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Optoelectronic properties of Ga_4Se_3S-layered single crystals

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Abstract
The optoelectronic properties of Bridgman method-grown Ga_4Se_3S single crystals have been investigated by means of room temperature electrical resistivity, temperature-dependent photosensitivity and temperature-dependent optical absorption. The photosensitivity was observed to increase with decreasing temperature, the illumination dependence of which was found to exhibit monomolecular recombination in the bulk at 300 K. The absorption coefficient, which was calculated in the incident photon energy range of 2.01–2.35 eV, increased with increasing temperature. Consistently, the absorption edge shifts to lower energy values. The fundamental absorption edge corresponds to an indirect allowed transitions energy gap (2.08 eV at 300 K) that exhibits a temperature coefficient of -9.5×10^{-4} eV K^{-1}.

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1. Introduction

The III–VI-layered compound semiconductors, such as GaSe, InSe, GaS and GaS_xSe_{1-x}, are promising candidates for future optoelectronic materials [1–10]. Because of the quasi-two-dimensional crystal structure with strong covalent bonds in two dimensions and only weak interactions of the van der Waals type in the third direction parallel to the *c*-axis, the optical transition is dominated mainly by the excitonic effect, which is also found in the quantum well or superlattice structure due to confinement effects. Besides, the compounds have large optical nonlinearity [9]. Therefore, these materials are promising for many applications in solid-state device fabrication. For example, they are used as the base material of the heterojunctions with window layers of SnO_2, ITO, In_2O_3 or used as window material together with the absorber layers such as InSe, CdTe, GaAs, Si, etc [1, 2]. MIS and Schottky barrier photovoltaic devices [3, 4] and semiconductor detectors made of GaSe [5–7] were also studied. Due to these potential applications, it is very important to determine the structural, electrical and optical properties of such materials. In addition to the GaSe crystals, most of the physical properties of the GaSe–GaS system crystals are being established as well [8–20]. In particular, the photoluminescence, Raman scattering, the thermally stimulated conductivity, the carrier-scattering mechanisms and the energy-localized levels in Ga_4Se_3S and Ga_4SeS_3 crystals have been studied.

Previously, we have studied the room temperature optical properties of Bridgman method-grown Ga_4Se_3S crystals by means of absorbance, transmittance and reflectance spectral analysis [21]. These optical data have revealed an indirect allowed transition band gap of 2.08 eV. The room temperature refractive index, which was calculated from the reflectance and transmittance data, allowed the identification of the dispersion and oscillator energies, static dielectric constant and static refractive index as 21.08 and 3.85 eV, 6.48 and 2.55, respectively.

In the present work, the room temperature electrical parameters and room temperature illumination intensity–photosensitivity dependence, the temperature-dependent photosensitivity and the temperature-dependent energy band gap of Ga_4Se_3S single crystals will be reported.

2. Experimental details

Single crystals of Ga_4Se_3S were grown by the Bridgman method from the stoichiometric melt of the starting materials

