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The effect of an external magnetic field on the luminescence of gallium phosphide crystals

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The effect of a constant magnetic field on photoluminescence spectra in single crystals of gallium phosphide was found in the work. It was found that the preliminary exposure of GaP crystals in a constant magnetic field (B < 0.5 T) at room temperature leads to the ignition of a luminescence band with a maximum of $\lambda = 565 \text{ nm}$ when exposed to a laser crystal with a wavelength of 405 nm and a power of no more than 10 mW. At the same time, the relaxation time of the strip to its initial state did not exceed 3 hours. The authors attribute the observed features to the influence of the magnetic field on both the rate of intercombination conversion $(S_1 \rightarrow T_1)$ in GaP crystals and the transition of gallium phosphide complexes with nitrogen to an excited state.

Keywords: gallium phosphide, permanent magnetic field, luminescence, relaxation, intercombination conversion.

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Gallium phosphide (GaP) continues to attract interest due to its application in a variety of semiconductor devices, including light-emitting structures [1]. Both the bulk semiconductor material and epitaxial layers, nanowires, and quantum dots based on GaP are used to form light-emitting structures.

For example, a method for production of GaP-based quantum dots was detailed in [2]. Quantum dots were formed by hot injection using a combination of precursors. The obtained samples demonstrated controlled emission within the range from 400 to 520 nm and high photoluminescence quantum yields (up to 40%) [2]. In addition to quantum dots, the authors of [3] propose the use of gallium phosphide nanowires doped with rare earth metals. Specifically, it was found that co-doping of GaP with samarium and gadolinium atoms affects the magnetic properties of gallium phosphide nanowires. In addition, double doping with Gd and Sm atoms leads to a reduction in band gap width E_g (from $E_g = 2.44 \text{ eV}$ to a semi-metallic state) [3]. This effect is proposed to be used to control the spectral composition of stimulated emission of GaP-based structures.

As was already noted, several authors propose the use of epitaxial GaP layers in construction of light-emitting structures. Specifically, polycrystalline GaP films with a thickness of 25-30 nm were deposited in [4] onto Si (100) by the plasma deposition method (duration, up to 20 s; power, 75 W) with the use of a mixture of Ar and H₂ with a partial pressure of 10 and 40 mTorr, respectively. Local epitaxial growth of GaP on GaAs with high stoichiometry (P/Ga = 1.05), low O content (~ 3.1 at.%), and smooth surface morphology (a surface roughness of 1.6 nm) was performed via atomic plasma deposition in [5]. These

methods provide an opportunity to form light-emitting heterostructures with thin GaP layers on various substrates.

An attempt to control the semiconductor properties with magnetic fields (MFs) is an interesting and promising research direction in GaP technology. Specifically, the authors of [6] have discovered that a single-crystal GaP layer is magnetized significantly due to the formation of a Ga vacancy. In this case, an unbalanced spin-dependent distribution of charges of P atoms closest to the vacancy site is the factor inducing a magnetic moment enhancement. In addition, it was found that GaP acquires the properties characteristic of magnetic semiconductors after doping with alkali metals (Li and Na) and Se atoms [6].

Another aspect that should be emphasized is the influence of MFs on the electrical, mechanical, and optical properties of non-magnetic semiconductors and dielectrics [7–9]. For example, preliminary exposure to a constant magnetic field (with magnetic induction $B \leq 1$ T) may raise the dislocation mobility and reduce the microhardness (GaAs, InSb, Si, NaCl, etc.). Preliminary exposure to a constant MF also affects the optical properties of materials. Specifically, it was found that the integrated brightness of electroluminescence increases several times after exposure of ZnS single crystals with microtwins to a magnetic field with an induction of 1 T or higher [10].

In addition, the effect of preliminary exposure to a constant magnetic field on the photoluminescence spectra of quenched NaCl:Eu crystals was reported. It is assumed that the observed changes are related to intracenter atomic rearrangements of dimers (decay and subsequent formation of dimers of a different type) [11]. The mechanisms of these changes are associated with spin-dependent reactions in the subsystem of structural defects. An MF enables

0.3 1 cm 0.2 0.1 0 500 550 600 650 700 750 800 λ , nm

Figure 1. Luminescence spectra of GaP(Zn,N) single crystals before (1) and 130 (2), 70 (3), 30 (4), and 5 min (5) after preliminary exposure to a constant 0.4 T magnetic field for 30 min at room temperature. A photographic image of a GaP wafer is shown in the inset.

the rearrangement of magnetosensitive complexes under the influence of external forces.

