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Mechanisms and possibilities of defect reorganization in III–V compounds due to the non-thermal microwave radiation treatment

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ABSTRACT

The influence of microwave radiation (2.45 GHz) treatment on processes of reorganization and generation of defects in epitaxial films of GaN and GaAs has been studied. Physical reasons of the observed transformations caused by specific non-thermal action of microwave radiation have been analyzed. Long-term processes of structural transformation after microwave radiation treatment have been modeled. Our approximation is based on the assumption that evolution processes in the defect subsystem, in the crystal are random events, and distribution of the random value – the time before a random event – is a subject to the Weibull-Gnedenko law. Qualitative and quantitative agreements between experimental data and theoretical models of long-term structural changes caused by microwave treatment have been obtained. These results enable to explain non-monotonous behavior of photoluminescence spectra after microwave treatment and could be applied to prediction the consequences of non-thermal action of microwave radiation.

1. Introduction

The results of numerous studies aimed at various semiconductors and structures based on them, testified that microwave radiation significantly influences on the defect-impurity structure over a wide power range [1]. These phenomena are usually associated with thermal interaction of microwave radiation with semiconductor substance. However, this approach cannot explain observed transformations of the semiconductor defect structure in some cases, even with account of irregularities in the heated areas, and changes of the material reflectivity [2]. It was noted [3] that in addition to microwave heating it was necessary to estimate the impact of non-thermal microwave radiation factors, and it was suggested that microwave radiation results in an additional ponderomotive force. This force acts on the charged vacancies directly, thus promoting a sharp increase of their mobility and, consequently, reorganization of the defect structure in the near-surface regions of the crystal. The ponderomotive effect is a most pronounced when powerful sources of microwave radiation are used. However, even at the moderate and low powers of microwave radiation, noticeable changes in the structural parameters of crystals have also been observed. Up to date, the mechanisms of the noted defects reorganization caused by the microwave field are not clear enough.

In this work, possible mechanisms of defect structure transformation at the non-thermal action of electromagnetic fields on the material have been analyzed using gallium nitride and gallium arsenide semiconductor compounds as examples.

2. Experimental

Objects of our study were the structures of epitaxial GaN and GaAs films. The first one doped with Si, thickness ~ 2.2 µm, was obtained using MOCVD- method on sapphire substrate. The charge carrier concentration was close to $8{\cdot}10^{17}\,cm^{-3}$. The second one (n-n^+-GaAs structure) was obtained by PVE method, doped with Te. The thicknesses of the epitaxial n-layer and n^+-substrate were 3 and 300 µm, respectively. The concentrations of free carriers in the epitaxial film and substrate were $\sim 5{\cdot}10^{16}$ and $\sim 1{\cdot}10^{18}\,cm^{-3}$, respectively. We studied photoluminescence (PL) at 77 K within the spectral range 0.6–2.0 eV by using the excitation light $h\nu \geq 2$ eV light for GaAs- based samples. PL spectra of GaN-based samples were measured at 300 K within the 2.0–3.5 eV spectral range with the excitation light energy 3.94 eV.

The PL spectra for both types of the samples were measured for the extended period after microwave treatment (up to 90 days). Microwave treatment of the samples was carried out at the frequency 2.45 GHz and power 7.5 W/cm^2. The duration of exposure was 60 s. The total exposure time was accumulated with 5-s periods of microwave irradiation and 3-min pauses between these periods. The temperature of our samples was measured using a thermocouple.

The specimen receiving no microwave treatment was used as the reference one. Atomic force microscopy (AFM) was applied to study modification of surface characteristics. The increase of analyzed area was accompanied by rise of the peak height distribution. This testifies

