DEGRADATION-RELAXATION PROCESSES STIMULATED BY STRUCTURAL DEFECTS IN GREEN GALLIUM-PHOSPHIDE LIGHT-EMITTING DIODES

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The structural defects in green GaP light-emitting diodes (LEDs), initial and irradiated by gamma-rays, were studied using optical and electrophysical methods. The researches of the temporal variation of the electroluminescence intensity showed that the emergence of long-term relaxation processes can be caused by intrinsic dislocation grids — large-scale structural defects — namely, dark-line and dark-spot defects (DLDs and DSDs, respectively). Irradiation does not generate additional relaxation centers but only assists in revealing those already available in the crystal. The fine structure of the current-voltage characteristics (CVCs) in the negative differential resistance (NDR) region, which has been found in the low temperature interval $T = 77 \div 110$ K, evidences for the availability of a considerable number of deep recombination levels in the depletion region of the GaP p—n junction. The character of current oscillations is governed by the alternating depletion and population of those levels. Irradiation of LEDs by Co^{60} γ-rays extends CVC intervals, where oscillations are observed; similar changes of CVCs are caused by the ultrasound treatment. Such a response of the green GaP LEDs results from the concentration increase of deep recombination levels.

The running of long-lasting relaxation processes in solid-state electronic devices is extremely undesirable owing to their negative influence on devices' performance, stability, reproducibility of signals, ability to operate without information distortion, etc. The crucial factor that governs the emergence of relaxation phenomena in a sample is the existence of large-scale potential barriers, which are capable to separate nonequilibrium current carriers from one another [1, 2]. The reason of such barrier formation can be a non-uniform distribution of dopants, dislocation grids, and clusters of radiation-induced point defects. The characteristic relaxation times depend on how large those barriers are and, obviously, should be expected rather prolonged in wide-band-gap semiconductors. Really, the recovery of conductivity in thermally excited gallium phosphide can last for tens of minutes. Such a process is especially typical of irradiated samples. It was also observed in indium phosphide [3, 4] bombarded with α-particles. In works [5, 6], a long-term recovery of luminescence in GaP samples subjected to the ultrasound treatment for one hour or more has been revealed. The intensity of relaxation processes, as a rule, becomes enhanced as the degree of compensation of crystal conductivity grows.

In this work, the reduction of the majority charge carrier concentration was attained by irradiating the specimens with Co^{60} γ-quanta. The powerful field of γ-radiation also served as the exciting factor, which causes the growth of the number of nonequilibrium charge carriers and stipulated the process of their trapping.

Nitrogen-doped GaP LEDs were studied. The peak of their luminescence intensity at room temperature corresponds to a quantum energy of 2.17 eV (Fig. 1). Point defects were introduced making use of a Co^{60} γ-source (300 K). The dose rate amounted to about 1 Gy/s. The luminescence intensity was measured, starting from a dose of 10 Gy, when the samples were immediately in the field of γ-radiation, as well as beyond the limits of the active zone. While plotting the degradation-relaxation curves, the constant background component created in the recording device by the irradiation of a photosensor, was calculated from the measured luminescence intensities. For some specimens, the radiation treatment was carried out when the current passed through a p—n junction. The CVCs of the original and irradiated samples were also measured in the current-generator mode within the temperature range $T = 77 \div 300$ K. The amplitude of the current through a diode was changed with a step $\Delta I = 1 \div 5$ mA.

The irradiation was found to result in the monotonous reduction of the diode luminescence intensity, similar to that revealed earlier for GaP [6]. After the specimen having been removed from the active zone, its brightness partially recovered, with the corresponding growth remaining substantially weaker than that at the red GaP:ZnO diode luminescence recovering. The intensity of such relaxation pulses at first increased with the dose up to $D = (2 \div 3) \times 10^4$ Gy and then started to fall down quickly. The characteristic

