Gaussian impurity bands in GaN and weakening of carrier confinement in InGaN/GaN quantum wells

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Abstract. Gaussian impurity bands in GaN responsible for intracenter optical absorption and photoluminescence, give rise to defect-assisted carrier tunneling (hopping) through the barriers in the pn nanostructures with InGaN/GaN quantum wells (QWs). The tunneling injection of majority carriers into the QW results in the current humps and in rapid increase in the radiative recombination efficiency at low enough forward bias. As the bias increases, the carrier confinement in the QW weakens, leading to tunneling injection of minority carriers into the barriers, which results in the emission efficiency saturation and droop.

I. Introduction
Gallium nitride is the most promising wide-band-gap semiconductor ($E_G=3.42$ eV at 300 K) for the energy-efficient solid-state lighting. High efficiency of the light emitting nanostructures based on GaN has been achieved in the presence of the high density of extended and point defects which is far in excess of what could be tolerated in any working devices based on the more narrow-band-gap materials such as GaAs or GaP [1]. The controversial and complex role of the defects in the electrical and optical properties of the nanostructures based on GaN is not fully understood. Further improvements in device performance hinge on an in-depth understanding of deep-level point defects.

2. Experimental
Photoluminescence (PL) and optical transmission measurements were performed at room temperature for the bulk 200 µm thick n-type GaN samples grown by the hydride vapour phase epitaxy (HVPE) technology on TiO$_2$ and Al$_2$O$_3$ substrates [2] using an Avantes spectrometer. A He–Cd laser ($\lambda =325$ nm) with the power density of 1 W/cm$^2$ was used as an excitation source. The optical absorption spectra were measured over the spectral range of 1.1-3.5 eV photon energy.

With the purpose of the tunneling spectroscopy of deep centers and their effect on the radiative recombination efficiency, the dependences of the forward current, $I(V_j)$, and light intensity, $L(V_j)$, on the junction forward bias for the pn nanostructures with the single InGaAs/GaAs quantum wells in the commercially available light-emitting diodes of Nichia company are studied. The junction bias was determined as $V_j = V - I r_s$, taking into account the voltage drop on the series resistance $r_s = dV/dI$ at nominal current 20 mA.

3. Results and discussion
3.1. Intracenter optical absorption and photoluminescence in GaN
High density of the deep level point defects and the continous distribution of defect states in the GaN forbidden gap have been revealed by the various optical measurements [3-9]. The deep-level point defects
in GaN are usually characterized by photoluminescence measurements [3,9], which give information about defect states involved in radiative recombination processes and their manifestation in the wide PL bands in visible and near UV spectral region, and thus cannot provide a full picture of the density of states distribution.

The optical absorption [5-7], the photocapacitance [8] and the photoconductance [4] spectra of n-type GaN often contain a few spectral steps at threshold photon energies in the ranges from 0.6 to 3.8 eV. The optical threshold energy of 2.1 eV was tentatively attributed to the commonly observed yellow (YL) defect–associated PL band centered near 2.2 eV by combining PL and transmission measurements [6]. However, a vast number of controversial results in the literature, a strong dependence of the experimental spectra on the growth technology and conditions, on the type and level of doping, on GaN epilayer thickness, and on the substrate material makes particular difficult to determine the main characteristic features in the spectra that may help to identify the electrically active defects and to understand their effect on the electronic transport and the efficiency in GaN-based devices.

Figure 1(a)-(c) presents the PL spectra observed for three representative 200 µm thick n-type GaN layers grown by HVPE on TiO$_2$ (samples A and B) and Al$_2$O$_3$ substrates (sample C).

The room-temperature PL spectrum of sample A contains the commonly observed YL PL Gaussian band centred at 2.2 eV (figure 1 (a)). The green (GL) PL band peaking at $h\nu_{GL}=2.5$ eV and the red (RL) PL band peaking at $h\nu_{RL}=1.85$ eV could be seen as shoulders of the YL band. The red PL band exhibit a low-energy tail that extends to $h\nu_{RL}=1.6$ eV. In addition, a near UV (UVL PL) band peaking at $h\nu_{UVL}=3.25$ eV and weak blue (BL) PL peaking at $h\nu_{BL}=2.85$ eV appeared in PL spectra.

