in the temperature range of 10–230 K. A curve-fitting method was utilized to evaluate the activation energies (52, 200 and 304 meV) of the revealed three trap centres. The heating rate dependence and trap distribution of the peaks have been studied using experimental techniques based on various heating rates and various illumination temperatures, respectively. An anomalous heating rate dependence of the high-temperature peak was found by carrying out TL measurements with various heating rates between 0.2 and 1.0 K/s. This behaviour was explained on the basis of a semi-localized transition model. Whereas normal heating rate dependence was established for low-temperature peak, that is, the TL intensity of the glow curve decreases and the peak maximum temperature shifts to higher values with increasing the heating rate. Moreover, a quasi-continuous trap distribution with the increase of activation energies from 52 to 90 meV, from 200 to 268 meV and from 304 to 469 meV for the observed three different traps was established employing the various illumination temperatures method.

Keywords: semiconductors; GaS; thermoluminescence; defects

1. Introduction

A wide variety of binary- and ternary-layered semiconductors have attracted much interest owing to possible optoelectronic applications from the ultraviolet to the infrared [1,2]. For many of these materials, the optoelectronic properties are controlled by defects of various types and the interactions between them. Gallium sulphide (GaS) crystal belongs to the family of III–VI layered semiconductors. It crystallizes in the hexagonal structure with lattice parameters of $a = 0.3578$ and $c = 1.547$ nm. Each layer in the crystal structure is composed of two gallium and two sulphur atoms stacked along the $\boldsymbol{c}$-axis with a repeating unit of S-Ga-Ga-S [3]. In GaS crystals, weak van der Waals forces dominate the interlayer interactions, while strong covalent bonds are effective on the intralayer forces. GaS is a wide band gap semiconductor, which is a promising material for fabricating near-blue light emitting devices [4,5]. The indirect band edge is about 2.5 eV at 300 K, and the direct one exists some 0.45 eV higher in energy [6]. In the literature, there exist some reports focused on the photoconductivity [7], interband optical transitions [8] and temperature-dependent absorption and piezoreflectance measurements

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of GaS layered crystals [9,10]. Characterization of GaS thin films has been reported in Refs. [11–16].

Previously, we have performed low-temperature photoluminescence (PL) measurements on GaS crystals [17]. Three bands at energies of 2.22, 2.02 and 1.59 eV have been observed in the PL spectra. The temperature and excitation intensity dependencies of the observed PL bands have revealed three levels with activation energies of 13, 17 and 151 meV. Moreover, thermally stimulated current measurements on GaS crystals in the temperature range of 10–300 K were carried out at a heating rate of 0.10 K/s [18]. The analysis of the data revealed six trap levels with activation energies of 50, 60, 120, 630, 710 and 750 meV.

One of the factors affecting the optical and electrical properties of the materials is the presence of defects and impurities. Thermoluminescence (TL) is one of the most sensitive techniques that has been employed for the investigations of lattice imperfections [19–21]. Upon excitation with light, with photon energy greater than the band gap of the material, free electrons and holes are created, a proportion of which can be trapped at lattice imperfections acting as electron and hole traps. TL is emitted as a result of recombination of thermally liberated trapped electrons with the trapped holes. Analysis of the TL below room temperature enables one to obtain information about shallow defects in the material even at very low defect concentrations.

In this study, we continue to further explore the characteristics of the GaS layered crystals by means of TL measurements carried out in the range of 10−230 K. In the following sections, we report the results of TL glow curves associated with defect centres in the band gap of GaS crystals where, besides the determination of thermal activation energies using various techniques, an anomalous heating rate effect is observed. The result of the present work dealing with the TL measurements will provide an important contribution to related research areas and expand the studies of luminescence measurements on GaS crystals.

2. Experimental details

Gallium sulphide polycrystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. GaS single crystals were grown by the Bridgman method in our crystal growth laboratory. The samples were prepared by easy cleavage of an ingot parallel to the crystal layer. For TL measurements, we used bulk samples with dimensions $6 \times 6 \times 0.9$ mm^3. The mass of samples was approximately 125 mg. The electrical conductivity of the studied samples was n-type as determined by the hot-probe method. TL measurements were carried out using a set-up built in the laboratory. The system was performed using a closed-cycle helium cryostat (Advanced Research Systems, Model CSW 202), which is able to operate in the temperature range of 10–300 K. The temperature of the sample was adjusted using a computer interfaced temperature controller (Lakeshore Model 331).

