

Non-equilibrium processes of defect transformations in semiconductors stimulated by non-thermal action of microwave electromagnetic radiation and magnetic fields

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Abstract. Non-thermal action of magnetic and microwave electromagnetic fields on semiconductor crystals is shown to cause transition of defect ensembles from a thermodynamically equilibrium state to a non-equilibrium one. After the external fields cease to act, a process of thermally activated displacement, namely relaxation of the defect ensemble to the thermodynamically equilibrium state, which is characterized by a relaxation time, is observed. A criterion of the loss of stability of the equilibrium state by defects is formulated allowing one to determine the threshold values of external field parameters that cause formation of a non-equilibrium state of a defect system in a semiconductor structure. Electroresonance mechanisms of creating the non-equilibrium state of linear and point defect ensembles in semiconductors are presented. It is proven that the relaxation of a defect system over time is described by the Weibull–Gnedenko distribution function, the scale parameter of which represents the relaxation time of the defect ensemble from the non-equilibrium state to the equilibrium one. The results of the experimental studies of the relaxation processes of integrated photoluminescence in *n*-GaAs and *n*-GaN structures stimulated by non-thermal treatments with microwave radiation are shown to agree with the theoretical concepts.

Keywords: semiconductor, defect, equilibrium state, non-equilibrium state, microwave radiation, magnetic field, resonance phenomena, random event, Weibull–Gnedenko distribution, relaxation, relaxation time, photoluminescence.

<https://doi.org/10.15407/spqeo29.03.323>

PACS 05.40.-a, 41.20.-q, 71.55.Eq

Manuscript received 18.06.26; revised version received 28.08.26; accepted for publication 16.09.26; published online 25.09.26.

1. Introduction

Study of nonthermal effects of both weak magnetic and microwave electromagnetic fields on evolution of defect ensembles in semiconductor crystals is a problem of both fundamental [1–6] and practical [6–8] interest. From a scientific perspective, attention to these phenomena is motivated by their non-triviality. Indeed, the interaction energies of the defects in semiconductor structures with such fields are negligibly small, much smaller than the energy barriers they must overcome during transformation. This fact motivates analysis of the underlying mechanisms of how such small effects lead to significant physical responses. From the practical point of view, a promising direction is controlling the structural perfection

of epitaxial semiconductor films by nonthermal action of external fields.

The transformation effects of point and extended defects in semiconductors stimulated by nonthermal action of microwave electromagnetic radiation and magnetic fields were experimentally confirmed in a large number of publications [9–21]. A distinctive feature of the most experiments was that the response of the physical system was studied directly under the action of an external field. In particular, the paths of dislocations in semiconductor and dielectric crystals under the action of magnetic fields were analyzed [10, 22–24]. These paths were interpreted based on the concepts of spin reactions, *i.e.*, singlet-triplet transitions in the defect-stopper radical pair, leading to detachment of dislocations [11, 25].

The question of how a defect ensemble behaves after external influences cease remains beyond the scope of research. It is reasonable to assume that exposure to magnetic and electromagnetic fields creates a new state of defects, which is generally unstable. Therefore, over time, after the external influences cease, physical processes of subsequent transformation of defects into a stable state should occur. This article is devoted to developing new concepts regarding dynamics of defect ensembles in semiconductor crystals activated by non-thermal action of microwave radiation and magnetic fields.

2. Equilibrium and non-equilibrium states of defects in semiconductor crystals

The possible energy states of any point and linear defect from the entire ensemble of defects in a semiconductor depending on the coordinate x can be described by potential functions $V(x)$ shown in Fig. 1a.

From a physical perspective, the function $V(x)$ describes the energy relief of a double symmetric potential well with a barrier E_a . The minima 1 and 2 correspond to the equilibrium states of the defects. When the equilibrium states 1 and 2 in the potential field $V(x)$ deviate from each other a force arises, which stimulates return of a defect to the equilibrium state.

Evolution of a defect ensemble in semiconductor structures can be described by the Fokker–Planck–Kolmogorov equation, the stationary solution of which gives the following relation for the probability density $\rho(x)$ of finding defects in the state x [26]:

$$\rho(x) = A \exp \left[-\frac{V(x)}{kT} \right], \quad (1)$$

where k is the Boltzmann's constant and T is the absolute temperature, respectively.