Thus, magnetic fields may be used to alter the mechanical and optical properties of dielectrics and semiconductors to a considerable extent. However, although a large volume of experimental data has been accumulated, virtually no studies into the effect of constant magnetic fields on luminescence of GaP single crystals have been performed. Therefore, the aim of the present study is to investigate the effect of preliminary exposure of gallium phosphide crystals to a constant MF on their luminescence spectra.

Single crystals of p-GaP(Zn,N), which are gallium phosphide wafers with a diameter of 30 mm and a thickness of 0.45 mm, were studied (see the inset in Fig. 1). A constant magnetic field with B < 0.5 T for their preliminary exposure was produced between the poles of neodymium magnets. An OHSP-350P spectrophotometer was used to record luminescence spectra at room temperature (5 min after the end of the magnetic exposure). In our experiment, luminescence spectra were recorded in a classical setup: luminescence was excited by radiation from a semiconductor laser diode with a power up to 10 mW and a wavelength of 405 nm.

The luminescence spectra before and after exposure of the crystal to a constant MF are shown in Fig. 1. It is evident that the luminescence spectrum of the studied samples features two bands with maxima at $\lambda_1 = 565 \text{ nm}$ (characteristic of nitrogen-doped GaP, $E_1 = 2.2 \text{ eV}$) and $\lambda_2 = 700 \text{ nm}$ (manifested in zinc-doped oxygen-containing single crystals; luminescence at Zn–O complexes, $E_2 = 1.8 \text{ eV}$ [12,13]. The ratio of intensity maxima $I_{\lambda_2}/I_{\lambda_1}$ measured 5 min after the magnetic exposure did not exceed 3.

These experiments revealed that preliminary exposure of crystals to a constant MF with B < 0.5 T leads to an increase in intensity I_1 of the luminescence band of the crystal with $\lambda_1 = 565$ nm. Figure 1 (curves 2–5) provides a clear illustration of variation of the I_1 luminescence intensity maximum ($\lambda_1 = 565 \text{ nm}$) with time elapsed after exposure of the crystal to an MF with B = 0.4 T.

Having performed multiple experiments, we found that maximum intensity I_1 first increases after the magnetic exposure, which is followed by its relaxation (Fig. 2) that takes up as much as 180 min (regardless of the magnetic field induction). It is easy to see that measurements at two magnetic field magnitudes provided similar results. We believe that the effect has already reached saturation in these fields; at lower values of induction B, "threshold" values of B below which the effect vanishes are to be expected. Examples of such effects are provided in review [7].

In our view, the observed change of the luminescence band is associated with the influence of the magnetic field on the rate of intercombination conversion $(S1 \rightarrow T1)$ in the GaP single crystals under consideration. In addition, this effect may be related to the formation of complexes of gallium phosphide with nitrogen in an excited state. It is known [2,14,15] that the internal quantum yield of the luminescence band with a maximum at $\lambda_1 = 565 \text{ nm}$ in gallium phosphide is close to 1-3%, which is much lower than the quantum yield of the luminescence band at $\lambda_2 = 700 \text{ nm} (10-20\%)$. Thus, preliminary exposure of samples to a constant MF allows one to raise the quantum yield of the luminescence band with $\lambda_1 = 565$ nm. As for the characteristic relaxation times of magnetosensitive changes, the observed times are apparently representative of diffusion processes in complexes of structural defects [16,17].

Thus, the influence of a constant magnetic field on luminescence spectra in GaP crystals was examined. It was found that the intensity of the luminescence band with a maximum at $\lambda_1 = 565 \text{ nm}$ excited by a laser with a wavelength of 405 nm and a power of 10 mW increases after exposure to a constant MF. The temporal dependence of maximum intensity I_1 of the luminescence band was also determined. Thus, a constant magnetic field may affect the spectral characteristics of various crystals. The presented results may facilitate the development of efficient methods for modifying the electronic properties of GaP monolayers,





Figure 2. Dynamics of variation of maximum intensity I_1 of the luminescence band with a maximum at $\lambda_1 = 565$ nm. I — Prior to exposure of the GaP crystal to a magnetic field; 2 — after exposure to a constant magnetic field with B = 0.25 (a) and 0.4 T (b) for 30 min at room temperature.

enabling the fabrication of novel multifunctional materials for optoelectronic applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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