TL emission was collected using a light-tight measurement chamber housing a photomultiplier tube (Hamamatsu R928, spectral response: 185–900 nm), a light source for illumination and light collecting optics, attached to the optical access port of a cryostat with a quartz window. The pulses from the photomultiplier tube (working in photon counting regime) were converted to TTL logic pulses (0–5 V) using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and counted using the counter

of a data acquisition module (National Instruments, NI 6211). The sample was illuminated at low temperatures for 600 s, which is the experimentally determined time to fill the traps using an LED producing light with a peak photon energy of 2.6 eV. After the light source was switched off and an expectation time (≈120 s) waited, the temperature of the sample was increased at a constant heating rate using a Lake-Shore 331 temperature controller. The flux at the sample position was estimated to be about a few mW/cm^2. The whole measurement set-up was controlled using a LabView (National Instruments) graphical development program. Further details of the system can be found in Ref. [22]. The emitted light was collected without filtering and/or wavelength discrimination. The spectral response of the measurement system is mainly restricted by the spectral response of the photomultiplier tube, that is 185–900 nm. However, the band gap of the crystal used restricts the measurement region to approximately 410–900 nm.

3. Results and discussion

3.1. *Determination of activation energy*

An example of a TL glow curve of GaS obtained by heating the sample from 10 to 230 K at a rate of 1 K/s is shown in Figure 1. As seen in the figure, the TL curve exhibited two strong overlapping peaks with maxima around 91 and 146 K labelled as 'peak A' and 'peak B', respectively. In addition, a weak third peak C (shoulder) is observed around 175 K. The TL curve did not exhibit any peak beyond 200 K, so for the remainder of the manuscript, the TL data recorded at higher temperatures will not be shown.

One can benefit from several analysis techniques that are available for observed TL curves to calculate the activation energies of trap levels. In this study, we applied a

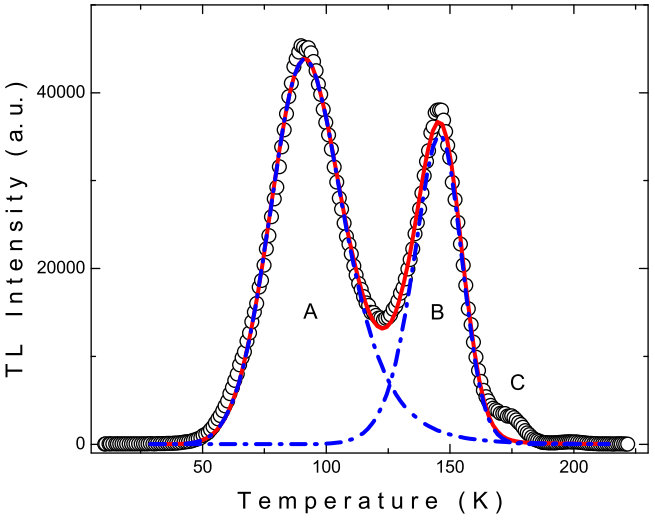

Figure 1. (colour online) Experimental TL curve of GaS crystal with a heating rate of β = 1.0 K/s. Notes: Open circles are experimental data. The solid curve and the dash-dotted line curves show the theoretical curve fitting and the deconvoluted peaks, respectively.

curve-fitting method to the experimentally obtained TL glow curves using the following expressions [20]

$$I_{\mathrm{TL}}(T) = n_0 s \exp\left\{-\frac{E_{\mathrm{t}}}{kT} - \int_{T(t=0)}^{T(t)} \frac{s}{\beta}\exp\left(-\frac{E_{\mathrm{t}}}{kT}\right)\mathrm{d}T'\right\} \quad \text{(for first-order kinetics)} \quad (1)$$

$$I_{\mathrm{TL}}(T) = n_0 s'' \exp\left(-\frac{E_{\mathrm{t}}}{kT}\right)\left[1 + (b-1)\frac{s''}{\beta}\int_{T(t=0)}^{T(t)} \exp\left(-\frac{E_{\mathrm{t}}}{kT}\right)\mathrm{d}T'\right]^{-\frac{b}{b-1}} \quad (2)$$

(for non-first order kinetics)

with $s'' = s'' n_0^{b-1} = s\left(\frac{n_0}{N}\right)^{b-1}$.

