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# Donor–acceptor pair emission via defects with strong electron–phonon coupling in heavily doped $AI_xGa_{1-x}N$ :Si layers with AI content x > 0.5

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We report the results of time-resolved and temperature-dependent stationary photoluminescence investigations of the defects responsible for emission in the visible spectral range in heavily silicon-doped  $Al_xGa_{1-x}N$  layers grown by molecular beam epitaxy on sapphire substrates. The emission band was attributed to donor–acceptor transitions. The transitions were described using the one-dimensional configuration coordinate model taking into account the high-doping regime. An increase in Al content from 0.56 to 1 leads to an increase in the acceptor ionization energy from 1.4 to 1.87 eV. The value of the Franck–Condon shift is about 1 eV at x = 0.56-0.74 and decreases to 0.8 eV at x > 0.74. The changes in the donor–acceptor transition energy parameters with increasing silicon concentration are discussed. © 2019 The Japan Society of Applied Physics

#### 1. Introduction

Aluminum nitride (AlN) and its alloys with gallium nitride (GaN), aluminum gallium nitride ( $Al_xGa_{1-x}N$ ), have emerged as important materials for high-power electronics and deep-UV light sources (light-emitting and laser diodes).<sup>1,2)</sup> The creation of effective light-emitting devices is impossible without doping the epitaxial layers. The formation of epitaxial *n*-GaN and Ga-rich Al<sub>x</sub>Ga<sub>1-x</sub>N layers using silicon (Si) as a donor does not cause significant difficulties and the electron concentration can be controllably increased to  $10^{20} \text{ cm}^{-3}$ . Similar behavior might be expected for Si doping in Al-rich Al<sub>x</sub>Ga<sub>1-x</sub>N and AlN. However, doping of Al<sub>x</sub>Ga<sub>1-x</sub>N becomes less efficient with an increase in Al content (x) higher than x > 0.6. The electron concentration becomes significantly lower than the concentration of silicon atoms due to two phenomena. First, Si is shallow donor in GaN assigned a wide range of ionization energies between 12 and 31 meV.<sup>7–12</sup>) It was shown that the ionization energy of Si is constant at x < 0.1 and increases with further increase of x up to x = 0.6.<sup>12</sup>) Si is a well-behaved shallow donor at x < 0.6 but undergoes a transition to deep DX-like centers for higher compositions.<sup>13,14</sup>) Experimentally, the DX-like center has been assigned a wide range of activation energies between 60 and 345 meV.<sup>15-22)</sup> The second issue is the self-compensation of Si donors. The electron concentration increases with increasing Si concentration in the low-doping regime but the electron concentration actually decreases with additional Si in the high-doping regime. The increase and subsequent decrease in carrier concentration as a function of Si concentration is often referred to as a compensation knee. This effect has been attributed to many factors, including the formation of cation vacancies,<sup>16,23)</sup> cation vacancy–oxygen complexes<sup>24)</sup> and cation vacancy-silicon complexes.<sup>25)</sup>

One of the side effects of self-compensation is the appearance of intense broadband luminescence in the visible spectral range that was observed in heavily doped  $Al_xGa_{1-x}N$ :Si epitaxial layers with x > 0.5.<sup>26)</sup> Further investigations showed that this emission band displays stimulated emission properties under electron beam (EB) excitation.<sup>27)</sup> This emission band demonstrates a high quantum yield that reaches 0.79 at x = 0.74.<sup>28)</sup> Amplified spontaneous emission

propagating near the critical angle of incidence along a zigzag path under total internal reflection conditions at the interfaces of the waveguide has been obtained under optical pumping. The optical measured gains are equal to 58 cm<sup>-1</sup> for x = 0.65 at 510 nm and 20 cm<sup>-1</sup> for x = 0.74 at  $\lambda = 528$  nm.<sup>28</sup>) As a result, coherent and non-coherent light-emitting structures from blue-green to far-red parts of the spectrum, including structures with a broad emission band in a single emitting element and tunable lasers in a large wavelength range, can be created. Moreover, the wideband emission spectrum of heavily doped Al<sub>x</sub>Ga<sub>1-x</sub>N samples is promising for the development of lasers with ultra-short pulses of femtosecond duration.

