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CONTROL OF THE PARAMETERS OF GaAs:Si p-n STRUCTURES BY GYROTRON IRRADIATION

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It is shown that using gyrotron irradiation it is possible to control the p-n junction in an already fabricated light-emitting structure. Shift of the compensated region of emitting structure based on GaAs:Si *is conditioned by the motion of impurities in the field of thermoelastic stresses appearing during cooling of the samples after gyrotron irradiation.*

Keywords: *GYROTRON IRRADIATION, LIGHT-EMITTING STRUCTURES, IMPURITIES, CONTROL OF THE p-n JUNCTION, THERMOELASTIC STRESSES.*

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1. INTRODUCTION

Except the traditional thermal annealing methods [1], non-traditional irradiation methods by the fluxes of neutral and charged particles [2-5] are widely used during last years in the production of semiconductor devices, in particular, at the control of the energy and geometric parameters of the *p-n* junctions (especially by the profile of doping impurity and position of the interface in the volume of the material). The achieved level of understanding of the physical processes occurring during interaction of these particles with non-homogeneous semiconductor structure allowed to propose technological control methods of the *p-n* junctions in an already fabricated optoelectronic device.

However, each of these methods has fundamental individual or general for all pulse methods disadvantages: substantial defect formation (injection of point and more complex defects), non-uniformity of heating of semiconductor structure, initiation of not only longitudinal but also transverse temperature gradients, appearance of thermoelastic stresses, etc.

In connection with this, in the present work we have analyzed the case of the control of the *p-n* junction in an already fabricated light-emitting structure (LES) using its irradiation by uniform in area electromagnetic microwave radiation of the millimeter range (gyrotron irradiation) that provides rapid, controlled, reproduced, and uniform heating of the whole volume of device up to the specified temperature.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

As the subject of the research, we have used semiconductor *p-n* junctions based on highly doped and compensated (HDC) by silicon gallium arsenide (GaAs:Si) and obtained in one technological cycle during growth of LES by the liquid-phase epitaxy method from the limited volume of arsenic and silicon melt in gallium solution on *n*-GaAs(Sn) substrates oriented in the plane (100). When growing *p-n* structures, mass fraction of silicon was equal to 0,2-0,4% that corresponds to the structures with maximum quantum yield of irradiation. At the growth temperature T_g more than 900°C silicon was incorporated into gallium sites mainly (substitutional impurities Si_{Ga}) and formed *n*-layer, and at $T_g < 900$°C – into arsenic sites (substitutional impurities Si_A) and formed *p*-layer. Concentration of the incorporated silicon impurities was $\leq 5 \cdot 10^{18}$ cm^{-3} and concentration of the majority charge carriers in *n*- and *p*-regions far from the space-charge region of the *p-n* junction (in particular, on the LES surface) did not exceed the value of $5 \cdot 10^{17}$ cm^{-3}, and in the vicinity of the *p-n* junction it was as minimum 1-2 orders less, and compensation factor of the material (k) was close to 1. The value of the factor k was estimated using shift of the wave-length in the maximum of the radiation band of the *p-n* structure.

Samples were irradiated by monochromatic coherent microwave radiation of gyrotron with the wavelength of $\lambda \approx 3$ mm ($f = 10^{11}$ Hz). Surface density of the flux of microwave radiation varied in the range of $P = 1$-10 kW/cm^2, radiation time varied in the range of $t = 1$-10 s. Absorption coefficient of this radiation by the material of GaAs structure did not exceed 0,3 mm^{-1}, and almost uniform radiation penetration over the whole thickness of the irradiated *p-n* structure took place.

Gyrotron irradiation of GaAs:Si structures was carried out in two stages.

1) Preheating during $t = 2$-3 s at $T = 300$ °C.

2) Main irradiation during $t = 1$-10 s at $T = 850$-1200 °C (melting temperature of GaAs was equal to $T_m = 1238$ °C). Here, the action of microwave radiation on the studied structures was exhibited in two aspects: thermal (in the form of heating) and electromagnetic (in the form of vortex electromagnetic field).

All electrophysical, kinetic, and radiation characteristics of the samples were measured at the room temperature.

Profile of dominating (in the active region of the *p-n* junction) impurity ($N_A - N_D$) and position of the *p-n* junction itself in the volume of the device structure were estimated using measurements of the dC/dV characteristics [6]. Moreover, effective lifetime of nonprincipal charge carriers by the method of the *p-n* junction switching [7] and integral and spectral characteristics of electroluminescence (EL) [8, 9] were studied as well.

