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# Study of gamma field induced degradation of green GaP light diode electroluminescence characteristics

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**Abstract.** Optical and electrical properties of green GaP light diode irradiated by gamma-irradiation have been studied. Long-lasting relaxation processes on electroluminescence curve of diodes had been observed which one could connect with dark line defects DLD and dark spot defects DSD. Fine structure of negative differential resistance (NDR) region has appeared in  $I(V)$ -characteristics at low temperatures (77–110K). Gamma-ray irradiation leads to the broadening of  $I(V)$ -curve where oscillations occur. The same action is observed in  $I(V)$ -characteristics treated by ultrasonic. Current oscillations are connected with deep recombination centers in depleted region of GaP light diodes. As these levels are located far enough from p-n junction no one can observe them in TLDS spectra. The much greater voltage oscillation amplitude in the NDR region of  $I(V)$ - green diode characteristics comparing with red diodes may be bound with their lower defect level.

**Keywords:** GaP light diode, electroluminescence, negative differential resistance, recombination centers.

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## 1. Introduction

Long-lasting degradation processes occurring in electronic devices are extremely undesirable due to its negative influence on the speed of response, operating stability, signal reproduction and ability to work without information distortion.

An existence of large-scale potential barriers which can divide nonequilibrium current carriers is the main factor in appearing of relaxation processes [1,2]. Such barriers may be caused by the heterogeneity in doping impurity, dislocation networks and clusters of radiation defects. Characteristic relaxation times are depended upon the value of these barriers and in wide zone semiconductors are expected to be rather essential.

Really one can see that restoring the conductivity in GaP after thermal excitation is lasting some dozens of minutes. This process is especially essential for irradiated samples: see, for example, restoring of emission characteristics in InP irradiated by  $\alpha$ -particles [3,4]. The

analogous long-lasting changes of emission characteristics were observed in GaP treated by ultrasonic an hour or more [5,6].

The purpose of this work is a further study of degradation-relaxation processes of GaP light diodes. Relaxation process intensity increase, as a rule, with the increase of the electroconductivity compensation level of the crystal. One can slow down the majority current carrier concentration by irradiation, so in order to investigate relaxation process we use gamma-rays of Co<sup>60</sup>. Powerful  $\gamma$  field is simultaneously the exciting factor, which causes the increase of nonequilibrium carriers and stimulates their capture by traps.

## 2. Experiment and discussion

In this experiment GaP light diodes were doped by N<sub>2</sub> and the maximum intensity in the emission curve responds to energy 2.17 eV (wavelength 570 nm) at room temperature (see Fig. 1). Point defects were incorporated by  $\gamma$

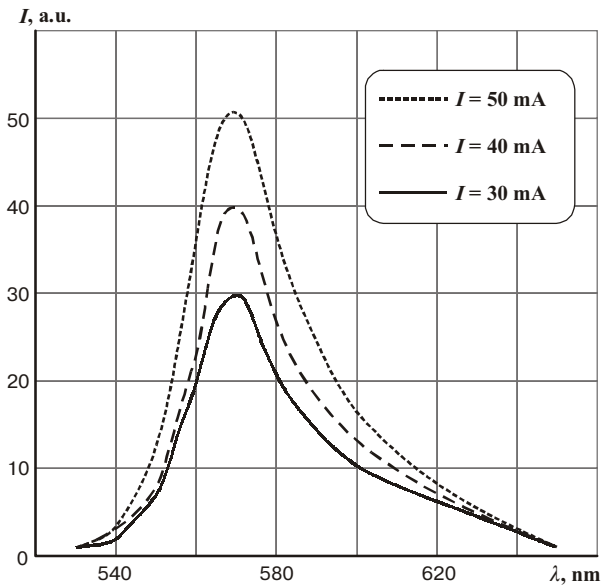


Fig. 1. Electroluminescence spectra of nitrogen doped GaP light diodes ( $T = 300\text{K}$ ). Electrical current is equal: 1)  $I = 50\text{ mA}$ ; 2)  $I = 40\text{ mA}$ ; 3)  $I = 30\text{ mA}$ .

source at 300K. Dose rate is equal 1 Gy/s. Emission intensity of irradiated structures was measured beginning from 10 Gy directly in the  $\gamma$ -field and outside. While studying degradation-relaxation process and plotting luminescence characteristics the constant background component of registered device, caused by photosensor irradiation was subtracted out of measured intensity values. Some samples were irradiated in dynamic mode (under direct current flow through the  $p$ - $n$  junction). Current-voltage characteristics of initial and irradiated diodes were measured in the current generator mode at room and lower temperatures (300–77K). Current was changed with the different steps:  $\Delta I = 1; 5\text{ mA}$ .

