Electrophysical characteristics of GaAs$_{1-x}$P$_x$ LEDs irradiated by 2 MeV electrons


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Abstract. Commercial orange and yellow GaAs$_{1-x}$P$_x$ LEDs were irradiated by 2 MeV electrons with fluences of $10^{14}$ - $2 \times 10^{16}$ cm$^{-2}$, and their electrophysical characteristics were investigated in the current and voltage generators modes. It has been shown that point radiation defects introduced into GaAs$_{1-x}$P$_x$ diodes reduce the electrical conductivity of the base. The series and parallel resistances of the device increase, compensating the electrical conductivity of the base and reducing the probability of forming the avalanche breakdown channels. Negative differential resistance regions that appear in current-voltage characteristics are the result of the presence of a GaP sublattice in the solid solution. During irradiation, the switching voltage into the low level state increases due to expansion of junction depleted region. The streamlined currents increase after irradiation is caused by changing in the free path length of charge carriers.

Keywords: GaAs$_{1-x}$P$_x$, LED, electron irradiation, defects, current-voltage characteristics.

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1. Introduction

Two main factors significantly limit the efficiency of radiative recombination in the first-generation gallium phosphide LEDs made by the simple double liquid epitaxy technology. In these LEDs, the emission is enhanced by an activator (nitrogen), since nitrogen solubility in the liquid phase is rather low. Thus, the first limiting factor is the insufficient concentration of nitrogen, which results in a low quantum yield of the devices. The second limitation is fundamental: the indirect band structure of GaP semiconductor reduces the probability of the desirable radiative transitions.

In an ideal crystal the $G$-$X$ interaction for free electron exciting is impossible due to the complete translation symmetry of the Hamiltonian. The emergence of spatial potential fluctuations in the solid solution GaAs$_{1-x}$P$_x$ removes the second prohibition and increases accordingly the probability of recombination. And if in GaAs the wave function of electron ($|ψ_0^0\rangle$), captured by the short-range potential of isoelectronic impurity N, is blurred in space, in the case of direct-band composition of GaAs$_{1-x}$P$_x$ (x $\approx$ 0.45) the $|ψ_0^0\rangle$ value is three orders higher [1, 2]. Due to the abovementioned advantages of the GaAs$_{1-x}$P$_x$ solid solution, the replacement of binary GaP compound by it in the process of LED manufacturing makes it possible to increase tangibly the quantum yield of emitters ($\eta_{GaAs} \sim 40\%$ vs $\eta_{GaP} \sim 1\%$).

The scope of applications for these devices made on the base of GaAs$_{1-x}$P$_x$ is extended from household appliances and computers, to fiber optic communication lines, systems of automatic regulation of nuclear-physical installations, spacecraft, etc. [3]. Prolonged operation under nuclear radiation or rigid cosmic rays results in degradation of characteristics followed by operational failure. Thus, it is necessary to obtain information of the effects of irradiation on the main parameters and characteristics of the devices.
There is a limited number of publications devoted to the study of radiation induced degradation processes in GaAs\textsubscript{1-x}P\textsubscript{x} crystals and LEDs, and most of them consider the effects of heavy particles (neutrons and protons). Munoz et al. [4] studied four groups of GaAs\textsubscript{1-x}P\textsubscript{x} samples of different composition \((x = 0.4, 0.65, 0.85, 1)\), irradiated by reactor neutrons with the fluence \(5 \times 10^{19} \text{n/cm}^2\). They concluded that EL2 trap \((E = 0.70 \text{ eV})\) is the main defect center. Measurements carried out by using the EPR method have shown that this center corresponds to the antisymmetric defect of As\textsubscript{0}Ga\textsubscript{0} in combination with other point defects. Later, Garsia et al. [5] suggested that the EL2 trap belongs to a group of antistructural defects, surrounded by a shell of point defect complexes on the periphery of the disordering region. The speed of the entering of this center is 1 cm\textsuperscript{-s}. The speed of the carrier removal \((dn/dF)_{F \rightarrow 0}\) is equal to 10 cm\textsuperscript{-s}, and this high value should testify (in the opinion of the authors) about the capture of charge carriers by the core of the cluster.