The sample A exhibit highest optical density in near IR, where the asymmetric absorbance peak with the steep low-energy side is observed at $h\nu=1.25$ eV. In the visible part of the spectrum the wide absorption maximum is observed in the energy range $h\nu=2.1-3.25$ eV, which may be deconvolved in four Gaussian bands with the full width at half maximum FWHM=0.4 eV and the optical threshold energies equal to the peak energies of the RL, YL, GL and BL bands. Such shift to a higher photon energy of the absorption peaks relatively the PL peaks implies the intracenter optical transitions mechanism of absorption and is typical for the centers, which absorbe in the visible spectral regions (for the color centers). The optical density decreases with photon energy achieving minimum at $h\nu=3.25$ eV, then again rapidly starts to increase with energy at the peak energy of UVL PL band, achieving in the near UV at $h\nu=3.36$ eV the same value as the optical density in near IR at $h\nu=1.25$ eV resulting in the window of light transmission with absorbance minimum at $h\nu=2.1$ eV.

![Figure 1](image.png)

**Figure 1.** Photoluminescence and absorption spectra of the bulk 200 µm thick n-type GaN layers grown by HVPE on TiO$_2$ (a), (b) and Al$_2$O$_3$ (c) substrates.

The sample B (figure 1 (b)) exhibited the weaker YL PL compared with that of the sample A and the relative stronger intensities of the RL PL band and of its deep absorption tail that extends to infrared. The intensity of the UV PL band becomes stronger. In the sample C with GaN layer grown on an Al$_2$O$_3$ substrate the
UV PL band, the GL-shoulder on YL-peak and RL-tail of RL-band disappear (figure 1 (c)). The PL intensity in the green–blueish and near UV spectral ranges $h\nu=2.6-3.25$ eV decreases with the photon energy.

The optical absorption in the samples B and C increases, most stronger at the high energy range and at RL-tail of the RL PL band, while the absorption at the maximum of IR-peak of $h\nu_p=1.25$ eV is saturated. The absorption minimum at $h\nu=2.1$ eV in the sample B shifts to $h\nu=1.5$ eV in the sample C, because of strong increase of the adsorption at RL-tail of RL-band and at the high energy range.

3.2. Optical density of n- and p-GaN layers and hopping in n- and p-barriers to the QW

Large subband optical absorption coefficient in GaN, which reaches values of $10^{2}-10^{3}$ cm$^{-1}$ in the visible and near-UV spectral ranges, implies the high energy density of states in the forbidden gap introduced by the absorption centers with total concentration of $10^{17}-10^{18}$ cm$^{-3}$ according to the known Smakula–Dexter formula. The impurity bands in the pn junctions in the heavily doped materials give rise to an increase in tunneling transparency of the potential barrier when the quasi–Fermi level achieves the impurity band, which is manifested in a conduction hump in I-V curve. Under these circumstances, dependence of the current on the pn junction forward bias provides a tunneling spectroscopy of the localisation energy and density of states in the impurity bands.

Since the PL spectra of heavily-doped p-GaN and n-GaN layers that were used as injecting holes and electrons in Nichia LEDs with the single InGaN/GaN QW have been well studied [1] and samples A and B show the same main bands in their PL spectra, it is interesting to compare forward bias current and light intensity behavior in these LEDs with the absorption spectra in samples A and B.

Shown in figure 2 the dependences of the forward currents $I$ and the light intensities $L$ on the junction voltage $V_j$ for the pn nanostructures with the single InGaN/GaN QW, emitting light in the blue and near-ultraviolet (NUV) regions of the spectrum with peak energies of $h\nu_p=2.7$ and 3.21 eV, respectively, are typical of GaN based light-emitting diodes (LEDs). The pn structures exhibit humps in the portions of $I(V_j)$ and $L(V_j)$ characteristics near the threshold voltages of light detection $V_{th}$. Since the light intensity $L(V_j)$ is determined by the current component responsible for the radiative recombination in the QW $I_{rad}(V_j)$, the $I(V_j)$ and $I_{rad}(V_j)$ characteristics can be approximated by an exponential functions $I = I_0 \exp(qV/n_j kT)$ and $I_{rad} = I_{0 rad} \exp(qV/n_{rad} kT)$ where the bias-dependent parameters $n_j(V_j)$ and $n_{rad}(V_j)$ are the ideality factors, $kT$ is the thermal energy, $I_0$ and $I_{0 rad}$ are preexponents.