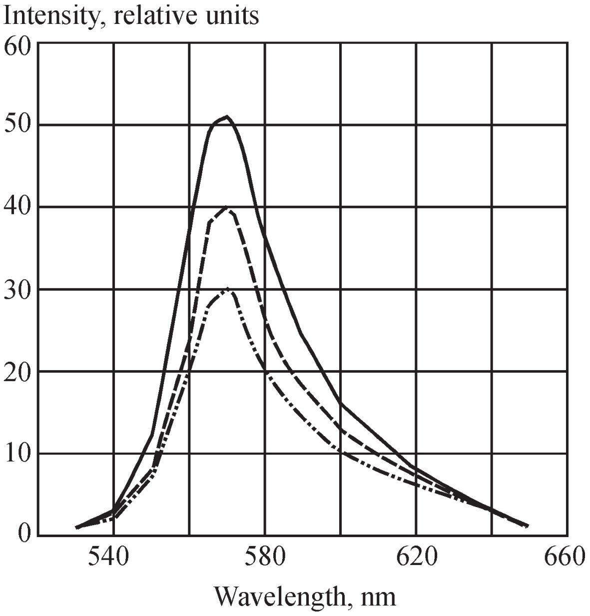

Fig. 1. Electroluminescence spectra of green GaP diodes at a temperature of 300 K

feature of the sample irradiated in the dynamic mode (when the current continuously passes through the sample) was a considerably higher rate of degradation under identical irradiation conditions. The brightness of its luminescence was observed to be rather stable up to an irradiation dose of 10^3 Gy. At higher doses, it started to decrease more rapidly than in other diodes.

The effect of low doses in green GaP p—n structures was expressed more weakly than in red ones [6]. Some samples demonstrated a small, up to 15%, growth of the luminescence intensity within the interval of absorbed doses 10^2—10^3 Gy.

The shape of the luminescence relaxation curves is not monotonous. After the removal of a diode from the irradiation zone, its emission increases at first, then starts to decrease (Fig. 2). Such a character of the brightness-recovery curves differs from their behavior for red GaP diodes. This phenomenon was observed, as a rule, only at the relaxation of the conductivity of thermally excited GaP Hall specimens and, especially, of InP [4].

It is quite evident that the processes of charge carrier capture at and escape from the levels that are associated with defects induced by γ-irradiation cannot be responsible alone for the complicated degradation-relaxation effects in the objects indicated above. Really, the leading role in the appearance of such long-term relaxation effects is played by large-scale concentrations of point-like structure distortions, whose formation by γ-quanta is unfeasible. Point defects, i.e. vacancies V_{P} and V_{Ga}, being stable in GaP at room temperature, can provoke only the recession of the luminescence intensity, by destroying excitonic centers and introducing extra centers of radiationless recombination.

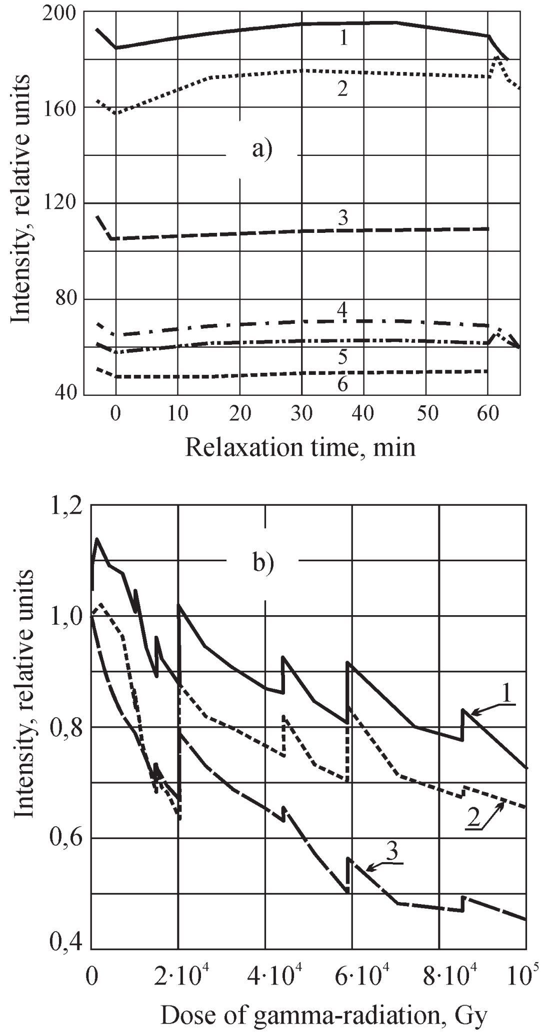

Fig. 2. (a) Relaxation of the luminescence intensity of irradiated green GaP diodes for various irradiation doses D: in the dynamical mode, $D = 10^4$ (*1*), 2×10^4 (*2*), and 10^5 Gy (*3*); and in the absence of the current through the p—n junction, $D = 10^4$ (*4*), 2×10^4 (*5*), and 10^5 Gy; (b) dose dependences of the luminescence intensity for three green GaP diodes