It was previously suggested that this broadband luminescence is connected with donor–acceptor (DA) and free electron–acceptor (eA) transitions involving the same acceptor.<sup>29–31)</sup> The donor is likely to be silicon. The acceptor might be a cation vacancy (V<sub>III</sub>) or its complexes with shallow donors. However, the energy structure of recombination centers has not been completely described. The ratio between DA and eA transitions is unclear. The insufficiency of the configuration coordinate model for heavy  $Al_xGa_{1-x}N$ doping has been demonstrated. This paper presents new results on the recombination mechanism and the energy structure of recombination centers in heavily doped  $Al_xGa_{1-x}N$ :Si epitaxial layers with x > 0.5 studied by photoluminescence (PL) spectroscopy.

#### 2. Experimental methods

Al<sub>x</sub>Ga<sub>1-x</sub>N:Si layers were grown by molecular beam epitaxy using ammonia as a source of active nitrogen on 400- $\mu$ mthick nitridated sapphire (0001) substrates with an AlN buffer layer about 300 nm thick. The thickness of the Al<sub>x</sub>Ga<sub>1-x</sub>N layers was 1.2  $\mu$ m. The Al content in the layers was set by the Al-to-Ga flux ratio during the growth. A mix of 0.7% silane (SiH<sub>4</sub>) with nitrogen (N<sub>2</sub>) was used as a source of Si atoms. The first series of studied layers was grown at a constant SiH<sub>4</sub> flux of 3 sccm and x was varied from 0 to 1. The second series of studied layers was grown at a constant x = 0.62 and the SiH<sub>4</sub> flux was varied from 0 to 6 sccm.

The silicon concentration in the layers was estimated by secondary-ion mass spectrometry (SIMS), using a IMS7f

(CAMECA) setup with primary Cs<sup>+</sup> ions. The sample charge was neutralized by electron beam (EB) irradiation of the samples. The concentration of free electrons ( $n_e$ ) 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. The Si concentration ( $N_{si}$ ) in the layers has a spread of (1.1–2.0) × 10<sup>20</sup> cm<sup>-3</sup> for the first series and linearly increases from 2.0 × 10<sup>16</sup> cm<sup>-3</sup> (background value due to residual Si in the growth camera) to  $3.0 \times 10^{20}$  cm<sup>-3</sup> with the increase of SiH<sub>4</sub> flux from 0 to 6 sccm for the second series.

Measurements of temperature-dependent stationary PL were conducted in a wide temperature range of 5-1100 K using a He:Cd laser (photon energy  $E_{\rm ph} = 3.81 \text{ eV}$ ) and a pulsed fourth harmonic of a Nd:YLF laser ( $E_{ph} = 4.71 \text{ eV}$ ) for excitation. The studied samples were mounted in a helium closed-circuit refrigerator for measurements at low temperatures below 300 K and in a home-made vacuum camera for measurements at high temperatures above 300 K. PL was dispersed using a double 1 m monochromator equipped with a cooled photomultiplier operating in the photon counting mode. The data obtained at low and high temperatures were crosslinked at room temperature. 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. A pulsed fourth harmonic of a Nd:YAG laser ( $E_{\rm ph} = 4.66 \, {\rm eV}$ ) was used for the excitation of non-stationary PL collected in the time range of 0–1000  $\mu$ s at room temperature.

