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Effect of pulsing magnetic field on radiative recombination spectra of GaP and InP single crystals

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Abstract. We present the results of investigations concerning the effect caused by weak magnetic field (B = 15 mT and 60 mT) treatment on GaP and InP single crystals of impurity-defect composition. This effect was found when studying the radiative recombination (luminescence) spectra within the range 0.6 to 2.5 μm at 77 K. It was obtained that a short-term influence of field initiates long-term changes in the intensity of radiative recombination inherent to centers of different nature. General regularities in behavior of the luminescence intensity have been found. This intensity changes with the concentration of recombination centers. A possible mechanism of observed transformations has been discussed.

Keywords: photoluminescence, weak magnetic field, impurity-defect composition.

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1. Introduction

Up to date, it is established that weak magnetic fields (MF) with the induction $B \leq 1$ T can essentially influence on the real structure and properties of various non-magnetic materials at room temperatures [1, 2]. The investigations carried out with alkali-halide crystals attribute the structural changes appearing due to magnetic treatments to the destruction of defect complexes inherent to these materials. Such destruction leads to formation of non-equilibrium natural and impurity defects that participate in quasi-chemical reactions of formation of new electrically active centers. An interesting feature is that the observed changes in the defect subsystem take place at the energy values that are some orders of magnitude lower than the activation energy for reorganization of structural defects.

There are numerous theoretical and experimental investigations of the changes of the state of defects caused by exposure in MF. Many of these investigations deal with ionic crystals. The amount of publications devoted to the study of MF induced effects in silicon and Si-SiO_2 structures is small [3-6]. And the question about the effect of perspective weak pulsing MFs [7-9] on the modification of physical properties of practically important III-V semiconductors still remains open.

For finding-out the nature of observable effects in these materials, using the spectral techniques, in particular the luminescent ones [10], for objects, which defect nature was reliably ascertained at the microscopic level, seems reasonable. In this work, the luminescent properties of indium and gallium phosphides were studied as a result of influence of pulsing MFs.

2. Experimental

Single crystals of GaP doped with Te (carrier concentration up to 10^{17} cm^{-3}), and CZ-grown n-type InP crystals without intentional doping were used in our investigations. Stationary photoluminescence (PL) spectra were measured at 77 K within the spectral range 0.5 to 2.4 eV. Magnetic-field treatments were carried out using MF single pulses (pulse duration ~30 ms, the induction 15 and 60 mT) and 60 s pulse series (with $B \sim 60$ mT, $f = 10$ Hz, and duration of pulse 2 ms). The samples were treated at room temperature in ambient atmosphere.

3. Results and discussion

Stationary PL spectra of GaP crystals measured before and after MF treatment at 15 and 60 mT are shown in Figs 1 and 2, respectively. The shape of the spectra of initial samples in the region of impurity-related emission testifies the imperfect crystalline structure of samples and high concentration of uncontrollable impurities. The

bands with $h\nu_{\max_1}^{\mathrm{GaP}} = 1.72$ eV and $h\nu_{\max_2}^{\mathrm{GaP}} = 1.28$ eV dominate in the initial samples.

Despite numerous investigations of optical properties of both GaP itself and impurities in it, identification of bands in radiation recombination spectra is a complicated problem, which is caused by many factors. They are: presence of various impurities, including uncontrollable (in the ground state and in excited states), various inter-impurity transitions in donor-acceptor (DA) pairs and phonon repetitions, various distances between impurities in lattice, etc.

According to [11-13], we attribute the band at 1.72 eV to the inter-impurity recombination, namely: donor (Te)/hole trap formed by the V_{Ga}-$3D_P$ complex. Here, D = S, Se, or Te. These complexes should be electrically neutral (isoelectronic), because three donor atoms substituting P supply three electron deficiencies to near-neighbor Ga vacancy. In the heavily Te-doped GaP crystals, the nature of isoelectronic centers is related to the V_{Ga}-$3Te_P$ complex, as shown in [12], contrary to the existing statement that the band at 1.7 eV appears due to the microcrystalline inclusions of phosphorus. In view of [14], we believe that the band with $h\nu_{\max_2}^{\mathrm{GaP}} = 1.28$ eV is related to the inter-impurity recombination in the long-range DA pairs with participation of oxygen, which is responsible for the emission in the narrow infrared region (1.25 to 1.50 eV).

