Determination of the energy structure of recombination centers in heavily doped Al$_x$Ga$_{1-x}$N:Si epitaxial layers with $x > 0.5$

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Abstract. The photoluminescence properties of the intensive defect-related emission in heavily doped Al$_x$Ga$_{1-x}$N:Si layers with $x > 0.5$ have been investigated by photoluminescence (PL) spectroscopy. The PL band in AlN was attributed to donor-acceptor (DA) transitions. At the lowest Al content, the impurity band merges with the conduction band and DA transitions are replaced by electron-acceptor transitions involving the same acceptor. The energy structure of recombination centers was obtained using the model of configuration coordinates for Al$_{0.67}$Ga$_{0.33}$N.

1. Introduction

GaN and its alloys with AlN have emerged as promising semiconductor materials for applications in laser sources emitting in the blue-green spectral range. The creation of effective light-emitting semiconductor devices is impossible without doping the epitaxial layers. The formation of epitaxial $n$-GaN layers using silicon (Si) as a donor does not cause significant difficulties, and the electron concentration can be controllably increased to $10^{20}$ cm$^{-3}$ [1–4]. However, doping of Al$_x$Ga$_{1-x}$N becomes less efficient with an increase in Al content ($x$). The electron concentration becomes significantly lower than the concentration of silicon atoms due to two phenomena: 1) the deepening of the Si donor level from 30 meV in GaN [5] to 250 meV in AlN [6, 7]; 2) the self-compensation of Si caused by the formation of negatively charged cation vacancies ($V_{III}$) [8, 9]. It is assumed that heavy doping with Si also leads to the appearance of intense broadband luminescence in the visible spectral range that was observed in Al$_x$Ga$_{1-x}$N epitaxial layers with $x > 0.5$ [10, 11]. This band is attributed to donor-acceptor (DA) and free electron-acceptor (eA) transitions involving the same acceptor. However, the ratio between DA and eA transitions was unclear. The donor was assigned to Si. The acceptor might be $V_{III}$ or its complexes with shallow donors. However, the energy structure of recombination centers has not been completely described. This work is a continuation of previous investigations. In this paper, the new results on the energy structure of recombination centers in heavily doped Al$_x$Ga$_{1-x}$N:Si epitaxial layers with $x > 0.5$ studied by photoluminescence (PL) spectroscopy are presented.
2. Experimental details

We investigated 1.2-μm-thick Al$_x$Ga$_{1-x}$N:Si layers grown by molecular beam epitaxy techniques (using ammonia as a source of active nitrogen) on nitridated (0001)-oriented 400-μm-thick sapphire substrates with an AlN nucleation layer about 300 nm thick. The Al content in the layers was controlled by the Al-to-Ga flux ratio during the growth and varied from 0.5 to 1. The real $x$ value was obtained by secondary-ion mass spectrometry (SIMS) and transmission spectroscopy. The latter method revealed the value of $x$ to be 5-7% lower than the value produced by SIMS, probably because of band gap narrowing at high impurity concentrations. Therefore, the $x$ value from the SIMS data was assumed to be close to the real values. The mix of 0.7% silane (SiH$_4$) with nitrogen (N$_2$) was used as a source of Si. Measurements of photoluminescence (PL) of the studied samples were conducted in a wide temperature range of 5-1200 K using a continuous He-Cd laser with a photon energy $E_{ph} = 3.81$ eV and a pulsed 4th harmonic of Nd:YLF laser ($E_{ph} = 4.71$ eV) for excitation. The studied samples were mounted in a helium closed-circuit cryostat for measurements below 300 K and in a custom-made vacuum camera for measurements above 300 K.