It had been found that irradiation led to the monotonous decrease of emission intensity of green diodes, the same as it was observed earlier for red structures[6]. After sample removal out of an active zone partial restoring of diode brightness occurs but this process is much weaker than those observed in red diodes doped by ZnO.

Relaxation pulse intensity increases quickly up to dose  $\sim 2\div 3 \cdot 10^4\text{ Gy}$ , than drops.

Samples irradiated under dynamic mode (when constant current flows through it) show some characteristic features: they degrade strongly under the same irradiation conditions. Its emission brightness is stable nearly to dose  $10^3\text{ Gy}$  and than begins to drop; even faster than for other diodes without applied voltage.

“Low dose effect” (improving of diode characteristics at the beginning of irradiation) is weaker in green GaP structures comparing with red ones [6]. Some increase of emission intensity (nearly 15%) is observed for separate diodes in the accumulated dose interval  $10^2\div 10^3\text{ Gy}$ . The shape of relaxation emission curve is not monotonous. After withdrawal from an active zone the emission intensity increases rapidly at once and then relaxes

slowly (Fig. 2). Such restoring behavior is not typical for red diodes. It was observed, as a rule, only for electroconductivity relaxation in thermally excited GaP Hall samples, and especially – in InP samples [4].

By analyzing relaxation-degradation of emission curve we can conclude that processes of simple carrier capture and release from defect levels(induced by  $\gamma$  irradiation) can't explain such time-dependend effect. Long-lasting relaxation must be connected with large-scale clusters of point defects, which  $\gamma$ -irradiation of given intensity and time can't produce. Phosphorous and gallium vacancies, stable in GaP at room temperature are able to cause emission intensity drop by destroying exciton carrier capture centers and inducing additional centers

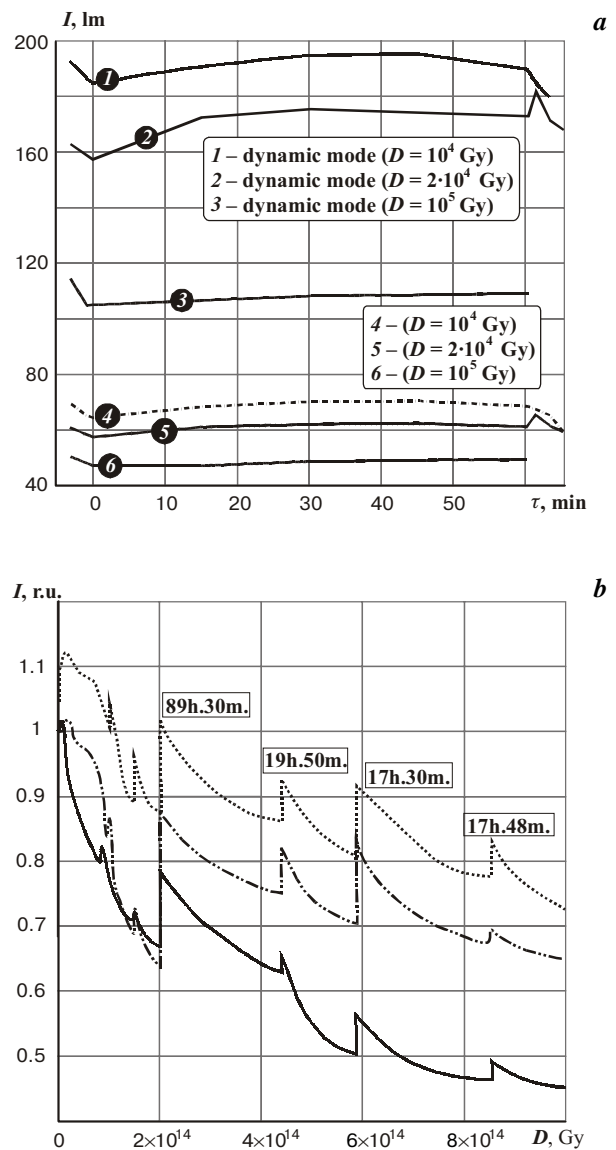


Fig. 2. a – relaxation of emission intensity of GaP light diodes, irradiated by gamma-rays. b – dose dependence of emission intensity for three green GaP light diodes (time of relaxation after withdraw from an active zone is mentioned in frames).

