

CHANGE OF DEEP CENTERS DURING OPERATION ALGAAS LIGHT EMITTING DIODES

Abdullaev Jamolitdin Solijonovich

jamoliddin196005@gmail.com

Associate Professor of the Department of Natural Sciences of the Fergana branch of the Tashkent University of Information Technology named after Muhammad al-Kharezmi.
Uzbekistan

Annotation: Light-emitting diodes (LEDs) are widely used in optoelectronics. In this regard, studying the degradation process of LEDs, that is, changes in their parameters during operation, is an urgent task both from the point of view of elucidating the physics of elementary processes causing degradation and their mechanisms, and to improve the reliability of devices. The paper presents the results of a study of the degradation process of LEDs based on $\text{Al}_x\text{Ga}_{1-x}\text{As}:\text{Te}(x > 0,34) - \text{Al}_{0,34}\text{Ga}_{0,66}\text{As}:\text{Zn}-\text{GaAs}:\text{Zn}$ heterostructures obtained by liquid-phase epitaxy. When studying the degradation phenomenon, along with classical methods of studying electroluminescence spectra in the temperature range 77-300K, capacitance-voltage and current-voltage characteristics, modern highly informative methods were used.

Key words: light-emitting diodes, liquid-phase epitaxation, photoluminescence, current-voltage characteristic, capacitance-voltage characteristic, electroluminescence, deep centers.

Introduction

Studies of the degradation of injection electro-luminescence (EL) in GaAlAs-GaAs heterostructures and devices have shown that the main reason for its decrease is an increase in the concentration of non-radiative recombination centers (CBR) in the active region of DM [1,2]. To explain this phenomenon, it was assumed, in particular:

- recombination-stimulated generation of defects with their subsequent unification into the CBR [3];
- diffusion-drift redistribution of impurity atoms and intrinsic defects in the p-n transition field;
- recombination-stimulated relaxation of elastic stresses in the heterosystem with the formation of dislocations – defects of dark lines (DTL) and dislocation loops [4]. The formation of DLB during degradation was eliminated by reducing the voltage in the systems. The reason for the appearance of point defects - CBR, which is associated with long-term degradation of devices, remains controversial.

Deep centers (HCs) affect the parameters of semiconductor materials and devices. The presence of deep centers: impurities with deep levels, radiation defects (RD), heat treatment defects (TDP) - in some cases gives semiconductor materials and devices useful or, conversely, undesirable properties [5]. Therefore, the study of the properties of GCs is one of the main areas of modern semiconductor physics.



Thanks to the development of various methods for the study of deep centers, it has become possible to determine the energy spectrum of deep levels in the active DM region in the process of degradation. These methods include the method of thermally stimulated current (TST) and thermally stimulated capacitance (TCE), tunneling spectroscopy (TS), as well as deep level relaxation spectroscopy (RSGU), the so-called DLTS method in foreign literature, etc.

Materials and methods

Capacitive spectroscopy of deep centers is based on a change in the barrier capacitance of the p-n- transition when the filling of the energy levels of the HZ with electrons or holes changes. The advantages of capacitive methods are high sensitivity, the ability to determine the parameters of the HC when changing their filling with both basic and non-basic carriers, etc.

An increase in the concentration of CBR during the degradation of DM is evidenced by an increase in the recombination and excess components of the direct current, an increase in the reverse current and low-frequency current noise, a decrease in the lifetime of non-basic carriers and their diffusion length, and an increase in the threshold of laser generation. Detailed studies of changes in the spectrum of energy levels in the active region of the DM by methods of terstimulated currents and transient capacitive spectroscopy of deep centers [6,7] have shown that in the process of degradation, a whole series of local centers arises. However, not for all emerging centers there is a correction of their appearance with the degree of degradation. For example, the degradation of GaAs_{1-x}P_x-based devices by almost 50% was accompanied by the appearance of traps with a concentration of $610 \cdot 10^{15} \text{ cm}^{-3}$ in the energy range of 0.2 – 0.4 eV from each of the zones [8].

Fig. Figure 1 shows the curves of the thermally stimulated LED current based on GaAl_{1-x}P_x obtained by diffusion of Zn into an n-type material doped with Te[11]. Comparing the curves (Fig. 1) before and after degradation (100 h), it can be seen that the concentration of some levels in the region of spatial charge (SPR) has increased, while others have decreased.

The authors [10] also made sure that the concentration of deep impurity centers in p-n junctions can both increase and decrease during DM degradation. In TST measurements, the sample was cooled to the temperature of liquid nitrogen with a direct current with a density of 10 A/cm². Then the reverse displacement voltage of 3 V was turned on, the sample was held for 5 minutes, at 80 K and then heated at a constant rate, which varied from 0.07 to 0.6 deg/s. After reaching the room temperature of subsequent cooling, holding at 80 K, and heating was carried out for the second time at a reverse displacement voltage of 3 V. TST was estimated as the difference in currents in these two measurements.