3. Results

Figure 1 shows the room-temperature PL spectra of silicon-doped Al$_x$Ga$_{1-x}$N layers with $x \approx 0.6$ grown at different silane fluxes. The PL spectra of doped Al$_x$Ga$_{1-x}$N grown at 1 sccm ($N_{Si} \approx 10^{19}$ cm$^{-3}$) comprise the band-edge ultraviolet (UV) band with maximum energy at $E_g = 4.5$ eV related to band-to-band transitions, the parasitic defect-related UV band split into two bands with $E_m = 3.6$ eV and $E_{em} \approx 3.9$ eV, and the defect-related visible band at $E_{em} \approx 2.2$ eV. An increase in silane flux up to 3 sccm ($N_{Si} \approx 1.5 \times 10^{20}$ cm$^{-3}$) leads to a strong decrease in the intensity of the defect-related UV band at 3.6 eV and total reduction of the band-edge band and the defect-related band at 3.9 eV. Thus, transitions through the levels of defects due to Si doping dominate over all other radiative recombination channels.

Figure 2 shows $E_{em}$ of the defect-related PL bands and $E_g$ of the heavily doped Al$_x$Ga$_{1-x}$N layers with $N_{Si} \approx 1.5 \times 10^{20}$ cm$^{-3}$, estimated using the Vegard law:

$$E_g = x_{Al} \cdot E_{gAlN} + (1 - x_{Al}) \cdot E_{gGaN} - b \cdot x_{Al} \cdot (1 - x_{Al}) = 1.0 x_{Al}^2 + 1.59 x_{Al} + 3.43,$$

where $E_{gAlN} = 3.43$ eV [12] and $E_{gGaN} = 6.015$ eV [13] are the GaN and AlN band gaps, respectively, and $b = 1.0$ eV [14] is the bowing parameter. The parasitic UV band demonstrates the lowest range of blue shift of $E_{em}$ with an increase in $x$ that reveals a stronger deepening of the acceptor energy level than in the case of the visible band.

Figure 1. The room-temperature PL spectra of silicon-doped Al$_x$Ga$_{1-x}$N layers with $x \approx 0.6$ with a silicon concentration ($N_{Si}$) of about $10^{19}$ cm$^{-3}$ and $1.5 \times 10^{20}$ cm$^{-3}$.

Figure 2. Dependences of the energy position of defect-related P bands ($E_{em}$) and the band gap ($E_g$) of heavily doped Al$_x$Ga$_{1-x}$N layers with $N_{Si} \approx 1.5 \times 10^{20}$ cm$^{-3}$ on the Al content ($x$) at T = 300 K.
The Al$_{0.67}$Ga$_{0.33}$N layer with $N_{Si} \approx 1.5 \times 10^{20}$ cm$^{-3}$ demonstrates the same behavior of the temperature-dependent visible PL band intensity that was observed before for a lower Si concentration [10], i.e., the PL intensity increases with an increase in temperature from 5 to 270 K, while a further rise in temperature causes PL quenching (see figure 3).

The enhancement and quenching of the PL intensity with temperature are described by the expression:

$$I(T) = A \frac{1 + B_0 e^{E_0/kT}}{1 + B_1 e^{E_1/kT}}$$

(2)

where $E_0$ and $E_1$ are the activation energies, and $A$, $B_0$, and $B_1$ are constants. Fitting of the PL quenching curve by equation (2) gives $E_0 = 9$ meV and $E_1 = 160$ meV. The enhancement of the PL intensity is explained by the emission of carriers from the states arising due to the band edge perturbations caused by the Al mole fraction fluctuation ($\Delta x$). The addition of the second exponential factor with an activation energy $E_2$ to the denominator [10] would be in excess of the accuracy of the approximation.

The increase in temperature up to 1100 K causes the blue shift of the visible PL band maximum, following a linear law $\Delta E_m = 1.2 \times kT$ (see figure 4). This linear coefficient of 1.2 was lower than the reported value of 1.7 obtained for $N_{Si} \approx 5 \times 10^{19}$ cm$^{-3}$ [10].

Figure 3. Temperature dependence of the intensity of the visible PL band in the Al$_{0.67}$Ga$_{0.33}$N layer with $N_{Si} \approx 1.5 \times 10^{20}$ cm$^{-3}$. The solid line depicts the approximation curve (see the text for details).