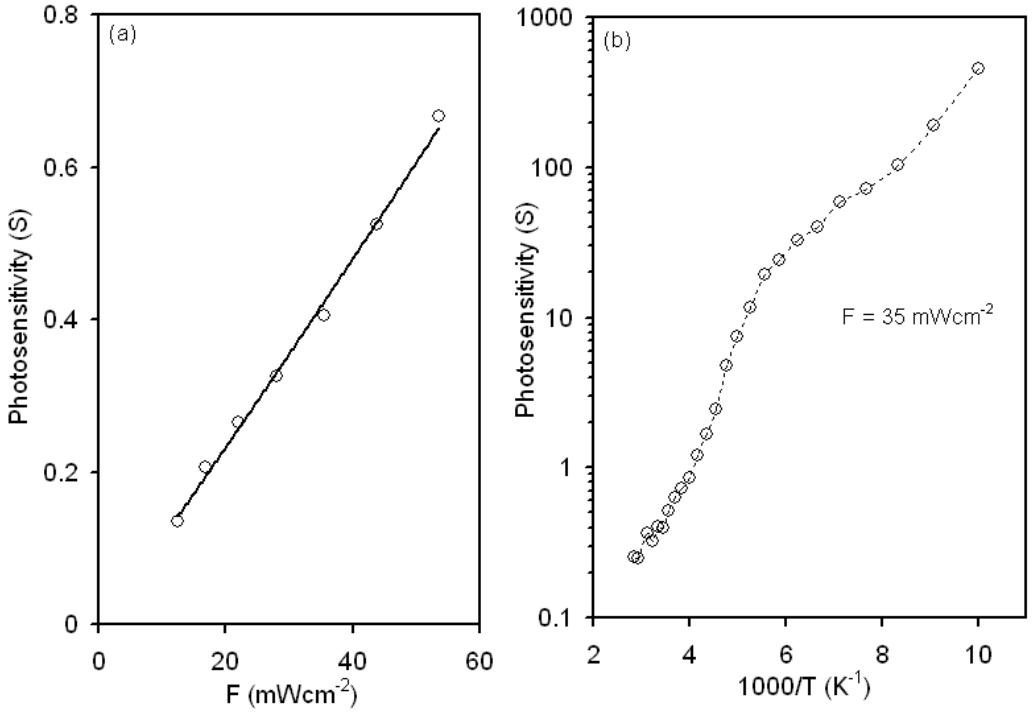

Figure 1. (a) The S–F variation. (b) The S–T^{-1} plot.

sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom. The ampoule was moved in a vertical furnace through a thermal gradient of 30 °C cm^{-1}, between the temperatures 1000 and 650 °C at a rate of 0.5 mm h^{-1}. The analysis of x-ray diffraction data showed that Ga_4Se_3S crystallized in a hexagonal unit cell with lattice parameters: $a = 0.3708$ and $c = 1.5915$ nm. The resulting ingots (orange in color) showed good optical quality and were easily cleaved along the planes, which are perpendicular to the c-axis of the crystal. Typical dimensions of the crystals suitable for electrical and optical measurements were $\sim 5 \times 5 \times 2$ mm^3 and $\sim 5 \times 5 \times 0.1$ mm^3, respectively. Using silver paste, four point contacts were fixed at the top surface of the sample. The ohmic nature of the contacts was confirmed by I–V characteristics. These characteristics were linear and independent of the reversal current in an applied voltage region of 1.0–200.0 V. Electrical resistivity and photosensitivity data were recorded in a Lake Shore 7507 Hall-effect measurements system. The data were collected using an IEEE computer interface and IDEAS software provided by Lake Shore. Cooling of the sample was achieved using a closed cycle cryostat (Advanced Research Systems) and Lake Shore 340 temperature controller. Light illumination was done using a halogen lamp. The light intensity was recorded using an IL1700 radiometer. The optical data were obtained using a Hewlet Packard 8453 A UV–VIS spectrophotometer.

3. Results and discussion

The sign of the Hall coefficient, R_h, indicates that the crystals exhibit n-type conduction. The room temperature dark electrical resistivity (ρ), carrier concentration (n) and Hall mobility (μ_h) of this crystal are found to be $7.7 \times 10^6\ \Omega$ cm, 8.3×10^9 cm^{-3} and 98 cm^2 V^{-1} s^{-1}, respectively. The value of the conductivity (ρ^{-1}) being of the order of $\sim 10^{-7}\ (\Omega\,\text{cm})^{-1}$, carrier concentration and Hall mobility are higher than that reported for Ga_4SeS_3 crystals as $\sim 10^{-9}\ (\Omega\,\text{cm})^{-1}$, 3.4×10^9 cm^{-3} and 48 cm^2 V^{-1}s^{-1} [19, 20], respectively, indicating that the replacement of Se atoms by S atoms significantly affects the electrical properties.