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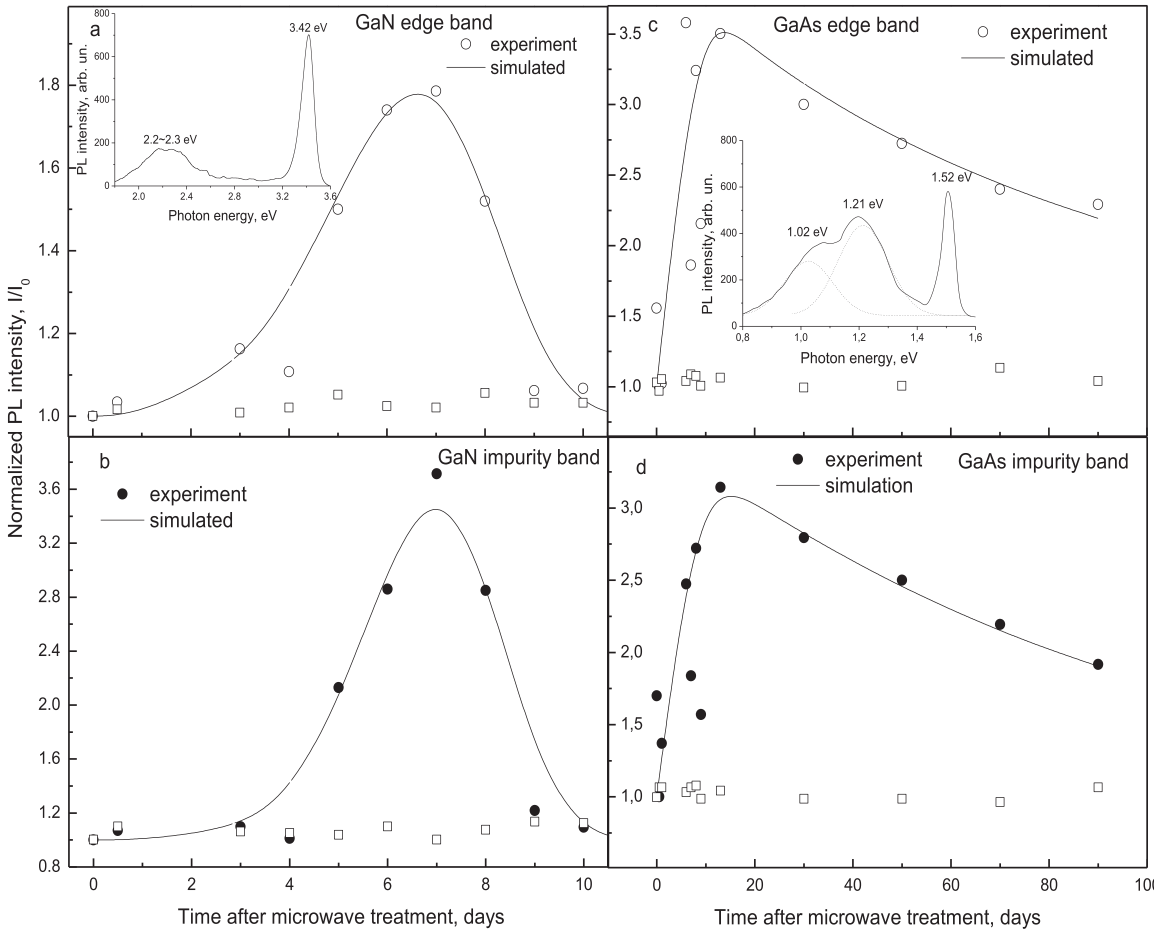

Fig. 1. Variation of the normalized integrated PL intensity of the observed bands as a function of time after microwave treatment (dots – experiment, line – averaging, empty squares for reference sample). Insets: initial spectra of corresponded structures.

about a fractal mechanism of relief formation for the samples under investigation. We used the approach proposed in [4] for fractal dimensionality analyzing by the triangulation method. It allows obtaining reliable information about the actual area of the scan. All measurements were repeated after the treatment to reveal the time-dependent features.

3. Results and discussion

Initial PL spectra of GaN and GaAs samples are shown in the insets of Fig. 1. The GaAs-related curve contained three bands peaking at 1.52, 1.21 and 1.02 eV. The first one is related with near-edge radiative transitions. According to literature data [5], two others are associated with donor-acceptor pairs (DAPs) that formed by impurity-defect complexes of different nature. The PL spectrum of GaN-structure consists of two bands peaking about 3.42 and 2.34 eV. The first peak is attributed to near-edge emission. The second one is assigned to the complex with V_{Ga} cooperation [6,7] and apparently is not trivial. Moreover, according to [7] radiative transitions take place not from donor (D) to V_{Ga} as it is often interpreted, but from a distant donor or from the conduction band to the $V_{Ga}+D$ complex.