Expression (1) provides the relationship between the distribution of the coordinates of defect positions and the potential energy. Maxima in the probability density correspond to equilibrium positions (Fig. 1b).

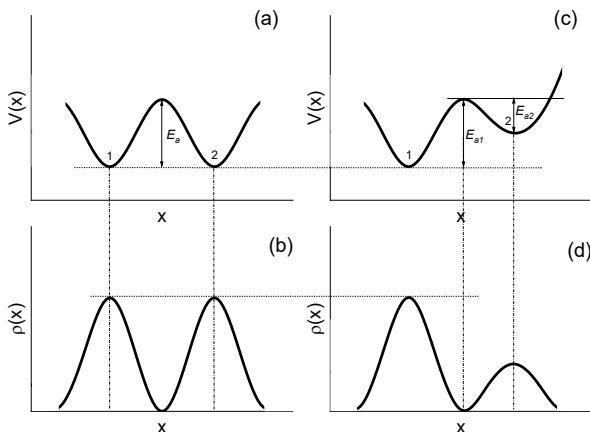


Fig. 1. Energy relief (a, c) and probability density (b, d) of the state of defects.

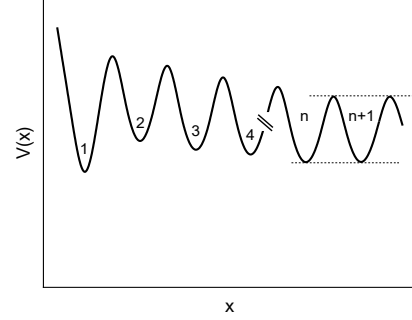


Fig. 2. Configuration of the potential field $V(x)$ of the defect state.

It follows from the expression (1) that any defect in a field with the potential energy $V(x)$ is subject to action of a force $F(x)$:

$$F(x) = -\frac{dV(x)}{dx}. \quad (2)$$

This force stimulates relaxation of the defect ensemble upon deviation from equilibrium.

The situation under consideration is related to the theory of activation energy: due to thermal fluctuations, defects overcome energy barriers E_a (E_a is the activation energy), jumping with equal probabilities from the state 1 to the state 2 and back. The probability densities of the defects in these states are equal. For the entire set of defects, these states are equivalent. These states, characterized by equal energy values, are in thermodynamic equilibrium from a statistical standpoint.

This scenario takes place if the sequence of possible energy states of the defect ensemble is characterized by translational symmetry. However, in practically observed situations, defects in the initial state are attached or bound, for example, attached dislocations or associates of impurity ions, which are stable complexes with possible clustering [27–29]. The energy relief of their states is an asymmetric double potential well with the barriers E_{a1} and E_{a2} (Fig. 1c). The states of the defects in the minima 1 and 2 are energetically unequal: the state 1 corresponds to the attached (bound) state of the defects, and the state 2 to the detached (dissociated) state of the defects.

The state 1 is energetically favorable and the probability density of finding a defect in this state is higher. Fig. 1d shows the probability density of the defect positions. Therefore, the state 1 of the defect is the ground state, *i.e.*, thermodynamically equilibrium (or simply equilibrium) state with a minimum energy value. The state 2 may be considered a thermodynamically non-equilibrium energy state (or simply a non-equilibrium state), since it is unstable and the defect tends to return to the ground state under the influence of thermal fluctuations. With some reservations, it may be called a state of local equilibrium or a metastable state of defects.

In the most general case, the configuration of the potential field $V(x)$ during movement of both neutral and charged point and extended defects in the crystal structure of a semiconductor is a sequence of double

symmetric potential wells, which are deformed by internal mechanical stress fields acting on them or by electric fields [26]. Action of the fields leads to an asymmetry of the energy barriers with respect to defect transitions under the influence of thermal fluctuations between any two nearest local minima of the potential energy. A possible energy profile is shown in Fig. 2.

From an energy standpoint, action of external magnetic and microwave electromagnetic fields can stimulate transition of defects from the thermodynamic equilibrium state 1 (Fig. 2) to the non-equilibrium state 2. Subsequently, after cessation of the action of external fields, the defects will move between the minima of the potential wells 3, 4, ..., n reaching thermodynamic equilibrium state in the $n + 1$ -th minimum. It can be said therefore that evolution process of the defect ensemble from the non-equilibrium state 2 to the equilibrium state n takes place.

