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METHODS OF THERMAL-STIMULATED CURRENTS FOR RESEARCH OF IMPURITY SITES AT LIGHT-EMITTING DIODES

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МЕТОДИ ТЕРМОСТИМУЛЬОВАНИХ СТРУМІВ ДЛЯ ДОСЛІДЖЕННЯ ДОМІШКОВИХ ЦЕНТРІВ У СВІТЛОДІОДАХ

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МЕТОДЫ ТЕРМОСТИМУЛИРОВАННЫХ ТОКОВ ДЛЯ ИССЛЕДОВАНИЯ ПРИМЕСНЫХ ЦЕНТРОВ В СВЕТОДИОДАХ

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Abstract. Impurity sites in LEDs based on of $Ga_{1-x}Al_xAs$ for fiber-optic communication lines using thermal-stimulated current method were researched. The causes of the degradation of such diodes are clarified. The installation for research using the method of thermal-stimulated currents is described. Given in p-n junctions based on *GaAlAs*. The dependence curves of thermal-stimulated currents and temperature are shown at various heating rates. Was made a research of light-emitting diodes degradation by their power supply of current pulses up to 10 A, with a duration of 100 ns and a frequency of 300 Hz, as well as at 50 mA, 20 mA and a temperature of 80^0C. A connection was found in the process of degradation of LEDs with an increasing of the concentration of impurity sites. The curves of thermal-stimulated currents determined the concentration of impurity sites before and after the degradation of LEDs. It is shown that the main reason for the change in the electrical characteristics of the p-n junctions of the studied samples upon passing a direct current is the accumulation of impurity sites.

Key words: light-emitting diodes, impurity sites, degradation, thermal-stimulated currents, heating rate, accumulation, efficiency, burial depth.

Анотація. Досліджені домішкові центри у світлодіодах на основі $Ga_{1-x}Al_xAs$ для волоконно-оптичних ліній зв'язку методом термостимульованих струмів. З'ясовуються причини деградації таких діодів. Описується установка для проведення досліджень методом термостимульованих струмів. Надано сутність даного методу та можливість його використання у *p-n*-переходах на основі *GaAlAs*. Показано криві залежності термостимульованих струмів від температури при різноманітних швидкостях нагрівання. Проведено дослідження деградації світловипромінюючих діодів при їх живленні імпульсами струму до 10 А, тривалістю 100 нс та частотою 300 Гц, а також при 50 мА, 20 мА та температурі 80^0С. Виявлено наявність зв'язку в процесі деградації світлодіодів зі зростанням концентрації домішкових центрів. По кривих термостимульованих струмів знайдені концентрації домішкових центрів до та після деградації світлодіодів. Показано, що основною причиною зміни електричних характеристик *p-n*-переходів досліджених зразків при пропусканні прямого струму є накопичення домішкових центрів.

Ключові слова: світлодіоди, домішкові центри, деградація, термостимульовані струми, швидкість нагріву, концентрація, ефективність, глибина залягання.

Аннотация. Исследованы примесные центры в светодиодах на основе $Ga_{1-x}Al_xAs$ для волоконно-оптических линий связи методом термостимулированных токов. Выясняются причины деградации таких диодов. Описывается установка для проведения исследований методом термостимулированных токов. Приведена сущность данного метода и возможность его использования в *p-n*-переходах на основе *GaAlAs*. Показаны кривые зависимости термостимулированных токов от температуры при различных скоростях нагревания. Проведено исследование деградации светоизлучающих диодов при их питании импульсами тока до 10 А, длительностью 100 нс и частотой 300 Гц, а также при 50 мА, 20 мА и температуре 80 ^{0}С. Обнаружено наличие связи в процессе деградации светодиодов с ростом концентрации примесных центров. По кривым термостимулированных токов определены концентрации примесных центров до и после деградации светодиодов. Показано, что основной причиной изменения электрических характеристик *p-n*-переходов исследованных образцов при пропускании прямого тока является накопление примесных центров.

Ключевые слова: светодиоды, примесные центры, деградация, термостимулированные токи, скорость нагрева, концентрация, эффективность, глубина залегания.

The rapid development of optoelectronics opens up new possibilities for the use of optical communications. Fiber-optic LEDs can serve as a material or medium for optical communication. Although, any light sources can be used in optronic and fiber-optic communication systems, it is more advantageous to use LEDs, since they have the highest quantum yield at low currents, the best optical connection with a transmission medium is a light guide (due to its small size and low operating temperatures) and the highest transfer rate.

