Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 1. P. 34-38.
doi: 10.15407/spqeo19.01.034

PACS 29.40.-n, 85.30.-z, 85.60.Dw

Acoustic-stimulated relaxation of $GaAs_{1-x}P_x$ LEDs electroluminescence intensity

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Abstract. The effect of ultrasonic (US) treatment on electroluminescence of initial and irradiated with 2-MeV electrons ($\Phi = 8.24\cdot10^{14}$ e/cm^2) GaAs-GaP LEDs grown on solid solution base was studied. It was found that luminescence intensity of samples previously loaded with US increased during long-term storage ($t = 15$ h). Passing the current through the diode generates the relaxation process of radiation brightness falling followed by the growth when ultrasound is switched on. The results of calculation of the dislocation density responsible for electroluminescence quenching within the region of electroluminescence degradation are adduced. It was found the ultrasound effect on diodes irradiated with high-energy electrons.

Keywords: $GaAs_{1-x}P_x$, GaP, LED, ultrasound, US-treatment, irradiation, dislocations, electroluminescence, defects of dark lines, dark spots' defects.

Manuscript received 03.11.15; revised version received 20.01.16; accepted for publication 16.03.16; published online 08.04.16.

1. Introduction

Ultrasonic (US) treatment of different industrial products and semiconductor devices is an effective tool of nondestructive influence on physical properties of materials in order to correct their characteristics in the right direction [1-20]. For example, the use of ultrasound during crystal growth homogenizes melt ingots and gives a larger volume, improves film adhesion to silicon and metal substrates [2, 3]. One can use ultrasound to clean chips by forming cavitations' bubbles on the surface of a module immersed into water. Also, it was reported that high-frequency MHz vibrations can strengthen the surface silicon layers (up to 100 μm), increasing the dislocation density in them [4]. Deformation stresses, by stimulating the dislocation movement, promote their reproduction, resulting in an additional amount of point defects. Disintegration of donor-acceptor complexes responsible for green luminescence in CdS causes reduction of luminescence intensity [5]; the analogous phenomena are observed after acoustic and photostimulated reactions. Qualitatively different results were obtained in [6], when M/n-n^+-GaAs structures were treated using ultrasound. The effect was positive: growth and narrowing the photoluminescence intensity lines were observed. Reducing the activation energy of diffusion of vacancies in the US field and appropriate weakening the non-radiative recombination channel is considered as a main reason of the observed features.

It is clear from the above brief review of the papers devoted to acoustic treatment of solids that the main focus concerns the ultrasound effects analysis on properties of crystals and devices. As for the mechanisms of interaction of US waves with various structural defects and the nature of phenomena of the ultrasound passage through the sample, now there is no single point of view.

This issue is partially revealed by the authors [7] summarizing the ultrasound treatment effects on GaAs tunnel diodes. According to their data, the main possible factors that affect the diode characteristics are the gettering of point defects by ultrasound swinging dislocations; US-stimulated defect diffusion in the space charge region; recharging the point defects and mutual conversion of complexes.

The problem of acoustic-defect interaction can be partially solved, at least in the interpretation of a large number of experimental data, being based on the concept of double-acting deformation disturbances (appearance of rapidly changing piezofields) and due to the deformation potential influence. The role of the first factor is particularly relevant for polar semiconductors that include A^3B^5 compounds. The alternating electric field ($E \approx 10^5$ V/cm) leads to the oscillatory motion of charged dislocations and causes them to climb.

The model of deformation potential is based on local bandgap changes that generate electric fields [5, 8].

Authors [9-11] prove the existence of another, fundamentally different way of high-energy sound wave transmitting to anharmonic heterogeneity at $\lambda_{US} >> L_{heter}$. Energy storage near the defect occurs as a result of parametric resonance between hypersonic lattice vibrations and heterogeneity vibrations.

The main purpose of our work is identifying the peculiarities of ultrasound action on solid GaAs-GaP solution. This object, by its definition, is characterized by a higher level of defects as compared to binary GaP or GaAs composition because of the statistical distribution existence of As and P atoms and is convenient to study acoustic-defect interaction in semiconductors.

2. Experimental

We used samples in the form of LED $GaAs_{1-x}P_x$ structures. The exciton emission component ensures maximum sensitivity to US treatment. Electroluminescence spectra were measured at room temperature in the automatic mode by using the equipment designed on the basis of monochromator MDR-23. Radiation intensity was investigated for more measurement cycles, the interval between them was 1 hour. The US wave with the frequency ν = 2.2 MHz and power $W \approx$ 0.5 W/cm^2 was introduced into the sample dynamically in the process of passing the current I = 40 mA through it. Hourly within each cycle, the measurements of changes in the luminescence intensity were carried out through both with the US treatment and without it.