Magnetic-field treatment at the induction close to 15 mT does not result in essential changes of the emission spectra (a small decrease in the PL intensity is observed). The intensities of PL peaks after short-term treatments increased and exceeded the initial ones. Long-term changes in the PL spectra after switching the field off had a non-monotonic character and were different for bands of various origin. Actually, synchronous changes in the intensity of PL bands were observed only at the initial stage after MF treatment. Then the time dependence showed the following features. The growth of 1.72 eV peak intensity with increasing the time period after treatment was accompanied by lowering the intensity of the peak at $h\nu_{\max_2}^{\mathrm{GaP}} = 1.28$ eV and vice versa.

Long-term changes in the intensity for certain time intervals are accompanied by shifts in the frequency positions of band peaks, namely, a blueshift of the band at $h\nu_{\max_2}^{\mathrm{GaP}} = 1.28$ eV and redshift of the band at $h\nu_{\max_1}^{\mathrm{GaP}} = 1.72$ eV.

The above described results as well as the change in the half-widths of bands allow us to conclude that MF treatment influences not only on the concentration of dominating centers that form the PL spectra but also promotes the appearance of new emission bands that overlap with the observed ones.

The increase of the magnetic field induction up to 60 mT results in qualitatively similar changes in long-term non-monotonic dependences of the band intensity. Differences are observed only at the initial stage of long-term relaxation: the intensity of the PL peak at $h\nu_{\max_1}^{\mathrm{GaP}} = 1.72$ eV is not practically changed, while the PL peak at $h\nu_{\max_2}^{\mathrm{GaP}} = 1.28$ eV is quenched.

At the same time, absolute changes of intensity values that occur after treatments are similar. It allows us to conclude that the effects of long-term relaxation do not depend on the value of MF and are a consequence of a general mechanism that influences on structural states of defects. Activation of this mechanism is caused by pulsing magnetic field.

It should be noted that residual changes in the luminescence spectra are observed for a long time after MF exposure (up to several days), which distinguishes the observed phenomena from those observed only in the cause of MF action. These are, for example, changes of photocurrent [14]. Besides, experiments on PL from GaP crystals were carried out under conditions when the

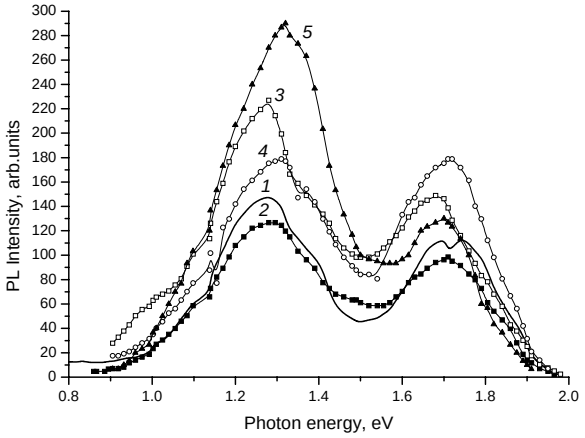

Fig. 1. PL spectra of the GaP samples before (*1*), after magnetic-field treatment B = 15 mT (*2*), and kept for 3 (*3*), 7 (*4*), and 17 (*5*) days after treatment.

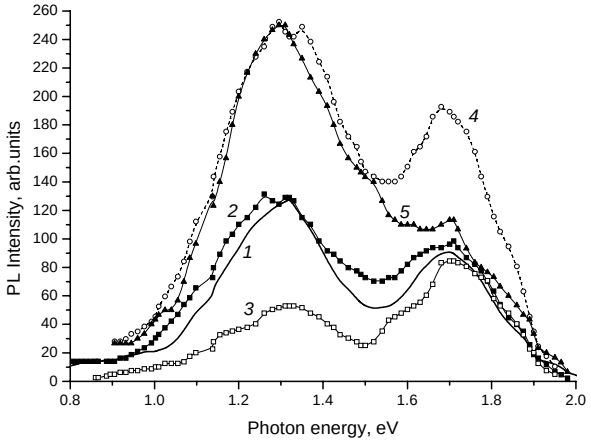

Fig. 2. PL spectra of the GaP samples before (*1*), after magnetic-field treatment B = 60 mT (*2*), and kept for 3 (*3*), 7 (*4*), and 17 (*5*) days after treatment.