3. RESULTS AND DISCUSSION

3.1 Shift of the p-n junction

In Fig. 1 we represent the profiles of dominating (in the active region of the *p-n* junction) impurity ($N_A - N_D$) which specifies the concentration of intrinsic charge carriers in the active *p*-region of the irradiated GaAs:Si structure ($p_0 = N_A - N_D$) before and after gyrotron irradiation (GI) ($\lambda \approx 3$ mm, $t = 6$ s, $P = 5$ kW/cm^2).

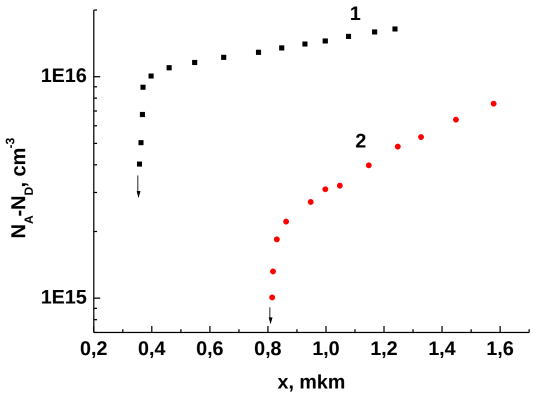

Fig. 1 *– Profiles of dominating (in the active p-region of GaAs:Si structure) impurity before (1) and after (2) intense gyrotron irradiation ($f = 10^{11}$ Hz, $P = 5$ kW/cm^2, $t = 6$ s)*

Distance reading was performed from the metallurgical interface of *p*- and *n*-regions inside LES. Plane, in which maximum electrical resistance of LES took place, was taken as the physical boundary of the *p-n* junction. Then we have observed the transition from the strongly compensated region, in which sharp decrease of the impurity profile occurred (vertical arrows in Fig. 1), that provides the highest resistance of this region to the region of the space-charge region, where concentration of dominating (in the active region of the *p-n* junction) impurity ($N_A - N_D$) coincided with concentration of intrinsic charge carriers in the active *p*-region.

Under the action of power microwave irradiation the heating process and, especially, further cooling of LES can be accompanied by the appearance of significant temperature gradients (see below) and elastic mechanical stress, which change the impurity-defect composition of local recombination centers.

As seen from Fig. 1, after GI *p-n* junction is shifted inside the sample on the distance of $\Delta w \approx 0{,}45$ μm. Moreover, after GI one can observe insignificant (~ 1,25 ± 0,05 fold) increase in the concentration gradient of the impurity and considerable decrease in the absolute value of the concentration of majority charge carriers (for example, on the depth of 1 μm from the initial physical boundary of the *p-n* junction – more than one order) in the space-charge region of the active *p*-region of device structure. Here, continuous increase in p_0 in the space-charge region for both initial and irradiated samples took place. If suggest that linear increase in the concentration of majority charge carriers spread to the sample surface, its values in both initial and irradiated sample will be equal to (2-3)·10^{17} cm^{-3} on the thickness of 30-40 μm which is close to real thickness of the active *p*-layer.

Thus, GI, probably, does not change the concentration of majority charge carriers on the LES surface. Such situation implies the appearance of the maximum temperature of overheating in compensated region of LES (on the thickness of the order of 1-2 μm (as minimum) in the region of the physical boundary of device) immediately after irradiation termination. This provides maximum temperature gradient in the direction to the heat extraction (see below).

As known, short-term power pulse electromagnetic irradiation of materials and devices of electronics have the following advantages.

1) Uniform treatment of large area structures.

2) High controllability and reproducibility of GI parameters that provides precise energy dosing which is supplied to the sample. Moreover, influence of microwave radiation on the electrical activity and impurity-defect composition of the material conditions the diffusion of impurities under the action of plastic deformation and thermal force [10, 11].

At the fluxes of GI, which were used in the present work, the maximum temperature of overheating of the *p-n* junction exceeded the temperature of environment as minimum on 1000 °C (see below). Temperature gradients arising in this case lead to the appearance of the force which moves impurity atoms from hot regions to cold ones. Expression for thermal force F_T acting on the impurity atoms in the field of temperature gradient has the view of [10, 11]

$$F_T = -\tfrac{1}{3}\Omega_o C\langle\sigma_o/\sigma_i\rangle\nabla T\,, \tag{1}$$

where Ω_o is the elementary volume of the base material atom; C is the crystal heat capacity; $\langle\sigma_o/\sigma_i\rangle$ is the averaged ratio of the scattering cross-sections by crystal and impurity atoms; ∇ is the Poisson operator.