Changes in the PL band intensities after the microwave irradiation treatment were non-monotonous for GaAs-based structures as well as for GaN-based ones (Fig. 1). First, the band intensity increases, but later it decreases to the initial values or close to them. The obtained results testify about the change of impurity-defect composition of near-surface layer in GaAs crystals due to the influence of microwave radiation. Moreover, processes of structural reorganization take place over a long period after the microwave radiation processing.

Initial AFM images of structures under investigation are shown in Fig. 2. The results of AFM studies qualitatively confirm the fact of microwave influence on the structure of III–V semiconductor compounds. It is clear that the relation of the quantitative characteristics of the transformation processes in GaN and GaAs surface layers to the regimes of microwave radiation treatment is not straightforward, but the changes of surface characteristics (root-mean-square deviation and arithmetic average deviation) as well as fractal dimensionality variation are observed (see Table 1).

According to these data, one can note a tendency to surface smoothing, long-term period of reorganization in microrelief of samples, and the last but not the least – the main changes in surface characteristics appear after some time period since the microwave radiation treatment. All that confirms the results of PL studies. Actually, smoothing the surface due to microwave radiation treatment was obtained earlier in silicon dioxide/silicon carbide structures [8].

As it was previously shown in study [9], microwave irradiation changes not only the PL spectra but also the magnitude of the internal stresses in the semiconductor structure. The process of internal stresses relaxation after microwave treatment is non-monotonous, and the value and sign of stresses are determined by the initial stress state of the studied samples. These changes are likely caused by transformation in the dislocation structure, which are accompanied by changes in the fields of the elastic deformation in near-surface regions of the crystal. The destruction of micro-defects was also observed.

The observed changes in PL spectra and elastically strained state of the studied structures cannot be due to thermal heating the