It should be noted that the flow of point defects is also caused by a thermodynamic force, the magnitude of which is proportional to the particle concentration gradient. In this case, thermodynamic equilibrium of defects is achieved when the particle concentration gradient becomes zero. The process of transition of an ensemble of defects from a thermodynamically non-equilibrium state to a thermodynamically equilibrium one is called relaxation. The time interval characterizing this transition is called the relaxation time.

Since relaxation, which is the process of transition to thermodynamic equilibrium in the state of a defect ensemble after turning off magnetic fields and microwave radiation, occurs over time, it will manifest itself in temporal changes in the parameters of semiconductor structures sensitive to this process. Let us analyze the energetic characteristics of forming non-equilibrium state of defects in semiconductor structures under influence of magnetic and microwave electromagnetic fields.

3. Energy criterion for formation of a non-equilibrium state of defects in semiconductor structures under influence of magnetic and microwave electromagnetic fields

Transition from a thermodynamically equilibrium state to a non-equilibrium state may be interpreted as a loss of stability of the equilibrium state of defects. Such a transition as a result of an action of external fields – magnetic or electromagnetic – leads to formation of a non-equilibrium state of an ensemble of defects. In [30, 31], an energy criterion for stability of defects in semiconductor crystals under the action of external fields was formulated. According to it, a defect loses stability of its equilibrium state when the field energy localized in the defect volume V is equivalent to such kT that during the time t of the field action, at least one defect particle experiences an energy fluctuation of the value E_a . This criterion yields the following relationships for the threshold values of the parameters of electromagnetic as well as homogeneous and constant magnetic fields causing formation of a non-equilibrium state of defects in semiconductor structures [30, 31]:

$$\bar{w}_{th} = \frac{E_a}{V \ln \left(\frac{VNt}{\tau_0} \right)}, \quad (3)$$

$$B_{th} = \left[\frac{2\mu\mu_0 E_a}{V \ln \left(\frac{VNt}{\tau_0} \right)} \right]^{\frac{1}{2}}, \quad (4)$$

where $\bar{w}_{th}$ is the threshold value of the average volume density of the field energy for a plane ultra-high-frequency electromagnetic wave, B_{th} is the threshold value of the magnetic field induction, N is the concentration of atoms in the crystal, τ_0 is the factor that is of the same order of magnitude as the period of thermal oscillations of a particle in the semiconductor lattice, μ is the magnetic permeability of the semiconductor, μ_0 is the magnetic constant, ϵ is the permittivity of the crystal, and ϵ_0 is the electric constant, respectively. In particular, calculation by the expression (4) of the threshold value B_{th} for edge dislocations in GaAs crystals with a length of 1 μm and a core radius equal to two lattice constants under an action of a magnetic field with a duration $t = 60$ s yields $B_{th} = 4.7 \cdot 10^{-2}$ T.

Let us now analyze specific mechanisms for the loss of stability of an equilibrium state by defects.

4. Mechanisms of formation of non-equilibrium defects in semiconductor structures under influence of magnetic and electromagnetic fields

4.1. Electroresonance mechanism under influence of microwave radiation [27–29, 31]

Edge dislocations carrying an electric charge and attached at their ends have own angular frequency of oscillation ω_D equal to

$$\omega_D = \frac{\pi}{L} \left(\frac{G}{\rho_V} \right)^{\frac{1}{2}}, \quad (5)$$

where G is the Poisson modulus, ρ_V is the bulk density of the material, and L is the dislocation length, respectively.

When the electromagnetic radiation frequency (the magnetron carrier frequency) coincides with ω_D , resonance phenomena are observed accompanied by a sharp increase in the amplitude of dislocation oscillations, leading to its detachment, *i.e.*, its transition from an equilibrium attached state to a non-equilibrium one. Subsequently, movement of the dislocation into the equilibrium state under the influence of a mosaic of internal mechanical stresses in the semiconductor crystal takes place. It should be emphasized that the detachment of dislocations from their stoppers is stimulated by thermal fluctuations, while their movement itself is a thermally activated process of overcoming the Peierls barriers by formation and expansion of double kinks.

These resonance phenomena are selective with respect to the length of the dislocations being detached.