Samples were irradiated with 2-MeV electrons at the electronic accelerator ILU-6 in the pulsed mode at room temperature. Within electron flow densities used (Φ = 8.24·10^{14} e/cm^2) darkening of LED polymer lens was not essential.

3. Results and discussion

Fig. 1 shows the change in the emitting efficiency of the orange initial $GaAs_{1-x}P_x$ LED during five cycles of loading (ν = 2.2 MHz, $W \approx$ 0.5 W/cm^2) and endurance. During the 1-st cycle of US loading (t = 6 h), the emitting efficiency η decreases (section A–B). However, after turning off the ultrasound source and long pause (t = 15 h), which prolongs up to the beginning of the next measuring phase (cycle 2), η eventually exceeded its initial value (point C). Further electroluminescence measurements without introducing ultrasound for this cycle were accompanied by decreasing the radiation intensity due to the passing the current through the diode. If to turn on US at the end of the recession curve, an opposite process occurs – diode efficiency grows (section D–E). A similar trend of the degradation-relaxation processes is inherent to minor deviations in subsequent cycles 3, 4, 5. The total time for five cycles of US load did not exceed 24 hours of treatment.

After increasing the US loading time over 25 hours, a slow decrease in the radiation intensity occurs. Fig. 2 shows the dependence of maximum emitting efficiency of the diode in a passive state (in the absence of current and ultrasound loads) on the total time of 8 previous US cycles. One can see that the initial intensity growth is offset by the following loading cycles (6, 7, 8). The positive effect is reduced and at the end of the latter cycle the light activity of LED is reduced by almost three times. After the 8-th treatment cycle, the diode behaves like an uncontrolled one: chaotic maximum and minimum peaks emerge on the average background values of the luminescence intensity curve and they are not reproducible with repeated measurements.

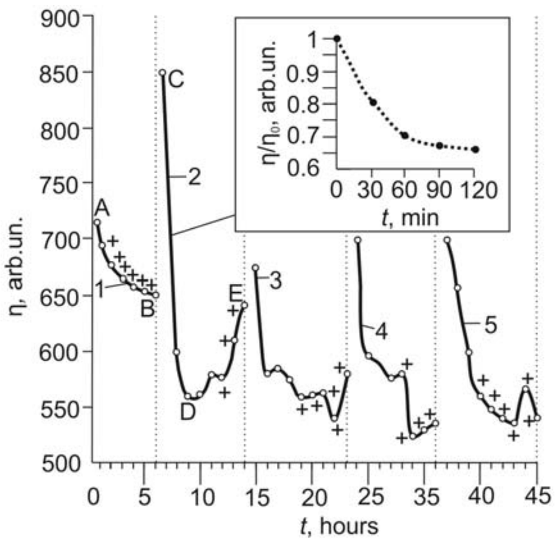

Fig. 1. Degradation-relaxation cycles of $GaAs_{1-x}P_x$ LEDs. "+" responds to US treatment of the sample. Inset: the change in the emitting efficiency η/η_0 depending on the time of injection of minority carriers for the 2-nd degradation-recovery cycle.

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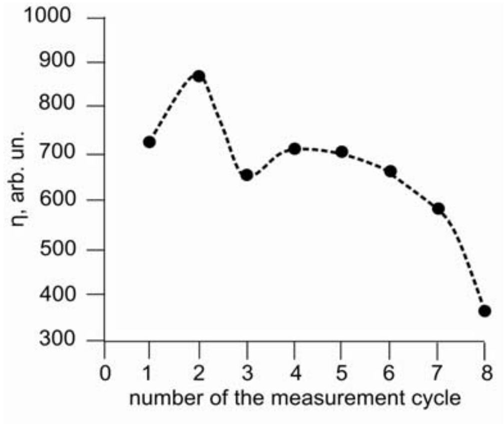

Fig. 2. Generalized relaxation curve for the LED emitting efficiency. The experimental points respond to the maximum emitting efficiency in each degradation-relaxation cycle.

The presence of long lasting relaxation processes in the crystal indicates the existence of large-scale defects and diffusion processes of point defects' restructuring.

One of the components of $GaAs_{1-x}P_x$ solid solution is gallium phosphide, where relaxation instability of the electrical parameters after electrical and thermal excitation was also found [12]. Therefore, it is likely that long-term relaxation of luminescence previously subjected to ultrasound $GaAs_{1-x}P_x$ LED is caused by the GaP sublattice, in which ultrasound-stimulated motion of dislocations causes the appearing of dislocation networks responsible for formation of "defects of dark lines" (DDL) and "defects of dark spots" (DDS) with a high non-radiative centers concentration. Accumulation of this type defects in the crystal is a natural consequence of the process of acousto-defective interaction, when the maximum loss of ultrasound wave energy is within the area of dislocation vibration [5, 13-15], which causes its release and subsequent movement to the formed before clusters – dislocation networks.