#### 3. Results

The room-temperature PL and PLE spectra of heavily silicon doped  $Al_xGa_{1-x}N$  layers for the first series are shown in Fig. 1(a). The PL spectra were measured in the visible spectral range and comprise only one broad band with peak marked as  $E_{em}$ . The excitation energy was 4.71 eV. The PLE spectra were measured at detection energy  $E_{em}$  in the UV spectral range and comprise two peaks. The main peak marked  $E_{bb}$  corresponds to band-to-band transitions in  $Al_xGa_{1-x}N$  layers because its energy position close to the band gap,  $E_{gAlGaN}$ , of the  $Al_xGa_{1-x}N$  layers was estimated using the Vegard law as:

$$E_{gAIGaN} = bx^{2} + (E_{gAIN} - E_{gGaN} - b)x + E_{gGaN}$$
  
= 1.0x<sup>2</sup> + 1.59x + 3.43, (1)

where  $E_{gGaN} = 3.43 \text{ eV}^{32}$  and  $E_{gAIN} = 6.015 \text{ eV}^{33}$  are the GaN and AlN band gaps, respectively, and  $b = 1.0 \text{ eV}^{34}$  is the bowing parameter. The edge of the optical transmission spectra of these samples matches with  $E_{gAIGaN}$ . The second peak marked  $E_{ab}$  is attributed to acceptor-to-band transitions. Figure 2(a) shows the dependences of  $E_{gAIGaN}$ ,  $E_{bb}$ ,  $E_{ab}$  and  $E_{em}$  on *x*.  $E_{em}$  and  $E_{ab}$  blue shift with an increase in *x* more slowly than  $E_g$ , revealing a deepening of the acceptor energy level. The large Stock shift between  $E_{em}$  and  $E_{ab}$  is typical for deep centers with strong electron–phonon coupling. It should be noted that the Stock shift has a constant value of about 2.0 eV at x = 0.56–0.74 but decreases to 1.85 eV at x > 0.74.

Figure 2 shows PL decay curves measured in the maximum of the PL band (2.2 eV) of the Al<sub>0.56</sub>Ga<sub>0.44</sub>N layer and a reference Al<sub>2</sub>O<sub>3</sub> layer. It is evident that, in this time range,



**Fig. 1.** (Color online) (a) Room-temperature PL and PLE spectra of heavily doped  $Al_xGa_{1-x}N$ :Si layers with variable x = 0.54, 0.74 and 1 grown with a constant Si concentration of  $(1.1-2.0) \times 10^{20}$  cm<sup>-3</sup>.  $E_{\rm em}$  is peak energy of the PL band,  $E_{\rm bb}$  and  $E_{\rm ab}$  are the main peak and the second peak energy, respectively, in the PLE spectra. (b) Dependence of  $E_{\rm bb}$ ,  $E_{\rm ab}$ ,  $E_{\rm em}$  and the Al<sub>x</sub>Ga<sub>1-x</sub>N band gap  $E_{\rm gAlGaN}$  on Al content.

the decay curve for the Al<sub>0.56</sub>Ga<sub>0.44</sub>N layer contains two components: at first the PL intensity decays exponentially with characteristic decay times ( $\tau$ ) of about 20  $\mu$ s and then the PL intensity decays slowly following the power law

$$I(t) \sim t^{-\gamma} \tag{2}$$

where  $\gamma = 0.95$ . The decay curve for the Al<sub>2</sub>O<sub>3</sub> layer contains only exponential components with the same  $\tau = 20 \,\mu s$ , therefore this decay time is hardware time. Slow nonexponential decay of the PL intensity was observed previously for heavily doped Al<sub>0.62</sub>Ga<sub>0.38</sub>N layers<sup>29</sup> but the value of the exponent was much lower at  $\gamma = 0.4$ . This indicates that the decay rate of the PL intensity decreases with increasing Al content.

Figure 3(a) shows the room-temperature PL spectra of Al<sub>0.62</sub>Ga<sub>0.38</sub>N layers measured in the visible spectral range for the second series. The excitation energy was 3.81 eV. The PL spectrum of the undoped layer contains two weak and broad bands with maxima near 2.0 eV and 2.6 eV. These bands are not related to Si and are attributed to another residual defect in Al<sub>x</sub>Ga<sub>1-x</sub>N. The PL spectra of layers with  $N_{\rm Si} = 5 \times 10^{19} \,{\rm cm}^{-3}$  and higher silicon concentrations



**Fig. 2.** (Color online) PL decay curves measured in the maximum of the PL band (2.2 eV) of the Al<sub>0.56</sub>Ga<sub>0.44</sub>N layer and a reference Al<sub>2</sub>O<sub>3</sub> layer at 300 K in the time range 0–1000  $\mu$ s.