![Figure 2](image-url) Absorption coefficient of 200 µm thick n-GaN layer grown by HVPE on TiO$_2$ substrate (sample B) versus photon energy and the forward current (closed symbols), the light intensity (open symbols) (a) and the quantum efficiency (b) of the nanostructures with the InGaN/GaN QWs emitted light at $h\nu_p=2.7$ eV and $h\nu_p=3.21$ eV, versus the junction forward bias (given in energetic units).

The pn structures exhibit humps in the portions of $I(V_j)$ and $L(V_j)$ characteristics near the threshold voltages of light detection $V_{th}$. The low ideality factor $n_j\approx1.7$ at $V_{th}=2.2$ V of the blue LED structure increases with increasing bias to $n_j\approx4.5$ followed by a decrease to $n_j=2.5$. Results very similar in character were observed in the NUV LED structure.
At high density of states in the forbidden gap a distance between localized centers is critical for the tunneling transparency of the potential barrier. The local hopping conductivity in the space charge region (SCR) can be written as $\sigma_{\text{hop}} = q^2 \mu \cdot g(E_t) \cdot kT$, where $g(E_t)$ is the distribution of the density of localized states on the localization energy, $\mu = qD/kT$ is the effective microscopic mobility. $D = R_{ij}^2 \cdot \nu_{\text{hop}}(E_t)$ is the effective microscopic diffusion coefficient, $R_{ij} = (g(E_t))^{1/2}$ and $\nu_{\text{hop}}(E_t)$ are the distance and the frequency of electron hops between two centers $i$ and $j$, respectively. Finally, we have:

$$\sigma_{\text{hop}} = q^2 g(E_t) R_{ij}^2 \nu_{\text{hop}}$$  \hspace{1cm} (1)

The hopping rate between occupied centers $i$ and unoccupied centers $j$ decreases exponentially with increasing the distance between two centers $[10]$: 

$$\nu(R_{ij}) = \nu_0 \exp(-2\gamma R_{ij} + \frac{qFR_{ij}}{kT})$$  \hspace{1cm} (2)

where $\nu_0=10^{12}$ s$^{-1}$ is the attempt frequency, $\gamma = a$ is the decay length of the wave functions, and $a$ is the Bohr radius, $F$ is the electric field.

We estimate the local hopping conductivity in the SCR along a isoenergetic transport level in the absence of an electric field ($F = 0$). The hopping rate for Gaussian energy distribution of the localized states:

$$\nu(E_t) = \nu_0 \exp(-2\gamma (\frac{2N_j}{\sigma \sqrt{\pi}} \exp(-\frac{(E_t-E_{0t})}{2\sigma^2})^{1/3}))$$  \hspace{1cm} (3)

where $\sigma = w_i / 2\sqrt{\ln 4}$, $w_i$ is the full width at half-maximum (FWHM) of the Gaussian band, $E_{0t}$ is the position of the maximum of the Gaussian, $N_j$ is the total number of states. Deep states in the maximum of the Gaussian provide the local conductivity $\sigma_{\text{hop}} = 2 \cdot 10^{-7}$ Ohm$^{-1}$ cm$^{-1}$, assuming $N_j=10^{17}$ cm$^{-3}$, $w_i=0.4$ eV, $a=2.5$ nm. Assuming that the deep states with $E_t=E_{0t}$ are uniformly distributed in the space in a part of the SCR, its conductance can be estimated as $G_{\text{SCR}}=2 \cdot 10^{-7}$ Ohm$^{-1}$ (SCR$^3$ = SCR=50 Ohm) at the width of $w_{\text{SCR}}=100$ nm.