In order to decrease quantum yield, known LEDs are arranged as follows [1]: *GaAs:Si* (32%), $Ga_{1-x}Al_xAs$ (14%), *GaP:ZnO* (12%), *GaAs* (3 … 5%) and $GaAl_{1-x}P_x$ (1 … 3%). The choice of a particular LED as a light source is determined by the requirements for the characteristics of the LED system - light guide - light receiver. The basic requirement for such a system is as follows: it is necessary that the current transfer coefficient (Iвых/Iвх) be close to 1 or more.

However, during the operation of LEDs, degradation occurs, and reliability decreases under radiation exposure [2 - 4]. The reliability of the device means its ability to perform working functions for a given time. A failure is considered to be the exit of one of the conditioned parameters of the device beyond the limits of predefined requirements. The most basic character is physical aging - a drop in the internal quantum yield.

The electrophysical and optical characteristics of the material, such as impurities in solid solutions, are strongly influenced by point defects (vacancies and interstitial atoms) and their simple complexes (“divacancies” and complexes with impurity centers). Controlling the concentration of point defects is very difficult. An excess of vacancies of one of the sublattices of a binary compound (as well as an excess of interstitial atoms of one sort) represents a violation of the stoichiometry of the crystal [5]. Point centers repeat many properties of impurity atoms; in particular, they participate in the formation of complexes and can form inclusions in the form of voids and clusters. Irradiation of crystals by fast particles leads to disorder. In [2, 3], degradation of the luminescent characteristics of $Ga_{1-x}Al_xAs$ under irradiation was noted. Recently, much attention has been paid to the study of new levels in the band gap, which are formed both during irradiation and current training and their behavior during annealing and during the operation of devices [5].

During operation, a gradual degradation of light-emitting diodes is observed. However, the current level of technology can ensure the durability of LEDs up to 10^4 – 10^5 hours or more. The aging process in LEDs is characterized by a rate that grows with a current density j approximately proportional to j^2. Its essence is reduced to a decrease in the internal quantum yield of radiation in the edge band due to an increase in the rate of nonradiative recombination [4, 5]. An increase in the rate of nonradiative recombination during aging of optical fibers can be explained by an increase in nonradiative centers. Among the factors that accelerate the process of degradation of diodes, is primarily the initial perfection of the structure.

A factor accelerating degradation is also temperature. Measurements at temperatures above room temperature show that aging accelerates as a thermally activated process. In the presence of intense electronic recombination, the migration rate of defects increases; point defects, impurities, and dislocations can come into motion [5]. During the degradation of optical fibers, usually no new luminescence bands arise [6], so the quantum efficiency of diodes decreases due to nonradiative recombination.

The centers that appear in A^3B^5 semiconductors upon degradation are usually more stable than radiation defects. The question of the defects' nature which responsible for the degradation of the A^3B^5 group semiconductors of and LEDs made on their basis is one of the most relevant for solving the degradation problem.

From the analysis of references, we can conclude that there are not many works on the study of impurity centers in LEDs and their effect on efficiency and stability for the A^3B^5 group semiconductors, and there is practically no description of such materials for *GaAlAs* LEDs and the study of centers by the method of thermally stimulated currents.

The purpose of current article - the study of deep impurity centers in *p-n*-junctions based on GaAlAs by the thermo-stimulated current method and the clarification of the mechanism of LED degradation based on these data.

In the process of this work, light-emitting diodes based on Ga1-xAlxAs, designed for fiber-optic communication lines (FOCL), were studied. Features of such structures are described in [2]. Two types of samples with a structure were studied $n-GaAs-n_1-Ga_{1-x_1}Al_{x_1}As-p_1-$ $-Ga_{1-x_2}Al_{x_2}As-p_2-Ga_{1-x_1}Al_{x_1}As-n_2-Ga_{1-x_1}Al_{x_1}As$ at $x_1 =$ 0,25…0,3; $x_2 = 0,1$. The thickness of the *GaAlAs* layers was respectively 7; 2 ... 3,5; 7 and 5 μm. The structures under study were obtained by the epitaxial growth of layers from solutions — melts with different Al contents and dopant species on n-GaAs substrates, where an ohmic contact from *Au-Ge-Ni-Au* was applied. On $n_2-Ga_{1-x_1}Al_{x_1}As$ was applied continuous ohmic contact inside of which was a window with a diameter of 50 μm. Since the diffusion length for electrons in *GaAlAs* is a few microns and the recombination of electrons can occur in a *p*-layer with a thickness of 2-3 diffusion lengths, so to limit the recombination near the *p-n*-junction to the layer with x_2 are adjacent to the more wide-band layer with x_1. Potential barriers arise at the boundaries with these layers, and recombination is thus carried out in a thin p_1-layer. Since the studied samples are intended for FOCLs, then, to limit the region of current flow and localize radiation through the window in the ohmic contact, diffusion was performed *Zn* in $n_2-Ga_{1-x_1}Al_{x_1}As$ in ones fibers and ion implantation in others. The radiation was transferred in the direction perpendicular to the plane of the *p-n*-junction through the window indicated above.