The photosensitivity, $S = I_p/I_d$, defined as the ratio of the photocurrent (I_p) to the dark current (I_d), measurements were carried out at different light intensities (F) in the intensity range 12.5–53.6 mW cm^{-2} and at fixed illumination intensity of 35.0 mW cm^{-2} in the temperature region of 100–350 K. The electrical field was fixed at 50.0 V cm^{-1}. The photocurrent was measured along the layer, while the light was incident, perpendicular to the layer. As illustrated in figures 1(a) and (b), the photosensitivity is found to increase with increasing illumination intensity and decreasing temperature. As for example in figure 1(a), the crystals exhibit a room temperature photosensitivity of 0.14 at illumination intensity 12.5 mW cm^{-2} and increases up to 0.67 at $F = 53.6$ mW cm^{-2}. Similarly, in figure 1(b), the crystals' photosensitivity increases from 2.5×10^{-2} at 350 K to 4.6×10^2 at 100 K. Figure 1(a) indicates that the S–F dependence follows the relation $S \propto F^{\gamma}$. The γ value calculated from the slope of the logarithmic S–F plot is 1.0 reflecting a linear dependence of sample photosensitivity on illumination intensity. The $\gamma = 1.0$ value indicates that the linear recombination with all the recombination centers being empty (monomolecular recombination in the bulk) are dominant at room temperature.

Figure 1(b) shows the representative data of the experimental photosensitivity as a function of reciprocal temperature for Ga_4Se_3S single crystals at fixed illumination intensity. As can be seen, the photosensitivity increases exponentially with decreasing temperature. The observation of the thermal quenching of photosensitivity at fixed

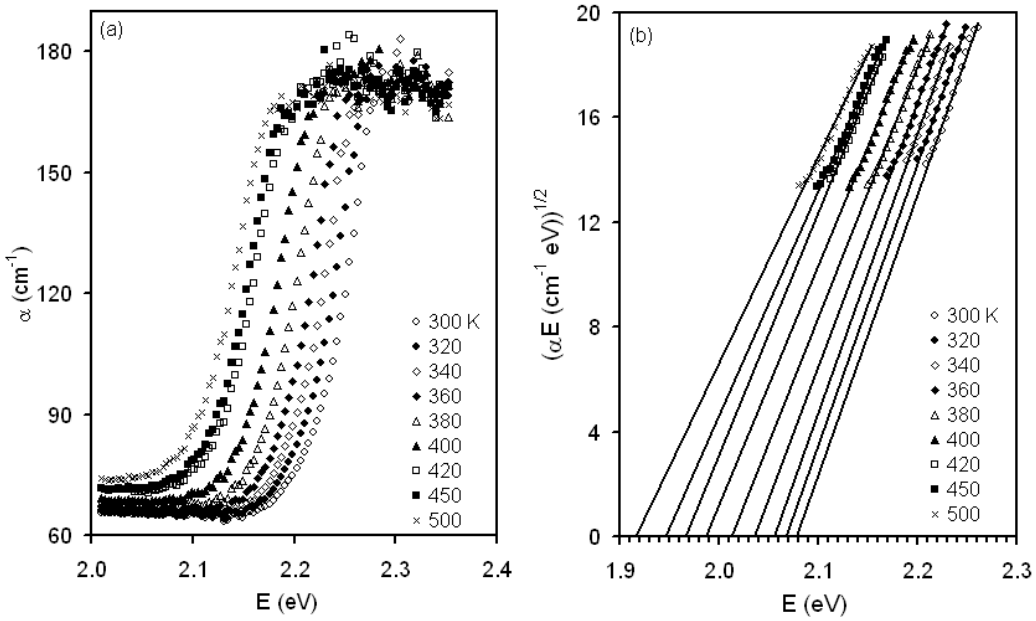

Figure 2. (a) Temperature dependence of the absorption coefficient for Ga_4Se_3S crystal. (b) The $(\alpha E)^{1/2}$–E plots at selected temperatures.

illumination intensity may be ascribed to the exchange in the behavior of the sensitizing centers. In other words, when sensitizing centers change their behavior from recombination centers to trapping centers at fixed illumination intensity thermal quenching of photosensitivity is observed [22].

In our previous work [21], we have reported the oscillator parameters of Ga_4Se_3S single crystals. In addition, we have also reported that the crystal under investigation exhibits the indirect allowed electronic transitions energy band gap of 2.08 eV. Following the same procedure of determination of the energy gap and as a continuation of that work, we now discuss the temperature dependence of this energy band gap in the temperature region of 292–500 K.