However, the presence of a broad spectrum of excited electromagnetic oscillations in the resonators eliminates this selectivity and leads to resonance phenomena in an ensemble of defects with different resonant frequencies. As a result, resonant detaching becomes possible, that is, formation of a non-equilibrium state of dislocations with a wide range of lengths. In particular, for n -GaAs, the range of the dislocation lengths L obeys the inequality $L \leq 4.05 \cdot 10^{-6}$ m.

Point defects in semiconductor structures can form associates (complexes). In particular, impurity complexes can form in n -GaAs crystals doped with tellurium and containing copper impurities. In turn, these complexes can form stable clusters. These clusters are characterized by their own (ion-plasma) angular oscillation frequency ω_P equal to

$$\omega_P = \left(\frac{e^2 N_i}{\epsilon \epsilon_0 \mu_i} \right)^{\frac{1}{2}}, \quad (6)$$

where e is the electron charge, N_i is the concentration of copper (tellurium) ions in the cluster, and μ_i is the reduced mass of the ion pair, respectively.

Coincidence of the microwave radiation frequency with the frequency ω_P leads to a strong increase in the amplitude of ion oscillations and subsequent decay of the clusters of charged point defects. As a result of the decay, ions being initially in a bound (integrated) state, *i.e.*, thermodynamically equilibrium state, transfer to a disintegrated – thermodynamically non-equilibrium state. As a consequence, thermally activated displacement of the ions formed under the action of mechanical stress fields and thermodynamic force – the concentration gradient – to the equilibrium state becomes possible.

In particular, for tellurium-doped n -GaAs structures, calculations yield the following oscillation frequency: $\nu_P = 2.01$ GHz, which is close to the microwave frequency of 2.45 GHz used in the experiments. As noted above, presence of a wide spectrum of excited electromagnetic oscillations in the resonators smooths out these frequency differences, leading to resonance phenomena in clusters, their destruction, and formation of a non-equilibrium state of charged point defects.

4.2. Electroresonance mechanism under action of pulsed magnetic fields [29, 31–33]

Under an influence of a magnetic field, mobile charge carriers in a semiconductor emit electromagnetic waves at the cyclotron frequency. Specifically, the (maximum) cyclotron frequency of electrons in n -GaAs subjected to influence of a pulsed magnetic field with an amplitude induction of 60 mT is 27 GHz. The pulsed magnetic field was generated by rotating the semiconductor structure through a magnet gap. As a result, the semiconductor sample also moved through regions of edge magnetic fields with an induction by orders of magnitude lower than the amplitude value. Accordingly, a spectrum of cyclotron frequencies took place. Furthermore, since charge carriers undergo scattering, broadening of the cyclotron emission line in both directions relative to the cyclotron frequency

was observed. Consequently, electromagnetic oscillations of a wide range of frequencies were generated in the semiconductor crystal, including frequencies equal to that of resonant oscillations of dislocations and clusters.

Hence, the mechanisms of formation of a non-equilibrium state of defects in semiconductor structures under influence of magnetic fields are the same as those under influence of microwave radiation.

5. Time-dependent regularities of relaxation of the non-equilibrium state of defects after exposure to magnetic fields and microwave radiation

As noted above, transition of a defect ensemble from a non-equilibrium state to an equilibrium one is generally determined by defect movement along a chain of asymmetric potential wells. From a statistical standpoint, a physical event – movement of a defect between adjacent minima of asymmetric double potential wells in a semiconductor crystal – is random. As noted above, this is due to the thermally activated (probabilistic) nature of such movement, namely, it is determined by a random event such as a fluctuation in the particle energy [34]. Consequently, relaxation of the defect ensemble from the non-equilibrium state to the equilibrium one is caused by a stream of the random events (or simply events) – defect movements.

We will perform probabilistic analysis of these random events, which will allow us to define the distribution law of a random variable – the time until a random event. The distribution function of this random variable will characterize time-dependent regularities of the transition of a defect ensemble from a non-equilibrium state to an equilibrium one activated by external fields.