The samples degraded both at a direct current of 50 mA and 20 mA at various temperatures, and at P-pulses with a density of more than 10^5 A/cm^2, a duration of 100 ns, and a frequency of 300 Hz. Relative changes in the radiation intensity were measured in direct current. To determine the energy spectrum of impurity levels located in the band gap of the semiconductor, thermal-stimulated current (TSC) curves in $Ga_{1-x}Al_xAs$ were emitted. An experimental setup was used to measure thermal-stimulated conductivity at *p-n-* junctions. The experiments were carried out in a vacuum cryostat filled with gaseous helium used as a coolant. The design of the cryostat allowed the heating in a wide range of temperatures (80 ... 400 K) and heating rates (0,05 ... 2 K/s). To record the temperature, a differential thermocouple was used, displayed through a millivoltmeter (thermocouple control unit) to the X coordinate of the two-coordinate recorder. The sample was cooled when the cryostat was immersed in liquid nitrogen. The design of the cryostat allowed quick (3 ... 4 minutes) cooling of the sample from maximum to minimum temperature. The cryostat with the sample was heated by the power source of the stove. In the measurements, the filling of traps by passing a direct current were mainly used. The sample, cooled to the temperature of liquid nitrogen, was connected to a stabilized voltage unit, and the input of the electrometric amplifier was shorted. The milliammeter measured the current flowing through the sample. Direct current was passed through the sample for 10 minutes, which made it possible to fill the charge carriers with the sticking levels in the crystal almost completely. The sample was connected to an electrometer and kept for 5 minutes at a low temperature and U = 0 V, then the cryostat with the sample started heating. The TSP signal was amplified by an electrometer and supplied to the coordinate Y of the recorder. In addition, a signal from a time stamp generator was supplied to the recorder. This made it possible to control the heating rate of the sample and determine it fairly accurately.

The essence of the TSC method in the classical version incorporates in a changing in the conductivity of a substance as a result of the release and recombination of nonequilibrium charge carriers with increasing crystal temperature. If the crystal temperature is sufficiently low, then after the excitation stops, nonequilibrium charge carriers turn out to be “frozen” at the trapping and recombination centers. During heating, the Fermi level goes down and thermal release of charge carriers occurs at those levels that cross the Fermi level, and the filling of the underlying levels remains unchanged. Thus, a phased "thermal highlighting" of local levels occurs. After thermal exhaustion, charge carriers have two ways: 1) recombination at recombination centers located below; 2) re-trapping on the centers. For an analytical description of the TSC curve, it is necessary to find the dependence of the concentration of nonequilibrium charge carriers on the temperature T.

Using the quasi-stationary principle [7], equations were obtained that are used as initial ones at substantiating various methods for calculating the parameters of impurity levels in a TSC. The main parameters of trapping centers include their occurrence depth E_t, trapping cross section S_t, and N_t concentration. The value of E_t in the TSC method is always determined independently of the kinetics of release and recombination of minority carriers.

As was noted above, the method for calculating the energy E_t of the occurrence of trapping centers by analyzing the position of the Fermi quasi-level is based on the assumption that the maximum TSC occurs when the Fermi quasi-level coincides with the level of trapping centers. This method gives the true value of the energy E_t. And regardless of the release kinetics and recombination of nonequilibrium carriers, the initial curved section of the TSC on the section $T < T_m$ (where T_m is the maximum temperature) can be represented as:

$$I = \text{const} \cdot \exp\left(-\frac{E_t}{kT}\right). \quad (1)$$

In coordinates $\ln I(1/T)$, this section of the TSC curve will be a straight line, from the slope of which it is possible to determine the activation energy of the trapping centers. To apply these calculations, it is necessary to “heat clean” the peaks, which allows reducing the processing time of the experimental data. With a high degree of filling of the trapping centers, the expression for the initial section takes the form:

$$I = \text{const} \cdot \exp\left(-\frac{Et}{2kT}\right), \quad (2)$$

but with a decreasing the degree of filling of the centers, (2) goes into (1). Therefore, the experiment should be repeated using a different degree of filling.

Using the TST method in the research of *p-n*-junctions, it must be taken into account that the condition of microscopic inhomogeneity of the sample is violated when it is heated, i.e. areas of space charge appear and its polarization occurs. For the occurrence of thermally stimulated polarization (TSP) currents, the nature of the contacts is crucial. At least one of them must be blocking. Due to the recording form, the TSP current is similar to the classical TSC in the conditions of weak re-trapping.

