GaN surface as the source of non-radiative defects in InGaN/GaN quantum wells

C. Haller, J.-F. Carlin, (iD) G. Jacopin, (iD) W. Liu, D. Martin, (iD) R. Butté, and (iD) N. Grandjean

View Online   Export Citation   CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Luminescence properties of defects in GaN
Journal of Applied Physics **97**, 061301 (2005); https://doi.org/10.1063/1.1868059

Defect-reduction mechanism for improving radiative efficiency in InGaN/GaN light-emitting diodes using InGaN underlayers
Journal of Applied Physics **117**, 134501 (2015); https://doi.org/10.1063/1.4916727

Optical absorption edge broadening in thick InGaN layers: Random alloy atomic disorder and growth mode induced fluctuations
Applied Physics Letters **112**, 032106 (2018); https://doi.org/10.1063/1.5010879

GaN surface as the source of non-radiative defects in InGaN/GaN quantum wells

C. Haller,[a)] J.-F. Carlin, G. Jacopin, W. Liu, D. Martin, R. Butté, and N. Grandjean

Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Blue light-emitting diodes based on III-nitride semiconductors are nowadays widely used for solid-state lighting. They exhibit impressive figures of merit like an internal quantum efficiency close to 100%. This value is intriguing when considering the high dislocation density running throughout the InGaN/GaN quantum well (QW) active region. This striking feature is currently ascribed to carrier localization occurring in the InGaN alloy, which hinders their diffusion toward dislocations. However, it was recently reported that another source of defects, disconnected from dislocations, dramatically decreases the radiative efficiency of InGaN/GaN QWs. Those defects, present at the surface, are usually trapped in an InGaN underlayer (UL), which is grown before the QW active region. To get insight into the trapping mechanism, we varied the UL thickness, In content, and materials system (InGaN or InAlN) and studied the photoluminescence decay time at 300 K of a single InGaN/GaN QW. Our data demonstrate that defects are incorporated proportionally to the indium content in the UL. In addition, we show that those defects are created during the high-temperature growth of GaN and that they segregate at the surface even at low-temperature. Eventually, we propose an intrinsic origin for these surface defects. © *2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5048010

III-nitride white light-emitting diodes (LEDs), which consist of a blue LED covered by a yellow phosphor, recently achieved a record luminous efficacy of 300 lm/W.[1] This spectacular performance must be credited to InGaN/GaN quantum wells (QWs), which form the active region of blue LEDs. When Nakamura *et al.* reported the first high-brightness InGaN based LED,[2] the scientific community was astonished since the device grown on sapphire was full of dislocations (density $> 10^9$ cm^{-2}), which act as non-radiative recombination centers (NRCs).[3] The defect-insensitivity of InGaN/GaN QWs was then ascribed to the intrinsic properties of the InGaN alloy: carriers are strongly localized due to large potential fluctuations induced by random alloy disorder[4] hindering their diffusion towards NRCs.[5] Besides dislocations, point defects such as impurities or vacancies are another common source of NRCs in semiconductor optoelectronic devices. In this vein, Armstrong *et al.* pointed out the detrimental impact of deep level defects on the efficiency of blue LEDs.[6] In particular, they showed that the density of NRCs in InGaN/GaN QWs decreases if a thick InGaN layer is deposited before the growth of the active region. In fact, such an InGaN underlayer (UL) or InGaN/GaN superlattice is commonly used in high efficiency commercial blue LEDs grown by metal-organic chemical vapor deposition (MOCVD). Its role is to trap surface defects (SDs) and avoid their further incorporation into the InGaN/GaN active region.[6–8] It was also noticed that this effect holds when InGaN QWs are grown on free-standing GaN substrates, which indicates that dislocations are not at play.[7]

In this study, we show that the defects buried in the InGaN UL are intrinsic to the GaN surface. They form at high temperature (>900 °C) and segregate at the surface even for low growth temperatures (<800 °C). In turn, they are incorporated in indium containing layers (InGaN or InAlN) where they create NRCs.