Therefore, the basic tendency that manifests itself in the course of diode irradiation and possesses the irreversible character — a monotonous fading of diode brightness — is related just to the vacancies V_{P} and

V_{Ga}, persistent at 300 K. All other lengthy degradation phenomena, which have the property to recover the initial state some time after the action of the exciting factor terminates — in our case, it is irradiation — may take place probably due to the influence of the structure distortions that are already available in a non-irradiated sample. The role of the extreme factor, which activates complex defects, is obviously played by the high degree of crystal ionization in the γ-field. Typical defects responsible for the long-term luminescence recession and the intensity recovery can be, e.g., DLDs and DPDs formed by dislocation grids [5–7].

Some information concerning the state of defects in the diode can be obtained from the measurements of its CVC. For this purpose, in this work, we used a current generator which allowed us to vary the current through the p—n junction with a step of 1—5 mA. The process of measurements was controlled by a computer. In the forward-bias branches of the CVCs and at temperatures of 77—100 K, we observed a region with an NDR, which revealed a fine structure, when the step of current scanning had been reduced. It is known that the current instability in solid-state objects is of two types, N- and S-shaped. In the former case, the current through the sample decreases with the growth of the applied voltage; the reduction occurs according to the following mechanism. Owing to the growth of the electric field, conduction electrons transfer from the lower minimum of the conduction band, where their effective mass is smaller, into the upper one, where it is larger. As a result, the electron mobility diminishes, and the conductance of the sample falls down, respectively. In gallium arsenide, e.g., the lower minimum is located at the center of the Brillouin zone, while eight upper minima are positioned at its edges. The effective carrier masses in those two positions differ from each other by almost an order of magnitude. Therefore, the reduction of the sample conductance, as the strength of the electric field in it grows, is rather noticeable and has found the application in the Gunn-effect diode production.

The S-shaped region in the NDR section is observed rather frequently in semiconductors. The reasons for this CVC feature to appear can be different. For its observation, the growth of the current through a sample is monitored while measuring the applied voltage. When the current reaches some threshold value, the voltage starts to decrease — the specimen conductance becomes dependent on the degree of charge carrier injection. On the basis of such an effect, e.g., the gallium-phosphide dynistor intended for high currents (5—10 A/cm^2) has been designed [8, 9].

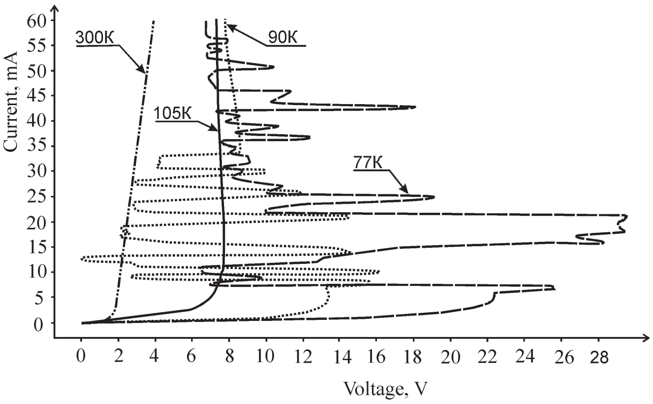

Fig. 3. CVCs of a green GaP LED at various temperatures

As concerns the origin of the S-shaped region in the NDR section of the GaP CVC, no consensus is available in the literature. In early works [10,11], the negative resistance was associated with the existence of a deep recombination level, which, being populated, converts the diode into the NDR mode, owing to the growth of the charge-carrier lifetime. The author of work [11] is more inclined to consider that the negative resistance section in the CVC of a GaP diode at 77 K is related to the heating of the depletion region of the p—n junction by a large current, which flows through the junction under conditions realized in the NDR region. Again, the authors of work [12], having measured the temperature of the junction by two methods, direct monitoring in the course of measurements and by analyzing the shifts of spectral lines, drew a conclusion that, at the initial stage of the S-region development, the essential roles are played by the populating of deep levels and the resulting drastic growth of the injected current carrier lifetime. The contribution of the thermal effect to the diode conductance dominates only in the final interval of the NDR section.