**Fig. 3.** (Color online) (a) Room-temperature PL spectra of the  $Al_{0.62}Ga_{0.38}N$ :Si layers grown with variable Si concentration from background (the undoped sample) to  $3.0 \times 10^{20}$  cm<sup>-3</sup>. (b) Dependence of the PL intensity and electron concentration in  $Al_xGa_{1-x}N$ :Si layers with constant x = 0.62 on Si concentration.

comprise only the intensive Si-related band with maximum  $E_{\rm em} \approx 2.4 \,{\rm eV}$ . The PL peak energy and the PL bandwidth do not change significantly with the increase of  $N_{\rm Si}$ . The increase of  $N_{\rm Si}$  up to  $1.5 \times 10^{20} \,{\rm cm}^{-3}$  leads to a strong increase in the PL intensity, then the PL intensity saturates with further increase in  $N_{\rm Si}$ . This dependence of the PL intensity is correlated with the compensation knee behavior of  $n_{\rm e}$  [see Fig. 3(b)]. In the low-



**Fig. 4.** (Color online) Temperature dependence of the PL intensity in Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers grown with variable Si concentration  $N_{\rm Si} = 5 \times 10^{19} \, {\rm cm}^{-3}$ ,  $N_{\rm Si} = 1.1 \times 10^{20} \, {\rm cm}^{-3}$  and  $N_{\rm Si} = 1.5 \times 10^{20} \, {\rm cm}^{-3}$ .

doping regime the concentration of compensation centers is low, therefore  $n_e$  is high and the PL intensity is low. In the highdoping regime the concentration of compensation centers is high, therefore  $n_e$  is low and the PL intensity is high. This correlation confirms that the acceptors involved in the radiative transitions are the Si compensation centers.

Figure 4 shows the temperature dependences of PL intensity in the Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers grown with the different Si concentrations. The PL intensity of the layer with  $N_{\rm Si} = 5 \times 10^{19} \,{\rm cm}^{-3}$  does not change significantly with increase of temperature up to 300 K and decreases very weakly at higher temperatures. The PL intensity of more heavily silicon-doped layers increases with increasing temperature from 5 to 270–300 K, while a further rise in temperature causes PL quenching. The value of the temperature enhancement increases from 25% to 520% with increase of  $N_{\rm Si}$  from  $1.1 \times 10^{20} \,{\rm cm}^{-3}$  to just  $1.5 \times 10^{20} \,{\rm cm}^{-3}$ . The dependence of the PL intensity on temperature is approximated by the expression

$$I(T) = A \frac{1 + B_0 \exp\left(-\frac{E_0}{kT}\right)}{1 + B_1 \exp\left(-\frac{E_1}{kT}\right) + B_2 \exp\left(-\frac{E_2}{kT}\right)},$$
(3)

where  $E_0$ ,  $E_1$  and  $E_2$  are activation energies and A,  $B_0$ ,  $B_1$  and  $B_2$  are constants. The exponential expression in the numerator and the two-exponential expression in the denominator describe well the enhancement and quenching of the PL intensity with temperature. The activation energy  $E_2$  is considered to correspond to the acceptor ionization energy and was taken as equal to 1.4 eV.<sup>31)</sup>

Figure 5 shows the temperature dependences of the PL band energy position  $E_{\rm em}$  in Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers with different Si concentrations.  $E_{\rm em}$  was constant in the layers with  $N_{\rm Si} = 5 \times 10^{19}$  cm<sup>-3</sup> and  $N_{\rm Si} = 1.1 \times 10^{20}$  cm<sup>-3</sup> up to 100 K. Further increase in temperature up to 1000 K causes blue shifting of the PL band maximum, following a linear law  $\Delta E_{\rm em} = \xi \times kT$ . This linear coefficient  $\xi$  lies in the range of 1.1–1.4.  $E_{\rm em}$  in the layer  $N_{\rm Si} = 1.5 \times 10^{20}$  cm<sup>-3</sup> increases rapidly ( $\xi = 3.2$ ) with increasing temperature up to 200 K with a further slow increase with temperature ( $\xi = 0.9$ ) up to 1000 K. An increase in temperature higher than 1000 K does not change  $E_{\rm em}$  in any layer.



