Nature of intensive defect-related broadband luminescence of heavily doped Al\textsubscript{x}Ga\textsubscript{1-x}N:Si layers

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Abstract. We report photoluminescence investigations of heavily doped Al\textsubscript{x}Ga\textsubscript{1-x}N:Si films grown by molecular beam epitaxy on sapphire substrates. The wide intensive defect-related band dominates in the photoluminescence spectra of Al\textsubscript{x}Ga\textsubscript{1-x}N:Si films with the Al content higher than 0.46 covering the whole visible spectral range. This band is attributed to donor-acceptor transitions. The acceptor ionization energy of about 1.87 eV for heavily doped AlN:Si was obtained, decrease of Al content leads to decrease of the acceptor ionization energy. The donor was assigned to the Si atom on the Ga/Al site; the acceptor might be the (2-/3-) transition level of the $V_{Al}$. 

1. Introduction

GaN and its alloys with AlN have emerged as promising semiconductor materials with applications to laser sources for the blue-green spectral range. Bokhan et al. recently reported the finding of a blue-green superluminescence related to optical transitions through levels of defects in heavily doped Al\textsubscript{x}Ga\textsubscript{1-x}N:Si layers with high Al content covering the whole visible and near-infrared region of the spectrum [1]. This luminescence band was attributed to superposition of donor-acceptor and free electron-acceptor transitions involving the same acceptor [2]. Super-radiance within the broad band was obtained by pumping these samples up with an electron beam with power more than 200 kW. Overall, however, the study of luminescent properties and obtaining stimulated emission in the optical transitions via defect levels in wide band-gap solid alloys Al\textsubscript{x}Ga\textsubscript{1-x}N:Si have not been given attention. The aim of this work was further study of the characteristics of broadband emission from heavily doped Al\textsubscript{x}Ga\textsubscript{1-x}N:Si layers by steady-state and time-resolved PL spectroscopy, as well as photoluminescence excitation (PLE) spectroscopy.
2. Experimental details

We investigated 1.2 \( \mu \)m-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-\( \mu \)m-thick sapphire substrates with an about 300-nm-thick AlN nucleation layer. The Al content (\( x_{Al} \)) in the layers was set by the Al-to-Ga flux ratio during the growth. The mix of 0.7% silane (SiH\(_4\)) with nitrogen (N\(_2\)) was used as a source of Si. The first series of studied layers was grown at the constant silane flux \( F_{SiH4} = 3 \) sccm, \( x_{Al} \) was varied from 0 to 1. The second series of studied layers was grown at the constant \( x_{Al} = 0.67 \), \( F_{SiH4} \) was varied from 0 to 6 sccm. The silicon concentration in the layers was estimated to be about \((1.5-2.0)\times10^{20} \) cm\(^{-3}\) at \( F_{SiH4} = 3 \) sccm by secondary-ion mass spectrometry (SIMS) using an IMS7f (CAMECA) setup with primary Cs\(^+\) ions. The real \( x_{Al} \) in Al\(_{x}\)Ga\(_{1-x}\)N layers was also obtained from SIMS data. The sample charge was neutralized by the EB irradiation of the samples. The concentration of free electrons in the samples under study was determined by measuring the Hall effect in the Van der Pauw geometry in a constant magnetic field of 0.5 T at room temperature. 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 refrigerator for measurements below 300 K and in a custom-made vacuum camera for measurements above 300 K. Measurements of photoluminescence excitation (PLE) spectra were carried out at room temperature on a FLS920 spectrofluorimeter with a 450 W xenon lamp as the excitation source. This setup allowed the measurement of both PLE and PL spectra.

3. Results

The PL spectra of heavily silicon doped Al\(_{x}\)Ga\(_{1-x}\)N layers for the first series at room temperature are shown in figure 1. PL spectra of the heavily doped GaN structure (\( x_{Al} = 0 \)) comprise only the band-edge ultraviolet band \( (E_{em} \approx 3.6 \) eV) related to band-to-band transitions, the defect-related “yellow” band typical for undoped GaN is reduced likely because of Si incorporation in Ga vacancies which are considered as the origin of the “yellow” band. The free-electron concentration in the GaN structure was about \( 1.1\times10^{20} \) cm\(^{-3}\). The rise of \( x_{Al} \) leads to decrease of both the intensity of band-edge PL and the free-electron concentration (see figure 2) whereas the very weak defect-related PL appears in the visible spectral range. The wide defect-related PL band dominates in PL spectra of the Al\(_{x}\)Ga\(_{1-x}\)N layers with \( x_{Al} > 0.46 \). The increase of Al content from \( x_{Al} = 0.5 \) to \( x_{Al} = 1 \) leads to the blue shift of the energy position of the PL band from the red-orange spectral range \( (E_{em} \approx 2.0 \) eV) to the violet spectral range \( (E_{em} \approx 3.1 \) eV).