Samples were grown by MOCVD in either a vertical Aixtron 3×2 in. CCS system (reactor 1) or a horizontal Aixtron 200/4 RF-S system (reactor 2). Substrates are *c*-plane sapphire (dislocation density of about 10^9 cm^{-2} in the GaN buffer) or c-plane freestanding (FS) GaN (dislocation density about $\sim 10^6$ cm^{-2} in the GaN buffer). The common structure for all the samples is a GaN buffer, an InGaN (InAlN) UL, a GaN spacer, an InGaN single (S)QW, and a GaN cap of 50 nm (see supplementary material Sec. 1). The buffer is grown using trimethylgallium (TMGa) and H$_2$ as carrier gas at a temperature of 1000 °C. For the growth of the InGaN (InAlN) alloy, the GaN spacer, and the GaN cap, the carrier gas is switched to N$_2$. The InGaN UL is grown using trimethylindium (TMIn) and triethylgallium (TEGa) at a temperature of 770 °C. The InAlN UL is grown using TMIn and trimethylaluminum (TMAl) at a temperature of 750 °C. The SQW growth temperature is about 755 °C, the nominal indium composition is 12%, and the thickness is 2.7 nm. Time-resolved photoluminescence (TRPL) was performed using a streak camera operating in synchroscan mode. We used the third harmonic of a mode-locked Ti:sapphire laser emitting at 280 nm as an excitation source. The pulse width is 2 ps and the repetition rate is 80.5 MHz. To extend the time window for long PL decay times, we used a pulse picker. The QW effective lifetime is measured over a spectral window for which the contribution of the yellow band, the InGaN UL, and the GaN band edge emissions is negligible. Time-integrated PL (TIPL) was performed with the same excitation source as TRPL, but the signal was integrated over several pulses (with an excitation power density of 0.26 W/cm^2).

[a)]camille.haller@epfl.ch

As shown in previous reports,[6–8] the role of the InGaN UL in an LED structure is to bury SDs and ensure a high efficiency InGaN/GaN active region. We first study the capture mechanism of these SDs by the InGaN UL. For that purpose, we grew a series of identical 2.7 nm thick $In_{0.12}Ga_{0.88}N$/GaN SQWs (series A) except for the thickness (d) of the $In_{0.03}Ga_{0.97}N$ UL, which was varied from 0 to 214 nm. PL measurements were performed at room temperature with a low excitation power density (0.26 W/cm²). The PL intensity increases by more than two orders of magnitude between a bare SQW sample (without UL) and the SQW with an UL of 214 nm [Fig. 1(a)]. The intensity first increases with the thickness and then saturates. Interestingly, the PL intensity of the InGaN UL also gets higher.

Additionally, we carried out TRPL experiments at 300 K to measure the QW effective lifetime and get insight into non-radiative (NR) processes. In agreement with the PL intensity behavior, the effective lifetime exhibits a huge improvement when the UL thickness increases [Fig. 1(b)]. From 170 ps when no UL is inserted, it goes up to about 20 ns for the thickest one indicating very low NR recombination. Notice that the nonexponential behavior at long delays has already been observed in InGaN/GaN QWs grown on bulk GaN substrates and was ascribed to the saturation of slow dynamics NRCs.[9]

The dependence of the InGaN/GaN SQW optical properties with the thickness of the InGaN UL suggests the following mechanism: SDs are incorporated if In atoms are present at the surface and, once buried in InGaN layers, they create NRCs. This is in agreement with former results, which showed, for instance, a strong improvement of the optical properties of multiple (M) QW structures compared to SQW ones.[10–12] Indeed, in this case, the first QWs in the MQW structure play the role of the InGaN UL by trapping SDs.

To account for the evolution of the QW decay time as a function of InGaN UL thickness, we developed a model where the NR lifetime is a function of the SD concentration in the InGaN/GaN QWs.[13] First, we suppose that SDs segregate at the surface, with a surface concentration given by $[SD] = \theta_0 R^N$, where θ_0 is the initial surface density after the GaN growth at high temperature, N is the number of monolayers (MLs) deposited ($N = d/e_{ML}$ with e_{ML} the InGaN ML thickness), and R is the segregation coefficient.[14] Previous observations by Akasaka *et al.*[6] indicate that the incorporation of SDs in GaN is negligible, i.e., R is close to 1. In contrast, SDs are incorporated in InGaN layers, i.e., R decreases. Assuming that SDs are buried upon interaction with In atoms, we can write $R = R_{GaN} - xp$ with R_{GaN} being the segregation coefficient of SDs in GaN, x the In composition of the InGaN layer, and p the interaction efficiency between In atoms and SDs. Then, we express the effective lifetime of the QW as $1/\tau_{eff} = 1/\tau_0 + 1/\tau_{NR,SD}$, with τ_0 being the QW lifetime when all SDs are trapped into the InGaN UL and $\tau_{NR,SD}$ the NR lifetime induced by the incorporation of SDs. The latter is given by $1/\tau_{NR,SD} \propto [SD]_{QW}$, with $[SD]_{QW}$ being the concentration of SDs in the QW. Finally, the QW effective lifetime can be expressed as