Thus, the parameters of impurity centers were calculated under the assumption that there was no re-trapping and the width of the depleted layer did not change during the emptying of traps, which was confirmed by the invariance of the capacitance of *p-n*-junctions filling and emptying the traps. It should be noted that in capacitive measurements, the following fact should be taken into account: the presence of deep centers at concentrations comparable to the concentration of the dopant species can lead to the formation of high-resistance layers adjacent to the *p-n*-junction. In this case, the experimentally measured capacitance of *p-n*-junction will not be equal to the barrier capacitance, and the cutoff potential will be the potential difference [8]. For the calculation, the following formula can be used [9]:

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E_t}{kT_m} - \ln\left(\frac{vkN_cS_t}{E_t}\right) \quad (3)$$

where $\beta = dT/dt$ – heating rate; v – the thermal velocity of the electron; N_c – the effective density of state in the conduction band; k – the Boltzmann constant. Expression (3) satisfactorily describes the experimental results for the case when the dependence $I(T)$ has one or more showed TSC maximum, the position of which along the temperature axis is determined by the heating rate of the sample. In this case, the value Et can be determined from the depending $\ln\left(\frac{T_m^2}{\beta}\right)$ on $\frac{1}{T_m}$.

During the research by the TSP method of the light emitting diodes samples based on $Ga_{1-x}Al_xAs$ for FOCL the latter were cooled to a liquid nitrogen temperature of 77 K. After cooling, the sample was biased for 10 minutes. The forward bias current on all samples was 10 mA and served to fill traps. Then, at zero voltage, the sample was kept for another 5 minutes at the temperature of liquid nitrogen and heating of the sample began.

The curves dependence of the current on temperature (TSC) for the samples was measured at different heating rates. In the region of maximum, thermal cleaning was used. Most of the studied samples showed the same maximum. The results of thermal cleaning showed that this peak consists of several adjacent peaks (Fig. 1).

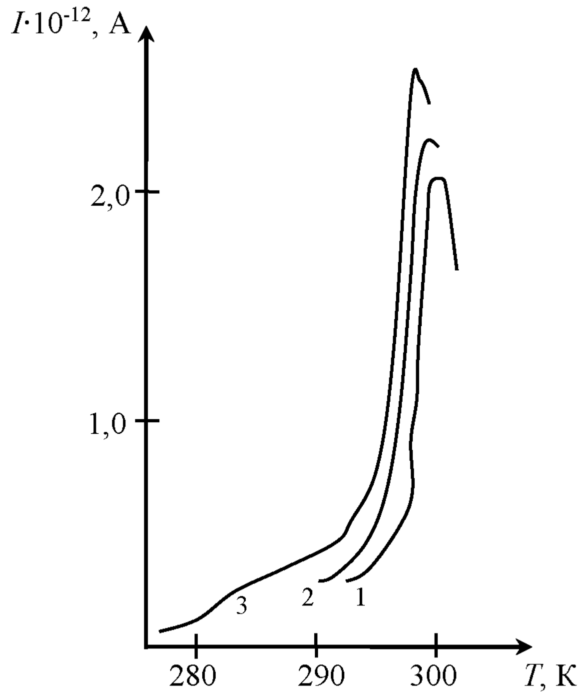

Figure 1 – Illustration of thermal cleaning of the TSC light emitted diode peak based on *GaAlAs* at a heating rate of β = 0,25 K/s

By increasing the heating rate, the peak maximum shifted to the low-temperature region. This, obviously, is explained by the "non-elementary nature" of the impurity level responsible for TSC. Curves 1, 2, and 3 in Fig. 1 were removed sequentially after repeated cooling of the sample. First, curve 1 was taken; immediately after reaching the maximum, the sample with a cryostat was immersed in liquid nitrogen and thus cooled. After that, heating was resumed again at a constant speed and curve 2 was taken. After reaching curve 2, the sample was again cooled with liquid nitrogen and curve 3 was taken. Fig 1 shows that this peak is the sum of several closely spaced TSC peaks. This is obviously explained by the fact that the levels recorded by the TSC are closely spaced from each other, forming a kind of sub-band of levels. At different heating rates, the levels have different effects on the initial portion of the TSC curve. Measurements and calculations have shown that the depth of impurity centers in all samples lies in the range from 0,55 to 0,58 eV.

A current of 50 mA was passed through part of the samples at a temperature of 300 K for 1500 hours. And other samples degraded as at constant current at a temperature of 80 ^{0}C for 1000 hours as by P-pulses of current with a density of more than 105 A/cm^2, duration of 100 ns, and a repetition frequency of 300 Hz.