**Fig. 5.** (Color online) Temperature dependence of the PL band energy position in  $Al_{0.62}Ga_{0.38}$ N:Si layers grown with variable Si concentration  $N_{\rm Si} = 5 \times 10^{19} \text{ cm}^{-3}$ ,  $N_{\rm Si} = 1.1 \times 10^{20} \text{ cm}^{-3}$  and  $N_{\rm Si} = 1.5 \times 10^{20} \text{ cm}^{-3}$ .

Figure 6 shows temperature dependences of the PL bandwidth in the  $Al_{0.62}Ga_{0.38}N$ :Si layers grown with different Si concentrations. The PL band broadens with increasing temperature. The temperature dependences of the PL bandwidth were similar for all Si concentrations. At temperatures below 100 K the PL bandwidth is constant. The temperature broadening of the PL band at higher temperatures follows a linear law and increases superlinearly with increase of temperature above 1000 K.

#### 4. Discussion

When discussing DA recombination, the following features of recombination centers should be taken into account.

Firstly, broad PL bands with a large Stock shift are typical for the recombination of carriers through acceptors with strong electron–phonon coupling. The one-dimensional configuration coordinate (CC) model well describes the recombination of carriers through such acceptors.<sup>34,35</sup> The CC diagram describing optical absorption and emission at defects with strong electron–phonon coupling is shown in Fig. 7. Adiabatic potentials in this diagram represent the total potential energy (*E*) including the crystal lattice, the electron and the defect in the crystal lattice as a function of the



**Fig. 6.** (Color online) Temperature dependence of the PL bandwidth in the Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers grown with variable Si concentration  $N_{\rm Si} = 5 \times 10^{19} \,{\rm cm}^{-3}$ ,  $N_{\rm Si} = 1.1 \times 10^{20} \,{\rm cm}^{-3}$  and  $N_{\rm Si} = 1.5 \times 10^{20} \,{\rm cm}^{-3}$ .



**Fig. 7.** (Color online) Configuration coordinate diagram describing optical band-to-band absorption and donor–acceptor pair emission at acceptor-like defects with strong electron–phonon coupling. The term  $A^-$  corresponds to an occupied state of the defect, and the terms VB, CB and  $D^0$  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.

configuration coordinate (Q). The term A<sup>-</sup> corresponds to an occupied (ground) state of the defect, and the terms VB, CB and  $D^0$  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 equilibrium positions of the ground and excited states are displaced according to the strength of the electron-phonon coupling. Transitions from the ground state to the excited state during absorption, and vice versa at emission, are followed by the atomic relaxation of the crystal lattice, i.e. emission of phonons with energies  $h\nu_{\rm g}$  and  $h\nu_{\rm e}$  in the ground and excited states, respectively. The measure of the electronphonon coupling is the Huang–Rhys factor, with  $S_{ab}$  and  $S_{em}$ representing the mean number of emitted phonons for photon absorption and emission processes. The amount of energy lost is the Franck–Condon shift,  $d^{e}_{FC}$  and  $d^{g}_{FC}$ , in the excited and ground states, respectively:

$$d_{FC}^e = S_{em} \cdot h\nu_e, \tag{4}$$

$$d_{\rm FC}^{\rm g} = S_{ab} \cdot h\nu_{g}.$$
 (5)