$$\tau_{eff} = \tau_0 \frac{1}{1 + \tau_0 \alpha (R_{GaN} - xp)^N}, \quad (1)$$

with α a constant, which depends on θ_0 and the electron-hole capture coefficient of the NR defect (see supplementary material Sec. 3). The experimental effective lifetime as a function of InGaN UL thickness is fitted using Eq. (1) [Fig. 2(a), green line]. The value for τ_0 is 18 ns. The composition and the thickness are measured by high resolution x-ray diffraction analysis. The best fit is obtained with an interaction efficiency of 0.7 ($R = 0.9782$), which confirms the strong interaction of SDs with indium (see supplementary material Sec. 3 for different values of p).

Next, a set of InGaN/GaN SQW samples (series B) was prepared keeping constant the InGaN UL thickness (55 nm) but varying the In content (up to 16% to ensure pseudomorphic layer). It is worth noticing that we used another reactor (horizontal reactor) and the substrate was sapphire. The InGaN UL was deposited under slightly different growth conditions ($T_g = 750\,°C$ with H_2 and N_2 used as carrier gases). The QW effective lifetimes for this sample series are displayed in Fig. 2(b). Equation (1) still with $p = 0.7$ reproduces well the QW effective lifetime. Note that τ_0 is 3.3 ns, which is smaller than the value measured on FS GaN substrate, which might be due to a higher dislocation density. A piece of information is that SDs are present whatever the reactor type: vertical design with a stainless steel showerhead for reactor 1 or horizontal design with a quartz liner (no stainless steel) for reactor 2.

We then checked whether SD trapping is specific to InGaN layers. To this end, we prepared a series of InGaN/GaN SQWs grown on FS-GaN substrate with $In_{0.15}Al_{0.85}N$ UL (series C). Notice that the $In_{0.15}Al_{0.85}N$ alloy is under slight tensile strain for this composition.[15] The PL decay time of the InGaN/GaN SQWs dramatically increases with the InAlN UL thickness [Fig. 2(a)]. Due to the high indium
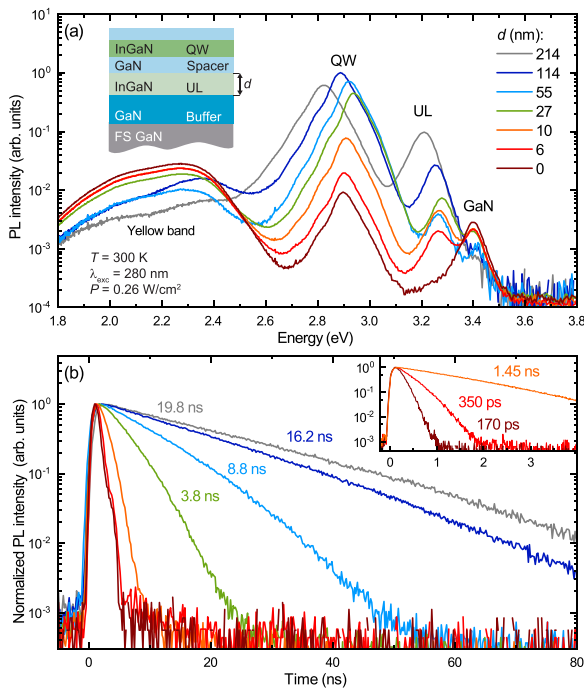