So, if at the beginning of US loading (~ 1 h) the diode emissivity may increase due to absorption of point defects by moving dislocations or bringing them to the surface through diffusion channel [13], at considerable long US treatment, luminescence degradation is observed, which is caused by the increase of DDL and DDS densities.

These large-scale structural defects have an excess energy after termination of US treatment. For a certain time, they relax to the state in which the radiative recombination intensity becomes higher than the original one (see Fig. 1). Relaxation process is accompanied by an increased efficiency of radiative recombination, apparently as a result of the restructuring of excited by US complex structure defects, the absorption of point defects by moving dislocations in the crystal regions between DDL and DDS, diffusion of simple defects to sewages, and because of changes in the charge state of non-radiative recombination centers, localized within these large-scale defects [14].

Next degradation-relaxation cycle, as already mentioned, begins with reducing the luminescence intensity in the absence of ultrasound exposure, when minority carriers are injected through the *p-n* transition in the operation mode (section C – D). It was reported in Barnes' early work [16] on the possibility of changes in the concentration of defects in GaAs LEDs under the forward bias. Obviously, in our experiment, minority carrier injection leads to a change in the charge state of recombination levels for the increasing number of non-radiative recombination acts.

The authors [14] studied the dislocation effect on effectiveness of green luminescence in GaP. According to [14], the relative change in radiation efficiency η/η_0 as a function of dislocation density is

$$\frac{\eta}{\eta_0} = 1 - 4\pi\rho_D L^2 \left[\ln\left(\frac{2L}{r_0} - 0.58 \right) \right]^{-1},$$

where L is the diffusion length of minority carriers, r_0 is the radial size of the linear defect – dislocation – within which non-radiative recombination is infinite. The impact of minority carriers within $r < r_0$ is equal to zero, ρ_D is the density of dislocations.

Using the above ratios, one can calculate ρ_D of initial and irradiated $GaAs_{1-x}P_x$ samples, which affects the efficiency of electroluminescence at r_0 = 50 Å and several values of L = 3, 5 and 10 μm.

The relative change in the efficiency η/η_0 as a result of changes in the charge state of dislocations, depending on the time of injection of minority carriers for the 2-nd degradation-recovery cycle (section C–E), is shown in the inset of Fig. 1. On its basis, the dependence of dislocation density ρ_D, affecting the luminescence intensity, as a function of time for current passage through the diode, is plotted in Fig. 3. As $\frac{\eta}{\eta_0}(t)$ and $\rho_D(t)$ curves exhibit a tendency to saturation,

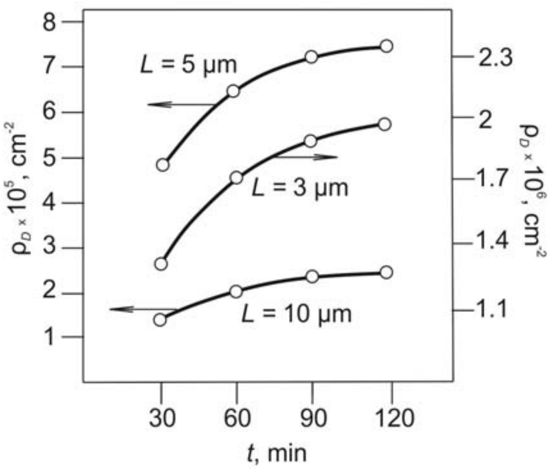

Fig. 3. Dependence of the dislocation density ρ_D, affecting the luminescence intensity, as a function of time for current passage through the unirradiated diode for various diffusion lengths of minority charge carriers.

due to the existence of such quantities ρ_D, when all dislocations accumulated in the DDL and DDS fields finally change their charge state. We see that it happens at $\rho_D = 7 \cdot 10^5 \ldots 2 \cdot 10^6$ cm^{-2}.

In [17], it was found that the US stimulated diffusion length of minority carriers in dislocation-free silicon can grow twice. Regarding to $GaAs_{1-x}P_x$ samples, similar sensitivity of L to ultrasound will probably not be observed due to significantly higher defectiveness' levels of solid solutions. Therefore, estimates are approximate; to calculate $\rho_D(t)$, we used the diffusion length value L = 3…6 µm, which is typical for GaP LEDs.