![Figure 1. PL spectra of heavily doped Al\(_{x}\)Ga\(_{1-x}\)N:Si layers grown at the constant silane flux \( F_{SiH4} = 3 \) sccm measured at room temperature.](image1)

![Figure 2. Dependence of the electron concentration on Al content.](image2)
Figure 3 shows the energy position of the defect PL band ($E_{em}$) and the band gap of the Al$_x$Ga$_{1-x}$N layers ($E_g$) estimated using the Vegard law:

$$
E_{g(x)} = x_{Al} E_{g(Al)} + (1 - x_{Al}) E_{g(Ga)} - x_{Al} (1 - x_{Al}) \cdot b = 1 \cdot x^2 + 1.59 \cdot x + 3.43
$$

(1)

where $E_{g(Al)} = 3.43$ eV [3] and $E_{g(Ga)} = 6.015$ eV [4] are the GaN and AlN band gaps, respectively, and $b = 1.0$ eV [5] is the bowing parameter. $E_{em}$ rises weaker with $x_{Al}$ increase than $E_g$. The intensity of the green band in PL spectra of the second series of samples ($E_m \approx 2.4$ eV) increases with the rise of the silicon concentration up to $F_{SiH4} = 4.5$ sccm then the PL intensity decreases with further rise of the silicon concentration (see figure 4). The electron concentration was about $1.6 \times 10^{19}$ cm$^{-3}$ and $4.1 \times 10^{17}$ cm$^{-3}$ for the samples grown at $F_{SiH4} = 1.5$ sccm and $F_{SiH4} = 3.0$ sccm, respectively, the undoped sample and samples grown in the highest silane flux were very low conductive. That is in agreement with our previous results [6].

Figure 3. Dependences of the band-gap ($E_g$) and the defect PL band energy position ($E_{em}$) on Al content.

Figure 4. Dependences of the intensity of the defect PL band in Al$_{0.67}$Ga$_{0.33}$N layers on silane flux.

Figure 5 shows the PL and PLE spectra of the Al$_{0.78}$Ga$_{0.22}$N and AlN ($x_{Al} = 1$) samples at room temperature. The peak in the PLE spectra marked $E_1$ at 5.2 eV and 6.0 eV for the Al$_{0.78}$Ga$_{0.22}$N and AlN layers, respectively, corresponds to band-to-band transitions in heavily doped Al$_x$Ga$_{1-x}$N layers because its energy position matches with the $E_g$ from equation (1). The second peak $E_2$ at 4.7 eV and 4.94 eV for the Al$_{0.78}$Ga$_{0.22}$N and AlN layers, respectively, was attributed to acceptor-to-band transitions in the heavily doped AlN layer. The large energy difference between the PL peak and the PLE peak $E_2$ (around 2.04 eV and 1.86 eV for the Al$_{0.78}$Ga$_{0.22}$N and AlN layers, respectively) indicates a large Stock shift due to strong electron-phonon coupling in a deep center. These results are in a good agreement with our previous PL and PLE investigations of heavily doped Al$_x$Ga$_{1-x}$N layers with high $x_{Al}$ [2]. Temperature-dependent PL spectra of the Al$_{0.78}$Ga$_{0.22}$N layer demonstrate unusual behavior of the PL intensity, i.e., the PL intensity increases with increasing temperature from 5 to 500 K, while the further rise in temperature causes the PL quenching (see figure 6). The enhancement of the PL intensity is explained by the emission of carriers from states arising due to the band edge perturbations caused by the Al content and Si concentration fluctuation. The quenching of the PL intensity with temperature is described by the expression:

$$
I(T) = \frac{E_0}{A / (1 + Be^{E_0/kT})},
$$

(2)

where $E_0$ is the activation energy, and $A$ and $B$ are constants. Fitting of the PL quenching curve (see figure 7) by equation (2) gives $E_0 = 1.57$ eV.
Figure 5. PLE and PL spectra of the Al$_{0.78}$Ga$_{0.22}$N and AlN ($x_{Al} = 1$) samples at a detection energy of 3.08 eV and 2.7 eV, respectively, and PL spectra measured at the excitation energy of 4.71 eV at room temperature.