FIG. 1. (a) PL spectra recorded at 300 K for different InGaN UL thicknesses. (b) Corresponding normalized PL decay traces of the QW for an 80 ns time window and, inset, for a time window of 4 ns.
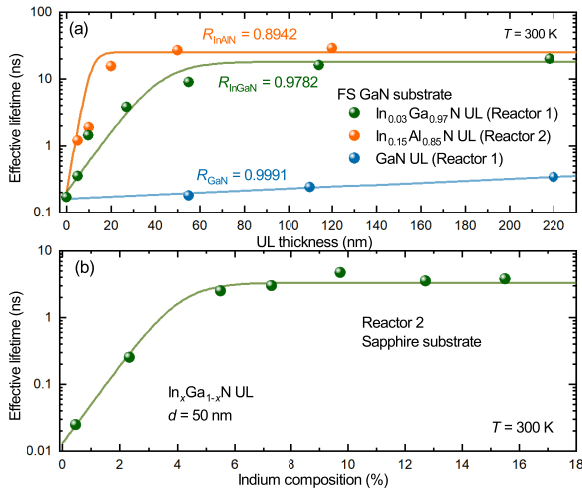
FIG. 2. (a) Effective QW lifetime as a function of UL thickness for three different materials: InGaN UL in green (series A), GaN UL in blue (series D), and InAlN UL in orange (series C). (b) Effective QW lifetime as a function of InGaN UL composition (series B). The dots are experimental data and the lines are fits based on Eq. (1) using an interaction efficiency $p = 0.7$.

content in the InAlN layer, the thickness needed to reach the saturation of the effective lifetime is about 20 nm. The data in Fig. 2(a) were fitted with Eq. (1) with $p = 0.7$ ($R = 0.8942$), as for InGaN ULs. To further emphasize the critical role of indium, we grew an additional series of InGaN/GaN SQW samples where the UL was replaced by a pure GaN layer grown at 770 °C (series D). The PL decay time exhibits a slight increase with the GaN thickness [Fig. 2(a)]. Fitting the data with Eq. (1) (with $x = 0$) leads to $R_{GaN} = 0.9991$. This high R value confirms the strong surface segregation of SDs in GaN even at a growth temperature as low as 770 °C. Consequently, 2 μm of GaN grown at 770 °C would be required to trap all SDs. This highlights the need for indium in the UL, as already pointed out by Akasaka *et al.*[6]

Although the phenomenological model we propose accounts well for the dependence of the QW effective lifetime on the InGaN (InAlN) UL thickness or composition, it does not provide any insights into the nature of those SDs. In the literature, capture coefficients for impurities and complexes range between 10^{-6} and 10^{-8} cm^3 s^{-1},[16–19] corresponding to impurity densities comprised between 10^{15} and 10^{17} cm^{-3}. Thus, we carried out secondary ion mass spectrometry (SIMS) and searched for Li, C, O, Na, Mg, P, K, Ca, Fe, and Mo, which might be detrimental to the radiative efficiency of InGaN QWs.[16,20–24] SIMS measurements did not allow us establishing any straightforward relationship between those impurities and the QW effective lifetime. However, one could argue that the SIMS detection limit was too high (see supplementary material Sec. 5) or that we missed the relevant impurity.

Based on previous results, SDs should have the following properties: (i) once incorporated into InGaN layers, they create efficient NRCs, (ii) they strongly interact with indium atoms, and (iii) their concentration should range between 10^{15} and 10^{17} cm^{-3}. Another intriguing observation is that SDs are present whatever the MOCVD growth reactor type. It is also a common feature that InGaN/GaN SQWs grown without InGaN UL exhibit a poor radiative efficiency.[10–12]

We therefore postulate that SDs could not be impurities but rather intrinsic point defects, which form during the growth of GaN at high temperature.

To investigate the dependence of the density of SDs on growth temperature, we prepared a series (series E) of InGaN/GaN SQW samples with InGaN UL but with a GaN spacer deposited at various temperatures T_{GaN} (Fig. 3). Increasing the growth temperature T_{GaN} from 770 °C to 1020 °C leads to a rapid collapse of the QW PL intensity (Fig. 3). The effective lifetimes measured at 300 K are displayed on a semilogarithmic scale as a function of 1000/T_{GaN} (inset, Fig. 3). Using the previous model and assuming that the SD density θ_0 scales as $\exp\left(-\frac{E_a}{k_B T_{GaN}}\right)$, we extracted an activation energy of 3.6 eV. Interestingly, this value is close to the activation energy reported in the literature for the decomposition of GaN.[25,26]

The dependence of the SD density on growth temperature suggests intrinsic point defects whose creation rate might be enhanced in the GaN near surface region. Indeed, the defect formation energy may be significantly different from the bulk formation energy.[27] In addition, vacancies tend to diffuse toward the surface, as observed in other materials.[28] We could thus infer that the GaN surface and near surface region provide a reservoir of point defects, which segregate at the surface until they react with indium atoms. Then, once buried, they form NRCs.

