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Changes in impurity radiative recombination and surface morphology induced by treatment of GaP in weak magnetic field

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Abstract. In this work, the results of studying the long-term changes in the intensity of photoluminescence bands and surface morphology of gallium phosphide caused by treatment in weak magnetic fields have been presented. A non-thermal mechanism based on the idea of defects transformation due to the random events related with defect subsystem modification has been proposed. The radiation power of electromagnetic waves emitted by electrons in the studied semiconductor has been estimated. Fitted parameters for the long-term transformation intensity of photoluminescence and diffusion factor for appearing defects have been calculated.

Keywords: photoluminescence, dislocation, random event, resonance, ion-plasma frequency, weak magnetic field, microwave radiation.

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1. Introduction

Controlling the changes in the microstructure of semiconductor materials by means of applying weak magnetic fields (WMF) (for these fields, the relation $\mu_B B \ll kT$ with μ_B being the Bohr magneton and B – magnetic induction, respectively, can be accepted) is a promising area of research. This control is possible only provided the mechanisms underlying the processes of defect transformations have been ascertained. Because of the small energy of interaction between point and linear defects as compared to the energy barriers required for initiation of motion (the so-called "kT-problem" [1]), one can suggest that weak magnetic field-induced phenomena could be related to alternative mechanisms. Realization of the spin-related mechanisms [1-6] as well as resonant mechanism [7, 8] for modification of structural parameters inherent to the structures under investigation can be observed at small energy values of external action. Transformations of defect subsystems stimulated by both spin-related processes and resonant phenomena do not require high energy values. Therefore, one can expect some combination of these processes under the real experimental conditions.

Analysis of the defect behavior in the diamagnetic dielectric and semiconductor crystals under action of weak magnetic fields has been presented from different points of view. According to one of them, magnetoplastic effects are caused by spin-related reactions occurring in radical pairs of paramagnetic defects (dislocation-stopper) [1, 2]. Paramagnetic centers in semiconductors are broken bonds in the cores of dislocations, carrying unpaired electrons [3], as well as oxygen atoms, ions of donors and acceptors acting as stoppers [2, 4, 5]. Singlet-triplet transitions in the mentioned pairs of paramagnetic defects result in the detachment of dislocations from the stoppers and their subsequent movement under the influence of a mosaic of internal mechanical stresses in the crystal [1, 2]. An alternative point of view was discussed in [9], where it was emphasized that a crucial role in the magnetoplastic effect can be attributed to the clusters of defects sensitive to the action of magnetic field. To explain the features of behavior of crystals in magnetic fields, a mechanism based on the concept of the destruction of paramagnetic defect complexes due to spin-dependent reactions within these complexes was proposed [10]. In [11], the concept of lattice-related defect induced magnetism was developed in the analysis of the destruction of defect complexes. At the same time, an important feature of semiconductor crystals is the presence of free-to-move charge carriers in them. Their dynamics in magnetic field can have a significant impact on the defect evolution in semiconductor materials.

The purpose of this paper is to present the results of experimental studies aimed at transformations of radiative recombination spectra and surface morphology of III–V semiconductor compounds induced by action of pulsed magnetic fields, as well as the analysis of corresponding mechanism of defect evolution that is based on the concept of magnetic field excitation of the electron subsystem (holes).

2. Experimental

The samples of GaP(111) under investigation were Czochralski grown and *n*-type doped with Te. The concentration of donors was $8 \cdot 10^{16}$ cm^{-3} and thickness was 350 μm.

Influence of WMF on the morphology (roughness) of the surfaces and integrated PL spectra of gallium phosphide were studied (all surfaces of the samples under study were under light excitation). PL spectra of GaP:Te were measured at room temperature within the spectral range 500–800 nm. The roughness parameters of material surfaces were estimated using the atomic force microscopy (AFM) data. The increase of analyzed area was accompanied by the rise of the peak height distribution. This indicates the fractal mechanism of relief formation in the samples under investigation. We used the approach proposed in [12] for the analysis of fractal dimensionality by the triangulation method. This approach enables to obtain reliable information about the actual area of the scan.

Pulsed magnetic field treatment of the structures under investigation was performed for 3 min by cyclically moving the sample through the gap of a permanent magnet with the induction B = 60 mT using a rotating modulator. The rotation frequency was 10 Hz. To control natural aging of samples and formation of surface oxides, the sample receiving no magnetic field (MF) treatment was used as the reference for each material. It was kept under the equal conditions with treated samples between the measurements.

