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Determination of donor and acceptor concentrations in GaN using yellow photoluminescence band

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Abstract. In this paper, we present the results of the calculated and experimental dependence of photoluminescence on the excitation power density for GaN:Si layers grown by molecular beam epitaxy. A model was constructed for transitions in a compensated semiconductor upon interband generation of electron-hole pairs. It is shown that the dependence of the photoluminescence intensity on the excitation power density can be used to determine the recombination mechanism and concentrations of donors and acceptors in semiconductor.

Keywords: GaN, ammonia-MBE, photoluminescence, heterostructures, point defects

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Материалы конференции
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Определение концентраций доноров и акцепторов в GaN по желтой полосе фотолюминесценции

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Аннотация. В настоящей работе представлены результаты расчетной и экспериментальной зависимости интенсивности фотолюминесценции от плотности мощности возбуждения для легированных кремнием слоев GaN, выращенных методом молекулярно-лучевой эпитаксии. Показано, что анализ зависимости интенсивности фотолюминесценции от плотности мощности возбуждения с помощью модели электронных переходов в GaN при межзонной генерации электрон-дырочных пар позволяет определить механизм рекомбинации и концентрации доноров и акцепторов в полупроводнике.

Ключевые слова: GaN, аммиачная МЛЭ, фотолюминесценция, гетероструктуры, точечные дефекты

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Introduction

III-nitrides and their alloys are direct-gap semiconductors, relevant for the manufacture of light-emitting devices for the visible and ultraviolet regions of the spectrum [1, 2]. Varying the Al content in AlGaN allows creating materials with band gap (E_g) from 3.43 to 6.2 eV, covering the spectral range from 200 to 365 nm. Formation of epitaxial GaN *n*-type conductivity layers using silicon (Si) as a donor is not difficult, the electron concentration can be increased to 10^{20} cm^{-3}. However, epitaxial growth of semiconductor structures is associated with formation of point defects, which can form acceptor-like states and compensate the doping impurity. Photoluminescence spectroscopy (PL) is a non-contact fast non-destructive method of characterizing such heterostructures, requiring a small amount of material to study. Several bands in the GaN luminescence spectra related to electronic transitions to the centers with energy levels in the band gap [3] are known, the most actively studied is the 'yellow band' of luminescence with the maximum of about 2.2 eV that is associated with the main GaN background impurities or their complexes with natural lattice defects: V_{Ga}-O_N complex [4–6] and C_N-O_N complex or isolated C_N impurity [7–9]. The yellow band provides information on the defects in the crystals and is actively used to improve their growth technology since the ratio of the intensities of the UV-edge band and the yellow band in the GaN luminescence spectrum can serve as a criterion of its crystalline perfection.

Usually the intensity of the yellow band linearly depends on the excitation power density (J) at low values of J and it saturates at high values of J. The approximation of this dependence by the function of the form $I(J) \sim \ln(1 + J/J_1)$ in [10] allows to determine the acceptor concentration from the magnitude J_1. This method requires the measurement of the external quantum efficiency of the yellow band, since within such a model this magnitude takes into account the influence of competing channels of the recombination. It is not possible to calculate the concentration of the donors by this model. A stricter account of other channels of the recombination consists in solving the system of the kinetic equations in the stationary case together with the electroneutrality equation. In the present work, we propose to use this approach to determine the mechanism of yellow band recombination in the Si-doped GaN layers and concentrations of donors and acceptors according to the dependence of yellow band intensity on the excitation power density. The proposed model is universal and can be used for any compensated semiconductors at high temperatures.