Let us consider the most likely points defects, which are gallium and nitrogen vacancies. Gallium vacancies (V_{Ga}) in GaN epilayers grown by MOCVD have been discussed back to 1996 and proposed to be responsible for the yellow-band luminescence.[29] In GaN homoepitaxial layers, two energy levels associated with V_{Ga} complexes have been determined by deep level spectroscopy: $E_c - 0.56$ eV and $E_c - 0.23$ eV,[30] with E_c the conduction band minimum. These values are far from the energy level $E_c - 1.62$ eV that was identified to be related to the creation of NRCs by SDs in InGaN/GaN QWs.[6] Recently, theoretical calculations have pointed out that V_{Ga} are unlikely in bulk GaN, but instead complexes with oxygen and hydrogen are.[19,31] This would mean that oxygen and hydrogen could be detected by SIMS if their density was high enough, which is not the case in our samples (see supplementary material Sec. 5). In addition, Dreyer *et al.* computed the impact of these V_{Ga} complexes on NR recombinations in

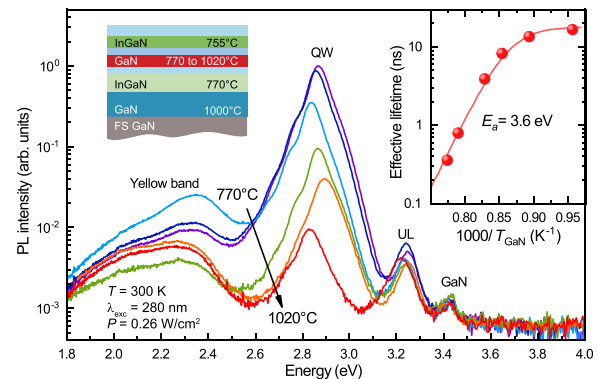FIG. 3. PL spectra recorded at 300 K for a sample with a spacer grown at different temperatures (T_{GaN}). Inset: InGaN SQW effective lifetime (red points) as a function of 1000/T_{GaN}. The red line corresponds to the calculated effective lifetimes assuming thermally activated SDs ($E_a = 3.6$ eV).

InGaN layers and found that they play a marginal role below 15% In content.[19] Thus, V_{Ga} and related complexes are not expected to dramatically impact the efficiency of the present InGaN/GaN QWs, which have an indium content of 12%.

It is commonly admitted that the concentration of nitrogen vacancies (V_N) in bulk GaN is low due to their large formation energy[27] but not negligible.[32] Furthermore, the formation energy of vacancies at the semiconductor surface may be significantly smaller.[33] It was also proposed that during the decomposition of GaN, nitrogen atoms dissociate from the surface and form N_2 molecules, leading to a nitrogen-poor growth front, which could be a source of V_N.[26,34,35] Therefore, $[V_N]$ could be high at the GaN surface. Notice that the predominance of anion vacancies near the surface was already pointed out in common III-V semiconductors.[33] Another hint comes from the so-called two-flow MOCVD reactor invented by Nakamura *et al.*[36] This reactor design allows improving the III-N material properties thanks to a higher NH_3 pressure close to the surface using an additional N_2 flow.

The present study points out the strong affinity of SDs with indium atoms. Thus, the mechanism could be the following: V_N are created near the surface during high temperature growth of GaN. Once formed, they segregate at the surface even for low-temperature growth GaN due to their high formation energy in bulk GaN.[37] In the presence of indium atoms, the segregation process is quenched: V_N are incorporated in the bulk due to a decrease in their formation energy in InGaN,[38,39] inducing in turn NRCs. Potential NRC candidates could be a complex formed by V_N and In as theoretically predicted,[40] and experimentally reported,[41] or a divacancy complex (V_N, V_{III}) as recently observed in GaN.[42]

In conclusion, we studied the origin of surface defects in GaN, which dramatically reduce the efficiency of InGaN/GaN QWs. We hypothesize that the rather low stability of GaN at high temperature induces nitrogen vacancies at the surface. Those V_N strongly segregate, even during low-temperature growth of GaN. In contrast, in indium containing layers, V_N are incorporated where they create NRCs. We thus propose that the role of the UL is to capture preexisting V_N at the GaN surface. Additionally, InAlN nearly lattice-matched to GaN proved to be an extremely efficient UL material through its high indium content while avoiding strain-related issues. Hence, our results shed new light on the physics and fabrication of high performance III-nitride based optoelectronic devices and potentially high power electronics.