For the case of an exponential energy distribution of localized states near the edges of the conduction and valence bands $g(E_t)=(N_j/E_U)\exp(-E_t/E_U)$ with the Urbach energy $E_U = 0.05$ eV $[4]$ the hopping rate for the transport level $E=E_t$:

$$\nu_{\text{hop}}(E_t) = \nu_0 \exp[-2\gamma N_j^{1/3} \exp(E_t/3E_U)]$$  \hspace{1cm} (4)

The localized states provide the local hopping conductivity $1<\sigma_{\text{hop}}>10^{-7}$ Ohm$^{-1}$ cm$^{-1}$ near the SCR edges, where $0<E_t<0.15$ eV by taking $N_j \approx N_c = 2.3 \cdot 10^{18}$ cm$^{-3}$.

Since the density of the localized states at the quasi-Fermi levels, $F_n$ and $F_p$, is lowest near the QW, the tunneling current is controlled by the local hopping conductivity at the boundary with the QW.

According the equation (3), as the quasi-Fermi level at the boundary with the QW is shifted to the Gauss impurity band edge by applying forward bias $qV_f$, and sweeps through $N_i$ states toward the maximum of the Gaussian, a rate of the $\sigma_{\text{hop}}$ increase with forward bias $qV_f$ increases exponentially with the characteristic energy $E_Q=2\sigma^2/(E_t-E_{0t})$, exceeding the Boltzmann factor $\exp(qV_f/kT)$.

The ideality factor $n_1$ can be less than unity $n_1<1$ provided that the quasi-Fermi level is not very close to the maximum of the Gaussian and the localisation energy difference $E_tE_{0t}$ is not small. For example, if $N_j=10^{16}$ cm$^{-3}$, the ideality factor $n_1$ less than unity, $n_1<1$, as quasi-Fermi level sweeps through states $N_i(E_t)$ in the range of $E_tE_{0t}>0.34$ eV and $n_1$ less than two, $n_1<2$, in the range of energies $E_tE_{0t}<0.24$, if $N_j=10^{16}$ cm$^{-3}$ $n_1<1$ at $E_tE_{0t}>0.42$ eV and $n_1<2$ at $E_tE_{0t}>0.3$ eV.

The exponential dependence of the hopping rate on the distance between two deep localized centers $R_{ij}$ determined by density of their states, and the exponential dependence of the density of states in Gaussian impurity band $R_{ij}$ on the square of localisation energy difference $(E_t-E_{0t})^2$ give rise a steep current-voltage I-V curve over a short range of bias. Before and after the transition the current may vary slowly with the bias and the ideality factor may increase to $n_2>2$ typical for defect-assisted tunneling $[11]$. 


A comparison of the behavior of the current as a function of bias $qV_f$ (given in energy units) with the behavior of the optical density as a function of photon energy (sample B) in figure 1 (b) shows that the regions of $I(V_f)$-curves near the threshold voltages for blue and NUV LED structures can be associated with an increase in the density of states in the GaN forbidden gap at the peak energies YL- and BL- PL bands, $h\nu_{YL}=2.2$ eV and $h\nu_{BL}=2.85$ eV, respectively.

The light intensity near the threshold voltages increases with the bias faster than the current, and the ideality factors of $I(V_f)$ – curves in the blue and NUV LED structures are equal to $n_{rad}=1.5$ and 1, respectively.

The main contribution to the total current at the bias $qV_f= F_nF_p$ is made by a component of the trap-assisted tunneling current $I_{TAT}$ which flows along the quasi-Fermi levels $F_n$ and $F_p$ (figure 3). The main contribution to the generation of light in the QW is made by a component of the tunneling current of the carriers $I_{eff}$ which are thermally activated at the top of the effective injection barrier with the height equal to the peak emission energy $E_{eff}=h\nu_p$ (figure 3). At low injection level the differential resistance of the effective barrier $r_{eff}=kT/qI_{eff}$ is higher than the tunneling resistance of the SCR. As a result, the emission intensity rapidly increases with increasing forward bias as $I_{rad}=\exp(qV/kT)$, providing the increase in the emission efficiency, as can be seen in figure 2(b). With increasing the injection level the $r_{eff}$ decreases, and the tunneling resistance of the SCR began to restrict the injection current. The increase in the voltage drop at the tunneling resistance of the SCR results in an increase of the minority carrier injection in the SCR of the barrier and the efficiency droop.

