Features of Electrical and Photoelectric Properties of GaS(Yb) Monocrystals

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Abstract: The electrical and photoelectric properties of GaS(Yb) monocrystal have been studied in the range of 100–300 K. It has been established that as the partial compensation of structure defects (V\text{Ga}) occurs due to the inclusion of ytterbium dopant, the electroconductivity of GaS monocrystal decreases. The simultaneously occurrence of substitution (Yb\text{Ga}) of cation vacancy – V\text{Yb} and Yb-Ga due to the formation of acceptor and donor type two charged local centers during the doping, leads to a self-compensating process. As a result, the specific resistance of the crystal increases, and thermal activation and extinction processes are observed in the temperature dependence of photoconductivity.

Keywords: Activation Energy; Anisotropy; Mobility; Photoconductivity; Vacancy.

1 Introduction

GaS monocrystals have strong structure anisotropy, like the layered A\text{III}B\text{VI} crystals [1–5]. The structure feature is related to the presence of strong ion-covalent bonding plane atomic packing inside the layer and weak van der Waals force between the layers. And it leads to the distribution of dopant atoms in the different spaces (inter-layer or intralayer). Although aforementioned facts are investigated in [5–8], the obtained results do not allow proposing the model describing the distribution mechanism of dopant atoms.

One of the other interesting properties of layered crystals is a low mobility and small diffusion path of free charge carriers in the direction of crystalline c-axis due to a large number of specific defects (cation and anion vacancies, Frenkel defects), especially cation vacancies (10^{17}–10^{18} cm^{-3}) [7]. Therefore, p-type conductivity is formed in them, and high-ohmic crystals are partially compensated. Although the influence of the concentration of dopant atoms (rare earth elements) on the photoelectric properties of layered crystals is investigated in the wide temperature range in the works of [7–9], the unit mechanism for the purposeful control of conductivity has not been given, as the nature of defects is not taken into account in the obtained results. Other studies [1, 9–13] show that it is more expedient to use ionising rays (γ-irradiation) in order to control the concentration of defects. However, as the amount of radiation defects depends on the obtaining method of crystals, it is impossible to have an idea of a unit mechanism.

Therefore, the purpose of the study is to investigate electroconductivity and photoconductivity of the doped monocrystal of GaS(Yb) in the wide temperature range in order to get more data on the effects of specific and dopant-type point defects on the electronic structure in the layered p-GaS monocrystal.

2 Experimental Part

GaS monocrystals have been obtained by Bridgman–Stockbarger’s oriented crystallisation method. The temperature gradient was 20–30 K/cm, and the growth rate was 0.13 mm/h in the crystallisation zone. The obtained monocrystals had p-type conductivity and their specific resistance (ρ) was (10^{7}–10^{8}) Ohm-cm at the room temperature. The excess of sulphur element has been taken into account in order to decrease the amount of sulphur vacancy during the crystal obtaining. The degree of anisotropy was ∼10^{2} in respect of crystal axis. The doping of crystals has been carried out during their growth. Ytterbium (Yb) has been chosen as a dopant atom, and its amount has been ∼(0.5; 1.0) at%. The grown GaS(Yb) monocrystal also has p-type conductivity like pure crystals, and it is equal to ρ∼10^{5} Ohm-cm. It has been determined on the basis of microstructure
and X-ray analyses that the obtained monocrystals are homogeneous, and crystalline accumulation has not been observed in them. The samples with a strong surface and 0.2-mm thickness, which are scaled in the direction of layer (0001), have been prepared for the research. Silver paste (in aqua) has been used to obtain an ohmic contact. The electrical and photoelectric properties of the prepared samples have been measured at the temperature of 100–300 K, and electrometric amplifier (V7-35), MS3504i-type monochromators to get a monochromatic light beam, and the halogen lamp as a source of light have been used during the measurement.

The obtained spectra have been normalised according to the amount of quanta of incident light. The measurements have been carried out in the wavelength range of λ = 380–850 nm and the temperature range of T = 10–300 K. The samples are illuminated after cooling down to 100 K in the dark and heated at low speeds in order to obtain thermostimulating current (TSC) curves. The intensity of electrical field between electrical contacts was \( E = 10 \text{ V/cm} \). The sample was heated at low speeds after keeping in an excited state for a certain period, and the current generated during the directed movement of loads generated by thermal ionisation is mentioned. The energy state of the traps has been determined according to maximums in TSC curves, which is obtained during the experiment [17].

The method of Rivkin [15] has been used during the measurement of photoelectric properties of the sample. Thus, the sample with the sizes 2, 5, and 0.1 mm is placed in air-absorbed crystallat after the inclusion of electroconductive contacts, and the measurements have been taken after cooling in liquid nitrogen. The monochromatic ray is so chosen that it falls to the linear region of \( f \sim f(L) \).