Temperature gradients lead to the diffusion of impurities whose velocity u is proportional to F_T that according to equation (1) specifies the relation $u \sim \text{qrad}\ T$.

Appearance and specific nature of the deformation stress in the crystalline structure promotes the anomalously sharp acceleration of the impurity diffusion processes. With the increase in the thermoelastic stresses during the process and at the moment of GI switching-off, the diffusion coefficients of impurities considerably exceed those not only for the stationary case, but also for the case of impurity diffusion in melt [12]. As a result, shift of the *p-n* junction boundary should take place, in our case, in GaAs:Si structure.

Motion of impurity atoms in the field of thermoelastic stresses, according to [9], was carried out under the action of the force

$$F_G = \frac{4}{3}\frac{1-\nu^2}{(1-2\nu)^2}G(\Omega_i - \Omega_o)\nabla(\beta T)\,, \tag{2}$$

where ν is the Poisson coefficient; G is the shear modulus; Ω_i is the elementary volume of impurity atom; β is the linear thermal expansion coefficient of GaAs:Si crystal.

Here we should note that forces acting on the impurity atoms in both the thermodynamic and deformation fields [compare expressions (1) and (2)] are conditioned by the same factor, temperature gradient, i.e. from the physical point of view they are identical. Differences are conditioned by the mechanical and thermal properties of the matrix material, and, the most important, these are differences in the geometric parameters of atoms of the base material and impurity, as well as the processes of their interaction with thermal phonons generated during and after GI.

Summing forces (1) and (2) and using the Einstein correlation for the charge carrier mobility one can write the expression for the drift velocity of impurity atoms in the fields of temperature gradients and thermoelastic mechanical stresses

$$u = \mu(F_T + F_G)/q\,, \tag{3}$$

where μ is the impurity mobility; q is the impurity charge.

Corresponding flux of impurity $J = N\cdot u$, where N is the concentration of impurity atoms, depending on the correlation between forces F_T, F_G and sign of the difference $\Omega_i - \Omega_o$ is directed either along the temperature gradient or contrariwise. In our case, almost uniform heating of the whole crystal volume by GI takes place, and temperature gradient is specified by the processes of cooling after GI termination only. This gradient is considerable, but not so large to provide the correlation $F_T > F_G$. Thus, elastic deformation force [see expression (2)] exceeds thermal force [expression (1)], i.e. inequality $F_G > F_T$ is fulfilled. In this case, direction of the flux of impurity atoms depends on the sign of the difference $\Omega_i - \Omega_o$. If Ω_i (elementary volume of impurity atom) is more than the elementary volume of the base material atom $\Omega_i > \Omega_o$, then direction of impurity flux and temperature gradient coincide, and impurity is transferred from cold regions to hot ones. If opposite correlation between elementary volumes takes place, then impurity diffuses from hot regions to cold ones.

Taking into account that ionic covalent radius of the negatively charged ion Si^-_{As} (2,71 nm) exceeds ionic radii of both arsenic (1,21 nm) and gallium (1,25 nm), then the direction of impurity flux is opposite to the direction of the temperature gradient and impurity diffuses from hotter region to colder one, i.e. away from the *p-n* junction boundary. As for certain moving direction of impurity atoms (toward the surface or heat extraction), we will speak below.

Generally, silicon impurities move in arsenic sites (Si_{As}), since there are much more of them in *p*-region than Si_{Ga} impurities. Motion is performed on both existing arsenic vacancies (V_{As}), whose high mobility remains up to the temperature of ~ 150 °C, and less mobile gallium vacancies (V_{Ga}) occupied by silicon and just formed arsenic vacancies generated by GI. The latter are generated on the level of 10^{15} cm^{-3} that slightly blurs profile dN/dx, especially in completely compensated region near metallurgical transition where profile becomes smoother. It is shown in the paper [13] that short-term post-implantation silicon annealing, in contrast to high-temperature thermal one (1100 K), does not distort profile of the interstitial impurity. Difference of our results consists in the fact that samples are highly doped and, the most important, they are highly compensated. This leads to the wide possibilities of displacement of silicon impurity in GaAs that conditions insignificant blurring of its profile. Dominating motion of silicon impurities is carried out on V_{As}, since their amount is one order more than of V_{Ga} in GaAs:Si samples.