The absorption and emission peak energies are given by

$$E_{\rm ab} = E_{\rm gAlGaN} - E_{\rm A} + d_{\rm FC}^{\rm e},\tag{6}$$

$$E_{\rm em} = E_{\rm gAlGaN} - E_{\rm D} - E_{\rm A} - d_{\rm FC}^{\rm g},\tag{7}$$

where  $E_{\rm D}$  and  $E_{\rm A}$  correspond to donor and acceptor ionization energies, respectively. We assume that the Franck– Condon shift is the same for absorption and emission  $(d^{\rm e}_{\rm FC} = d^{\rm g}_{\rm FC} = d_{\rm FC})$ . Equations (6) and (7) allow us to estimate  $d_{\rm FC}$  and  $E_{\rm A}$  from obtained values of  $E_{\rm ab}$  and  $E_{\rm em}$ :

$$d_{\rm FC} = 0.5(E_{\rm ab} - E_{\rm em} - E_{\rm D}),\tag{8}$$

$$E_{\rm A} = E_{\rm gAlGaN} - E_{\rm ab} + d_{\rm FC}.$$
 (9)

The Si donor energy was assumed as  $E_{\rm D} = 250 \text{ meV}$ in AlN<sup>17,19,21</sup> and  $E_{\rm D} = 50 \text{ meV}$  in Al<sub>x</sub>Ga<sub>1-x</sub>N with x = 0.56-0.74.<sup>12</sup> Figure 8 shows the dependences of  $d_{\rm FC}$  and  $E_{\rm A}$  on the Al content. The increase in Al content from 0.56 to 1



**Fig. 8.** (Color online) Dependences of the acceptor ionization energy  $E_A$  and the Franck–Condon shift  $d^e_{FC}$  on Al content.

leads to an increase in  $E_A$  from 1.4 to 1.87 eV. The value of  $d_{FC}$  is about 1 eV at x = 0.56-0.74 and decreases at x > 0.74-0.8 eV.

Secondarily, the donor concentration is high and the assumption of isolated donors ceases to be true. Acceptance of Eqs. (8) and (9) is not obvious for heavily doped  $Al_xGa_{1-x}N$  because the donor concentration is high. Electrons are not localized on single donors in heavily doped semiconductors. The criterion for heavy doping is expressed by<sup>36)</sup>

$$N_{\rm Si}a_{\rm B}^3 = 1 \tag{10}$$

where  $a_{\rm B}$  is the Bohr radius of the donor state. Within the framework of the hydrogen atom model  $a_{\rm B}$  can be estimated as<sup>37)</sup>

$$a_{\rm B} = a_0 \epsilon \frac{m_0}{m_{\rm e}} \tag{11}$$

where  $a_0$  is the Bohr radius of an electron in a hydrogen atom,  $\epsilon$ is the dielectric constant,  $m_0$  is the mass of a free electron, and  $m_{\rm e}$  is the effective mass of an electron. By using  $\epsilon = 9.5^{38}$ and  $m_e = 0.22m_0^{39}$  for GaN, Eq. (10) is satisfied at  $N_{\rm Si} \approx 7.5 \times 10^{19} \, {\rm cm}^{-3}$ . This means that the impurity band merges with the conduction band and electrons are not localized at donor levels at  $N_{\rm Si} > 10^{20} \,{\rm cm}^{-3}$ . In this case semiconductors are degenerate and the recombination radiation in the spectral maximum region is determined by electron transitions from levels lying near the Fermi level, i.e. far into the conduction band, to holes localized at the acceptor levels and at deep levels of the tail of the density of states of the valence band, as well as with free holes. Since the concentration of compensation centers is low the recombination of free electrons with free holes dominates. On the contrary, silicon is a deep donor in AlN and forms an impurity band below the conduction band; the concentration of compensation centers is high and DA recombination is dominant.  $E_{\rm D}$  increases with increasing Al content at x > 0.5<sup>12,16</sup> This means that  $a_{\rm B}$  should be lower at x = 0.56-0.74 than in GaN. By using  $\epsilon = 8.5^{40}$  and  $m_e = 0.33m_0^{41}$  for AlN and the Vegard law for  $Al_{0.5}Ga_{0.5}N$  equation (11) is satisfied at  $N_{\rm Si} \approx 1.5 \times 10^{20} \, {\rm cm}^{-3}$ . Al<sub>x</sub>Ga<sub>1-x</sub>N with x = 0.56-0.74 is a heavily compensated semiconductor, unlike GaN.