Equations (1) and (2) give the TL intensity (I_{TL}) under conditions for negligible and non-negligible retrapping at the defect level, respectively. In these equations, E_{t} is the activation energy of the trap level, n_0 is the initial concentration of trapped charge carriers, s is the attempt-to-escape frequency, β is the heating rate, T_0 is the starting temperature of heating process, N is the concentration of traps and b is the order of the kinetics. Detailed studies of curve-fitting analysis are reported in Refs. [23,24].

The intensity of the high-temperature peak C around 175 K (see Figure 1) is very low compared to its neighbouring peak at around 146 K. Therefore, we decided not to include this peak in the curve-fitting analysis and to perform the analysis in the temperature range of 30−170 K. Curve-fitting analyses were tried for a contribution of two trapping centres in the TL emission spectra. Figure 1 shows the two underlying components (peaks A and B) of the TL glow curve of GaS obtained by deconvolution using curve fitting. A first-order kinetic approach (application of Equation (1)) was not successful in describing the TL glow peaks. However, the glow curve could be deconvoluted into its components using a model function based on Equation (2). The curve was fitted to Equation (2) by gradually varying the kinetic order parameter b between 1 and 2 separately for peaks A and B. The best fitting was obtained with parameters $b_{\mathrm{A}} = 1.6$ and $b_{\mathrm{B}} = 1.2$ for peaks A and B, respectively. This outcome implies that mixed-order kinetics dominates the excitation process from the traps. Using curve fitting, the thermal activation energies of peaks A and B were determined as 52 and 200 meV, respectively. Since the studied crystals were not intentionally doped, these centres are thought to originate from anion vacancies caused by non-stoichiometry and/or stacking faults, which quite possibly exist in layered GaS owing to the weakness of the van der Waals forces between the layers [25].

3.2. *Anomalous heating rate dependence*

Measurement of the TL using various heating rates (and analysis of the associated shift of the peak temperature) is another technique used for determining the trap parameters from a TL glow peak. TL glow curves of the GaS crystal, measured at various heating rates ranging between 0.2 and 1 K/s, are given in Figure 2. As can be seen from the figure, a shift of the peak temperatures is observed for both peaks A and B. It is interesting to observe that the intensities of the peaks behave differently. The intensity of the low-temperature peak (peak A) behaves in an expected manner, that is the intensity decreases on increasing the heating rate. However, the intensity of peak B is observed

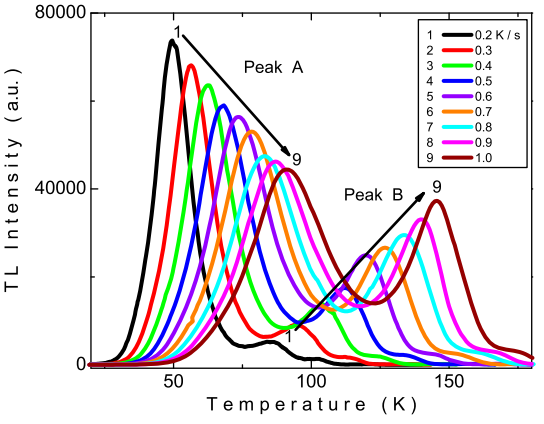

Figure 2. (colour online) Experimental TL curves of GaS crystal with various heating rates between 0.2 and 1.0 K/s.

to increase with increasing heating rate. A close inspection of the figure shows that the intensity of peak B increases sevenfold as the heating rate varies from 0.2 to 1 K/s. Such an increase can be ascribed to an increase in the probability of radiative transitions over that of the non-radiative transitions.

In normal circumstances, when the observed TL peak can be approximated using a one-trap/one-recombination mechanism model, a decrease of the TL peak intensity is expected and many of phosphors studied exhibit such a dependence on heating rate [20]. However, recent observations made on crystalline YPO_4 have shown that the peak intensity increased on increasing the heating rate [26]. In the literature, such a behaviour has been called an anomalous heating rate phenomenon and can be explained using a two-stage model where the stimulation of the trapped electrons takes place via an intermediate localized excited state and radiative transitions are possible via the conduction band [27]. A variation of such an approach is the semi-localized transition (SLT) [28,29] model, which considers an additional non-radiative transition that may take place directly from the localized excited state into a recombination centre. Details of the models can be found in references [27–29]. Briefly speaking, at low heating rates, the probability of non-radiative transitions is higher and as the heating rate increases (when the peak is reached at higher temperatures), the probability of transitions from the localized excited state into the conduction band increases. As the non-radiative transition probability is assumed to be temperature independent, the radiative recombination probability increases as the temperature increases, resulting in a higher TL peak at high heating rates.