3.2 Temperature gradient

Heat source (GI) is considered to be uniform over the whole volume of LES, since its absorption coefficient is very small. For simplified calculation of the temperature gradient, dimensions of the radiation source were equal to the *p-n* junction area, since after termination of irradiation the heat extracted in LES (the maximum heating temperature of LES took place in the region of the *p-n* junction due to its high imperfection) was spread to the lower contact (heat-sink) not avoiding each layer located between the *p-n* junction and heat-sink. Such situation is conditioned by the fact that after termination of irradiation bulk copper heat-sink almost immediately (very fast) was cooled to the temperature of environment. In this case, a very large temperature gradient promoting the impurity diffusion took place in the direction toward the heat-sink. We have to note that temperature gradient (by the absolute value) increases as the sample is cooled. Moreover, its maximum is shifted in the direction toward the heat-sink. This leads, on the one hand, to the situation that movement velocity remains maximum in the region of maximum gradient and, on the other hand, to the increase in the gradient of impurity profile dominating in AO LES. Moreover, since silicon moves on both arsenic and gallium vacancies, p_0 decreases in the space-charge region in comparison with initial sample.

Using estimations of the overheating temperature of GaAs samples carried out in the work [14], where at the GI intensity of 1 kW/cm^2 and time of ~ 3 s it was equal to 600 °C, then maximum temperature at our irradiation parameters (P = 5 kW/cm^2, t = 6 s) was equal to 1050-1150 °C. Taking into account that distance between p-n junction and heat-sink is about ~ 250 μm (200 μm is the substrate thickness and 50 μm is the thickness of n-region of LES), temperature gradient in the direction toward the heat-sink was not less than $4\cdot10^6$ K/m.

Taking into account that thermal resistance R_T of any region inside LES is proportional to the thickness of d-region and inversely proportional to the area of metal contact S, i.e. $R_T \sim d\cdot S$, and knowing the estimated areas of the upper contact ($2{,}5\cdot10^3$ μm^2) and the lower heat-sink ($2{,}5\cdot10^5$ μm^2) [15], one can suggest that correlation of thermal resistances of the regions located between the p-n junction and heat-sink, as well as between the p-n junction and upper ohmic contact, differs almost 20-30 times. Thus, thermal flux to the lower ohmic contact (heat-sink) 20-30 times exceeds the thermal flux to the upper contact. In this case, since temperature gradient in the direction toward the substrate (and body as well) considerably exceeds that in the direction of free p-surface, then during calculations one should take into account only the first of the mentioned gradients, i.e. impurity diffusion from the p-n junction boundary inside the sample (toward body) was taken into account. Thus, one can neglect the propagation of thermal flux and connected with it processes of thermoelastic displacements of impurities in the direction toward the LES surface.

3.3 Analysis of the lifetimes and irradiation processes

First of all, we have to note that one wide emission band with the energy of $h\nu_{\max}$ = 1,30 eV and half-width of $\Delta E_{1/2}$ = 80 meV with slightly delayed short-wave front [8] was irradiated in the samples before GI. Large value of $\Delta E_{1/2}$ is connected with a strong compensation of the material conditioned by the concentration narrowing of the band gap of GaAs:Si HDC material due to the interaction between electrons and holes located in tails of state density.

GI promoted insignificant shift of $h\nu_{\max}$ toward higher energies (approximately on 0,01 eV) and decrease in the value of $\Delta E_{1/2}$ on 5-10 meV (in particular, because of the decrease in the delay of the short-wave front of the spectral curve) connected with the decrease after GI in the concentration of p_0 in the whole active region of LES.

In Fig. 2 we present the experimental results concerning the influence of an intense GI ($f = 10^{11}$ Hz, $P = 5$ kW/cm^2, $t = 6$ s) on the lifetimes of charge carriers measured by the method of the *p-n* junction switching from the forward direction to the reverse one.

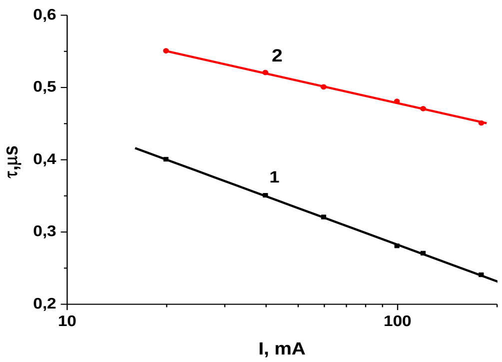

***Fig. 2** – Dependence of the lifetimes of charge carriers measured by the method of the p-n junction switching from the forward direction to the reverse direction versus the passing current for unirradiated (1) and irradiated (2) samples by microwave GI*