energy "transmitted" to structural defects in magnetic field with the induction B satisfied the requirement $\mu_B B << kT << Q_a$, with μ_B being the Bohr magneton, $T = 290$ K the MF treatment temperature, and Q_a the activation energy of the reorganization of defect complexes. In view of these factors, it is natural to attribute the observed changes in PL spectra to the spin-dependent conversion of structural complexes, into which composition paramagnetic defects enter [1, 2]. MF influence on PL under condition of $\mu_B B << kT$ results in changes of the multiplicity of defect complexes and thermally induced break of weak bonds between defects, removes spin forbidding for reactions between defects in GaP. These transformations occur with defects of both radiative and non-radiative recombination, which are most probably in metastable state.

To reveal how the weak MF influences on the reorganization of defects in InP crystals, we consider the changes in the parameters of PL bands in details. It is natural that the microstructure of centers of radiative recombination differs from that in GaP.

Stationary PL spectra of Cz-InP crystals measured before and after the treatment by a single pulse of MF with $B = 60$ mT, $\tau = 30$ ms are shown in Fig. 3.

PL spectra of initial InP consist of only two bands with the peaks at $h\nu_{\max_1}^{\mathrm{InP}} = 1.41$ eV and $h\nu_{\max_2}^{\mathrm{InP}} = 1.14$ eV. We believe in view of data of PL researches of undoped crystals InP *n*-type [11-15] and experimental values of peaks position for radiation recombination, it is possible to assume that the passes through shallow donor and partially band to band transitions of free electrons and holes participate in forming of the peak near 1.41 eV.

The calculated ionization energy, drawing on a position of a spectral band maximum, makes ~7 meV, which is in a good agreement with the energy position of Si donor level in InP [15], atoms of which together with Fe atoms are spread non-controlled impurities in the above semiconductor.

According to that stated above, the band at $h\nu_{\max_2}^{\mathrm{InP}} = 1.14$ eV probably originates from the $[Fe_{In}+V_P]$ complexes [16]. It should be noticed that in [17] a more grounded model of the center responsible for the band close to 1.14 eV is presented. According to this model, this center is formed by Fe atoms in the positions of In atoms and P vacancies, $Fe_{In}V_P$.

As a result of MF treatment of indium phosphide, like to the earlier experiments with GaP, long-term and oscillatory changes in the intensity and half-width of PL bands are observed. Values of the intensity after MF exposure can be both higher and lower than the initial ones. The biggest changes in the intensity are observed in some time interval after MF exposure. The changes of the radiative recombination spectra of InP and GaP crystals are qualitatively similar. This supports the common mechanism of defect structure reorganization as a result of MF treatment. From this statement, one can expediently compare the effects of the single pulses of MF with series of symmetric pulses with definite duration.

PL spectra of InP samples before and after pulsing MF treatment ($B = 60$ mT, $f = 10$ GHz, $t = 60$ s) are shown in Fig. 4. The intensity of PL bands immediately after this treatment was not practically changed like to that observed for single-pulse MF treatment. For some time period after MF exposure, non-monotonic changes in the intensity of both impurity and near-edge bands were observed. Small displacements of the positions of band maxima were observed, too. Reproducibility of these shifts however, was not established accurately. Absence of synchronous changes in intensities of the observed bands specifies that their behaviour cannot be explained as the change of the channel for non-radiative recombination only. Most probably, like to the case of single pulses, the reorganization of centers responsible for radiative recombination takes place, too. The shifts of maxima and change in the half-width of impurity band as well as observed in some samples bands at $h\nu_{\max_3}^{\mathrm{InP}} = 1.05$ eV and $h\nu_{\max_4}^{\mathrm{InP}} = 1.21$ eV, which nature