See supplementary material for complementary information.

[1]S. Nakamura, "Background story of the invention of efficient InGaN blue-light-emitting diodes (Nobel Lecture)," Angew. Chem., Int. Ed. **54**, 7770–7788 (2015).

[2]S. Nakamura, M. Senoh, and T. Mukai, "P-GaN/N-InGaN/N-GaN double-heterostructure blue-light-emitting diodes," Jpn. J. Appl. Phys., Part 2 **32**, L8–L11 (1993).

[3]D. Cherns, S. J. Henley, and F. A. Ponce, "Edge and screw dislocations as nonradiative centers in InGaN/GaN quantum well luminescence," Appl. Phys. Lett. **78**, 2691–2693 (2001).

[4]S. F. Chichibu, A. Uedono, T. Onuma, B. A. Haskell, A. Chakraborty, T. Koyama, P. T. Fini, S. Keller, S. P. DenBaars, J. S. Speck, U. K. Mishra, S. Nakamura, S. Yamaguchi, S. Kamiyama, H. Amano, I. Akasaki, J. Han, and T. Sota, "Origin of defect-insensitive emission probability in In-containing (Al,In,Ga)N alloy semiconductors," Nat. Mater. **5**, 810–816 (2006).

[5]J.-M. Gérard and C. Weisbuch, "Semiconductor structure for optoelectronic components with inclusions," U.S. patent application US5075742A (December 24, 1991).

[6]T. Akasaka, H. Gotoh, T. Saito, and T. Makimoto, "High luminescent efficiency of InGaN multiple quantum wells grown on InGaN underlying layers," Appl. Phys. Lett. **85**, 3089 (2004).

[7]A. M. Armstrong, B. N. Bryant, M. H. Crawford, D. D. Koleske, S. R. Lee, and J. J. Wierer, "Defect-reduction mechanism for improving radiative efficiency in InGaN/GaN light-emitting diodes using InGaN underlayers," J. Appl. Phys. **117**, 134501 (2015).

[8]C. Haller, J.-F. Carlin, G. Jacopin, D. Martin, R. Butté, and N. Grandjean, "Burying non-radiative defects in InGaN underlayer to increase InGaN/GaN quantum well efficiency," Appl. Phys. Lett. **111**, 262101 (2017).

[9]M. Dworzak, T. Stempel, A. Hoffmann, G. Franssen, S. Grzanka, T. Suski, R. Czernecki, M. Leszczynski, and I. Grzegory, *Luminescence Efficiency of InGaN/GaN Quantum Wells on Bulk GaN Substrate* (Mater. Res. Soc. Symp. Proc., 2006), Vol. 892, p. 825.

[10]M. S. Minsky, S. B. Fleischer, A. C. Abare, J. E. Bowers, E. L. Hu, S. Keller, and S. P. Denbaars, "Characterization of high-quality InGaN/GaN multiquantum wells with time-resolved photoluminescence," Appl. Phys. Lett. **72**, 1066–1068 (1998).

[11]C. Prall, C. Kaspari, F. Brunner, K. Haberland, M. Weyers, and D. Rueter, "*In-situ* photoluminescence measurements during MOVPE growth of GaN and InGaN MQW structures," J. Cryst. Growth **415**, 1–6 (2015).

[12]S. F. Chichibu, H. Marchand, M. S. Minsky, S. Keller, P. T. Fini, J. P. Ibbetson, S. B. Fleischer, J. S. Speck, J. E. Bowers, E. Hu, U. K. Mishra, S. P. DenBaars, T. Deguchi, T. Sota, and S. Nakamura, "Emission mechanisms of bulk GaN and InGaN quantum wells prepared by lateral epitaxial overgrowth," Appl. Phys. Lett. **74**, 1460–1462 (1999).