3. Results and discussion

The initial PL spectrum of GaP:Te crystals in the red range contains one impurity band near 1.83 eV (Fig. 1a) attributed to complexes [11]. We had therefore the samples with typical defect structures and background impurities. Initial roughness parameters as well as fractal dimensions obtained by the triangulation method based on approximation with a straight line of the data (Fig. 1c) for the studied samples are summarized in Table 1.

Magnetic field treatment did not significantly change both the PL spectra and the surface parameters of III–V semiconductors. However, after processing long-term (up to 1 month) restructuring of semiconductor defect subsystems takes place, which can be deduced analyzing the obtained PL spectra and AFM data of the samples under investigation. Fig. 1 shows evolution of the PL spectra and fractal dimensions of GaP:Te after WMF processing. It should be noted that changes in the PL spectra of studied semiconductor are accompanied by

Table 1. Morphological characteristics of GaAs:Te samples determined from AFM data (R_{ms} – root-mean-square deviation, R_a – arithmetic average deviation).

State of samples	R_{ms} (nm)	R_a (nm)	Fractal dimensionality
Initial state	6.90	5.28	2.31
1 day after treatment	6.92	5.82	2.36
7 days after treatment	5.88	5.71	2.46
14 days after treatment	7.41	5.98	2.49
21 days after treatment	6.8	5.33	2.35
35 days after treatment	6.52	5.14	2.29

modification of their morphological parameters, and an increase of roughness is observed at the first stage. However, return to the initial parameters of both PL spectra and morphological characteristics were observed later. Moreover, in some cases even smoothing of the surface was observed, similar to that observed in silicon samples [13] after magnetic field treatments.

The observed changes in the intensity of PL band and surface morphology can be explained using the concept of dynamics inherent to dislocation behavior and impurity complexes in the near-surface regions (*i.e.*, the regions in which the electron-hole pairs are generated by PL excitation light). This dynamics corresponds to detachment of dislocations from local stoppers and destruction of impurity complex clusters [8, 14]. These phenomena are accompanied by migration of defects [8, 14–16] and activation of oxidative processes [17].

When a semiconductor crystal is placed into homogeneous magnetic field with constant induction, free electrons with scalar effective mass begin to move along spiral trajectories that are screw lines with the axis coinciding with the direction of magnetic field induction. The angular frequency of electron rotation is called the cyclotron (Larmor) frequency. For non-relativistic particles (for electrons in a semiconductor crystal, the thermal velocity is much smaller than the speed of light), it is equal [18]:

$$\omega_B = \frac{eB}{m_n}, \quad (1)$$

where e is the elementary charge, B – magnetic field induction, and m_n – effective electron mass in the semiconductor crystal, respectively.

Since electron undergoes acceleration during rotation, which has a constant magnitude and is directed along the normal to the linear velocity, it is a source of electromagnetic radiation with the frequency ω_B [18]. The radiation power of electromagnetic waves emitted by electrons in a volume unit of a semiconductor crystal is expressed as follows [19]:

$$W = \frac{ne^2 \omega_B^2 \upsilon_T^2}{12\pi \varepsilon_0 \varepsilon c^3}, \qquad (2)$$

where ε_0 is the electric constant of vacuum, ε – dielectric function of semiconductor, υ_T – thermal mean square velocity of electrons, c – speed of light in vacuum, and n – concentration of free electrons in this semiconductor, respectively.

In particular, for GaP:Te we have obtained the following results. In this semiconductor compound, the effective mass of electrons is a tensor quantity. In our approach, we replace it by the effective mass of states density. Our calculations by using Eqs (1) and (2) are: $\nu_B = \omega_B/2\pi = 2.1\cdot10^9$ Hz, $W = 0.15$ W·m^{-3} (the effective mass of states density is $m_c = 0.79m_0$, where m_0 is the electron rest mass, $\varepsilon = 11.1$, $\upsilon_T = 2\cdot10^5$ m·s^{-1} [20]).

It should be noted that the regions where magnetic field has the induction orders of magnitude smaller than 60 mT were also present (at the edge of magnet). The samples moved through these regions during rotation as well. That is, the result is by orders of magnitude smaller for the cyclotron frequency. Therefore, electromagnetic waves in a wide frequency range will be generated in the semiconductor crystal.

Thus, one can expect that the mechanisms of defect structure transformation in epitaxial films treated in pulsed magnetic fields could be the same as those proposed at the non-thermal effect of wide range microwave electromagnetic irradiation [21]. Transformation of the defect subsystem under the action of microwave radiation is caused by a detachment and displacement of dislocations as well as destruction of the clusters of impurity-defect complexes with subsequent diffusion of destruction products. This diffusion is favored by resonant phenomena related to the coincidence between the electromagnetic wave frequency and proper frequencies of dislocation oscillations and plasma oscillations of impurity ions [8, 14, 22]. At the resonant frequency with small attenuation, the amplitude and, hence, the oscillation energy increase sharply. As soon as the oscillation energy becomes higher than the binding energy of defects, the observed changes of the state of the latter occur.