Our current observation of an increase in intensity of peak B in the GaS TL glow curve can be explained using the same approach. It should be noted that the coexistence of normal (peak A) and anomalous heating rate (peak B) dependences is reported here for the first time.

In addition to the above-mentioned observation of heating rate dependences of the peak intensities, the heating rate dependences of the two peak temperatures (T_{max}) and the full-width-half-maximum (FWHM) values were also analysed. Figures 3(a) and (b)

presents the heating rate dependencies of the FWHM, T_{max} and intensity of peaks A and B. As can be seen from the figures, for peak A, both the peak temperature and FWHM increase from 49.5 to 91.2 K and from 14.5 to 35.0 K, respectively. For peak B, these values increase from 85.3 to 145.6 K and from 16.9 to 22.9 K, respectively.

3.3. *Determination of traps distribution*

Although some crystals may contain a single discrete trap level, others exhibit a continuous distribution of defect levels. In order to understand the nature of the traps associated with our observed glow peaks, we applied a technique based on changing the temperature at which illumination occurred in order to investigate the distribution of traps. In this technique, the sample was illuminated at a temperature (T_{0i}) higher than the starting temperature (which was 10 K) and, after switching off the illumination, the sample was cooled down to 10 K and the TL glow curve measured by heating up the sample at a rate of 1 K/s. Then, the experiments were repeated for successively higher illumination temperatures.

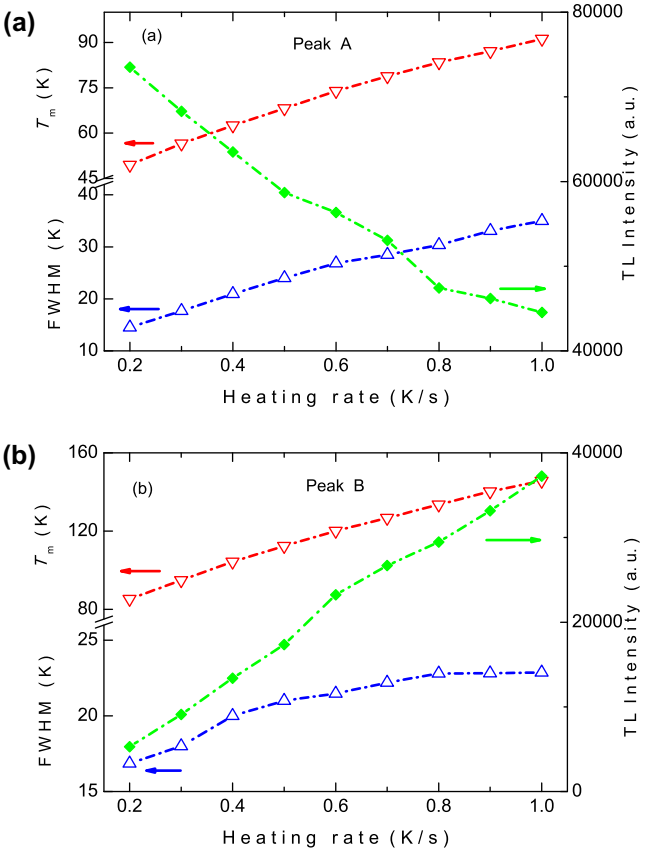

Figure 3. (colour online) (a, b) Heating rate dependencies of FWHM, peak maximum temperature (T_m) and intensity of TL curves (peaks A and B).
Note: The dash-dotted lines are only guides for the eye.

In this study, this process was undertaken with illumination temperatures ranging from $T_{0i} = 10$ K to $T_{0i} = 70$ K. Figures 4(a) and (b) shows the measured TL curves obtained after illuminating the GaS sample at various temperatures. With elevating illumination temperature, peak C in the TL spectra becomes more distinctive owing to 'thermal cleaning' of peaks A and B. As the concentration of trapped charge carriers diminishes gradually, the intensity of the TL curve exhibits a tendency to decrease and the peak maximum temperature (T_{max}) shifts towards higher temperatures with increasing illumination temperature (T_{0i}). This behaviour can be explained on the assumption of a quasi-continuous trap distribution [30–33]. The total number of charge carriers released from the traps corresponds to the total area enclosed under the curve obtained at a certain illumination temperature T_{0i}. The activation energies of released charge carriers were found using a curve-fitting method. The increase of the activation energy from 52 to 90 meV (peak A), from 200 to 268 meV (peak B) and from 304 to 469 meV (peak C) with rising illumination temperature from 10 to 30 K, from 10 to 50 K and from 30 to 70 K, respectively, can be explained in terms of charge carriers