### 3 Discussion of Experimental Section and Conclusions

The temperature dependence of the electroconductivity of GaS and GaS(Yb) monocrystals in the dark (black and red curves) and GaS(Yb) various lighting (blue and pink curves) is shown in Figure 1. It is also seen in Figure 1 that the dependence of \( \sigma(T) \) (black and red curves) obeys the exponential law \( \sigma(T) = \sigma_0 \exp(-\Delta E_\text{F}/kT) \) and has a nature of compensated doped semiconductor. The activation energy of the dependence \( \sigma(T) \) (black curve) defined from the linear region of \( T < 200 \text{ K} \) corresponds to \(-0.15 \text{ eV} \) and from the high temperature range \( T > 300 \text{ K} \) corresponds to 0.8 eV. It can be said on the basis of obtained results that the conductivity and concentration of undoped GaS monocrystal are determined by two acceptor-type levels, which are sharply different from each other: \( E_\text{A} + 0.15 \text{ eV} \) and \( E_\text{A} + 0.8 \text{ eV} \). It should be noted that the thermal discharge rate of the level is very low in the low-temperature range than the high-temperature range. And it shows that the concentrations of the observed levels of \( E_\text{A} + 0.15 \) and \( E_\text{A} + 0.8 \text{ eV} \) are different. It is known that anion and cation vacancies and rapid volatile component (in our case, sulphur) in the binary-type double compounds create the condition for the formation of acceptor- and donor-type defects in the band gap of the compound. And it leads to self-compensation, and as a result, the electroconductivity of the sample decreases. This fact proves itself during the doping of p-GaS monocrystal with ytterbium atom. It is seen from Figure 1 (red curve) that the electroconductivity of the sample decreases in the low-temperature region during the inclusion of Yb atom and increases at temperatures of \( T > 250 \text{ K} \). The activation energy defined from the rectilinear parts of the dependence of \( \sigma(T) \) (red curve) was 0.16 and 0.8 eV, respectively. The obtained result allows us to say that the Yb atom creates a shallow donor-type level by filling the gallium vacancy (V\text{Ga}), and as a result, the conductivity of the sample decreases, but Yb\text{Ga} substitution creates a deep acceptor-type level. And it leads to the increase in conductivity at temperature of \( T > 250 \text{ K} \). The samples have been illuminated with different-intensity monochromatic rays in order to determine the nature of the defect and doping levels (Fig. 1, blue and pink curves). It has been established that the conductivity increases due to the filling of the defect levels under the influence of light.

The integral photosensitivity \( \sigma_\text{light}/\sigma_\text{dark} \sim 10^2 \) increases as a result of the decrease in dark current during the doping of GaS crystals with Yb atoms, and it has been determined that the increase in photosensitivity depends on the temperature and light intensity.

Temperature dependence of photocurrent in GaS(Yb) monocrystals is given in various light intensities in Figure 2. It is seen in Figure 2 that two processes – thermooxidation of photocurrent in low-temperature range and thermal extinction of photocurrent (TEP) in high-temperature range – are observed in the temperature dependence of photoconductivity in the doped GaS(Yb)
It should be noted that the dependence of TEP on the light intensity and temperature has been determined from obtained results. This fact is clearly seen from the dependence graph of photocurrent on light intensity given in Figure 2. It is seen in Figure 2 that the photocurrent increases by the growth of temperature during the constant-intensity monochromatic (specific lighting) lighting in GaS(Yb) crystal, and the TEP occurs at the temperature value of \( T > 250 \) K. The depth of TEP decreases with the increase in light intensity, and it is not observed at higher values.

The dependence of photoconductivity on light intensity in GaS(Yb) crystal at various temperatures is given in Figure 3. It seems from the figure that the dependence of photocurrent on the light intensity changes with linear law at 100 and 300 K temperatures (Fig. 3, black, red, and blue curves), and gradual activation of photocurrent by the increase in temperature is observed. The photocurrent has a linear nature in the low intensities, and it sharply increases in high intensities during the measurements at \( T = 300 \) K. The value of the upper coefficient of \( n \) has been determined from the straight line part of the \( J \sim f(E) \) dependence and, respectively, was 0.7 and 0.9. The studies show that the activation and extinction processes of photocurrent are characteristic for the crystals having wide band gap [14], and it is also observed in the doped layered crystal of GaS(Yb). Thus, the processes observed during the experiment prove that there are two types (\( r \)-slow and \( s \)-fast) of recombination and deep traps in the band gap of doped GaS(Yb) monocrystal, and the photoconductivity can be explained based on the multichannel recombination model [15].