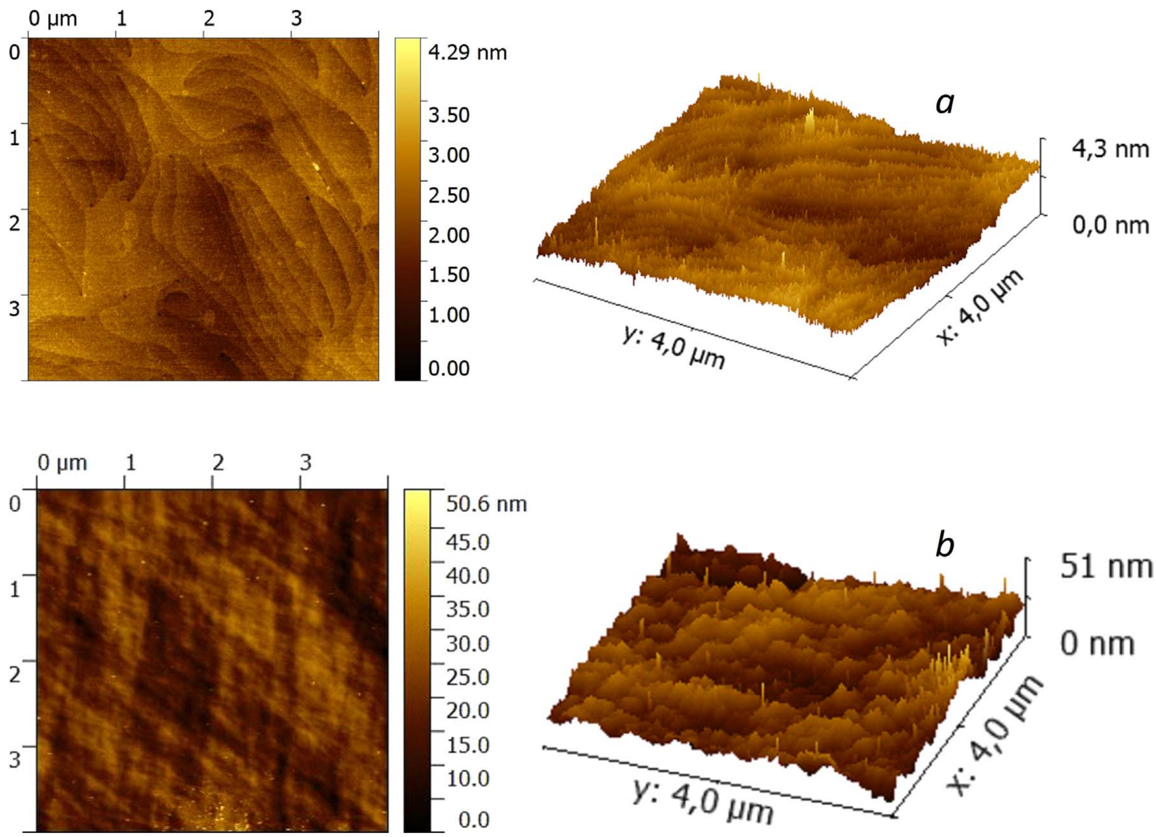

Fig. 2. AFM images of initial GaN (*a*) and GaAs (*b*) samples.

Table 1
Variations of morphology characteristics from the AFM results.

GaN	State of samples	R_{ms} (nm)	R_a (nm)	Fractal dimensionality
	Initial state	0.364	0.289	2.47
	3 days after treatment	0.378	0.302	2.52
	7 days after treatment	0.531	0.488	2.64
	10 days after treatment	0.352	0.285	2.32
n-n^+-GaAs	State of samples	R_{ms}(nm)	R_a(nm)	Fractal dimensionality
	Initial state	5.15	4.12	2.40
	10 days after treatment	6.85	5.22	2.82
	20 days after treatment	6.81	5.24	2.84
	60 days after treatment	5.13	4.01	2.30

semiconductor material in the used regime of microwave radiation treatment, because the temperature of samples did not differ significantly from the ambient one (~ 2 °C). For structural modification of semiconductors due to their instant heating, which results in the nonstationary elastic stresses in the crystal and changes of defects charge state, the microwave power should be at least one order of magnitude higher than that used in our experiments [10].

Thus, it is necessary to admit the existence of non-thermal microwave radiation action leading to changes in the structural parameters of the semiconductor. One of these possible mechanisms has been proposed in our paper [11]. It was shown that under resonance conditions (the coincidence of eigenfrequencies of the dislocation segment vibrations and electrical component of the microwave radiation), multiple dislocation loops occur. A released loop by the source creates mechanical tensions at the location of the source. These tensions block further generation of dislocation loops, when their certain "critical" value is reached. The considered mechanism of dislocation multiplication influences both internal stresses of the crystal and curvature of the lattice. Their changes relax with time due to increasing the size of dislocation loops and/or their ordering.

Along with the multiplication of dislocations caused by microwave radiation treatment, their movement can take place, when an energetic barrier is absent. Let us consider some possible mechanisms of dislocations detachment from the barriers (stoppers).

It was shown in [11] that dislocations anchored at the ends have their own (basic) frequency of vibrations ω_1 equal to

$$\omega_1{}^2 = \pi^2 \frac{G}{L^2 \rho_v}, \tag{1}$$

where G is the shear modulus, ρ_v – bulk density of material, L – dislocation length.

When the dislocation is electrically charged and fixed by two stoppers at the ends, the frequency of electromagnetic radiation ω_{em} is equal to the frequency of intrinsic oscillations of dislocation ω_1, then under the influence of the electric component of an electromagnetic wave, the phenomenon of resonance is observed. At the resonant frequency, the amplitude and energy of oscillations sharply increase at low damping. Since the energy of oscillations exceeds the binding energy of the dislocation with stoppers, the dislocation detaches and becomes able to move. However, this effect is characterized by strong selectivity of lengths of detached dislocations to the frequency of microwave radiation. For example, at $\omega_{em} = 1.54 \cdot 10^{10}$ Hz for GaAs $\rho_v = 5.317 \cdot 10^3$ kg/m^3 [12], $G = 32.85$ GPa [13], for GaN $\rho_v = 6.15 \cdot 10^3$ kg/m^3 [14], $G = 67$ GPa [15] in accordance with (1) only the dislocations with $L_{GaAs} = 5.07 \cdot 10^{-7}$ m and $L_{GaN} = 6.73 \cdot 10^{-7}$ m are detached.