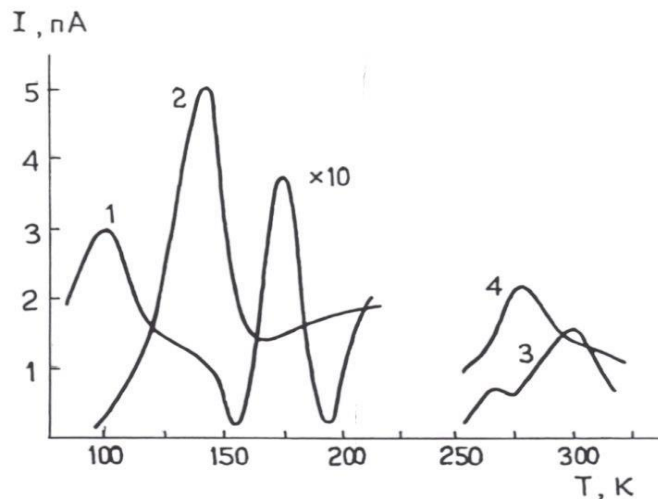


Fig. 1. TST sectors p-n – transitions based on GaAs_{1-x}P_x before (1,3) and after (2,4) degradation at heating rates of 0.55 (1,2) and 0.07 (3,4). (K·⁻¹).

The parameters of the impurity centers were calculated on the assumption of the absence of re-adhesion and the invariability of the width of the depleted layer in the process of emptying the traps. The validity of the latter assumption was confirmed by the invariability of the capacity of p-n – transitions when filling and emptying traps. The depth of impurity levels was determined by the dependence of the position of the corresponding TST maxima on the heating rate [11].

Changes in the parameters of deep centers in AlGaAs DM under conditions of recombination of significant concentrations of electrons and holes were recorded in [12,13]. On the basis of the analysis of the tunneling components of the forward and reverse currents, a change in the concentration of the two traps $E_t = 0.45$ and 0.60 eV was found. An increase in the concentration of traps with $E_t = 0.89$ eV in the process of rapid ($t = 100$ h) degradation of AlGaAs lasers was recorded by the DLTS method.

In [14] it was found that in the initial state of GaAs: Si DM there are centers with an ionization energy of 0.1 eV and a concentration of $(1.87: 4.14: 10^{18} \text{ cm}^{-3})$. After accelerated degradation at $T_g = 100^\circ\text{C}$ for 1500 hours, the concentration of these centers tripled.

In a number of degraded DMs, new centers with an energy of 0.36 eV and a concentration of $(1.4 - 2.9)$ of 10^{18} cm^{-3} were found.

It should be noted that a number of deep levels in the GaP and GaAs of the SD have been identified. In particular, the level of $E_v + 0.55$ eV in GaP, as well as the acceptor level with ionization energy $(0.43 + 0.45)$ eV for GaAs, is associated by the DM with Cu. The level of $E_v + 0.22$ eV in GaP DM and the level with ionization energy $E_v + 0.08$ eV and $E_v + 0.17$ eV arising from the degradation of GaAs DM may correspond to centers containing Si, while the majority of HZ in GaP and GaAs DM have not been identified. It should be noted that not in all cases there is the appearance of new deep levels with DM degradation. In particular, no changes in the energy spectrum in the active region of GaP:N were detected in [15].



Such a difference in results is apparently due to different degradation conditions, as well as different technologies for manufacturing LEDs.

However, the kinetics of degradation of red AlGaAs DMs is complex and is due to the course of several elementary processes. Therefore, it was expedient to trace the change in the spectrum of deep levels with shorter time intervals, using modern research methods, as well as in connection with the simultaneous emission of changes in the phenomenological characteristics of diodes to establish a correlation between the nature of changes in phenomenological parameters and the appearance of certain types of deep centers.