Neutron fields are the main destructive factor in nuclear reactors, but in the case of radio-electronic equipment of satellites, devices degrade under fluxes of high-energy protons \((E_p \sim 50 \text{ MeV})\). Unlike fast neutrons, which interaction with atoms is described by the model of solid spheres, the scattering mechanism of protons (as charged particles) is Rutherford’s. Comparison of the energy transferred to As atom by one neutron or proton (provided that \(E_p = E_n\) that the energy transferred by proton as a result of this scattering is about 100 eV. It is about one thousand times less than the energy obtained in an elastic collision with neutron [6]. At the same time, the experiment shows that degradation parameters of proton irradiation are much higher than that of the neutron one. For example, proton with \(E = 1 \text{ MeV}\) produces in silicon 40 times more defects than neutron with a similar energy [6]. The reason for the discrepancy of the calculations and the experimental data is that the number of displacements is determined by the cross-section of the particle-atom interactions (\(\sigma\)), which is much higher for protons as compared to that of neutrons \((\sigma_p^0 = 10^3 \text{b} vs \sigma_n^0 = 3...5 \text{b})\). Therefore, if for example, the energies of two particles are close to the threshold energy of formation of the disordered region (DR), then the number of DRs in both cases can not be greater than unity. However, since \(\sigma_p^0 >> \sigma_n^0\), a significant fraction of the proton energy is transferred through pulsed interactions with the media atoms, generating a large number of point defects.

As mentioned above, in scientific literature there are almost no reports concerning point defects introduced by electrons with the energy 1...2 MeV into GaAs\textsubscript{1-x}P\textsubscript{x} LEDs, in contrast to binary GaP and GaAs. A lack of information about influence of point defects on the characteristics of such emitters obscures the study of the nature of complex defects caused by heavy particles, which is especially noticeable in Refs [2-7]. Therefore, in our work, we focused on the study of radiation effects caused by 2 MeV electrons and on degradation of the main operational characteristics of the GaAs\textsubscript{1-x}P\textsubscript{x} devices.

2. The samples and experiment

Commercial GaAs\textsubscript{1-x}P\textsubscript{x} LEDs grown on GaP substrates with the phosphorus content \(x = 0.45 \) (orange) and \(x = 0.85 \) (yellow) were studied. The current-voltage \((I-V)\) characteristics were measured by automated system in the modes of a voltage generator and a current generator with the temperature interval 77...300 K under conditions of a pulsed diode power supply. Diods were irradiated by 2 MeV electrons at room temperature with the fluences within the range \(F = 10^{14} \ldots 2 \times 10^{16} \text{cm}^{-2}\).

3. Results and discussion

Irradiation of the samples with electrons of intermediate energies \((1...2 \text{ MeV})\) makes it possible to introduce a controlled number of point defects. Fig. 1 shows the results of calculation of the cross-section of interaction of fast electrons with Ga, As and P atoms obtained using the McKinley–Feshbach model [8], according to which

\[
d\sigma = \frac{4\pi\alpha_0^2 z_2^2 E_R^2}{m_0^2 c^4} \left(1 - \beta^2\right) \times
\]

\[
\times \left[1 - \beta^2 \sin^2 \frac{\theta}{2} + \pi \alpha \beta \cdot \sin \frac{\theta}{2} \left(1 - \sin \frac{\theta}{2}\right)\right] \cos \frac{\theta}{2} \cos \theta \frac{\theta}{2} d\theta,
\]

where \(\theta\) is the angle of scattering, \(\alpha_0\) – Bohr radius, \(z_2\) – atomic number of the target, \(E_R\) – Rydberg energy, \(m_0\) – mass of electron residue, \(c\) – velocity of light, \(\alpha = \frac{z_2}{137}\), \(\beta = \frac{V_c}{c}\), \(V_c\) – electron velocity.