Materials and Methods

We investigated 1-μm-thick GaN layers grown by molecular beam epitaxy (MBE) from ammonia on Riber's CBE-32 machine. The substrates used were (0001) oriented polished 400 μm thick 2" sapphire wafers. The layers were doped with silicon (Si) from a monosilane gas source. The concentration of silicon atoms in the layers was determined by secondary ion mass spectrometry (SIMS) using the technique described in [11] and was approximately 8×10^{18} cm^{-3}. The electron concentration was determined by Hall effect measurements in Van der Pau geometry in a 0.5 Tesla magnetic field at room temperature and was about 3×10^{17} cm^{-3}. The PL spectra were measured at room temperature. The 4th harmonic of the stationary YAG laser (λ_{las} = 266 nm) with a maximum radiation power density of 12.6 W/cm^2 was used to measure the PL over a wide range of excitation power.

Results and Discussion

Fig. 1, *a* shows the experimentally measured PL spectra of a typical GaN sample, in which the near-band-edge PL band with a maximum at 3.45 eV and yellow PL band with a maximum at 2.18 eV dominate. Both bands are characterized by a monotonic growth of the integral intensity with the increase in the excitation power density (Fig. 1, *b*). The near-band-edge PL band intensity increases by the superlinear law throughout the range of excitation power density, approximation by the exponential function gives a power index $\gamma = 1.17$. The yellow band intensity increases linearly up to $J \sim 1$ W/cm^2, at higher values the dependence becomes sublinear, approximation by the exponential function gives a power index $\gamma = 0.66$, close to the value from work [12], which is typical for donor-acceptor recombination. The intensities of the edge and yellow bands are compared at $J_0 \sim 4.5$ W/cm^2. The approximation of the yellow band intensity by a function of the form $I(J) \sim \ln(1 + J/J_1)$ [10] gives the value $J_1 \sim 3.4$ W/cm^2, which depends on N_A as follows:

$$J_1 / E_{las} = N_A / \alpha\tau\eta, \qquad (1)$$

here $\tau = (n_0 W_{eA})^{-1}$ is the lifetime and η is the external quantum efficiency of the yellow band, respectively. Substituting the value $\eta = 0.06$, typical for the yellow band [10, 13], into relation (1) gives the estimation $N_A = 2\times10^{18}$ cm^{-3}.

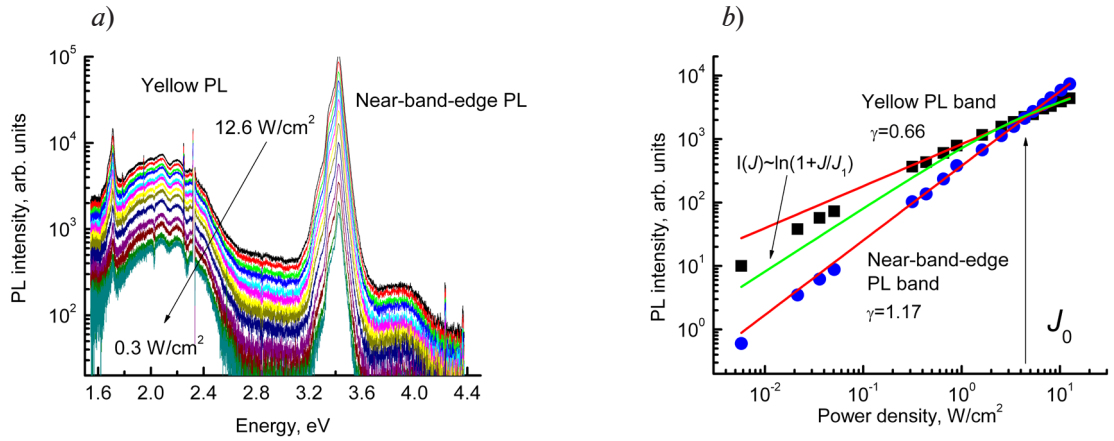

Fig. 1. Room-temperature PL spectra of GaN (*a*) and dependences of the intensity of the edge and yellow PL bands on the excitation power density (*b*). The solid lines depict the approximation curves (see the text for details)

Within the framework of the above model, the influence of competing recombination channels is taken into account by the value of η. This model does not allow us to calculate the concentration of donors. A more rigorous consideration of other recombination channels consists in solving a system of kinetic equations in the stationary case together with the electroneutrality equation. The dependence of intensity of various PL channels in a compensated semiconductor on the excitation power was calculated for the interband mechanism of electron-hole pair generation, Fig. 2 shows a scheme of electronic transitions. The semiconductor contains donors (D), acceptors (A), and non-radiative recombination (NR) centers. Within the model there are three channels of radiative recombination – band-band (BB), band-acceptor (eA) and donor-acceptor (DA) with participation of one type of acceptors and one channel of non-radiative recombination (NR).