In this work, we attempted to consider thoroughly the processes that manifest themselves in the CVCs of the green diode. In particular, it is a scenario where the diode, starting from the temperature $T \approx 110$ K, converts into the state with the NDR (Fig. 3). In Fig. 4, the diode CVCs measured at 77 K are depicted for two steps of the current scanning, $\Delta I > 1$ mA and $\Delta I = 1$ mA. For the longer step, the dependence $I(V)$ is smooth and looks like the analogous CVC given in work [11]. But when the scanning step becomes shorter, the NDR section reveals oscillations. The envelope curve drawn through the points of maximal deviations to the right side reproduces the CVC recorded at longer ΔI steps.

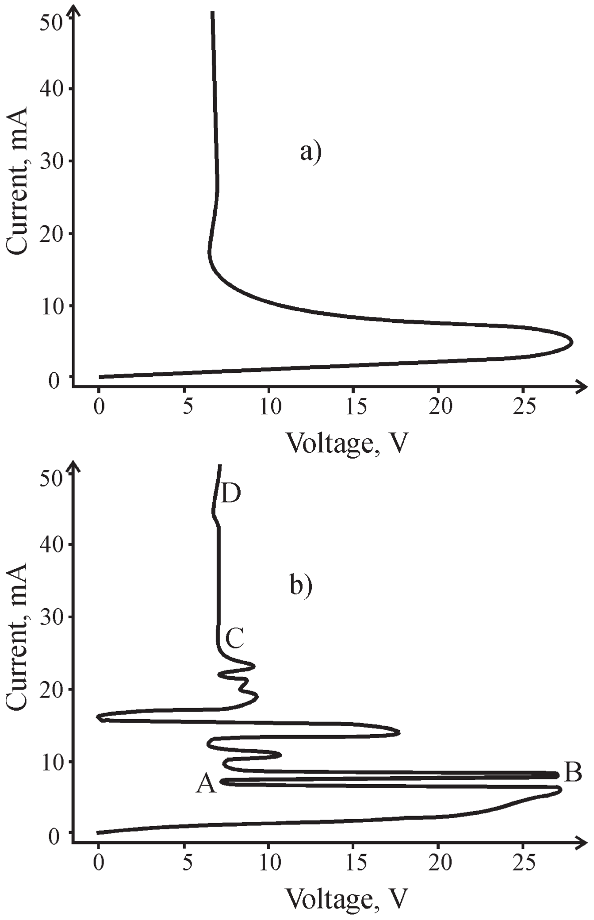

Fig. 4. CVCs of a green GaP LED measured at $T = 77$ K in two regimes of the current scanning $\Delta I = 5$ (*a*) and 1 mA (*b*)

It is obvious that the very existence of the NDR section in the CVC of GaP diodes evidences for the availability of recombination levels in the depletion region of the *p*—*n* junction and that those levels determine the lifetime of minority charge carriers. The transition of the diode into a low-resistance state within a single oscillation (Fig. 4,*b*; point A) is caused by the population of levels with the increase of the forward current. This current heats the diode, then recombination levels become thermally depleted, and the diode returns back to its initial state (Fig. 4,*a*; point *B*). The increase of the current (by enhancing the charge carrier injection) repeats the process many times; the oscillations terminate when the number of injected charge carriers considerably exceeds the number of existing recombination levels. Really, provided, e.g., the current $I = 26$ mA, the number of injected charge carriers is so large as compared with the number of recombination centers that a variation of the population of the latter cannot substantially affect the charge carrier lifetime τ_n; so that τ_n becomes infinite, and the current drastically — almost vertically — increases (Fig. 4,*b*; section *CD*).