of non-radiating recombination. So, monotonous decrease of diode brightness is connected with vacancies: phosphorous ( $V_p$ ) and gallium ( $V_{Ga}$ ). Other degradation phenomenon, which can be restored after stoppage of the exciting factor action (irradiation – in our case) might be tribute to the structure imperfections, which exist in initial samples before irradiation. High ionizing level could be such extreme factor, activating complex defects (dark line defects-DLD and dark spot defects DSD, formed by dislocation networks, for example [5–7]).

Especially interesting information one can receive by studding the direct part of current-voltage characteristics  $I(V)$  of GaP green diodes. The main feature of it there is negative differential resistance (NDR) in the temperature region 77–100K.

As it is known there are two types (N- and S-) of current instability in solid devices. The first type is realized when current through the sample decreases under the increase of the bias. Due to the increase of the electrical field electrons from the lowest minimum in conductive zone (where their effective mass is the lowest) transmit to the higher minimum (where their effective mass is higher). This leads to the decrease of electron mobility and consequently – of conductivity drop. In GaP, for example, the lowest minimum is situated in the Brillouin’s zone center and 8 upper minima are on the edges of zone. Effective masses in both positions differ by near one order of the value. The effect of the conductivity drop under the increase of the electric field strength is rather strong and is realized in Gunn diode design.

S-type  $I(V)$  characteristics are often realized in semiconductors. There are different conditions of its appearing. In order to observe it one needs to control the current increase by measuring its voltage. When current reaches curtain boundary value, the voltage begins to decrease and conduction of the sample has become depended upon the current injection level. This effect is used in GaP dynistor, which can operate under high current values (5–10 A/cm<sup>2</sup>) [8,9].

It is difficult to explain S-type  $I(V)$ -dependence appearing in GaP. In earlier papers [10,11] negative resistance was explained by the concept of deep recombination centers, whose filling caused the diode transit to NDR-mode due to the increase of carrier lifetime. The author of the paper [11] prefer to think that negative resistance at 77K is connected with the heating of the depletion region of  $p-n$  structure by large current flying through the junction after its going to NDR-region.

Soon, by measuring junction temperature by two method: direct examination during current transport and spectral line displacement – authors [12] had decided that deep levels and accompanying process of sharp increase of injection current carrier life-time, caused by their filling, dominated at the beginning stage of the S-type curve  $I(V)$ . And heating effects are preferable at the end part of NDR.

In this work we try to study in detail the processes which occurs in  $I(V)$ -curve (when the diode transits to low-resistance state), and – to understand mechanism of

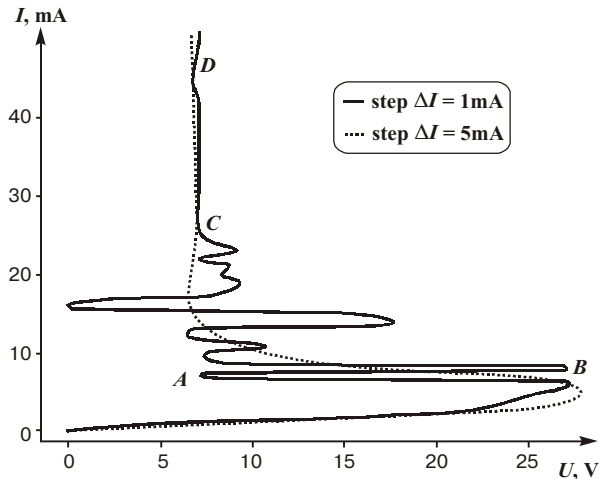


Fig. 3. Current-voltage characteristics of green GaP light diodes at 77K, measured at two injection modes: current steps are equal  $\Delta I = 1\text{mA}$  and  $\Delta I = 5\text{mA}$ .

the NDR. For this purpose the current generator was used in order to change current through the  $p-n$  junction with the step 1 mA. This allows to observe the fine structure of  $I(V)$ -characteristics in NDR-region. The computer controlled this measuring process.