The differences in the doping levels and in the energy distribution of localized states in the electron and hole injecting $n$- and $p$-layers of the $p$-$n$ structure lead to the difference in the tunneling resistances of the $n$- and $p$-barriers, causing an asymmetry of the pn nanostructure. The current is determined mainly by the barrier with the lower tunneling transparency.

![Figure 3. Proposed defect-related tunneling model for a pn nanostructure with an InGaN/GaN QW at low (a) and high (b) injection levels. Gaussian impurity bands responsible for the blue PL in p-GaN and n-GaN (shadowed by light grey) and for near UV PL (shadowed by dark grey) are shown.](image-url)

A broad BL band with a maximum at $h\nu_p=2.75$ eV typically dominates the PL spectrum of heavily doped Mg-doped GaN epilayers, that is routinely used to obtain a $p$-type GaN hole-injecting layer in the LEDs [1,3]. The YL and UVL PL bands peaking at $h\nu_p=2.2$ eV and $h\nu_p=3.25$ eV, respectively, dominate the PL spectrum of Si-doped GaN epilayers, that is routinely used to obtain a $n$-type GaN electron-injecting layer in the LEDs [1].

Comparing the behavior of the absorption spectra in samples A and B, showing the same characteristic bands in the PL spectra as the $p$-GaN and $n$-GaN layers, with the behavior of the current with voltage in $p$-$n$ nanostructures, we can estimate the contribution of each impurity band to the current.

In the blue LED structure with the peak emission energy $h\nu_p=2.7$ eV a steep increase in the current and the emission intensity is observed at the bias $qV_{th}=\Delta F=2.3$ eV ($\Delta F= F_p-F_n$), at which the quasi-Fermi levels begin to sweep the edge of YL absorption band in $n$-GaN layers. This allows us conclude
that the tunneling current is controlled by the tunneling resistance of the \( n \)-barrier due to the presence of undoped \( n \)-Ga\( \text{N} \) layer before the QW.

However, in the range \( \Delta F = qV_c = 2.85 - 3.25 \text{ eV} \), corresponding to the BL absorption band in the \( n \)-Ga\( \text{N} \), the emission intensity begins to increase more slowly than the current does. As the quasi-Fermi levels cross the Gaussian maximum in the density of states at \( \Delta F = qV_c = 3.05 \text{ eV} \) of the BL-related defects in the \( p \)-Ga\( \text{N} \), the current starts to be controlled by the hole injection. The electrons are injected from the QW in p-barrier, resulting in the efficiency droop.

In the NUV LED structure with the peak emission energy \( h\nu_p = 3.21 \text{ eV} \) the current and the emission intensity rapidly increase in the range of the bias \( \Delta F = qV_c = 2.85 - 3.25 \text{ eV} \), corresponding to the BL absorption band in the \( n \)-Ga\( \text{N} \), that indicates the high density of BL-related defects in the \( p \)-Ga\( \text{N} \) and the restriction of the current by the tunneling resistance of the \( n \)-barrier. The slower increase in the current and the emission intensity starts near \( \Delta F = 3.15 \text{ eV} \), when the quasi-Fermi levels achieve the high-energy edge of the Gaussian band of BL-related defects in the \( p \)-Ga\( \text{N} \). The current start to be controlled by the tunneling resistance of the \( p \)-barrier and the hole injection in the QW, similar to the blue LED structure with the peak emission energy \( h\nu_p = 2.7 \text{ eV} \).

4. Conclusion
Gaussian impurity bands in Ga\( \text{N} \) responsible for intracenter optical absorption and photoluminescence, give rise to defect-assisted carrier tunneling (hopping) through the barriers in the \( p \)-\( n \) nanostructures with InGa\( \text{N} \)/Ga\( \text{N} \) quantum wells (QWs). Low density of the defect states responsible for the UVL PL band in the \( p \)-type Ga\( \text{N} \) hole injected layers in \( p \)-\( n \) nanostructures with InGa\( \text{N} \)/Ga\( \text{N} \) QWs leads to an increase in the tunneling resistance of \( p \)-barrier and in the tunneling leakage of electrons from QW resulting in the emission efficiency saturation and droop.

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