Let the probability of the absence of an event at time t be $P(t)$ for the set of all possible events. Then the probability of the absence of an event before the time $t + dt$ can be represented as $P(t + dt)$. The probability $P(t + dt)$ is the probability of a composite event consisting of two independent events, namely, the absence of defect movement during the time t and over the interval dt . The independence means that the desired probability is equal to the product of the probabilities of the component events:

$$P(t + dt) = P(t)P(dt). \quad (7)$$

Let $\lambda(t)dt$ be the probability of an event during an interval dt . Then the probability of the opposite event is equal to $1 - \lambda(t)dt$ and (7) is transformed into

$$P(t + dt) = P(t)[1 - \lambda(t)dt]. \quad (8)$$

Let us explain the meaning of the quantity $\lambda(t)$. Since $F(t) = 1 - P(t)$ is the probability of an event before the time t and $F(t + dt) = 1 - P(t + dt)$ is the probability of an event before the time $t + dt$, it follows from (8):

$$\lambda(t) = \frac{F(t + dt) - F(t)}{[1 - F(t)] dt}. \quad (9)$$

In turn, $F(t) = n(t)/n_0$ by definition, and $F(t+dt) - F(t) = dn(t)/n_0$, where n_0 is the total number of events, $n(t)$ is the number of events up to the time t , and $dn(t)$ is the number of events during the interval dt , respectively. Taking these remarks into account and also replacing differentials with increments, we have

$$\lambda(t) = \frac{\Delta n(t)}{[n_0 - n(t)] \Delta t}. \quad (10)$$

The expression (10) is the classical definition of a quantity that is called the event intensity [34]. Hence, the quantity $\lambda(t)$ appearing in (8) is the event intensity (the intensity of defect displacements).

Transforming (8) based on the mathematical definition of derivative, we obtain the following expression for $P(t)$:

$$\frac{dP(t)}{dt} = -\lambda(t)P(t). \quad (11)$$

Let us first consider the case of time independent event intensity. We have

$$\frac{dP(t)}{dt} = -\frac{P(t)}{\tau}, \quad (12)$$

where $\tau = 1/\lambda$.

We make the following important remark. If we ignore the performed probabilistic analysis and formally mean $P(t)$ to be some parameter characterizing the semiconductor material, then this relationship is a classical relaxation equation, and expression (11) may be considered a generalized relaxation equation. As will become clear from the discussion below, this assumption is valid.

Integrating (12) leads to an exponential distribution of the probability of the absence of an event during the time t :

$$P(t) = \exp\left[-\left(\frac{t}{\tau}\right)\right]. \quad (13)$$

Accordingly, for the distribution function $F(t)$ of the random variable – the time to an event – we obtain

$$F(t) = 1 - \exp\left[-\left(\frac{t}{\tau}\right)\right]. \quad (14)$$

In this distribution, τ is the mathematical expectation, *i.e.* it represents the average time until the event. Since all the events are thermally activated, τ is numerically equal to the average time $\bar{t}_f$ until fluctuation of the particle energy with the value E_a [31, 34]:

$$\bar{t}_f = \tau_0 \exp\left(\frac{E_a}{kT}\right). \quad (15)$$

Here, τ_0 is the pre-exponential factor, which, as noted above, is of the same order of magnitude as the period of thermal oscillations of a particle in the semiconductor lattice ($2\pi\hbar/kT$, where $\hbar$ is the Planck's constant).

We take into account that the exponential function $F(t)$ characterizes the probabilistic process of occurrence of random events. At $t = \tau$, this function will reach $\approx 63\%$ of its steady-state value ($\approx 63\%$ of random events from

the entire set of events occurred). This means that, by formal criteria, τ is the time constant of this process or, in other words, the time constant of a random event.

On the other hand, since the exponential functions (13) and (14) define the time regularities of the probabilistic process of transition of the defect ensemble from a non-equilibrium state (when $F(t=0) = 0$ and $P(t=0) = 1$) to an equilibrium state, for which $F(t \rightarrow \infty) = 1$ and $P(t \rightarrow \infty) = 0$, τ formally represents the relaxation time of this process.

Let us now consider the case, when the event intensity is a power function of time, which is characterized by an exponent m [34]:

$$\lambda(t) = \frac{m}{\tau^m} t^{m-1}. \quad (16)$$

Integration of (11) leads to the Weibull–Gnedenko distribution of a random variable. The probability of the absence of an event during the time t is [31, 34]

$$P(t) = \exp\left[-\left(\frac{t}{\tau}\right)^m\right]. \quad (17)$$

For the distribution function of the random variable – the time before the event – we have [31, 34]:

$$F(t) = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^m\right], \quad (18)$$

where the exponent m is called the shape parameter (form factor) of the distribution, and τ is called the scale parameter.