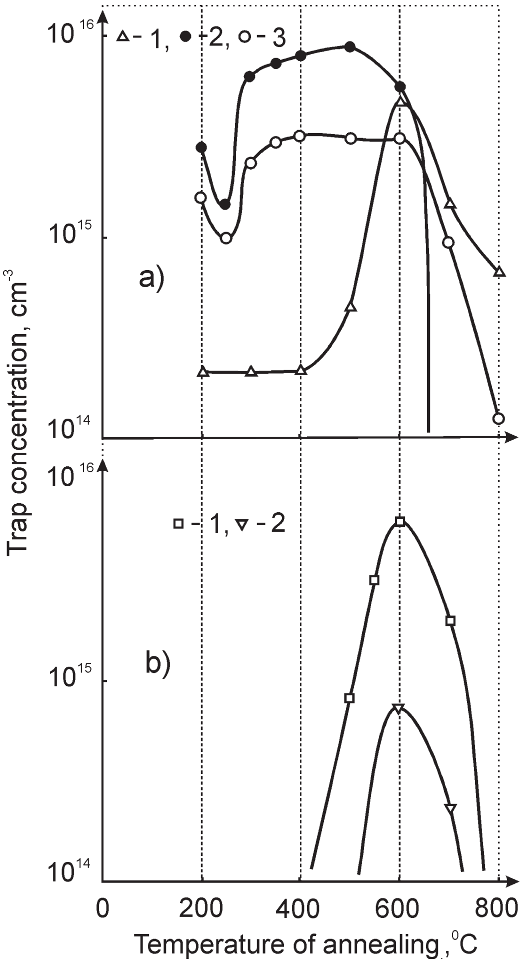

Fig. 5. Concentration variations of traps that are generated in a non-irradiated GaP sample in the course of isochronous annealing: (*a*) in vacuum, the energies of trap activation are 0.32 (*1*), 0.89 (*2*), and 1.04 eV (*3*); and (*b*) in air, the energies of trap activation are 0.44 (*1*) and 0.63 eV (*2*)

The method of deep-level transient spectroscopy (DLTS) enables one to determine the energy positions of defect-induced levels, which are responsible for the effect concerned. The measurement carried out on untreated samples showed that the overwhelming majority of defects in GaP, which can be revealed by the DLTS method, arise only after the heat treatment at $T \geq 200$ °C. In Fig. 5, the dependences of the concentration of several trap levels on the specimen annealing temperature in vacuum or in air are shown.

In both cases, the concentrations monotonously increase while the diode is heated and, only when the temperature $T = 600$ °C is achieved, starts to decrease. At the same time, it is known that, at $T > 600$ °C, a sharp recovery of the near-band-edge absorption resulted from the thermal annealing of thermally induced defects is observed. The quoted data testify that the deep levels that are available in the GaP sample can selectively influence the characteristics of the semiconductor, e.g., through increasing the optical absorption and simultaneously leaving the capacity of the p—n junction to be constant. The prevalence of the scattering of light quanta over their absorption owing to electron transitions can be the reason of why defects acts selectively in the case of growing absorption.

The authors of work [12], having evaluated the temperature of the p—n structure at the time moment of the diode transition into the NDR mode both by direct contact measurements and by analyzing a shift of the near-edge-emission band, came to a conclusion that it does not rise even to the room temperature. Therefore, there is no reason to expect that the thermal effect of the forward current might generate a deep level, whose availability could explain the NDR region in the CVCs. In order to elucidate what level ensures the transition of the structure into the state with NDR, we must consider two equally probable variants:
— the required level is located at a considerable distance from the depletion region of the p—n junction, e.g., in the bulk of the base p-regions; it is the level of oxygen [3];
— or such an electrically active level does exist within the scope of the p—n junction, but its location in the energy gap is close to $E_g/2$, and it cannot be registered owing to the limited capabilities of measurement facilities.

Which of those two hypotheses is correct cannot be answered unequivocally; additional researches are needed.

While irradiating the samples with Co^{60} γ-quanta, as well as when treating them by ultrasound for a long time ($t \approx 100$ h), the range of CVC oscillations extends along the current axis (Fig. 6). Such modifications are directly associated with the growth of the recombination center concentration in the device. As is known, in GaP, such levels are created by the $V_{\rm P}$ and $V_{\rm Ga}$ vacancies, as well as their complexes [13].