Results and Discussion

Degradation occurred when a direct current with a density of $I = 16 \text{ A/cm}^2$ was passed through diodes at a temperature of 500 C for 3000 hours. At various stages of degradation, the integral luminescence efficiency, electroluminescence (EL), watt-volt-ampere, volt-ampere and volt-farad characteristics (I-V and VCF) were controlled

The spectrum of the LE study of the SD at 300 K contained two luminescence bands: red (K) with a wavelength maximum of the spectral emission bandwidth

$\lambda_m = 675 - 655 \text{ nm}$ and a half-width of 17-20 nm, associated with recombination in the active $p\text{-Al}_{0.34}\text{Ga}_{0.66}\text{As}$ layer and infrared (IR) $\lambda_m = 885\text{-}888 \text{ nm}$ and half-width of 30-40 nm, due to re-emission in the GaAs substrate or transition layer, due to the absorption of the main K-band there. ÷ ÷

The direct branch of I-V of the studied LEDs had four regions corresponding to the tunnel-thermal /16/ $ITT = I_0 \exp(-\frac{E_t}{kT}) \exp(-\alpha U)$, where $8.8 \alpha = V_{-I}$ does not depend on the temperature (recombination $I_{tp} \sim \exp, n = 2$) and recombination-emission ($I_{nkt}^{pe} = \exp, m = 1.3$) current component, as well as the region of current limitation by series resistance. $\frac{eU}{mkT}$

The current on the reverse branch of the I-V of these SDs in the low voltage range of 1.0 – 1.5 V was due to the thermal generation component, and in the region of 1.5 V and 10 V it had a tunnel-thermofield nature (810) $I_{\div Tn} = I_0 \exp(-\frac{E\beta}{kT}) \beta U \beta =$, and also does not depend on temperature. At $U = 10\text{--}11 \text{ V}$, an avalanche breakdown of the diode occurred, as evidenced by the positive temperature coefficient of the breakdown voltage. ÷

The kinetics of the change in the intensity of the basic K-band of luminescence W_k measured in the process of degradation of a typical SD is shown in Fig. 2.a. -2.b shows the change in the degradation of the values of the above current components ITT, ITP, IPE, ITP, at the specified voltage values.

Periods of degradation. As is known, the luminescence efficiency of the main K-electroluminescence band in AlGaAs LEDs is determined by an expression of the form:

$$W_k = k n I_{nk}$$

Where, **k** is a coefficient that depends on the geometry of the crystal and the optical parameters of the structure; **I_n**—full current through the diode; **nk** is the internal quantum output of the K-band luminescence in the volume of the active layer,

$nI = I_{EE} / I_n = I_{2e} / I_{EE} + I_{pe} + I'$ is the coefficient of electron injection into the p-layer, where the emission of the K-band occurs, **I_{EE}**, **I_{pe}** is the emission current of electrons and holes in the p and p layers, respectively, **I'** is the sum of all other non-radiative components of the current. For the future, it is possible that the change with time of the intensity W_k



measured at $I_n=60$ mA (curve 2, Fig. 2.a) reflects the change in the operating value, since in this case $I_{ee} + I_{pei}$ and nI - const. Measurement at W_k at $I_n=10$ mA carries information about changes in nI and n_k .

Analysis of the degradation kinetics of the studied LEDs shows that during the operating period corresponding to the intervals A-B, B-C, C-D on the curves of Figure -2, a, the decrease in the intensity of the red luminescence band is due to various reasons. Indeed, in the period A-B, the value of W_k practically does not change (Fig. 2, a, curve 2), and in some diodes it even increases. At the same time, an increase in forward and reverse tunneling-thermal and thermorecombination currents is observed at the I-V (Fig-2, b, curves 1-3). At the same time, the current increases in the area where the thermionic component dominated, and the parameter m increases from 1.3 to 1.5, which indicates an increase in the share of the recombination current there and a decrease in the injection coefficient nI (Fig. 2, b, curve 2). This effect causes a decrease in the luminescence efficiency measured at a low current through the diode (Fig. 2, a, curve 1).

It should be noted that in the DM where the tunnel-thermal currents increase more strongly in the A-B segment, the recombination current increases more significantly and the value W_k , ($I_n=10$ mA), decreases.

In those DMs where the recombination current did not increase in the A-B segment, the value W_k , ($I_n=10$ mA) remained constant.

During the period of B-C operation, the degradation of W_k is due to a decrease in the volumetric quantum efficiency of the luminescence n_k at a constant value of currents on the I-V system. Apparently, an increase in the concentration of deep centers that determine the competing recombination channel causes a decrease in the value of n_k and W_k .

Finally, in the C-D operating area, the rate of decrease in volumetric luminescence efficiency decreases (Fig. 2, a, curve 2). At the same time, tunnel-thermal and recombination currents begin to grow again on the forward and reverse branches of the I-V (Fig. 2, b). The same change is accompanied by an increase in the deep centers and a decrease in the number of electron traps.