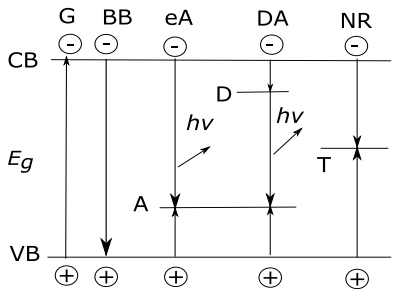

Fig. 2. Scheme of transitions in a compensated semiconductor at band-band generation of charge carriers

Following the transition scheme, we can write a system of continuity equations for free electrons n, free holes p,

neutral donors N_D^0, neutral acceptors N_A^0 and neutral non-radiative centers N_T^0 together with the electroneutrality equation.

$$\begin{gathered}
0 = \alpha J + W_t \cdot N_D^0 - W_f \cdot n \cdot p - W_{eD} \cdot n \cdot (N_D - N_D^0) - W_{eA} \cdot n \cdot N_A^0 - W_{eT} \cdot n \cdot N_T^0 \\
0 = W_{hT} \cdot p \cdot (N_T - N_T^0) - W_{eT} \cdot n \cdot N_T^0 \\
0 = W_{hA} \cdot p \cdot (N_A - N_A^0) - W_{eA} \cdot n \cdot N_A^0 - W_{DA} \cdot N_D^0 \cdot N_A^0 \\
0 = W_{eD} \cdot n \cdot (N_D - N_D^0) - W_{DA} \cdot N_D^0 \cdot N_A^0 - W_t \cdot N_D^0 \\
p + (N_D - N_D^0) = n + (N_T - N_T^0) + (N_A - N_A^0),
\end{gathered} \tag{2}$$

here N_D, N_A and N_T are total concentrations of donors, acceptors, and non-radiative centers, $\alpha = 1.8\times10^5$ cm^{-1} is absorption coefficient at the laser wavelength [14], $W_f = 1.1\times10^{-8}$ cm$^{-3}\times$c^{-1} is probability of radiative recombination of free charge carriers [14]. The probability of thermal ejection of an electron from the donor level into the conduction band was estimated as

$$W_t = W_{eD} \cdot N_{eff} \cdot e^{-\frac{E_d}{kT}}, \tag{3}$$

here N_{eff} is the effective density of states in the band, k is the Boltzmann constant, T is temperature, $E_d = 26$ meV is the ionization energy of the donor [15]. W_{eD}, W_{eA} and W_{eT} are probabilities of electron capture to the donor, to the acceptor and to the non-radiative center, W_{hA} and W_{hT} are probabilities of hole capture to the acceptor and to the non-radiative center [16]. Since the recombination probability in DA pairs depends on the distance between the donor and acceptor in the pair (r), it is impossible to describe the DA-channel by a simple expression for the transition rate with a fixed value of the transition probability W_{DA}. To avoid complicating the calculation scheme, we introduced an average value of the recombination probability showing the most possible value of this value:

$$\begin{gathered}
W_{DA} = \int_0^\infty W(r) f(r) dr, \\
W(r) = W_0 e^{-\frac{2r}{a}}, \\
f(r) = C_1 r^2 e^{-\frac{e^2}{\varepsilon r k T}} e^{-\frac{4\pi N r^3}{3}},
\end{gathered} \tag{4}$$

here $W(r)$ is the recombination probability in a donor-acceptor pair of radius r, $f(r)$ is the density distribution function of randomly located non-interacting donor-acceptor pairs along radius r. Here W_0 is a constant indicating recombination probability at $r = 0$, a is the Bohr radius of the electron on the donor, N is the concentration of the dominant impurity (donors in this case), ε is the dielectric permittivity, e is the elementary electric charge, C_1 is the normalization multiplier.