Figure 4. Temperature dependence of the visible PL band maximum in the Al$_{0.67}$Ga$_{0.33}$N:Si layer. The solid line depicts the approximation curve (see the text for details).

Figure 5 shows the temperature dependence of the PL bandwidth. The full width at half maximum (FWHM or W) of the PL band depends on temperature ($T$). The temperature broadening of the PL band is described by the expression [15]:

$$W(T) = W(0) \sqrt{\coth \left( \frac{h\nu_e}{2kT} \right)}$$

(3)

where $W(0)$ is the bandwidth at $T = 0$ and $h\nu_e$ is the local phonon energy. Fitting of the temperature broadening of the PL band by equation (3) gives $W(0) = 562$ meV and $h\nu_e = 62$ meV.
4. Discussion

4.1. Type of transitions in heavily doped Al$_x$Ga$_{1-x}$N:Si layers

Broad PL bands are typical for recombination of carriers through deep levels of defects due to strong electron-phonon coupling. The configuration coordinate (CC) model describes such systems well [15, 16]. The measure of the electron-phonon coupling is the Huang–Rhys factor ($S$). In the case of strong electron-phonon coupling, $S$ represents the mean number of the emitted phonons for each photon absorption or emission process. Previously, we assumed that $S$ is equal for absorption and emission [11] but in general, $S$ should be different for both processes. The CC diagram describing optical absorption and emission at defects with strong electron-phonon coupling is shown in figure 6. $S_{em}$ and $S_{ab}$ are the Huang-Rhys factors and $h\nu_g$ and $h\nu_e$ are the photon energies involved in the transitions, while optical energies are $E_{em}$ and $E_{ab}$, respectively. We assume that

$$S_{em}h\nu_e = S_{ab}h\nu_g.$$  \hspace{1cm} (4)

The emission peak energy is given by equations (5) and (6) for DA and eA transitions:

$$E_{em} = E_{g\text{AlGaN}} - E_D - E_A - S_{em}h\nu_e,$$  \hspace{1cm} (5)

$$E_{em} = E_{g\text{AlGaN}} - E_D - E_A - S_{em}h\nu_e.$$  \hspace{1cm} (6)

An important aspect of the applicability of equations (5) and (6) is delocalization of electrons in heavily doped semiconductors. The criterion of heavy doping is expressed by the inequality:
\[ N_D a_B^3 > 1, \]  

(7)

where \( N_D \) is the donor concentration and \( a_B \) is the Bohr radius of the donor state [17]. For GaN, the expression (7) is satisfied at \( N_D \approx 7.5 \times 10^{19} \text{ cm}^{-3} \) within the framework of the hydrogen atom model [18]. In heavily doped semiconductors, the impurity band merges with the conduction band and electrons are not localized at donor levels. Therefore, only \( eA \) transitions should be observed at \( N_D \approx 1.5 \times 10^{20} \text{ cm}^{-3} \) in cases where \( Si \) remains a shallow donor in \( Al_{0.67}Ga_{0.33}N \). Since \( Si \) is considered a deep donor with \( E_D = 250 \text{ meV} \) in \( AlN \), it still forms an impurity band below the conduction band and \( DA \) transitions take place. A \( Si \) donor level deepens at \( x \approx 0.85 \) [5], therefore equation (4) is applicable in the case of \( AlN \) and equation (5) should be used for \( x = 0.5-0.7 \).

4.2. Energetic parameters of acceptors in \( Al_{0.67}Ga_{0.33}N:Si \)

According to the one-dimensional CC model (see figure 6), the Stock shift of PL should be given by equations (8) and (9) in case of \( DA \) and \( eA \) transitions:

\[ E_{ab} - E_{em} = E_D + 2S_{em} h\nu_e, \]  

(8)

\[ E_{ab} - E_{em} = 2S_{em} h\nu_e. \]  

(9)