**Fig. 9.** (Color online) Scheme representing possible radiative and nonradiative transitions in cases of weak (a) and strong (b) doping regimes. The VB, CB, A, D and T terms correspond to the valence band, the conductivity band, the donors, the acceptors and the non-radiative centers, respectively. The average depth of the distorted region in the strong doping regime is marked  $\Gamma$ . The green arrows indicate DA transitions; the black arrows indicate carrier capture at centers, donors and acceptors and the non-radiative centers.

Moreover, PL intensity decay that follows the power law is a well-known characteristic feature of the DA recombination mechanism.<sup>42)</sup> Therefore DA recombination is also dominant in PL at  $N_{\rm Si} \approx 1.5 \times 10^{20} \, {\rm cm}^{-3}$ .

Despite the fact that the criterion of heavy doping is not formally satisfied, fluctuations of Si atom concentration affect the PL characteristics. In particular, fluctuations of Si atom concentration explain the non-monotonic behavior of the PL temperature dependence. Figure 9 shows possible radiative and non-radiative transitions for weak and strong doping regimes. In the low-doping regime the band edges are flat. Free electrons can be captured by donors with following DA transitions or non-radiative centers. Temperature affects the ratio between radiative and non-radiative recombination. When the temperature is low enough, radiative recombination is dominant because the non-radiative recombination process is significantly suppressed. In the high-temperature range, the non-radiative process dominates radiative recombination. So it is reasonable that the intensity decreases monotonously with increase in temperature. The activation energies of high-temperature PL quenching  $E_1$  and  $E_2$ correspond to the ionization energies of recombination centers.

In the high-doping regime, the band edges and the donor and acceptor levels are distorted due to the formation of potential wells in the regions of Si concentration fluctuations and shrinking of effective  $E_{gAlGaN}$ . The average depth of the distorted region is marked  $\Gamma$ . At low temperatures electrons are localized in the lowest donor states in regions of Si concentration fluctuations. Holes cannot approach the donors closely and become trapped in the acceptors nearest to them. Therefore, a localized electron can only recombine with holes located on distant acceptors, and the probability of such a process is small. As a result, the thermal emission of electrons from the wells prevails over their recombination even at low temperatures as temperature decreases. A similar phenomenon has been observed in Si nanocrystals.43-45) Carriers are localized at closer states with increasing temperature, and the probability of DA recombination increases. The activation energy  $E_0$  might correspond to a difference in energies between donor states corresponding to distant and close DA pairs. High-temperature quenching of the PL is explained by the thermal destruction of donor concentration fluctuations as well as the release of holes from acceptors into the valence band. The activation energy  $E_1$  might correspond to  $\Gamma + E_D$ . The activation energy  $E_2$  remains the same as in low-doping regime.

The above model taking into account the formation of potential wells in the regions of Si concentration fluctuations explains PL intensity enhancement with increase of temperature up to 300 K and the high value of the activation energy  $E_1$ . The increase of  $N_{\rm Si}$  from  $1.1 \times 10^{20} \,{\rm cm}^{-3}$  to  $1.5 \times 10^{20} \,{\rm cm}^{-3}$  leads to an increase in the number of distorted regions and the deepening of  $\Gamma$  from 70 to 125 meV. Unfortunately, high-temperature PL quenching of the layer with  $N_{\rm Si} = 5 \times 10^{19} \,{\rm cm}^{-3}$  does not reveal the expected energy  $E_1 = 50 \,{\rm meV}$ .