$I(V)$ -characteristics of green GaP diodes, measured at 77K with the step  $\Delta I > 1\text{mA}$  and  $\Delta I = 1\text{mA}$  are given in Fig. 3. In the first case ( $\Delta I = 5\text{mA}$ ) the curve is smooth and resemble  $I(V)$ -characteristics received in [11]. When the value of the step decreases and reaches 1mA the oscillations appear (Fig. 4). For this step diode transits to NDR-state when the temperature drops (beginning from 110 K). If to draw  $I(V)$ -characteristic by using values of maximum voltage deviations to the right, one can obtain easily the curve, characteristic for samples, measured with the large current step.

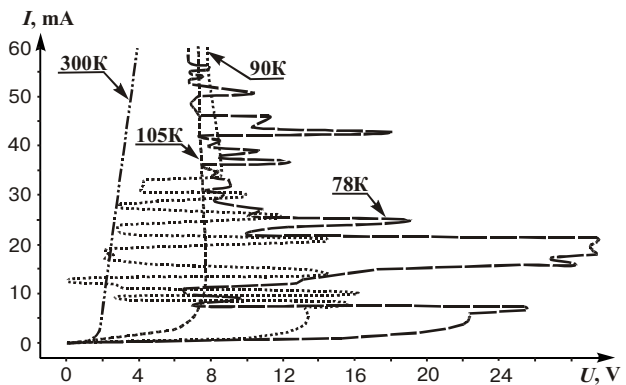


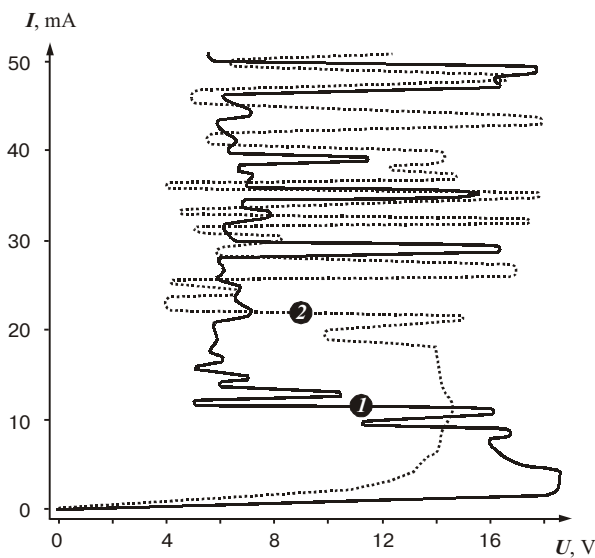
Fig. 4. Current-voltage characteristics of nitrogen doped GaP light diodes for different temperatures at: 77, 90, 105, and 300K.

It's obvious that NDR region in  $I(V)$ -curve is an evidence of existence of recombination centers in depletion region of GaP  $p-n$  junction, which influence on minority current carrier lifetime. The diode transition to the low resistance state in the frame of the single oscillation (Fig. 3, dot. A) is caused by recombination center filling while direct current rises. This rather large current leads at once to the diode heating, resulting in the thermal devastation of recombination centers. Thus diode recovers to the previous state (Fig. 3, dot. B). Next current increase (an injection level increase) repeats this process (filling-devastation) over and over again. Such oscillations cease when the number of injected current carriers exceeds the number of recombination levels.

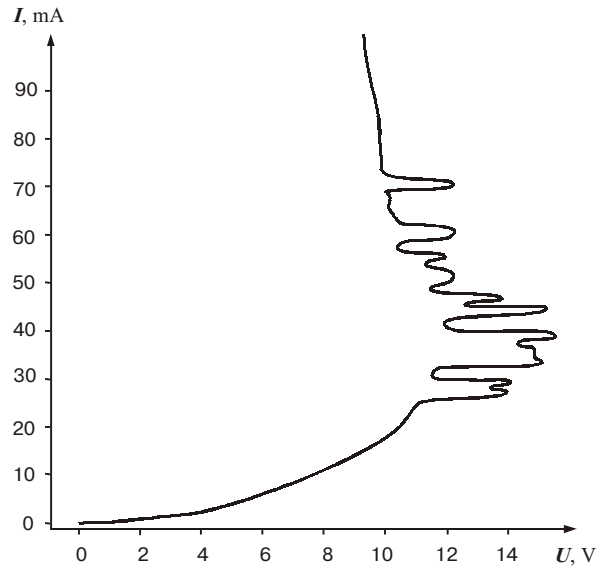
In our case, when current reaches the value of 26 mA, the number of induced carriers is so large comparing with the recombination center numbers that the changes of their filling do not essentially influences on the current carrier lifetime. This value has become enormous large and current increased sharply (as vertical line, see Fig. 3, CD region).