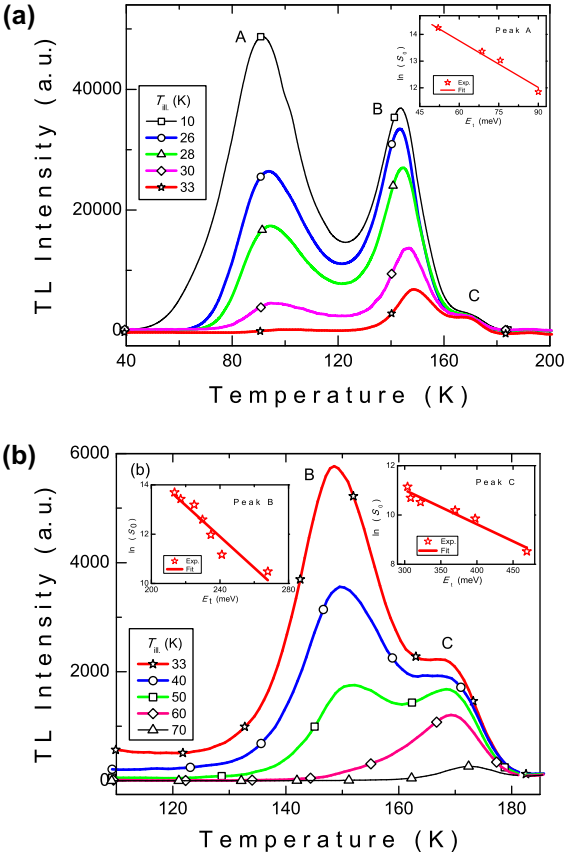

Figure 4. (colour online) (a, b) Experimental TL curves of GaS crystals at various illumination temperatures T_{0i}. Insets: ln S_0 plotted as a function of activation energy.

residing in deeper levels. The excitation energy for deeper levels should increase gradually to enable the release of carriers from trap levels during each preheating treatment [19,20,34]. Similar results on traps distribution were also reported previously in references [35–37].

The density of the traps can be assumed to be exponentially proportional to the activation energy as given by $N_{ti} = A_{exp}(-\alpha\ E_{ti})$, where α is a parameter characterizing the trap distribution. This assumption allows us to write the following equation for S_0 – the area enclosed under the glow curve, which is proportional to the number of traps filled at the illumination temperature T_{0i} [30]

$$S_0 \propto A\exp(-\alpha\ E_{ti}).$$

Plots of ln S_0 versus the activation energy are straight lines with slopes of $\alpha = 0.063$, 0.058 and 0.013 meV^{-1} for peaks A, B and C, respectively (see insets of Figures 4(a) and (b). These determined values imply a variation of one order of magnitude in the density of traps for depths of 36, 39 and 166 meV associated with peaks A, B and C, respectively.

4. Conclusions

TL of GaS single crystals has been investigated in the temperature range of 10–230 K. The TL exhibits glow curves composed of two intensive overlapping peaks at around 91 and 146 K and a weak third peak at 175 K. The thermal activation energies of the associated trapping states were determined using a curve-fitting method. As a result of the analysis, the activation energies of three trapping centres were determined as 52, 200 and 304 meV. The heating rate dependences of the revealed peaks were also studied. An anomalous heating rate behaviour of the high-temperature TL B peak was observed, while the normal behaviour was found for the low-temperature A peak. The TL intensity of peak B rises with increasing the heating rate between 0.2 and 1.0 K/s. This behaviour can be explained using a SLT model, which assumes competing radiative and non-radiative transitions. On the contrary, the TL intensity of peak A decreases with increasing heating rate. Moreover, a quasi-continuous trap distribution was inferred from the observation of increasing activation energies from 52 to 90 meV (peak A), from 200 to 268 meV (peak B) and from 304 to 469 meV (peak C) with rising illumination temperature in the ranges of 10–30, 10–50 and 30–70 K, respectively. Variations of one order of magnitude in the density of traps for depths of 36, 39 and 166 meV associated with peaks A, B and C, respectively, were determined.

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