Figure 6. PL spectra of the Al$_{0.78}$Ga$_{0.22}$N sample at different temperatures

Figure 7. Temperature dependence of the PL intensity. Solid line depicts the approximation curve (see the text for details)

4. Discussion
The large Stock shift is typical for the centers with strong electron-phonon coupling. The configuration coordinate model describes such systems well [7, 8]. The configuration coordinate diagram describing optical absorption and emission at defects with strong electron-phonon coupling is shown in figure 8. $S_{em}$ and $S_{ab}$ are the numbers of photons with energies $h
\nu_g$ and $h\nu_e$ involved in the transitions, $E_{em}$ and $E_{ab}$ are energies of the transitions. We assume that $S_{em} = S_{ab} = S$ and $h\nu_g = h\nu_e = h\nu_0$. The emission peak energy is given by:

$$E_{em} = E_{AlGaN} - E_D - E_A - S_{em} h\nu_0,$$

where $S_{em}$ is the number of photons with the energy $h\nu_g$ involved in the transitions. The Stock shift in this model should be:

$$E_2 - E_{em} = 2S_{em} h\nu_0 + E_D.$$

Since the intensity of green PL of the samples with $x_{Al} = 0.67$ increases with increasing Si concentration, the observed PL band is related to the silicon impurity in Al$_x$Ga$_{1-x}$N. The Si atom on the aluminum site Si$_{Al}$ is considered as a deep donor with a binding energy of 250 meV in AlN [9-11]. This allows estimating the $S_{em} h\nu_0$ value:
After that we obtain the acceptor ionization energy in AlN
\[ E_A = E_{g\text{AlN}} - E_{em} - E_D - S_{em} \nu_0 \approx 1.87 \text{eV}. \]  
Because of its ionization energy, possible candidates for a deep acceptor are the (0/-) transition level of the C\text{N} situated at about 1.88 eV [12] or the (2-/3-) transition level of the cation vacancy V\text{III} [13] above the valence-band maximum. It could be possible that Si\text{N} acts as an acceptor, however, the formation energy of Si\text{N} is so high that its formation is highly unlikely [14]. The carbon concentration in studied Al\text{x}Ga\text{1-x}N layers was about (1.0-5.0)×10\text{18} cm\text{−3} and reached a significant value of about 8×10\text{19} cm\text{−3} only in the AlN layer. The triple acceptor V\text{III} is known to be an effective electron compensator [13, 15], it’s formation energy decreases with the increase of the Fermi level, referenced to the valence-band maximum [13]. The intensity of the broadband PL rises with decrease of electron concentration due to compensation. Consequently, the strongest candidate for an acceptor is V\text{III}.

\[ S_{em} \nu_0 = 0.5(E_2 - E_{em} - E_D) \approx 0.8 \text{eV}. \] (5)

\[ E_A = E_{g\text{AlN}} - E_{em} - E_D - S_{em} \nu_0 \approx 1.87 \text{eV}. \] (6)

The decrease of x\text{Al} from 1 to 0.78 leads to decreasing difference in the energy position of E\text{1} and E\text{2} peaks from 1.06 eV to 0.5 eV. It’s known that Si on a cation site is considered as a shallow donor with a binding energy of 28-30 meV in GaN [16-18], and remains a shallow donor with a similar energy up to x\text{Al} ~ 0.85 with further deepening to 250 meV in AlN [10]. Assuming E\text{D} \approx 0.03 \text{eV}, we obtain S_{em} \nu_0 \approx 1.1 \text{eV} and E_A \approx 1.6 \text{eV} for Al\text{0.78}Ga\text{0.22}N. The last value is close to the value obtained from the temperature dependence of the PL intensity. So, the decrease of Al content leads to decrease of E_A and increase of S_{em} or \nu_0. From expression (3) and a weaker dependence of E_{em} on x\text{Al} than the one of E\text{D} (see figure 3), we obtain:
\[ \Delta(E_A + S_{em} \nu_0 + E_D) = \Delta(E_{g\text{AlN}} - E_{em}) \approx 1.1 \cdot \Delta x_{\text{Al}} \] (7)

5. Conclusions
The photoluminescence properties of the defect related emission attributed to the donor-acceptor transitions in heavily doped Al\text{Ga}_{1-x}N:Si layers with x\text{Al} > 0.46 have been investigated. The increase of Al content from x\text{Al} = 0.5 to x\text{Al} = 1 leads to the blue shift of the energy position of the PL band from the red-orange spectral range to the violet spectral range. The acceptor ionization energy was estimated to be 1.87 eV at x\text{Al} = 1, decrease of x\text{Al} leads to decrease of this value. The donor is supposed to be Si\text{III}, a possible candidate for an acceptor is the (2/-3-) transition level of the V\text{III}.

\[ \text{Figure 8. Configuration coordinate diagram describing optical band-to-band absorption and donor-acceptor pair emission at acceptor-like defects with strong electron-phonon coupling. The A' term corresponds to an occupied state of the defect, and the VB, CB, and D}^0 \text{ terms correspond to unfilled excited states of the defect where an electron is in the valence band, the conductivity band, and occupies the shallow donor state, respectively. The blue and green arrows indicate optical transitions during excitation and recombination, respectively.} \]
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