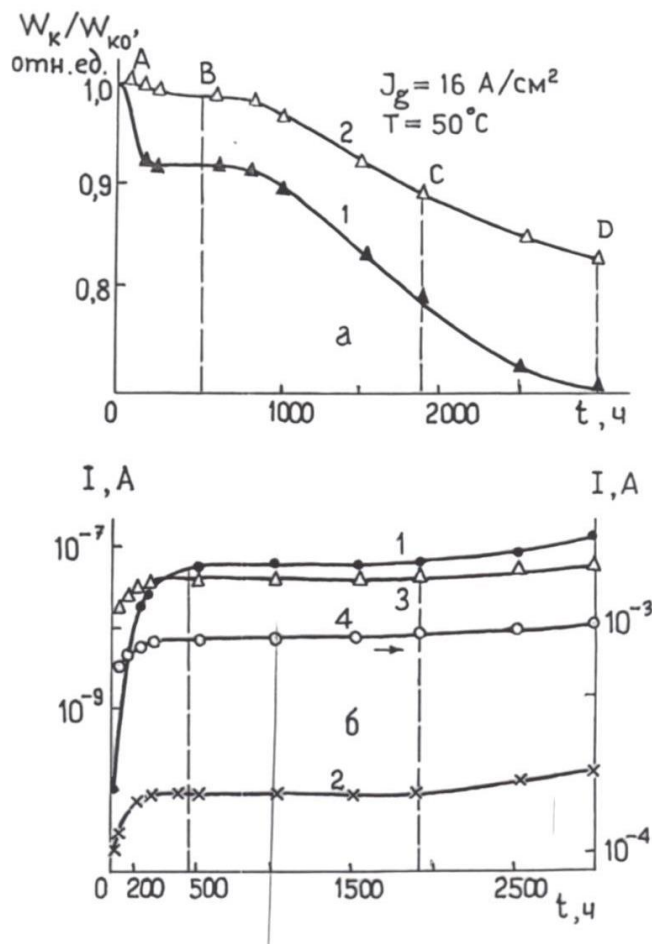


Fig. 2. Kinetics of relative change $W_k/W_{k0'}$ measured at tq equal to I_0 (1) and 60 mA (2). Operating time was carried out at $T = 50^\circ\text{C}$ and $I = 40 \text{ mA}$ (a); kinetics of changes in currents (1), (2), (3) and (4) on the forward and reverse branches of BAX (b)

It was previously shown that the increase in tunnel-thermofield current on the reverse branch of the I-V is an indicator of an increase in the p-n transition of the density of structural defects. The appearance of the latter at the initial stage of degradation of our D(A-B) can be caused by recombination-stimulated reproduction of dislocations or the formation of dislocation loops, due to relaxation in the heterosystem of elastic stresses.

The connection between the processes occurring in the A-B phase of DM degradation and the heteroboundary is confirmed by the dependence of the concentration of deep centers on the width of the spatial charge region. The concentration of centers arising in the period A-B increases in the direction of the heteroboundary between the n- and p-layers, and the concentration of disappearing traps in the same direction decreases.

We associate the B-C section of the DM degradation process with a decrease in the internal quantum yield of the K-band of luminescence in the active layer of the diode. This can occur: a) due to an increase in the rate of non-radiative recombination, due to an increase in the concentration of the corresponding centers; b) as a result of a decrease in the rate of radiative recombination due to a decrease in the concentration of luminescence centers, as well as c) during the transformation of radiative recombination centers into non-radiative ones, for



example, when **ZnGa atoms** participating in radiative recombination are released, and the internode with the formation of **VGa** centers of non-radiative recombination is evident. The appearance of traps in the forbidden zone during this period, which play the role of recombination centers in the lattice, clearly indicates in favor of the first reason.

And finally, during the period of C-D operation, the change in all characteristics is similar to the changes occurring in the A-B phase of DM degradation.

The described kinetics of the decrease in the efficiency of the DM luminescence during degradation becomes clear if we assume that during the period of B-D degradation the DM is caught by the diffusion of mobile impurities or defects in the heterostructure regions remote from the p-n junction, namely from the highly doped GaAs substrate. Easily mobile (donor) defects in GaAs are, as is known, internode Zn atoms.

Conclusion

From the analysis of experimental data, conclusions can be drawn, which are given by the following conclusions.

1. The degradation phenomenon of red AlGaAs LEDs, the light-emitting structures of which contain a GaAs substrate, is due to the injection-stimulated processes of relaxation of elastic stresses in the heterosystem and the diffusion of Zn atoms from the GaAs substrate to the p-n junction.

2. On the basis of the study of the dependence of the rate of relaxation processes of elastic stresses and the diffusion of Zn atoms, it was established that the process of injection-stimulated diffusion of zinc atoms in the layer

AlGaAs is not recombination-stimulated. At the same time, the process of relaxation of elastic stresses in AlGaAs-GaAs heterostructures turned out to be recombinationally stimulated.

The degradation model of red AlGaAs LEDs proposed here cannot be considered fully proven. However, the considerations expressed make it possible to uncontradictorily explain the complex nature of changes in the parameters of DM and shed light on the physicochemical nature of the forming centers.

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