It is known that different radiation transitions, namely, band-band, band-impurity, band-"tail of localized states", "tail"-"tail", "tail"-impurity, etc [16] take place in HDC semiconductors. And at sufficiently low temperatures and excitation levels, as a rule, all types of transitions are realized, especially for materials with intermediate doping level of 10^{16}-10^{19} cm^{-3}, i.e., in principle, recombination can not be monoexponential. Thus, during irradiation there is the situation, when amplification of ones and weakening of others recombination mechanisms connected with the change in the depth and configuration of potential wells in HDC semiconductors take place.

We note that in HDC semiconductor materials, in principle, a wide set of relaxation times is observed [16, 8]. Small potential wells (high-energy irradiation) which cause transitions with the shortest relaxation time are the most effective in radiation processes. Participation in radiation processes of electrons and holes captured by the deepest potential wells leads to the increase in the lifetimes of charge carriers. Non-exponential behavior of EL relaxation is displayed also in the dependence of the type of kinetics on the amplitude of pulse current [8].

Decrease in the lifetime, measured by the switching method from the forward direction to the reverse one, with the increase in the current corresponds to the tunnel radiation recombination of localized (in the Gauss density tails) states of non-equilibrium charge carriers with localized due to strong compensation of majority charge carriers (holes) in the *p*-region of LES [17, 8]. Such spatial separation of charge carriers promotes tunneling of electrons above the barrier of the specified height generated by the root-mean-square fluctuation of concentration with the size R [16] which is connected with the depth of the potential well $g(R)$ and estimated as follows

$$\frac{\gamma(R)}{e} = \frac{e(NR^3)^{1/2}}{\varepsilon R},$$

where ε is the dielectric permeability.

Thus, fluctuation of charged impurities of the scale R can, at an average, decrease the electron energy on the value of $g(R)$. Therefore, the mentioned effect of the decrease in the effective lifetime can be connected with the fact of the decrease in the potential well depth connected with the passing current, i.e. with the fact of the field smoothing of potential relief. We should note again that larger recombination times correspond to the electrons and holes located in the deepest potential wells and, as a result, the most remote from each other [18].

It is seen from Fig. 2 that the value of τ measured by the switching method on the initial samples decreased from 0,4 to 0,25 μs (with the current change from 20 to 180 mA) with the current. GI led to the approximately 1,4-1,8 fold increase of τ in the whole current range. Its decaying behavior was constant, but insignificant slowing-down was observed.

Close to the parallel, shift of the dependence $\tau(I)$ indicates that the processes of radiation recombination take place not in the compensated and even not in the space-charge regions, but in the quasi-neutral region of LES. Correlation effect in the distribution of charge particles, probably, also promotes the slowing-down of the current dependence of the effective lifetime in LES treated by GI [19]. GI leads to the amplification of inequality $N >> p_0$ due to the decrease in the value of p_0 that decreases fluctuations of the potential and shielding radius. Moreover, correlation effect promotes the increase in the effective lifetime in the whole current range.

Since heating is one of the main mechanisms of energy dissipation at GI, it considerably influences the structural characteristics of the studied rather uniform structures. Increase in the compensation level of the samples and, as a result, decrease in the concentration of the majority charge carriers in the active region of LES take place after GI. Such situation promotes the increase in the lifetimes of charge carriers that is connected with migration of recombination-effective centers toward sinks, since in our case there was high initial compensation of the samples and its larger increase at GI conditioned by the fragmentation of deep potential wells.

Typical size of the large-scale fluctuation is given by the correlation [16]

$$r_s = N^{1/3} \cdot p_0^{-2/3}.$$

We note that decrease in p_0 after GI leads to the fragmentation of the large-scale fluctuations and decrease in the number of electrons in a drop, since concentration of charged impurities N is changed insignificantly in this case. This also leads to the slight shift of the absorption band maximum toward large energies. Thus, small potential wells are the most efficient before GI in irradiation transitions and after GI – their efficiency increases more. As for the velocity of the radiation increase τ, it was found to be insignificant. High initial uniformity and perfection of the samples act in the same way.

Observed features of the change in the electrophysical and kinetic characteristics of LES can be the result of the stimulating diffusion of recombination-active impurities and defects on the energy-stable defects and sinks, i.e. GI conditions generating action which stimulates annihilation of the output structural defects on the sinks. Such situation leads to the decrease in the concentration of recombination-active centers that promotes slight increase in τ after GI.