The initial quasi-equilibrium state of the crystal changes in the elastic field of moving dislocation. The concentrations of point defects and impurities, level and sign of internal tensions change too. New state of the material is non-equilibrium, and crystal relaxes to the initial one or close to it for some time interval.

Internal tensions and the existence of clusters of point defects make significant influence on the structure of PL spectrum. The first factor is caused by relaxation of elastic deformations due to microwave treatment. These deformations influence on appearance of directed fluxes of point defects and impurities. This mechanism of PL spectra changes was analyzed in [16].

The second one is related to the change in PL spectra caused by to destruction of clusters and appearance of a small number of atomic-complexes and DAPs. Let's consider the mechanism of PL spectra changes by using the example of destruction of the clusters formed by tellurium and copper impurities.

Let the concentrations of Te^+ and Cu^- in the above clusters are the same and equal to N. Then, this cluster in the surface region of the semiconductor, where there is impoverishing band bending, resembles an ionic crystal. The equation of the motion of ions is given by the harmonic oscillator with the ion-plasma frequency [17]

$$\omega_p = \sqrt{\frac{e^2N}{\varepsilon_0\varepsilon\mu}} \tag{2}$$

If the frequency of the electromagnetic wave coincides with the plasma frequency of impurity ions, one can observe a resonance phenomenon accompanied by a significant increase in the amplitude of oscillations of ions and further destruction of impurity complexes.

Let us calculate ω_p for the epitaxial structures under investigation with the concentration of a doped impurity $N_{Te} = 5{\cdot}10^{16}\ cm^{-3}$ (for the GaAs-based structure). Taking into account that $\mu = 0.7043{\cdot}10^{-25}$ kg (reduced mass of Te and Cu ions), we obtain $\omega_p = 12.6$ GHz ($\nu_p = 2.01$ GHz). The obtained value of the ion-plasma frequency is sufficiently close, but, nevertheless, differs from the radiation frequency of microwave generator $\nu_{em} = 2.45$ GHz. Calculations for the GaN-based structure give a similar result.

Analogous approaches could be used to analyze destruction of intermediate complexes of another kind (impurity-vacancy, metal, *etc.*), which form quasi-crystalline inclusions in the semiconductor lattice.

The non-monotonic change of PL intensities of impurity bands inherent to the semiconductor material is a specific feature caused by the microwave radiation treatment. It is related with a non-trivial character of relaxation in the excited subsystem of structural defects. To explain this feature, one can use the results of [18], assuming that the intensities of the oscillations are caused by random events (e.g., appearance of local regions enriched (depleted) by point and extended defects). The corresponding random values – times to events – obey the distribution by Weibull–Gnedenko [18].

For this approach, we need to introduce the following random events: random event of movement of a defect (dislocations, gallium vacancies) from the subsurface area to the surface (boundary) and random event of defect motion to the subsurface area from the epitaxial layer (source) adjacent to this subsurface area and commensurate with the sizes of the latter. We assume that the subsurface area is the layer, in which the electron-hole pairs are generated, when the crystal is exposed to light of PL excitation. Then, the random variable is the time to a random event. Accordingly, $F_1(t)$ is the distribution function of time before movement of a defect from the subsurface area to the boundary (the probability of motion from the subsurface area to the boundary); $F_2(t)$ is the distribution function of times before movement of a defect into the subsurface area from the source (the probability of movement into the subsurface area from the source).

If we consider a random event – the absence of a defect in the subsurface area, - then we should take to account two possible cases. The first one is as follows. This event is complex and consists of a random event – movement of a defect from the subsurface area to the boundary – and of the random one – the lack of movement of a defect into the subsurface area from the source. Assuming these events to be independent, the probability of the given complex event is equal to the product of probabilities for the constituent events.