![Fig. 1. Calculated value of the cross-section for fast electron interaction with As (1), Ga (2) and P (3) atoms, received by the McKinley–Feshbach model.](image-url)
The threshold bias energies of the Ga and P atoms for the GaP crystal were determined in two ways: (1) changes of the rate of the carriers removed in the process of changing the energy of electrons in the beam; (2) changes of the luminescence intensity of the exciton bound on the nitrogen atom. In the literature, there are no data on the threshold energy for displacement of the As atom inside GaAs$_{1-x}$P$_x$ lattice. Therefore, for calculating the cross-section of electron–As interaction, we used an average value of $E_d$(P) and $E_d$(Ga). This is justified by the fact that the masses of Ga and As are close, and correspondingly in Fig. 1, the energies differ only slightly in GaP crystal: $E_d$(Ga) = 35 eV, $E_d$(As) = 33 eV, $E_d$(P) = 30 eV. From Fig. 1, it is also seen that for 2 MeV electrons the value of $\sigma$ for three components of the alloy is at least one order of magnitude higher than that for Si in the case of neutron irradiation [6]. But at the same time, the magnitudes of the maximum transferred energy for all three atoms are clearly insufficient to form the disordered region, because the average number of secondary displacements $\nu$ that phosphorus atom can create in accordance with the Kinchin–Pisa model $\nu \approx \frac{211}{60} = 3$ ($E_{\text{max}}^p = 211$ eV, $E_{\text{max}}^a = 93$ eV, $E_{\text{max}}^s = 87.4$ eV). Consequently, point defects should be considered to be the main defects in electron irradiated GaAs$_{1-x}$P$_x$ structure, and their concentration is rather high due to the large value of $\sigma$.

Current-voltage characteristics of orange GaAs$_{1-x}$P$_x$ diodes are shown in Fig. 2. In the low current regime (up to $\sim 10^{-3}$ A) within the range of 77...300 K the dependence of $I(U)$ is exponential:

$$I = I_s \left( e^{\frac{qU}{m_kT}} - 1 \right),$$

(2)

where $I_s$ is the reverse current of saturation, $m$ – non-ideality coefficient.

Within the Shockley model, this coefficient $m = 1...2$; when $m = 1$, the diffusion component of the total current is dominant, while $m > 1$ indicates significant contribution from carrier recombination. In our case, at $T > 100$ K recombination current is dominant in both initial and irradiated diodes.

In Fig. 3, the rapid growth of the non-ideality coefficient, $m$, at the low temperature region is possibly caused by the increase of carriers recombination due to the change of the charge state of the defect levels causing recombination. Additional possible factor is the decrease of the thermal velocity of carriers, which increases the capturing probability. Similar behavior of $m$ is observed in both GaP and GaAs irradiated samples with an increased concentration of radiation defects as effective recombination centers [9-11].

Changing the current mechanism after irradiation is directly reflected in its parallel ($R_p$) and series ($R_s$) resistances. An estimate of the value of $R_p$ can be made in the region of low voltage, where $U \ll E_s/e$ ($E_s$ is the bandgap of crystal) and $R_p = dU/dI$.

Considering that $R_s$ is large, the magnitude of the series resistance can be estimated being based on the modified Shockley equation:

$$I = I_s e^{\frac{q(U+R_s)}{m_kT}}.$$  \hspace{1cm} (3)

Then

$$R_s = \frac{dU}{dI} - \frac{m_kT}{ql}.$$  \hspace{1cm} (4)

Calculations were carried out in the area of direct bias where $U \gg kT/q$ [12].

Fig. 2. Current-voltage characteristics of the orange GaAs$_{1-x}$P$_x$ diode in the mode of the current generator at different sample temperatures: initial: $1' - 300$ K, $2' - 180$ K, $3' - 95$ K, $4' - 77$ K; irradiated ($E = 2$ MeV, $F = 2.64 \times 10^{16}$ cm$^{-2}$): $1' - 300$ K, $2' - 180$ K, $3' - 95$ K, $4' - 77$ K.