Since $F(t = \tau) \approx 0.63$ and $P(t = \tau) \approx 0.37$ for the Weibull–Gnedenko distribution, the time constant τ of a random event is also understood as the relaxation time of the process of transition of a defect ensemble from a non-equilibrium state to an equilibrium one.

A distinctive feature of the Weibull–Gnedenko distribution is that it is an extremal distribution of minimum values, in other words, a limiting distribution of the minimum value [31, 34]. Therefore, during relaxation of an ensemble of defects in a semiconductor crystal from a non-equilibrium state to an equilibrium one, the trajectory of the change in the probability of the events over a fixed time interval is described by the distribution function of a random variable, which is the minimum of a large number of independently acting variables. As can be seen, there is an analogy with the least-action principle, which obeys the trajectory of a physical system moving between two states over a fixed time.

Therefore, the distribution function of a random variable determines time regularities of the transition of a defect ensemble from a non-equilibrium state to an equilibrium one stimulated by magnetic and ultra-high-frequency electromagnetic fields. The dynamics of change of any parameter $\alpha(t)$ of the semiconductor structure, sensitive to the relaxation process of the defect ensemble, after cessation of the external fields, is described by the functions (17) and (18) up to constants [31, 34]. Consequently, we obtain:

$$\alpha(t) = \alpha_0 \exp \left[-\left(\frac{t}{\tau} \right)^m \right], \quad (19)$$

$$\alpha(t) = \alpha_0 \left\{ 1 - \exp \left[-\left(\frac{t}{\tau} \right)^m \right] \right\}, \quad (20)$$

where α_0 is the proportionality coefficient. We especially emphasize that, when applied to (19) and (20), by τ we mean the relaxation time of the parameter $\alpha(t)$. Returning to the above-mentioned analogy of (11) and (12) with the relaxation equations, the following can be stated. If, from the very beginning, we multiply the left- and right-hand sides of (11) and (12) by the proportionality coefficient α_0 , we will operate with the relaxation equations of the parameter $\alpha(t)$ and obtain the relations (19) and (20).

Let us make one more important remark. Based on the analysis of random events in physical-and-chemical processes carried out in [31, 34], one obtains that relaxation laws of the form (12) and (19), (20) with $m = 1$ hold when the activation energy is a deterministic value for the entire set of thermally activated (random) events – defect displacements. In turn, the relaxation laws of the form (11) and (19), (20) with $m \neq 1$ hold when the activation energy is a random value for the entire set of the events.

The relations (19) and (20) are valid when the transition of a set of defects from the non-equilibrium state to the equilibrium one is caused by a flow of elementary random events that cannot be broken down into components. In practice, defect ensembles in semiconductor structures have heterogeneous compositions. They contain subsystems formed by various types of point and linear defects. The random event – displacement of a defect – is complex and consists of a combination, *i.e.* a product of elementary independent events – the displacements of defects of each type. In turn, the probability of such a complex event is equal to the product of the probabilities of the constituent events with generally different time constants. Consequently, transition to the equilibrium state of such a defect ensemble is characterized by several relaxation times. For example, for a particular case of two types of defects, relaxation of the parameter $\alpha(t)$ of a semiconductor structure can be described by three possible combinations of functions (17) and (18):

$$\alpha(t) = \alpha_0 \left\{ 1 - \exp \left[-\left(\frac{t}{\tau_1} \right)^{m_1} \right] \right\} \left\{ 1 - \exp \left[-\left(\frac{t}{\tau_2} \right)^{m_2} \right] \right\}, \quad (21)$$

$$\alpha(t) = \alpha_0 \left\{ 1 - \exp \left[-\left(\frac{t}{\tau_1} \right)^{m_1} \right] \right\} \exp \left[-\left(\frac{t}{\tau_2} \right)^{m_2} \right], \quad (23)$$

$$\alpha(t) = \alpha_0 \exp \left[-\left(\frac{t}{\tau_1} \right)^{m_1} \right] \exp \left[-\left(\frac{t}{\tau_2} \right)^{m_2} \right], \quad (24)$$

where m_1 and m_2 are the form factors and τ_1 and τ_2 are the relaxation times, respectively.