The solution of the system of equations (2) allows us to obtain the dependence of the concentrations of charge carriers and neutral centers on the excitation power density J. From these we can derive the dependences of recombination channel rates as a function of J.

$$\begin{gathered}
I_{BB}(J) = W_f \cdot n(J) \cdot p(J), \\
I_{eA}(J) = W_{eA} \cdot n(J) \cdot N_A^0(J), \\
I_{DA}(J) = W_{DA} \cdot N_D^0(J) \cdot N_A^0(J), \\
I_{NR}(J) = W_{eT} \cdot n(J) \cdot N_T^0(J).
\end{gathered} \tag{5}$$

Fig. 3 shows the calculated dependences of the rates of BB, NR, eA and DA recombination and G generation rate channels on the excitation power density J. The concentrations of donors, acceptors, non-radiative centers, and equilibrium electrons are taken to be $N_D = 8\times10^{18}$ cm^{-3}, $N_A = 2\times10^{18}$ cm^{-3}, $N_T = 3.5\times10^{18}$ cm^{-3} and $n_0 = 3\times10^{17}$ cm^{-3}. The calculated dependences of the rates of BB and DA channels coincide with the experimental dependences for the band-

band and yellow PL bands. In the experiment, it is most convenient to register the value of power density J_0, at which the intensities (or recombination rates) of BB and DA channels are equal, which depends on the selected concentrations. Donor concentration $N_D = 8\times10^{18}$ cm^{-3} which corresponds to $J_0 = 4.5$ W/cm^2 observed in the experiment coincides with the value of total silicon concentration obtained by SIMS method. This means that this technique provides reliable information on donor and acceptor concentrations. It should be noted that the kinetics of photoluminescence decay would allow to accurately determining the donor concentrations [17]. This is a point of further development of the proposed approach.

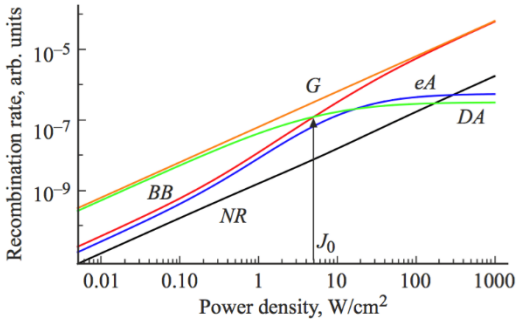

Fig. 3. Calculated dependences of the NR, BB, eA and DA recombination rate and the generation rate G on the excitation power density. The concentration of donors, equilibrium electrons, acceptors and non-radiative centers are $N_D = 8\times10^{18}$ cm^{-3}, $n_0 = 3\times10^{17}$ cm^{-3}, $N_A = 2\times10^{18}$ cm^{-3}, $N_T = 3.5\times10^{18}$ cm^{-3}

Conclusion

In this work, a model of electronic transitions in compensated GaN was established that takes into account radiative band-band, band-acceptor, donor-acceptor transitions and non-radiative transitions at band-band generation of electron-hole pairs. The dependences of the rates of these recombination channels on the excitation power density were calculated within this model. The dependences of the intensity of the near-band-edge and yellow photoluminescence bands on the excitation power density for n-doped GaN layers grown by molecular beam epitaxy were measured. It is shown that the yellow band in GaN is caused by donor-acceptor optical transitions. The analysis of band-band and donor-acceptor photoluminescence bands intensity dependences on the excitation power density allowed estimating the concentrations of donors and acceptors in GaN. The correctness of the concentration estimate demonstrates the coincidence of the donor concentration with the total silicon concentration.

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