Figure 2(a) illustrates the change in the behavior of the absorption coefficient with temperature. It is possible to observe, that the absorption edge shifts toward lower energy value when the sample temperature was raised. Figure 2(b) represents the best linear plot that covers the widest range of data in accordance with equation (2) of [21], which as reported was obtained for the $(\alpha E)^{1/2}$–E dependence. The extrapolation of straight line—shown by the solid lines in the figure—down to $(\alpha E)^{1/2} = 0$ gives the value of the indirect allowed transition energy band gap (E_{gi}). As the figure displays, the value of E_{gi} decreases with increasing temperature. Namely, it shifts from 2.09 to 1.92 eV as temperature increases from 292 to 500 K. The temperature dependence of the energy band gap can be represented by the relation [23]

$$E_g(T) = E_g(0) + \frac{\gamma T^2}{T + \beta}. \quad (1)$$

Here, $E_g(0)$ is the absolute zero value of the band gap, $\gamma = dE_g/dT$ is the rate of change of the band gap with temperature and β is approximately the Debye temperature. The Debye temperature for Ga_4Se_3S crystal $\beta = 211$ K was estimated by Lindemann's melting rule [24] using x-ray results reported in the previous section. The data of the E_{gi}–T dependence (figure 3) are fitted using equation (1). The fitting of the equation, which is represented by the solid line in the figure, revealed fitting parameters of $E_{gi}(0) = 2.25$ eV and $\gamma = -9.5 \times 10^{-4}$ eV K^{-1}.

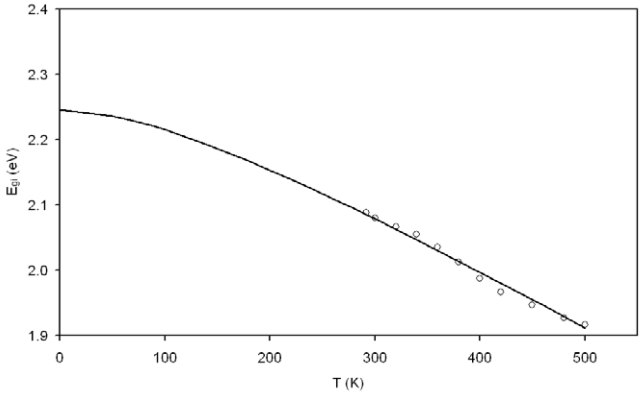

Figure 3. The energy band gap as a function of temperature. The solid line represents the theoretical fit using equation (1).

The room temperature indirect band gap being 2.08 eV, calculated through this study for the Ga_4Se_3S crystal, is close to that reported in literature for similar crystals [25]. The temperature dependence of the band gap of the Ga_4Se_3S crystal in the high-temperature region (292–500 K)—up to our knowledge—is not studied yet. The behavior of the E_{gi}–T dependence is similar to that reported for GaSe- and GaS-layered crystals [26–28]. For GaSe crystal, the E_{gi}–T dependence revealed a γ value of -4.4×10^{-4} eV K^{-1} and $E_{gi}(0) = 2.11$ eV. For GaS-crystal, γ and $E_{gi}(0)$ were reported to exhibit the values of -5.6×10^{-4} eV K^{-1} and 2.69 eV, respectively.

4. Conclusions

In this work, the electrical, photo-electrical and optical properties of Ga_4Se_3S crystal have been investigated. In

particular, the room temperature electrical parameters, the photosensitivity dependence on light intensity and on temperature and the dependence of the energy band gap on temperature are studied. The photosensitivity–illumination intensity dependence is found to be linear at 300 K. Similarly, at fixed illumination intensity, the photosensitivity is observed to increase with decreasing temperature. The absorption edge was observed to shift toward lower energy values as temperature increases. The data are used to calculate the indirect energy band gap of the crystal as a function of temperature. The rate of change of the band gap with temperature is $-9.5 \times 10^{-4}\,\mathrm{eV\,K^{-1}}$ and the absolute zero value of the band gap energy is $E_{\mathrm{gi}}(0) = 2.25\,\mathrm{eV}$.

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