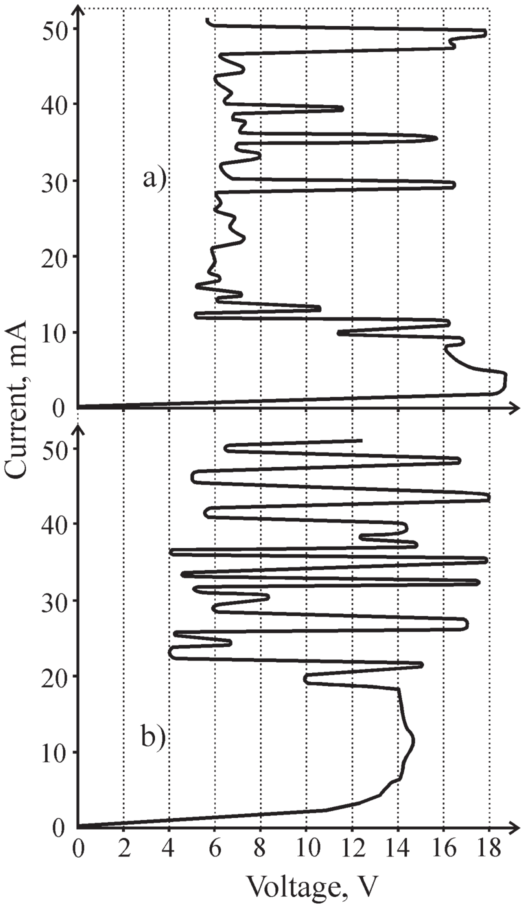

Fig. 6. CVCs of nitrogen-doped GaP diodes measured at $T = 77$ K: (a) irradiation by γ-quanta to a dose of 10^5 Gy; (b) ultrasound treatment for 100 h

Conclusions

The research of the intensity variations of the electroluminescence of GaP LEDs irradiated with γ-quanta has demonstrated that the emergence of long-term relaxation processes can be stimulated by their initial large-scale structural defects, in particular, dislocation grids (dark-line and dark-pixel defects). Their irradiation with Co^{60} γ-quanta does not generate additional relaxation centers and only assists in the manifestation of large-scale inhomogeneities that already exist in the crystal.

The fine structure of the CVC, which was revealed in the NDR region at low temperatures (77—110 K) evidences for the existence of a considerable number of deep recombination levels in the depletion region of the GaP p—n junction. The character of the dependence $I(V)$ within the NDR region (oscillations) is a manifestation of the mechanism of alternative population and depletion of the recombination levels.

The irradiation of diodes with Co^{60} γ-quanta leads to the extension of that CVC region, where oscillations are observed, along the current axis. Such an effect of γ-irradiation stems from the concentration growth of deep recombination centers. Ultrasound gives rise to a similar effect on the CVCs. A certain analogy between the effects produced by the radiation and ultrasound factors can serve as an additional confirmation of the conclusion that an ultrasound wave, while stimulating the motion of dislocations in the GaP crystal, also generates some number of point defects.

One of the possible reasons why the level, which could be related to the existence of the NDR section in the CVCs of GaP diodes, is absent from the transient spectroscopy spectra can be its localization in a distant depletion region of the p—n junction.

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ДЕГРАДАЦІЙНО-РЕЛАКСАЦІЙНІ ПРОЦЕСИ У ЗЕЛЕНИХ ФОСФІДО-ГАЛІЄВИХ СВІТЛОДІОДАХ, ЗУМОВЛЕНІ ДЕФЕКТАМИ СТРУКТУРИ

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Резюме

Оптичними й електрофізичними методами досліджено дефекти структури вихідних та опромінених гамма-квантами зелених світлодіодів. Дослідження часових змін інтенсивності електролюмінесценції показали, що довготривалі релаксаційні процеси можуть бути зумовлені вихідними крупномасштабними дефектами структури — дислокаційними сітками, а саме дефектами темних ліній (ДТЛ) та дефектами темних плям (ДТП), а опромінення лише сприяє виявленню наявних у кристалі неоднорідностей. Виявлена за низьких температур (77—110 К) тонка структура вольт-амперних характеристик (ВАХ) в області негативного диференціального опору (НДО) вказує на існування у збідненій області GaP p—n-переходу значної кількості глибоких рекомбінаційних центрів. Характер струмових осциляцій визначається почерговим заповненням та звільненням цих рівнів. Опромінення γ-квантами Co^{60} приводить до розширення області ВАХ, де спостерігаються осциляції. Подібні зміни у ВАХ виникають також під дією ультразвуку. Така реакція діода зумовлена зростанням концентрації глибоких рекомбінаційних центрів.