Fig. 3. Temperature dependence of the non-ideal coefficient $m$ in irradiated orange GaAs$_{1-x}$P$_x$ LED: $1 - F = 2 \times 10^{15}$ cm$^{-2}$, $2 - F = 9.5 \times 10^{15}$ cm$^{-2}$.

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Fig. 4 shows the temperature dependences of $R_p$ and $R_s$ of an orange diode before and after irradiation. The increase of the series resistance after irradiation is a result of the capture of the majority charge carriers by the levels of point radiation defects, which, in both GaP and GaAs, compensates the electrical conductivity of the $p$- and $n$-regions of the junction, increasing the resistance of the base of the diode. Reduction of $R_s$ with temperature growth is due only to the increase of carrier concentration in the conduction band, since their mobility is not considerably affected by the point radiation defects.

Parallel resistance $R_p$ shunts $p$-$n$ junction and its value mainly depends on the state of diode surface. Streamlined currents through it are parasitic and worsen operation of electrical circuits. From Fig. 4 that shows the temperature dependences of $R_p$, for diodes irradiated with different doses, it is evident that the increase in temperature leads to an increase in the resistance of the shunt. A similar effect is also caused by the irradiation. Taking into account both of these effects, one can make an assumption about the forming mechanism of the streamlined currents.

It is known that the increase of the sample temperature reduces the magnitude of the avalanche breakdown current as a result of a decrease in the length of the free run of carriers. Radiation-induced defects have a similar effect, so it is obvious that the existence of streamlined currents is provided by separate micro-breakdown channels of avalanche nature. Irradiation which causes the electroconductivity compensation might strengthen the role of near-contact dislocations as an additional factor of carrier scattering. It leads to the drop of streamlined currents [13, 14].

Current-voltage characteristics of GaAs$_{1-x}$P$_x$ LEDs at low temperatures ($T = 77\ldots95$ K) contain two regions of negative differential resistance, which is also characteristic of GaP diodes. The origin of the upper region, as suggested in Ref [15], may be related to band-to-band transitions between $E_{1c} \rightarrow E_{k}$, when the electric field within the $p$-$n$ junction reaches $E = 10^8$ V/m. It is possible to estimate the value of this field in the case of the GaAs$_{1-x}$P$_x$ diode within 77...95 K intervals from Fig. 4. Being based on the fact that the development of the negative differential resistance (NDR) region begins at $I = 0.02$ A and $U = 4$ V for 77 K and $U = 3.5$ V for 95 K, when the base resistances are: $R_{77K} = 85$ Ω and $R_{95K} = 75$ Ω, one can determine the strength field in the $p$-$n$ junction region. These values are 7.7·10$^5$ and 6.67·10$^5$ V/m, respectively, and are sufficient to stimulate $E_{1c} \rightarrow E_{k}$ transitions. Introduction of radiation defects leads to the expansion of the $p$-$n$ junction and switching voltage into the low-level state increases (Fig. 2). The reverse current $I_r$ of the diode increases mostly with increasing the temperature and radiation fluence.

It is known that the total reverse current at $|U| > 3kTq$ is the sum of the diffusion component in the neutral region and the generation current in the depleted region [16]

$$I_r = q \frac{D_0}{\tau_p} n_i^2 + \frac{qN_D W}{\tau_r}, \quad (5)$$

where $W$ is the width of $p$-$n$ junction.

The concentrations of intrinsic carriers in GaP, GaAs, and, accordingly, in GaAs$_{1-x}$P$_x$ are small enough, and the first part of the equation might be neglected. Consequently, the generation current in the space charge region is the main component of the reverse current in GaAs$_{1-x}$P$_x$ LED, and its growth during irradiation is caused by the decrease in the $\tau_r$ lifetime of charge carriers due to the introduction of deep recombination levels of radiation defects.