Also, internal quenching of luminescence is possible within the CC model. 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, non-radiative transitions occur from the excited state to the ground state. According to Fig. 7 the classical barrier for a transition from the upper curve to the lower potential energy curve, determined as the difference between the intersection point of the two curves and the minimum energy of the excited state, is given by

$$E_{\rm b}^{\rm em} = \frac{(E_{\rm gAIGaN} - E_{\rm D} - E_{\rm A} - d_{\rm FC})^2}{4d_{\rm FC}} = \frac{E_{\rm em}^2}{4d_{\rm FC}}.$$
 (12)

The obtained value  $E_b^{em} = 1.44 \text{ eV}$  is close to  $E_A$  and therefore does not appear as a separate term in the denominator in Eq. (3).

Accounting for the formation of potential wells in regions of Si concentration fluctuations allows us to explain the blue shift of the maximum of the PL band and the broadening of the PL band with increasing temperature. According to the CC model the temperature broadening of the PL band can be described by the expression<sup>46)</sup>

$$W(T) = W(0)\sqrt{\coth\left(\frac{h\nu_{\rm e}}{2kT}\right)},\tag{13}$$

where W(0) is the bandwidth at T = 0. At high temperatures, the bandwidth should be proportional to  $T^{1/2}$  but it follows a linear law and increases superlinearly with the increase of temperature above 1000 K because of additional broadening of the bandwidth due to fluctuations in Si concentration. Unfortunately, Eq. (4) is only suitable at low temperatures. The CC model predicts the following expression for a temperature-related shift:<sup>47)</sup>

$$\Delta E_{\rm CC} = \left[\frac{v_{\rm g}^2 - v_{\rm e}^2}{v_{\rm e}^2} + \frac{8v_{\rm e}^4}{v_{\rm g}^2(v_{\rm g}^2 + v_{\rm e}^2)}\right] \left(\frac{E_{\rm ab}(0) - E_{\rm em}(0)}{E_{\rm em}(0)}\right) kT$$
(14)

where  $E_{ab}(0)$  and  $E_{em}(0)$  are, respectively, the absorption and emission energies at T = 0. Figure 9 shows the temperature dependence of the PL band energy position shift  $\Delta E_{cm}$  in Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers with  $N_{Si} = 1.1 \times 10^{20} \text{ cm}^{-3}$ , the calculated  $\Delta E_{CC}$  and the calculated thermal band gap reduction  $\Delta E_{gAlGaN}$ . It is evident that  $\Delta E_{CC}$  is much less than



**Fig. 10.** (Color online) The temperature dependence of the PL band energy position shift  $\Delta E_{\rm em}$  in Al<sub>0.62</sub>Ga<sub>0.38</sub>N:Si layers with  $N_{\rm Si} = 1.1 \times 10^{20}$  cm<sup>-3</sup>, the calculated temperature-related blue shift  $\Delta E_{\rm CC}$  predicted by the configuration coordinate model and the calculated thermal band gap reduction  $\Delta E_{\rm gAlGaN}$ .

 $\Delta E_{\rm gAIGaN}$  and another contribution to the temperature shift of the PL band should be taken into account. The nature of the extra blue shift can be similar to the usual DA recombination blue shift: at high temperatures holes occupy the acceptors near donor concentration fluctuations so the nearest "DA" pairs are more strongly involved in the total recombination process, thus the energy position of the PL band is shifted to high energies.

### 5. Conclusions

The results on the recombination mechanism and the energy structure of recombination centers in heavily doped  $Al_xGa_{1-x}N$ :Si epitaxial layers with x > 0.5 studied by photoluminescence spectroscopy are presented. The PL band was attributed to the donor-acceptor transitions at silicon concentrations higher than  $10^{20}$  cm<sup>-3</sup>. The acceptors responsible for the transitions are the Si compensation centers. An increase in Al content from 0.56 to 1 leads to an increase in acceptor ionization energy from 1.4 to 1.87 eV. The value of the Franck–Condon shift is about 1 eV at x = 0.56-0.74 and decreases at x > 0.74-0.8 eV. The criterion of heavy doping is not satisfied for silicon in  $Al_xGa_{1-x}N$  with silicon concentrations higher than  $10^{20}$  cm<sup>-3</sup> but due to PL properties the  $Al_xGa_{1-x}N$  layers are revealed as heavily doped semiconductors.

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