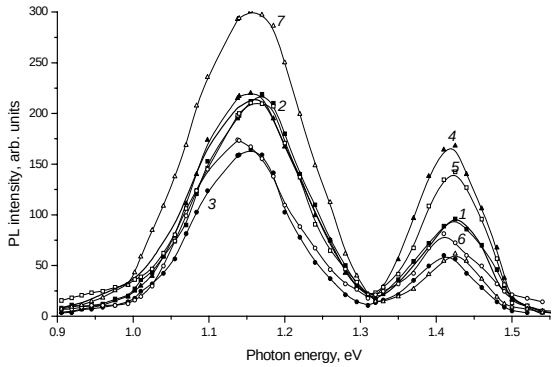

Fig. 3. PL spectra of the InP samples before (*1*), after magnetic-field treatment ($B = 60$ mT, $\tau = 30$ μs) (*2*), and kept for 1 (*3*), 7 (*4*), 9 (*5*), 14 (*6*), and 15 (*7*) days after treatment.

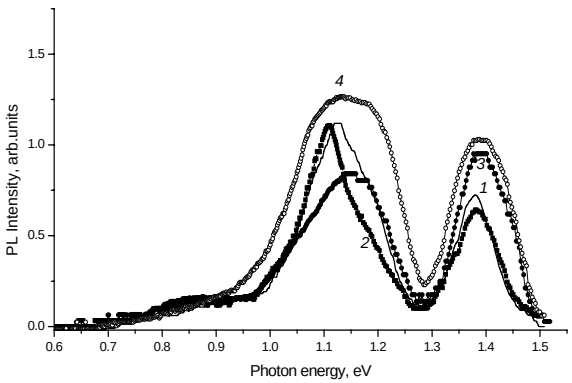

Fig. 4. PL spectra of the InP samples before (*1*), after magnetic-field treatment ($B = 60$ mT, $f = 10$ Hz, $t = 60$ s) (*2*), and kept for 1 (3) and 11 (*4*) days after treatment.

are related to the donor-acceptor pairs V_P-impurity and P_i-impurity, respectively [18], confirm it.

Although some differences in changes of PL spectra are observed (which can be caused by differences of the structural state of initial InP samples), general regularities can be summarized as follows:

i) MF treatment results in essential changes of radiation recombination spectra;
ii) changes in the intensities of impurity bands are feebly pronounced immediately after MF treatment, but for amplification of these changes, which are grounded on a structural changes in lattice of semiconductors, the time interval after switching the MF off is necessary;
iii) the changes in PL bands intensities are long-term and oscillatory;
iv) the effect of magnetic field is the change of both radiative and non-radiative channels of recombination.

Despite many reports on the influence of MF treatment on properties of semiconductors [1-9], it was not possible up to now to offer a comprehensive well-grounded model of the observed phenomena. The main obstacle is the lack of convincing data about the type of atoms and the defects that form complexes sensitive to MF. The analysis of the nature of PL centers done in this paper confirms convincingly what was noted above. But it should be noted that magnetic-sensitive centers consist of paramagnetic defects and impurity atoms with non-zero nuclear spin in all the cases. According to [4], destruction of impurity-defect complexes occurs as caused by the increase of filling the excited triplet states of defects during relaxation of electron-nuclear spin system polarization after exposure to MF. As a result, non-equilibrium native point and impurity defects appear that induce local quasi-chemical reactions. However, it is impossible to definitely establish the nature and concentrations of structural defects that arise from mentioned destructions. It is possible to ascertain only that these defects can form the radiative and non-radiative recombination centers, which result in the changes of intensities in the observed luminescence bands. Their long-term changes are determined by diffusion rates of the components of impurity-defect complexes that are destructed as a result of pulsing MF treatments.

The last but not least, structural reorganizations induced by MF will occur most efficiently in a near-surface area of semiconductor. This is characterized by the increased concentration of initial structural disturbances. This area was studied in the present paper.

4. Conclusions

For the first time, the effect of weak (60 and 15 mT) pulse magnetic field on the spectra of defect states in GaP and InP was observed experimentally. It was defined that the short-term influence of MF initiates long-term changes in the photoluminescence intensity of centers of different nature. The observable changes in these PL spectra are probably caused by the influence of MF on a spin-dependent quasi-chemical destruction reactions and subsequent association of point defects and impurities.

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