Thus, the appearance of S-shaped regions of NDR in current-voltage characteristics is obviously related with the presence of a phosphide-gallium component in a solid solution GaAs$_{1-x}$P$_x$. The temperature dependence of the reverse current is a direct consequence of a sharp increase of $n_i$ with an increase in the temperature of the sample.

Exciton traps created by the nearest nitrogen pairs NN$_1$ and NN$_2$ with the activation energy $E_g = 138.4$ meV are the main luminescent centers in GaAsP. Irradiation leads to the luminescence intensity drop caused by the increase of the non-radiating transitions in comparison with the radiating ones. (This behavior is typical to many irradiated emitters except the sources based on SiC.)

Radiation hardness $K$ is obtained using the equation

$$\frac{1}{\tau} = \frac{1}{\tau_0} + KF, \quad (6)$$

where $\tau_0$ and $\tau$ are the lifetime of the minority current carriers in the initial and irradiated samples.
where \( n \) depends on measuring regimes and current transport mechanism throughout \( p-n \) junction; can be as \( n=1, 1/3, 2/3 \).

In this case, the total current through the diode can be controlled as a process of recombination in the space charge region \( (n=1/3) \) and diffusion by minority carriers. It is obvious that in the investigated samples, both processes are equally probable, as can be seen from Fig. 3 the coefficient of non-ideality lies in the range from 1 to 2.

The radiation hardness \( K \) obtained from Fig. 5 is low and equal to \( K_{1/3}=1.67\times10^{-14} \text{cm}^2 \) for \( n=1/3 \), and \( K_{2/3}=3\times10^{-17} \text{cm}^2 \) for \( n=2/3 \), which is considerably smaller than the values obtained in [17], where diodes grown on GaAs and GaP and irradiated by electrons \( E=2…2.5 \text{MeV} \).

Fig. 5 shows \( \left( \frac{L_0}{L} \right)^n -1 \) dependence on the dose of irradiation, and Fig. 6 shows the luminescence intensity dependence on the voltages applied. Linear log\( (L/U) \) testifies about correctness of radiation hardness definition [17]. Both values \( n=1/3 \) and \( n=2/3 \) (Fig. 5) respond to the luminescence caused by the diffusion current \( (n=1) \) (Fig. 6).

The radiation hardness of GaAsP diodes irradiated by neutrons \( (E_n > 100 \text{ keV}) \) and protons \( (E_p = 16 \text{ MeV}) \) [5, 6] is also lower \( (K \approx 10^{-13} \text{cm}^2) \), most probably because of the disordered regions in the irradiated samples. Thus, a rude estimate of \( K \) is made according to the results of the work [17] for binary GaAs and GaP compounds. \( \tau_0 K \) is equal to \( 4\times10^{-16} \text{cm}^2 \) for GaP and \( 2\times10^{-15}…1.5\times10^{-14} \text{cm}^2 \) for GaAs diodes. Two order differences between dates for GaP and GaAsP testifies about the higher radiation hardness of the diodes grown on the solid solution base.

4. Conclusions

It has been shown that point defects introduced into the GaAs\(_{1-x}\)P\(_x\) diode during irradiation reduce the electrical conductivity of the base due to the capture of the majority current carriers by the levels of radiation defects. Appearance of the NDR regions in current-voltage characteristics is the consequence of the presence of GaP sublattice in the solid solution.

The switching voltage into the low-level state increases after irradiation of the diode due to the expansion of its depleted region.

Irradiation leads to the increase in the series and parallel resistances of the device, compensating the electrical conductivity of the base and reducing the probability of formation of avalanche breakdown channels. Reducing the streamlined currents of irradiated diodes is caused by the change in the free path length inherent to charge carriers.

It has been shown that the radiation hardness of GaAsP LEDs is more than two orders higher as compared with GaP and GaAs diodes.

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