Irradiation of structures by gamma-rays of  $Co^{60}$  leads – as in the case of long-lasting ultrasound treatment (~ 100 h) – to the broadening of oscillation region in the vertical axis, that is directly connected with the increase of the recombination center concentration (Fig. 5). Recombination levels in GaP are known to be created by phosphorous and gallium vacancies and their complexes[12].

Comparing green and red diodes, it is necessary to state that NDR region of their  $I(V)$ -characteristics differs: oscillation amplitude of GaP(Zn:O) diodes (Fig. 6) is smaller than for green ones. Such difference is evidently connected with smaller concentration of green diode initial defects.



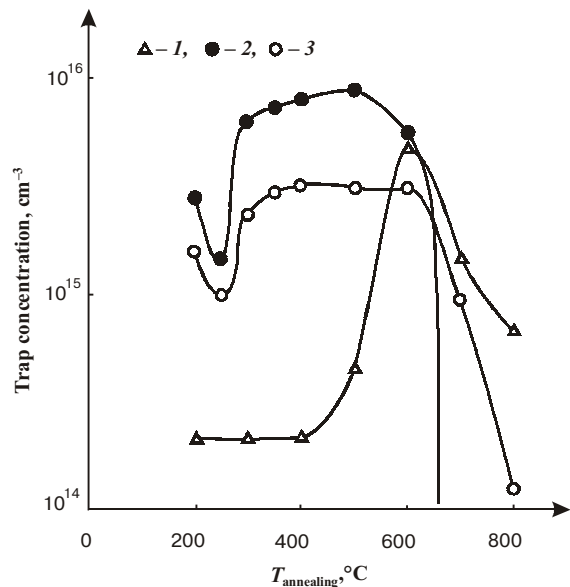
**Fig. 5.** Current-voltage characteristics of nitrogen doped GaP light diodes:  
 1 – irradiated by gamma-rays,  $D = 10^5$  Gy ( $T = 84$ K);  
 2 – treated by ultrasound during 100 h ( $T = 84$ K).



**Fig. 6.** Current-voltage characteristics (S-region) of Zn:O doped GaP light diodes at  $T = 77$ K.

While using the deep level transient spectroscopy (DLTS) one can find the energetic state position of the defect responsible for the phenomenon observed.

From our measurements performed on the initial samples it is clear that the most of defects (which one can discover in GaP by using DLTS method) appear after thermal treating at temperature  $T \geq 200^\circ\text{C}$ . The dependence of discovered level concentration as the function of temperature for annealing in vacuum and in the air are shown in the Figs 7 and 8. It is seen in this figures that the



**Fig. 7.** The dependence of trap carrier concentration of initial samples as the function of annealing temperature in vacuum (levels with activation energy: 1 – 0,32 eV; 2 – 0,89eV; 3 – 1,04 eV, discovered by DLTS method).

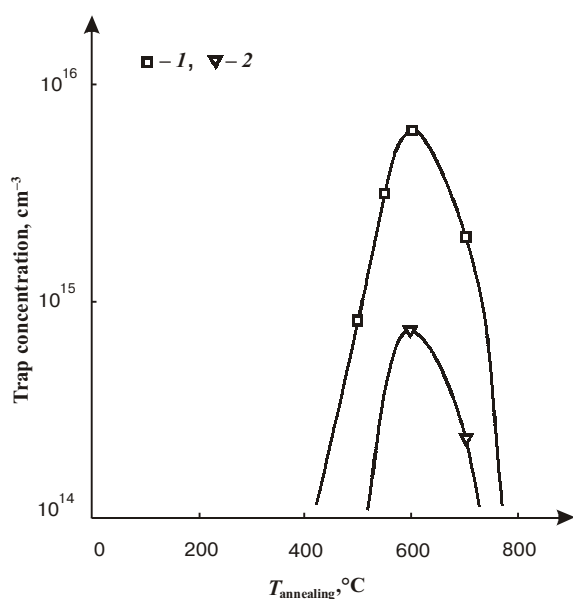


Fig. 8. The dependence of trap carrier concentration of initial samples as the function of annealing temperature in air (levels with activation energy: 1 – 0.44 eV; 2 – 0.63eV, found using DLTS method).