6. Theoretical and experimental studies of relaxation processes of integrated photoluminescence of *n*-GaAs and *n*-GaN structures stimulated by microwave radiation

A telling example is the time transformation of photoluminescence spectra during the transition of a defect ensemble from a non-equilibrium state to an equilibrium one, which is activated by an action of magnetic fields and microwave radiation on a semiconductor structure. The relaxation of the integrated photoluminescence is caused by flows of random events – displacements of defects both into the near-surface region of the semiconductor, where electron-hole pairs are generated under the action of photoluminescence excitation light, and beyond this region. Consequently, the transition of the defect ensemble from the non-equilibrium state to the equilibrium one is caused by independent events of two types. A random event of the first type is a displacement of a defect from the near-surface region to the surface. A random event of the second type is a displacement of a defect from the bulk of the crystal to the near-surface region. We denote $F_1(t)$ to be the probability of an event of the first type and $F_2(t)$ the probability of an event of the second type. The probability $P(t)$ of the absence of a defect in the near-surface region is equal to the product of the probabilities $P(t) = F_1(t)[1 - F_2(t)]$ [27, 31]. The value of the intensity of the integrated photoluminescence $I(t)$ calculated by (23) is [27, 28, 31–33]:

$$I(t) = I_{in} + I_0 \left\{ \left[1 - e^{-\left(\frac{t}{\tau_1} \right)^{m_1}} \right] e^{-\left(\frac{t}{\tau_2} \right)^{m_2}} \right\}, \quad (25)$$

where I_{in} is the initial value of the photoluminescence intensity, I_0 is the proportionality coefficient, m_1 and m_2 are the shape parameters, and τ_1 and τ_2 are the relaxation times of the integrated photoluminescence intensity, respectively.

Table 1 present the results and parameters of the least-squares approximation by the expression (25) of the change in the integrated photoluminescence intensity for the edge and impurity bands of *n*-GaAs and *n*-GaN epitaxial structures after non-thermal exposure to ultra-high-frequency radiation with a frequency of 2.45 GHz [27, 28, 31].

Table 1. Parameters of the approximating function (25).

Fitted parameter	<i>n</i> -GaN		<i>n</i> -GaAs	
	Edge emission	Impurity emission	Edge emission	Impurity emission
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

Table 2. Relaxation times τ for transition of a defect ensemble from a non-equilibrium state to an equilibrium one.

E_a , eV	τ , twenty-four hours
0.7	2.1
0.74	10
0.79	69
0.8	102

Let us estimate the relaxation time of the transition of an ensemble of defects from a non-equilibrium state to an equilibrium one. We assume that in a semiconductor structure, an ensemble of identical defects – edge dislocations with a number N_d and length L – transfer to a thermodynamically non-equilibrium state under an influence of microwave electromagnetic radiation. During subsequent transition to equilibrium, each dislocation moves a distance l within the semiconductor crystal under influence of thermal fluctuations and internal mechanical stresses. Then, for the relaxation time, we have

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) N_d \frac{Ll}{d^2}, \quad (26)$$

where d is the crystal lattice parameter.

We assume that in a GaAs-based structure with $d = 5.65325 \cdot 10^{-10}$ m, dislocations from a set with a number $N_d = 5$ and a length $L = 10^{-6}$ m move a distance $l = 10^{-7}$ m during their evolution from a non-equilibrium state to a thermodynamically equilibrium one. The calculated relaxation times τ for various values of the activation energy E_a are presented in Table 2 (the values used in the calculations were $\tau_0 = 1.61 \cdot 10^{-13}$ s and $T = 298$ K).

These estimated calculations provide a general idea of the physical phenomena underlying the above discussed experimental and theoretical studies of relaxation of the integrated intensity of photoluminescence. Overall, we note good agreement between the theoretical predictions and experimental results.

7. Conclusions

From a thermodynamic viewpoint, action of external magnetic and microwave electromagnetic fields on semiconductor structures causes transition of defects from an equilibrium to a non-equilibrium state. After the external fields cease to act, the defect ensemble evolves to a thermodynamically equilibrium state. The process of transition of a defect ensemble from the thermodynamically non-equilibrium state to the thermodynamically equilibrium one is called relaxation. The time period characterizing this transition is called the relaxation time.

The transition from a thermodynamically equilibrium state to a non-equilibrium one may be interpreted as a loss of stability of the equilibrium state of defects. For a defect to lose the stability of its equilibrium state, the field energy localized within the defect volume must be equivalent to that energy of thermal fluctuations, at which at least one defect particle changes its state during the field action.