The spectra of photoconductivity and absorption band in the layered crystal of GaS(Yb) at \( T = 100, 300 \) K, are shown in Figure 4.
It is seen from the comparison of the spectra of photoconductivity (black, red, and blue curves) and absorption band (pink and green curves) that the maximum of photocurrent in the spectrum (black curve) of the undoped GaS crystal corresponds to $h\nu_{\text{max}} = 2.5$ eV, is located on the absorption band (pink curve), and corresponds to band-to-band transition. This result agrees with the results obtained in previous studies [1, 11, 12, 16, 17]. At the same time, the low maximum that connected with the nonlinear transition is observed in the value of $h\nu_1 = 2.3$ eV in the spectrum. It is seen from Figure 4 that the additional maximum is observed in the doping region of photoconductivity spectrum ($T = 100$ K; $h\nu_2 = 1.85$ eV), beyond the absorption region due to the inclusion of dopant atom (Yb). It can be said from the comparison of energy state of additional maximum and the edge of permitted band that this maximum belongs to the donor-type level ($V_{\text{Yb}}$) formed due to the substitution of gallium vacancy with Yb atom.

Thermostimulating current curves in GaS(Yb) monocrystal are shown in Figure 5. It is seen from the graph that the maximum values of the current are observed in the curve at temperatures of 145, 200, and 270 K. Considering that the starting point of the curve obeys to $I_T \sim \exp(-E_t/kT)$ law and the Fermi quasi-level coincides with the capture centre [14, 17] in the given temperatures, the energy state of the capture levels has been determined. We observe acceptor-type levels for GaS and GaS(Yb) samples based on the TSC curves in Figure 5. It has been discovered that the energy levels are the same in both monocrystals of GaS and GaS(Yb), but their concentration are different; the capture levels with energy of 0.16, 0.40 and 0.75 eV exist in the band gap of doped GaS(Yb). The concentration of 0.4 eV level is not observed in electrical conductivity during the experiment as it is smaller than 0.16 and 0.75 eV. Exactly the sharp difference in their concentrations and energy states leads to the thermal activation and thermal extinction processes of the photoconductivity.

The most efficient method for the effective modification of electrical and photoelectric properties of wide-band semiconductors is the doping with halogen atoms. We consider that the major defects in the GaS monocrystals grown by the excess of S atom are the Ga vacancy. P-type conductivity in GaS monocrystal is formed due to the high concentration of defects ($10^{17}$–$10^{18}$ cm$^{-3}$). In some cases, the level of $E_V + 0.8$ eV is also observed. The inclusion of the Yb atom creates a donor- and an acceptor-type level in the band gap of GaS crystal, and they form a condition for the activation and TEP. These results correspond to the results in previous studies [11, 12, 16]. It should be taken into account the band structure of crystals and state density of defects in order to define the defect–dopant interaction during the doping of layered crystals. In the studies [18–22], considering the results obtained from the study of the band structure of A$^{\text{III}}$ B$^{\text{IV}}$ crystals and state density of defects and our experimental results, it has been determined that the electronic structure of layered crystals depends on interaction of the element components and valence electrons of the included dopant atoms. The obtained experimental results show that acceptor and donor states are generated as a result of the interaction of component elements and p-orbital of dopant atom due to the substitution of Ga atom with Yb atom ($V_{\text{Yb}}, Yb_{\text{Ga}}$) during the inclusion of dopant atoms. There occurs the filling of cation vacancies when dopant atom is $N_{\text{Yb}} < 1$ % and the generation of $Yb_{\text{Ga}}$-type states when it is $N_{\text{Yb}} \sim 1$ %. This fact is seen from Figure 1. Thus, the electroconductivity of the sample decreases, and partial compensation of the acceptor level occurs as a result of the inclusion of Yb atom. The processes of activation and TEP observed in Figure 2 prove the existence of the recombination centres – slow (r) and fast (s). On the basis of obey of the nature of TSC curves to $I \sim \exp(-E_t/kT)$ and considering the study of Bub [17], it has been determined that the depth of defined capture level shows the relative change in the concentration of initial levels as a result of inclusion of Yb atom. The change of concentration of capture levels, i.e. the unequal filling of recombination centres by capture centres, strongly influences the recombination process in the GaS(Yb) monocrystals.

It can be said on the basis of noted facts that the reason of a decrease in conductivity due to the inclusion of Yb

![Figure 5: Thermostimulating current in GaS (red) and GaS(Yb) (black) monocrystals.](image-url)
dopant atom in p-GaS monocrystal and thermal activation and extinction processes of photocurrent is related to a decrease in the concentration of structure defects. Thus, the regulation of defects at low concentrations of Yb dopant \( (N_{Yb} < 1\%) \) and the increase in local nonhomogeneity at high concentrations of Yb dopant \( (N_{Yb} \sim 1\%) \) [23] are observed.

References