Properties of intensive defect-related band in photoluminescence spectra of heavily doped Al$_x$Ga$_{1-x}$N:Si layers

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Abstract. We report photoluminescence investigations of heavily doped Al$_x$Ga$_{1-x}$N:Si films grown by molecular beam epitaxy on sapphire substrates. The wide intensive defect-related band dominates in the photoluminescence spectra of Al$_x$Ga$_{1-x}$N:Si films with the Al content higher than 0.38 covering the whole visible spectral range. This band is attributed to donor-acceptor and free electron-acceptor transitions involving the same acceptor. 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 (0/-) transition level of the CN or (2/-3-) transition level of the V$_{Al}$.

1. Introduction

GaN and its alloys with AlN have emerged as perspective semiconductor materials with applications to laser sources for a blue-green spectral range. It was recently reported the finding of a blue-green superluminescence related to optical transitions through levels of defects in heavily doped Al$_x$Ga$_{1-x}$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$_x$Ga$_{1-x}$N:Si has not been given attention. The aim of this work was further study of the characteristics of photoluminescence of heavily doped Al$_x$Ga$_{1-x}$N:Si layers.

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 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 the 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 $x_{Al} = 0.62$, $F_{SiH4}$ was varied from 0 to 6 sccm. The silicon concentration in the layers was estimated about $5 \times 10^{19}$ cm$^{-3}$ at $F_{SiH4}=3$ sccm. The concentration of free electrons in the samples under study was determined by measuring the Hall effect in 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 at the room temperature using a continuous He-Cd laser with a photon energy $E_{ph} = 3.81$ eV and a pulsed 4$^{th}$ harmonic of Nd:YLF -laser ($E_{ph} = 4.71$ eV) for excitation. 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 belong to the first series at room temperature are shown in Figure 1. PL spectra of 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 that are considered the origin of the “yellow” band. The free-electron concentration in GaN structure was about $1.1 \times 10^{19}$ cm$^{-3}$. The rise of $x_{Al}$ leads to decrease of the intensity of band-edge PL and free-electron concentration (see the insert in Figure1) both 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 $x_{Al}>0.38$. The increase of Al content from $x_{Al}=0.47$ to $x_{Al}=1$ leads to the blue shift of the energy position of the PL band from red-orange spectral range ($E_{em}\approx 2.0$ eV) to violet spectral range ($E_{em}\approx 3.1$ nm).

![Figure 1. PL spectra of heavily doped Al$_x$Ga$_{1-x}$N layers grown at the constant silane flux $F_{SiH4} = 3$ sccm. Spectra were measured at room temperature. The insert shows dependence of the electron concentration on Al content.](image)

Figure 2 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:

$$E_{gAlGaN} = x_{Al}E_{gAlN} + (1-x_{Al})E_{gGaN} - x_{Al}(1-x_{Al})b = 1 \cdot x^2 + 1.59 \cdot x + 3.43$$  \hspace{1cm} (1)

here $E_{gAlN}=3.43$ eV [3] and $E_{gAlN}=6.015$ eV [4] are the GaN and AlN band gaps, respectively, and $b=1.0 \text{ eV} [5]$ 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 ($E_{em}\approx 2.4$ eV) increases with the rise of silicon concentration up to $F_{SiH4} = 4.5$ sccm then the PL intensity decrease with the further the rise of silicon concentration (see Figure 3). 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 highest silane flux were very weak conducting. That is an agreement with our previous results [6].

Figure 2. Dependences of band-gap ($E_g$) and the defect PL band energy position ($E_m$) on Al content.

Figure 3. Dependences of the intensity of the defect PL band in Al$_{0.62}$Ga$_{0.38}$N layers on silane concentration.

Figure 4 shows the PLE spectra of the Al$_{0.74}$Ga$_{0.26}$N and AlN ($x_{Al}$=1) samples at detection energy of 3.08 eV and 2.7 eV respectively and PL spectra measured at the excitation energy 4.71 eV at room temperature. The peak in the PLE spectra marked $E_1$ at 5.2 eV and 6.0 eV for the Al$_{0.74}$Ga$_{0.26}$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 expression (1). The second peak at $E_2$ eV at 4.7 eV and 4.94 eV for the Al$_{0.74}$Ga$_{0.26}$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 and PLE band $E_2$ peaks indicates a large Stock shift due to the strong electron-phonon coupling in a deep center. This results 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].

Figure 4. PLE and PL spectra of the Al$_{0.74}$Ga$_{0.26}$N and AlN ($x_{Al}$=1) samples at room temperature.

4. Discussion
The large Stock shift is typical for the centers with the 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 the strong electron-phonon coupling is shown in Figure 5. $S_{em}$ and $S_{ab}$ are the numbers of photon with energies $h\nu_g$ and $h\nu_e$ involved in the transitions whole optical energies are $E_m$ and $E_{ab}$, respectively. We assume that $S_{em} = S_{ab} = S$ and $h\nu_g = h\nu_e = h\nu_0$. The emission peak energy ($E_{em}$) is given by

$$E_{em} = E_g AlGaN - E_D - E_A - S_{em} h\nu_0$$  \hspace{1cm} (2)

here $S_{em}$ is the number of photons with the energy $h\nu_g$ involved in the transitions. The Stock shift in this model should be
The photoluminescence properties of the defect related emission attributed to the superposition of donor-acceptor and free electron-acceptor transitions in heavily doped AlGaN:Si layers with $x_{Al}>0.38$ have been investigated. The increase of Al content from $x_{Al}=0.47$ to $x_{Al}=1$ leads to the blue shift of the energy position of the PL band from red-orange spectral range to violet spectral range. The acceptor ionization energy was estimated to be 1.87 eV at $x_{Al}=1$, decrease of to $x_{Al}$ leads to decrease of this value. The donor is supposed to be Si$_{Al}$, while the origin of the acceptor is not completely clear. Possible candidates are (0/-) transition level of the C$_N$ or (2/-3-) transition level of the V$_{Al}$.

### 5. Conclusions

The photoluminescence properties of the defect related emission attributed to the superposition of donor-acceptor and free electron-acceptor transitions in heavily doped AlGaN:Si layers with $x_{Al}>0.38$ have been investigated. The increase of Al content from $x_{Al}=0.47$ to $x_{Al}=1$ leads to the blue shift of the energy position of the PL band from red-orange spectral range to violet spectral range. The acceptor ionization energy was estimated to be 1.87 eV at $x_{Al}=1$, decrease of to $x_{Al}$ leads to decrease of this value. The donor is supposed to be Si$_{Al}$, while the origin of the acceptor is not completely clear. Possible candidates are (0/-) transition level of the C$_N$ or (2/-3-) transition level of the V$_{Al}$.

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