The mechanisms of forming non-equilibrium state in ensembles of linear and point defects in semiconductor structures under influence of magnetic fields and ultra-high-frequency radiation are of an electroresonant nature. When the electromagnetic radiation frequency coincides with the own oscillation frequency of attached charged edge dislocations, resonance phenomena are observed, leading to dislocations detachment, *i.e.* their transition from an equilibrium attached state to a non-equilibrium one. Subsequently, a relaxation process occurs, *i.e.* a thermally activated movement of the dislocation ensemble to an equilibrium state under the influence of a mosaic of internal mechanical stresses in the semiconductor crystal. Coincidence of the ultra-high-frequency radiation frequency with the own frequency of clusters of charged point defects causes their decay.

As a result of this decay, the ions being initially in a bound, thermodynamically equilibrium state, transfer to a disintegrated, thermodynamically non-equilibrium state. As a result, relaxation, or, in other words, thermally activated movement of the formed ions to the equilibrium state under the influence of mechanical stress fields and a concentration gradient becomes possible. The formation of the non-equilibrium state of defects in semiconductor structures under influence of magnetic fields is caused by excitation of the defect subsystem by electromagnetic cyclotron radiation.

Since the transition of a defect ensemble from a non-equilibrium state to an equilibrium one is caused by a stream of random events – thermal fluctuation movements along a chain of asymmetric potential wells – the relaxation process is probabilistic in nature. The distribution function of a random variable – time until a random event – will characterize time-dependent regularities of relaxation of a set of defects from a non-equilibrium state to an equilibrium one activated by external fields. During the relaxation of a system of defects in a semiconductor crystal, the time trajectory of the change in the event probabilities is described by the distribution function of a random variable, which is the minimum of a large number of independently acting variables. Such a distribution is the Weibull–Gnedenko distribution. The scale parameter of this distribution represents the time of relaxation of the defect ensemble from the non-equilibrium state to the equilibrium one.

Since relaxation, which is the process of establishing thermodynamic equilibrium for a set of defects after cessation of magnetic fields and microwave radiation, occurs over time, it will manifest itself in time changes in the parameters of the semiconductor structures sensitive to this process. The dynamics of any parameter sensitive to the relaxation process is described, up to a constant, by the Weibull–Gnedenko distribution function, in which the scale factor is understood as the relaxation time of the semiconductor parameter.

The results of the experimental studies of the relaxation processes of integrated photoluminescence in *n*-GaAs and *n*-GaN structures stimulated by non-thermal action of microwave radiation agree well with the theoretical predictions.

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Нерівноважні процеси трансформації дефектів у напівпровідниках, стимульовані нетепловою дією надвисокочастотного випромінювання та магнітних полів

Г.В. Міленін, Р.А. Редько

Анотація. Показано, що атермічна дія магнітних і надвисокочастотних електромагнітних полів на напівпровідникові кристали спричиняє перехід ансамблю дефектів із термодинамічно рівноважного в нерівноважний стан. Після припинення дії зовнішніх полів спостерігається процес термоактиваційного переміщення – релаксації ансамблю дефектів до термодинамічно рівноважного стану, який характеризується часом релаксації. Сформульовано критерій втрати дефектами стійкості рівноважного стану, що дає змогу визначити порогові значення параметрів зовнішніх полів, які спричиняють формування нерівноважного стану системи дефектів у напівпровідникових структурах. Представлено електрорезонансні механізми створення нерівноважного стану ансамблів лінійних і точкових дефектів у напівпровідниках. Доведено, що релаксація системи дефектів у часі описується функцією розподілу Вейбулла–Гнеденка, параметр масштабу якої є часом релаксації ансамблю дефектів під час переходу з нерівноважного в рівноважний стан. Продemonстровано узгодження результатів експериментальних досліджень процесів релаксації інтегральної фотолюмінесценції структур *n*-GaAs і *n*-GaN, стимульованої атермічною обробкою надвисокочастотним випромінюванням, із теоретичними уявленнями.

Ключові слова: напівпровідник, дефект, рівноважний стан, нерівноважний стан, надвисокочастотне випромінювання, магнітне поле, резонансні явища, випадкова подія, розподіл Вейбулла–Гнеденка, релаксація, час релаксації, фотолюмінесценція.