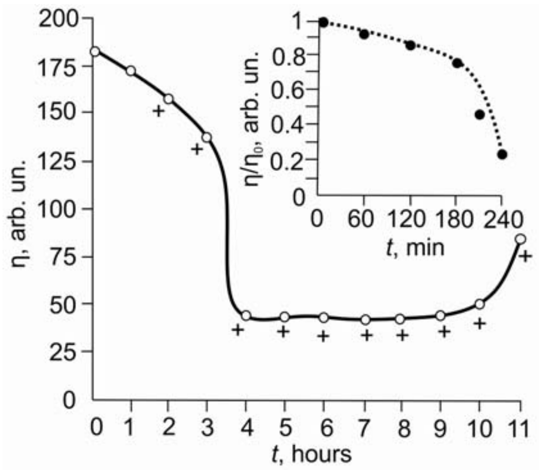

Fig. 4. Degradation-relaxation curve for one cycle of $GaAs_{1-x}P_x$ LEDs irradiated by 2-MeV electrons ($\Phi = 8.24 \cdot 10^{14}$ e/cm^2). "+" responds to US treatment of the sample. The change in the emitting efficiency η/η_0 depending on the time of injection of minority charge carriers is shown in the inset.

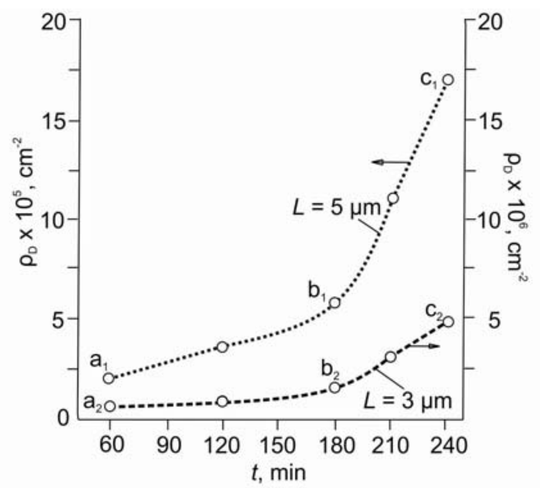

Fig. 5. Dependence of the density of optically active dislocations in 2-MeV electron irradiated $GaAs_{1-x}P_x$ LED as a function of time for current passage through the diode for L = 3 µm and 5 µm.

The degradation relaxation-curve of diode irradiated with electrons possessing the energy $E = 2$ MeV, $\Phi = 8.24 \cdot 10^{14}$ e/cm^2 is adduced in Fig. 4. The inset shows the dependence of efficiency $\frac{\eta}{\eta_0}(t)$ for the same sample; on its basis $\rho_D(t)$ calculations were made (Fig. 5).

Dependences $\frac{\eta}{\eta_0}(t)$ and $\rho_D(t)$ for irradiated sample are qualitatively different, although the growth trend with increasing t is the same for both curves. The curve $\rho_D(t)$ for irradiated samples in comparison with the initial dependence $\rho_{D0}(t)$ possesses two slopes that characterize the speed of acoustic induced changes in the charge of dislocations $\frac{d\rho_{D_1}}{dt} \approx 4.5 \cdot 10^3\,\text{cm}^{-2} \cdot \text{min}^{-1}$ and $\frac{d\rho_{D_2}}{dt} \approx 2 \cdot 10^4\,\text{cm}^{-2} \cdot \text{min}^{-1}$ versus $\frac{d\rho_D}{dt} = 2.2 \cdot 10^3\,\text{cm}^{-2} \cdot \text{min}^{-1}$ for the initial sample (L = 5 µm).

The density of dislocations in the irradiated sample for 120 min relaxation time is almost the same as for the unirradiated one ($\rho(t)_{ir} = 10^6$ cm^{-2}, $\rho(t)_0 = 2 \cdot 10^6$ cm^{-2}). Intense accumulation of non-radiative centers of radiation origin within DDL and DDS, stimulated by dislocation motion, starts only at considerable US exposure times ($t > 3$ h), indicating a relatively high defectiveness' level in the initial samples.

Obviously, the presence of radiation defects introduced by fast electrons is the decisive factor that dramatically changes the ratio between the number of non-radiative transitions involving dislocations and radiation defects. The existence of two slopes for the $\rho_D(t)$ dependences may serve as an evidence of formation of large clusters of simple defects in the region comprising dislocation networks caused by long-lasting US treatment.

4. Conclusion

It was found that US causes the number of degradation-recovery processes in $GaAs_{1-x}P_x$ LED. In the passive mode, it is expressed by the increase of luminescence intensity after long-term storage ($t = 15$ h), in the operation mode the luminescence intensity decreases. The subsequent treatment with ultrasound increases the efficiency of radiative recombination.

Partial increase of the luminescence intensity in the early US cycles is associated with the absorption of non-radiative centers by moving ultrasound-activated dislocations. The emission brightness drops under current passage. It is due to changes in the charge state of defects, which makes the DDL and DDS centers to serve as centers of non-radiative recombination.

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