In Fig. 3 we represent the experimentally measured on the pulse current before and after GI lux-ampere characteristic of LES. Linear connection between the current amplitude and radiation intensity (slope of the dependence is $\beta = 1,1 \pm 0,1$) is observed. At $I > 100$ mA deviation from linearity takes place that is conditioned by the current overheating of the structure in spite of the fact that porosity of pulses was chosen in the range of Q = 100-200.

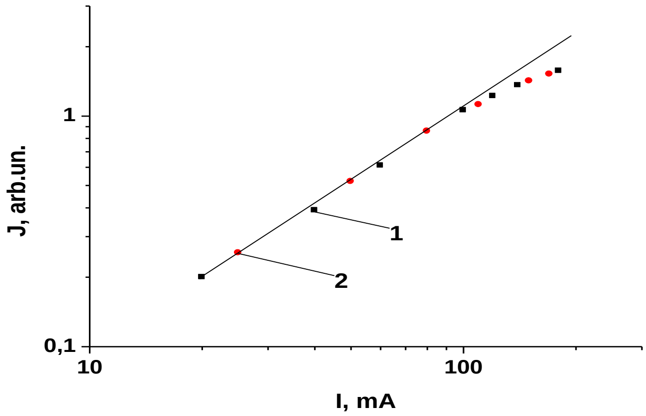

Fig. 3 *– Dependence of the integral intensity of LES on the pulse current amplitude before (1) and after (2) GI*

Integral radiation intensity of LES and slope of the lux-ampere characteristic after GI remains almost constant (slope $\beta = 1,1 \pm 0,1$) that implies the constancy of recombination mechanism after GI; mechanism of recombination radiation (mainly "tail"-"tail") remains prevail and constant.

Constancy of the slope of the lux-ampere characteristic and radiation amplitude with the increase in the effective lifetime of charge carriers after GI is conditioned by the fact that in HDC internal quantum yield of radiation, as minimum, exceeds 50%. In the case, according to [8]

$$\tau \sim (C \cdot p_0 + C_{Nr} \cdot N_r)^{-1},$$

where $C \cdot p_0$ is the probability of radiation zone-zone recombination; C_{Nr} is the trapping coefficient of the corresponding charge carrier on the impurity level or to the potential well; N_r is the concentration of the corresponding centers in the samples.

Since intensity of different radiation transitions J in HDC semiconductors is proportional to the product of τ and current amplitude passing through the structure, i.e.

$$J \sim (C \cdot p_0 + C_{Nr} \cdot N_r) \cdot \tau \cdot I^{\beta},$$

where $\tau = 1,1 \pm 0,1$ is the slope of the lux-ampere characteristic, and sum $(C \cdot p_0 + C_{Nr} \cdot N_r)$ figures in expressions for τ and intensity J with the opposite exponents, then intensity of radiation transitions J in HDC semiconductors (irrespective of the prevalence of the first or second term) does not depend on $(C \cdot p_0 + C_{Nr} \cdot N_r)$ and depend on the passing current amplitude I only.

Thus, increase in the value of τ makes intensity of radiation recombination in HDC GaAs:Si structures after GI almost constant and dependent on the current only. It is clear, if take into account the fact that GI does not incorporate any additional recombination centers, and, therefore, it does not change radiation intensity, it only can redistribute recombination fluxes from some radiation channels to others.

4. CONCLUSIONS

The observed change in the electrophysical and kinetic characteristics of LES after GI is the result of the structural-chemical reconstruction of recombination-active centers in the active region, change in the level of non-stationary internal mechanical stress generating GI actions. All these factors promote change in the thermoelastic stresses, shift of the *p-n* junction, and increase in the lifetimes of charge carriers in the active region of LES. Based on the results of the performed investigations, we can state the following.

1) Shift of the compensated region of LES based on GaAs:Si conditioned by the motion of impurities in the field of thermoelastic stresses, which appear during the cooling process of the samples after GI, is revealed

2) Increase in the effective lifetime of charge carriers in the active region of LES after GI connected with the decrease in the concentration of majority charge carriers in the active region of LES is established. It is shown that in spite of this increase, integral radiation intensity remains almost constant due to the fact that any recombination centers are not incorporated at GI, and only the re-distribution of initial recombination centers takes place.

3) It is shown that temperature gradient, which appears during the cooling process of the irradiated by GI sample, promotes diffusion of impurity atoms along this gradient (toward the heat-sink of LES).

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