4. Concept of equivalence

The proposed concept of equivalence of the effects caused by pulsed magnetic field treatments and non-thermal action of microwave radiation with the frequencies in the wide range is consistent with the following experimental facts.

(i) Experimental studies of changes in the structural perfection of the surface layers of III–V semiconductor compounds after exposure to magnetic field pulses indicating generation, transformation, and destruction of Frenkel defect clusters, as it was presented in [23]. These changes enhanced in the series of GaAs–InAs–InSb materials. This feature can be explained by the fact that the effective masses of free charge carriers decrease in this series. Therefore, taking into account (1) and (2), both the frequency ω_B (the range of frequency spectrum expands) and the power of electromagnetic radiation increase. These both circumstances result in the changes of structural perfection inherent to the surface layer of semiconductor compounds under action of magnetic field pulses.

(ii) Physical-statistical analysis of the long-term dependences of PL intensity changes after processing in WMF and under electromagnetic radiation indicates the equivalence of mechanisms responsible for transformation of defects under these two types of actions.

It was shown [24] that the considered physical processes can be represented by random events and the corresponding random variables (times to events) and are the subject to the Weibull–Gnedenko distribution. We assume that motion of a defect from the subsurface region to the surface and migration of a defect to the subsurface region from the epitaxial layer adjacent to this subsurface region are random events. Then this physical-statistical approach (as well as at microwave radiation treatment) allows us to obtain the following relation for the time dependence of the normalized intensity of integrated PL [8, 14, 21]:

$$I(t) = 1 \pm I_0 \left\{ \left[1 - e^{-\left(\frac{t}{\tau_1}\right)^{m_1}} \right] e^{-\left(\frac{t}{\tau_2}\right)^{m_2}} \right\}, \qquad (3)$$

where I_{in} is the initial value of the intensity of photoluminescence band, I_0 – proportionality factor, τ_1, τ_2 are the time constants of random events, and m_1 and m_2 – form factors of the distribution function of time to a corresponding random event.

Shown in the inset of Fig. 1a are the results of approximation obtained using the expression (3) and the least-square method for intensity changes in the integrated PL inherent to the III–V structures under investigation. One can see a good agreement between experimental and theoretical data. The fitted parameters for approximation are summarized in Table 2.

Table 2. Fitted parameters for the expression (3) and calculated diffusion factor.

Fitted parameter	GaP:Te
I_0	4.51
τ_1 (days)	13.01
τ_2 (days)	20.02
m_1	11.21
m_2	3.74
Calculated D, 10^{-14} cm^2/s	8.9