trap concentration increases monotonously with the heating and only when temperature reaches 600°C this value begins to drop. At the same time at  $T > 600^\circ\text{C}$  a sharp restoring of the near-edge transmission occurs (Fig. 9), caused by the thermodonor annealing. Data obtained has shown that deep levels in GaP can influence selectively on semiconductor properties: increasing, for example, the optical absorption value and leaving the  $p$ - $n$ -junction capacity without change. In the case of the absorption increase such selective defect action may be connected

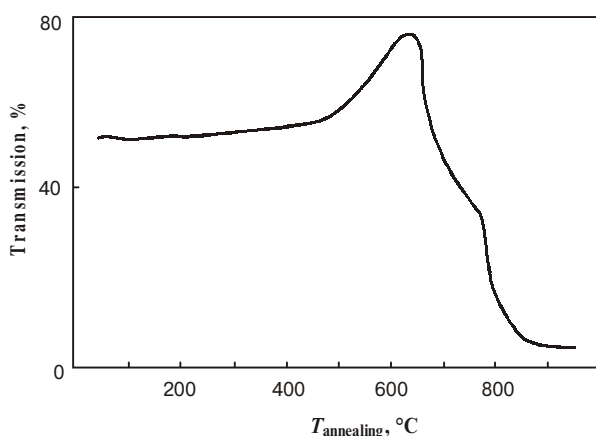


Fig. 9. Near edge optical transmission of green diodes as the function of annealing temperatures.

with the preferable influence of a light scattering comparing with it absorption due to the electron transition.

The authors of the paper [13], by estimating  $p$ - $n$  structure temperature (directly by the contact method and by displacement of edge emission band) at the moment of diode transition into NDR mode found that temperature does not reach even room value. So there is not any reason to think about incorporation of the deep level, which caused the appearing of NDR in  $I(V)$ -curve with heat effect of direct current. In order to answer which level responses for it one must examine two possible situations:

- necessary level, for example, the oxygen level [3], is situated far from the depletion region of a  $p$ - $n$ -junction.
- such electrically active level has just existed in the bound  $p$ - $n$ -junction, but its position is near  $E_g/2$  in the forbidden zone and it's impossible to fix it due to a limited opportunity of the measuring equipment.

It is still a doubt, which concept is preferable and further study is necessary.

### 3. Conclusions

Time study of electroluminescence intensity changes of GaP light diodes, irradiated by gamma-rays of  $\text{Co}^{60}$  has shown long-lasting relaxation processes, which one can connect with large scale structure defects – *dislocation* networks or dark line- DLD and dark spot defects DSD. Gamma-irradiation doesn't induce additional relaxation centers but only promote the reveal of large-scale non-homogeneity, which exist previously in crystals.

The fine structure of  $I(V)$ -characteristic's NDR region, discovered at low temperatures (77–110K) allows to state that there is rather large number of deep recombination centers in depleted region of GaP  $p$ - $n$  junction. NDR region behavior of  $I(V)$ -curve (appearing of oscillations) is an evidence of filling-release mechanisms of recombination centers: the voltage drop at the time of the filling and its restoring due to heat release, caused by the previous current increase.

Gamma-ray irradiation leads to the broadening of  $I(V)$ -curve where oscillations occur. The same action is observed in  $I(V)$ -characteristics treated by ultrasonic. Such analogy in the influence of both factors could be an additional confirmation of conclusion that ultrasound wave, while stimulating dislocation movement, at the same time generate certain amounts of point defects in GaP crystals.

The much greater voltage oscillation amplitude in the NDR region of green diode  $I(V)$ -characteristics comparing with red diodes may be bound with their lower defect level.

One of the possible explanation of absence in the DLTS spectrum of the deep level, responsible for NDR region of  $I(V)$ -characteristics, there is its position – far enough from region of  $p$ - $n$  junction.

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