Equation (9) is acceptable for \( x = 0.67 \). The Stock shift \( E_{ab} - E_{em} \approx 2.3 \text{ eV} \) [10] estimates \( S_{em}h\nu_e \approx 1.15 \text{ eV} \). The temperature broadening of the PL band is given by equation (3). The \( W(0) \) is given by

\[ W(0) = 8\ln 2 \cdot S_{em} h\nu_g / \sqrt{S_{ab}}. \]  

(10)

Equations (3), (4), (9) and (10) allow estimating CC parameters for an acceptor in \( Al_{0.67}Ga_{0.33}N:Si \). We obtained \( S_{ab} \approx 19.9, S_{em} \approx 18.5, h\nu_e \approx 62 \text{ meV}, h\nu_g \approx 58 \text{ meV} \). The differences between \( S_{em} \) and \( S_{ab} \) and \( h\nu_e \) and \( h\nu_g \) are at the level of error. After that, we obtain \( E_A \approx 1.4 \text{ eV} \) from equation (6). These results follow the previously observed trend: a decrease in Al content leads to a decrease in \( E_A \) and an increase in \( S_{em}h\nu_g \).

The activation energy \( E_1 = 160 \text{ meV} \) obtained from equation (2) is an order of magnitude less than \( E_A \) and close to the previously reported value of 170 \text{ meV} [10]. Most likely, this activation energy corresponds to internal quenching of luminescence. Due to the fact that the potential curve of the excited state is shifted relative to the potential curve of the ground state, it is possible to intersect these two curves so that, while in an excited state, the system can assume the same configuration as it has in the ground state at a sufficiently large value of the vibrational energy. In this case, nonradiative transitions from the excited state to the ground state occur.

Another feature is the linear blue shift of the maximum of the visible PL band with an increase in temperature, depending on the particulars of the adiabatic potentials of the recombination centers. The CC model predicts the following expression for a temperature-related shift [19]:

\[ \Delta E_{CC} = \frac{v_g^2 - v_e^2}{v_e^2} + \frac{8 v_g^4}{v_g^2 (v_g^2 + v_e^2)} \left[ \frac{E_{ab}(0) - E_{em}(0)}{E_{em}(0)} \right] kT, \]  

(11)

where \( E_{ab}(0) \) and \( E_{em}(0) \) are the absorption and emission energies at \( T = 0 \). Assuming that \( E_{ab} - E_{em} \) is about 2.3 \text{ eV} at \( T = 0 \), we obtain \( \Delta E_{CC} \approx 2.7kT \). Due to the band-gap reduction, the observed \( \Delta E_{em} \) follows the same law but with a less linear coefficient. However, the CC model does not explain the decrease in the linear coefficient from 1.7 to 1.2 with an increase in \( N_{Si} \) from \( 5 \times 10^{19} \text{ cm}^{-3} \) to...
1.5×10^{20} \text{ cm}^{-3}. This fact suggests that the theory of heavily doped semiconductors should be taken into account.

5. Conclusions
The new results on the energy structure of recombination centers responsible for the intensive visible emission band in heavily doped Al_{x}Ga_{1-x}N:Si epitaxial layers with $x > 0.5$ have been obtained by photoluminescence (PL) spectroscopy. The PL band in AlN was attributed to donor-acceptor (DA) transitions. At the lowest Al content, the impurity band merges with the conduction band and DA transitions are replaced by electron-acceptor transitions involving the same acceptor. Using the model of configuration coordinates, the parameters of recombination centers for Al_{0.67}Ga_{0.33}N were estimated to be $S_{ab} \approx 19.9$, $S_{em} \approx 18.5$, $h\nu_e \approx 62 \text{ meV}$, $h\nu_g \approx 58 \text{ meV}$. The acceptor energy level was $E_A \approx 1.4 \text{ eV}$.

The activation energy of internal quenching of luminescence of about 160 meV was obtained. The blue shift of the maximum of the PL band with an increase in temperature exceeded the temperature narrowing of the band gap but decreased with an increase in the Si concentration. This indicates the inadequacy of the configuration coordinate model for heavy Al_{x}Ga_{1-x}N doping.

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