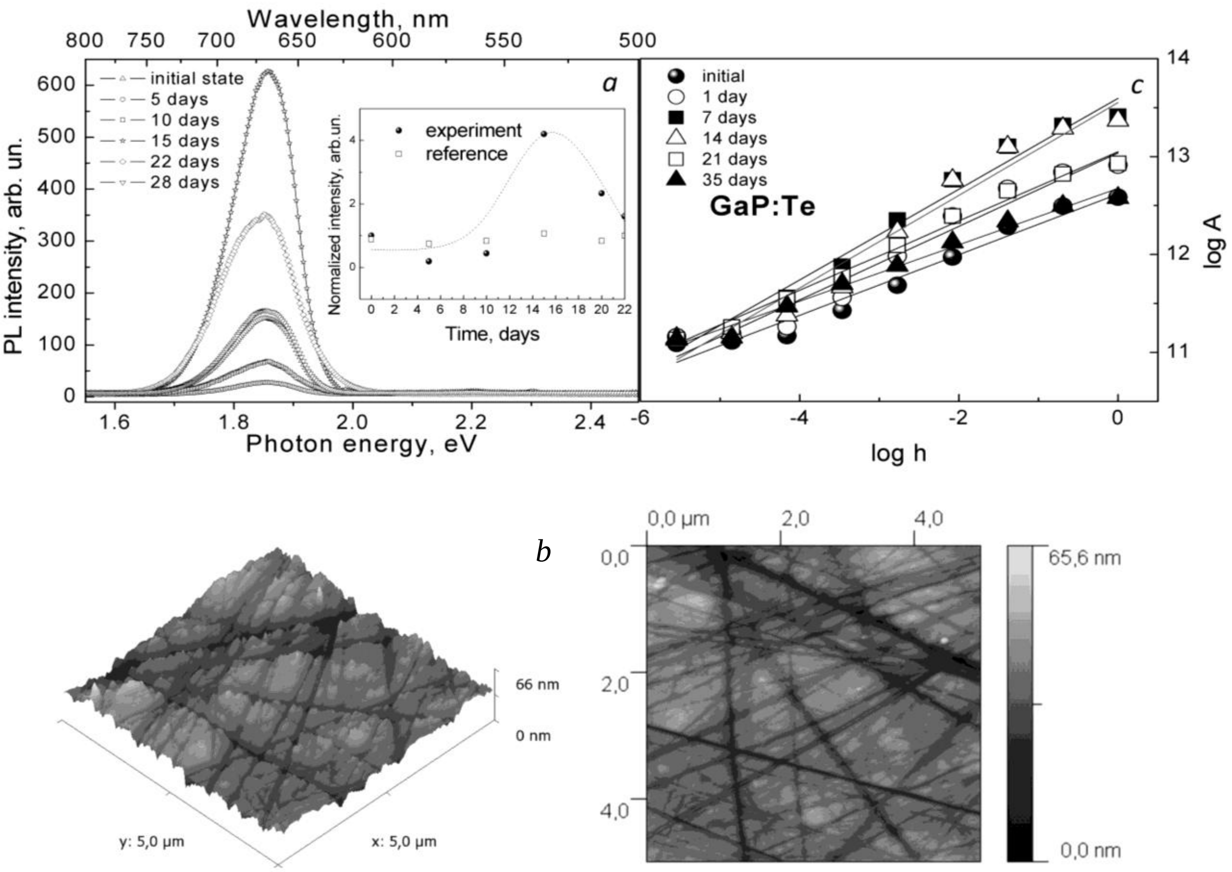

Fig. 1. Evolution of GaP:Te PL spectra after magnetic field treatment (a) (inset: the dependence of integrated PL intensity on the time after processing), AFM image of the initial state of the sample (b) and bundle of lines to obtain the values of fractal dimensionality using the triangulation method (c).

Let's estimate the parameters characterizing transformation of the defect structure. If the motion of defects has a diffusion character, in accordance with [24], $\tau_1 = d^2/D$, where D is the effective diffusion factor and d – thickness of the layer, in which the electron-hole pairs are generated under exposure to light of PL excitation. Since the absorption coefficients of III–V compounds under investigation in the studied spectral range are $\sim 10^4$ cm^{-1}, and $d \sim \alpha^{-1}$, in our experiments d is equal to about 10^{-4} cm. The calculated value of D is presented in Table 2. The obtained values, at least within one order of magnitude, are in fairly good agreement with similar estimates of the diffusion factors of migrating impurities appearing due to the non-thermal treatment with microwave electromagnetic radiation: $1.65 \cdot 10^{-14}$ cm$^2 \cdot$s^{-1} (for GaN), $2.06 \cdot 10^{-14}$ cm$^2 \cdot$s^{-1} (for GaAs) [8, 14]. This feature indicates generality of the non-thermal mechanisms responsible for the processes stimulated by microwave electromagnetic radiation and those taking place at the interaction of weak magnetic field with semiconductor structures.

5. Conclusions

In conclusion, the dependences of PL intensity and surface morphology on the time after the WMF treatment of III–V semiconductor compounds have been investigated. The results and conclusions of this study can be summarized as follows. (i) The after-effect (oscillatory changes of PL intensity and roughness parameters) is qualitatively the same for all the compounds studied and confirms earlier results obtained using other III–V compounds [25]. (ii) There is a strong correlation between PL intensity and AFM-data changes, which testifies the same nature of these phenomena. (iii) To explain the observed features, alternative mechanisms are required (because of "*kT*-problem"), such as, *e.g.*, the spin-conversion mechanism [1, 10, 11] or/and the resonant-related one [8].

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Зміни домішкової випромінювальної рекомбінації та морфології поверхні, викликані обробкою GaP у слабкому магнітному полі

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Анотація. У цій роботі наведено результати вивчення довготривалих змін інтенсивності смуг фотолюмінесценції та поверхневої морфології фосфіду галію, спричинених обробкою в слабких магнітних полях. Запропоновано нетепловий механізм, що базується на ідеї перетворення дефектів внаслідок випадкових подій, пов'язаних з модифікацією дефектів підсистеми. Оцінено потужність випромінювання електромагнітних хвиль, збуджених рухом електронів у досліджуваному напівпровіднику. Розраховано емпіричні параметри для довготривалої трансформації інтенсивності фотолюмінесценції та коефіцієнти дифузії для дефектів, які з'являються.

Ключові слова: фотолюмінесценція, дислокація, випадкова подія, резонанс, іонно-плазмова частота, слабке магнітне поле, мікрохвильове випромінювання.