In accord with [18,19], we use the Weibull-Gnedenko distribution for $F_1(t)$ and $F_2(t)$ functions. Thus, the dependence of the normalized PL intensity via the time after treatment could be expressed as follows:

$$I(t) = I_{in} + I_0\left\{\left[1 - e^{-\left(\frac{t}{\tau_1}\right)^{m1}}\right]e^{-\left(\frac{t}{\tau_2}\right)^{m2}}\right\}, \tag{3}$$

where τ_1, τ_2 are the time constants of random events; m_1, m_2 – form factors of the distribution function of time to a corresponding random event, I_{in} is the initial value of the intensity of the photoluminescence band, I_0 –proportionality factor. This function has an extreme (maximum) and could be used for simulation of experimental data.

The second case of the considered random event is realized when random event of the movement of a defect from the subsurface area to the boundary and random event of the movement of a defect into the subsurface area from the distant areas of the epitaxial layer (remote source) take place. By analogy with the above stated, we shall obtain a function that has several maxima. For our experimental results, the first approach is more appropriable. Thus, the probabilistic approach predicts the presence of at least one maximum in the long-term changes in the intensity of PL bands, which is observed in our studies.

Fig. 1 presents the results of the least squares approximation with the expression (3) of change in the intensity of integrated PL for the edge and impurity bands of epitaxial GaN (Fig. 1a, b) and GaAs (Fig. 1c, d) structures with the parameters summarized in Table 2.

One can note a good agreement between the experimental and theoretical results. Moreover, some of parameters these approximations are very similar for both the impurity and edge PL bands (τ_1, τ_2 and m_2) for GaN and GaAs, respectively. The other ones (I_0, m_1) are different. It could be caused by two possible factors. The first one is the same for impurity and near-edge bands. So, these parameters could be responsible for the changing of non-radiative recombination channel. Since variations in non-radiative recombination will modify intensity values of observed bands in the same way. The second factor, apparently, is related to the radiative recombination changes. So, it will always different for different spectral bands. Detailed properties of fitted parameters, its dependence on the impurity-defect composition and initial state of structure under investigation will be analyzed in another work.

One can estimate the parameters that characterize transformation of the defect structure. If the movement of defects has a diffusion character, in accordance with [18] $\tau_1 = d^2/D$, where D is the effective diffusion coefficient, and d – thickness of the layer in which the electron-hole pairs are generated under PL excitation. In our experiments, d is of the order of 10^{-4} cm. The obtained results are summarized in Table 2. The resulting values agree well with similar estimations for structural defects [20,21].

Table 2
Fitted parameters for expression (3).

Fitted parameter	GaN/Al_2O_3		n-n^+-GaAs	
	Edge emission	Impurity emission	Edge emission	Impurity emission
I_{in}	1	1	1	1
I_0	1.92	6.22	3.1	2.46
τ_1 (days)	7.03	6.99	5.62	5.8
τ_2 (days)	8.02	8.05	95.01	90.08
m_1	3.15	5.02	1.74	1.51
m_2	6.94	7.08	0.87	1.10
Calculated $D{\cdot}10^{-14}$, cm^2/s	1.65	1.66	2.06	1.99

4. Conclusions

PL experiments performed in this work suggest that the complete model of the evolution of the microstructure in semiconductors due to the microwave treatment should include not only the temperature factor but also contribution of non-thermal effects. Analysis of the PL data, indicates changes in impurity-defect composition of the near-surface layer due to the microwave field with further migration, restructurization and generation of defects of different origin. Reorganization of semiconductor defect structures due to microwave radiation action was confirmed by AFM studies. This method enabled to reveal the long-term modification of morphology parameters of materials under investigation. Thus, two mechanisms associated with the resonant microwave irradiation were proposed: the destruction of clusters of point defects and detachment of dislocations from the barriers (stoppers) that influence the mobility of dislocations. These mechanisms are not related to the microwave heating in contradiction to [22–24]. To provide these non-thermal mechanisms, no additional factors and conditions are required (as well as spin-selective nanoscale reactor [25], ponderomotive force [3,26], present of sufficient internal mechanical stresses [27]). So to explain non-thermal interaction between III-V compounds and microwave radiation treatment, they are more appropriable than the other ones proposed for ionic, dielectric and semiconductor materials. And the last but not the least proposed in this paper mechanisms could be applied to predict consequences of non-thermal action of microwave radiation on semiconductor material as well as for non-destructive estimation of defect diffusion factors of already formed devices based on epitaxial structures.

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