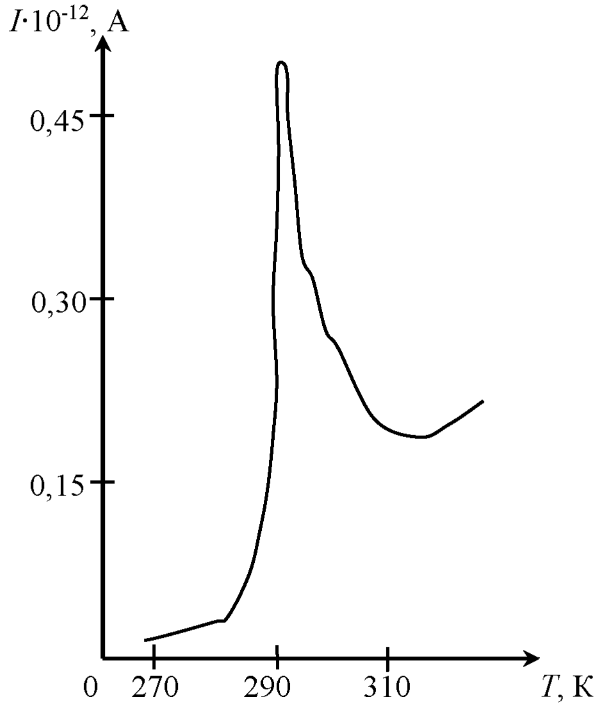

Figure 2 – Curve of the TSC current of a non-degraded LED at a heating rate of β = 0,112 K/s

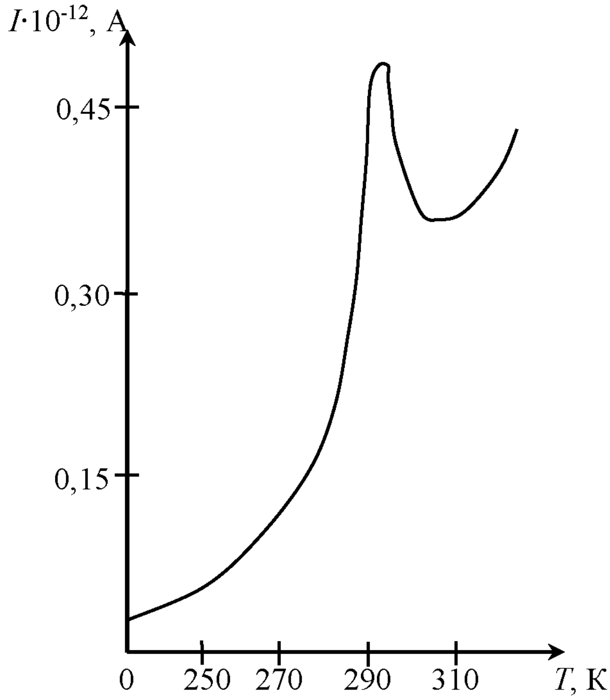

Figure 3 – Curve of the current TST of the LED after degradation at heating rate of β = 0,09 K/s

Comparing the TSC curves of a sample that did not degrade (Fig. 2) with the TSC curves of degraded samples (Fig. 3), it can be seen that the degradation of the TSC curve after the main maximum is much less than that of non-degraded ones. This suggests that the concentration of deep centers has increased, the TSC curves of which lie after the main peak. Evaluation of the TSC curves of the studied samples in the region of the main peak states that the TSC current has not changed, and so the concentration of the deep center responsible for this peak. From the analysis of TSC, it follows that there are a number of impurity centers that are responsible for TSC currents that appear in the temperature range from 200 to 340 K.

The concentration of impurity centers during degradation changed by approximately 15%. In the calculation, the area under the TSC curves of various samples was compared. Calculating the concentration of impurity centers, it was assumed that the width of the high-impedance layer of the samples does not change during the measurement of TSC. Calculation of capacitive characteristics gave a value of W of the order of 0,2 μm. The concentration of impurity centers was 1,2 … $1{,}4 \cdot 10^{16}$ cm^{-3} before degradation and 1,6 … $2 \cdot 10^{16}$ cm^{-3} after degradation.

Thus, a comparison of the TSC curves of the studied samples shows that the main reason for the change in the electrical characteristics of the *p-n*-junction upon passing a direct current is the accumulation of impurity centers. In degraded light emitted diodes based on *GaAlAs*, was detected an increasing in the concentration of impurity centers with ionization energy of 0,58 eV, as well as deeper levels.

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