[13]Y. Kawakami, K. Omae, A. Kaneta, K. Okamoto, T. Izumi, S. Sajou, K. Inoue, Y. Narukawa, T. Mukai, and S. Fujita, "Radiative and nonradiative recombination processes in GaN-based semiconductors," Phys. Status Solidi A **183**, 41–50 (2001).

[14]K. Muraki, S. Fukatsu, Y. Shiraki, and R. Ito, "Surface segregation of In atoms during molecular beam epitaxy and its influence on the energy levels in InGaAs/GaAs quantum wells," Appl. Phys. Lett. **61**, 557–559 (1992).

[15]R. Butté, J.-F. Carlin, E. Feltin, M. Gonschorek, S. Nicolay, G. Christmann, D. Simeonov, A. Castiglia, J. Dorsaz, H. J. Buehlmann, S. Christopoulos, G. Baldassarri Höger von Högersthal, A. J. D. Grundy, M. Mosca, C. Pinquier, M. A. Py, F. Demangeot, J. Frandon, P. G. Lagoudakis, J. J. Baumberg, and N. Grandjean, "Current status of AlInN layers lattice-matched to GaN for photonics and electronics," J. Phys. D: Appl. Phys. **40**, 6328–6344 (2007).

[16]D. Wickramaratne, J.-X. Shen, C. E. Dreyer, M. Engel, M. Marsman, G. Kresse, S. Marcinkevičius, A. Alkauskas, and C. G. Van de Walle, "Iron as a source of efficient Shockley-Read-Hall recombination in GaN," Appl. Phys. Lett. **109**, 162107 (2016).

[17]T. K. Uždavinys, S. Marcinkevičius, J. H. Leach, K. R. Evans, and D. C. Look, "Photoexcited carrier trapping and recombination at Fe centers in GaN," J. Appl. Phys. **119**, 215706 (2016).

[18]M. A. Reshchikov, D. O. Demchenko, A. Usikov, H. Helava, and Y. Makarov, "Carbon defects as sources of the green and yellow luminescence bands in undoped GaN," Phys. Rev. B **90**, 235203 (2014).

[19]C. E. Dreyer, A. Alkauskas, J. L. Lyons, J. S. Speck, and C. G. Van de Walle, "Gallium vacancy complexes as a cause of Shockley-Read-Hall recombination in III-nitride light emitters," Appl. Phys. Lett. **108**, 141101 (2016).

[20]J.-X. Shen, D. Wickramaratne, C. E. Dreyer, A. Alkauskas, E. Young, J. S. Speck, and C. G. Van de Walle, "Calcium as a nonradiative recombination center in InGaN," Appl. Phys. Express **10**, 021001 (2017).

[21]E. C. Young, N. Grandjean, T. E. Mates, and J. S. Speck, "Calcium impurity as a source of non-radiative recombination in (In,Ga)N layers grown by molecular beam epitaxy," Appl. Phys. Lett. **109**, 212103 (2016).

[22]N. Okada, K. Tadatomo, K. Yamane, H. Mangyo, Y. Kobayashi, H. Ono, K. Ikenaga, Y. Yano, and K. Matsumoto, "Performance of InGaN/GaN light-emitting diodes grown using NH_3 with oxygen-containing impurities," Jpn. J. Appl. Phys., Part 1 **53**, 081001 (2014).

[23]J. Yang, D. G. Zhao, D. S. Jiang, P. Chen, Z. S. Liu, L. C. Le, X. J. Li, X. G. He, J. P. Liu, S. M. Zhang, H. Wang, J. J. Zhu, and H. Yang, "Investigation on the compensation effect of residual carbon impurities in low temperature grown Mg doped GaN films," J. Appl. Phys. **115**, 163704 (2014).

[24]S.-H. Han, C.-Y. Cho, S.-J. Lee, T.-Y. Park, T.-H. Kim, S. H. Park, S. W. Kang, J. W. Kim, Y. C. Kim, and S.-J. Park, "Effect of Mg doping in the barrier of InGaN/GaN multiple quantum well on optical power of light-emitting diodes," Appl. Phys. Lett. **96**, 051113 (2010).

[25]N. Grandjean, J. Massies, F. Semond, S. Y. Karpov, and R. A. Talalaev, "GaN evaporation in molecular-beam epitaxy environment," Appl. Phys. Lett. **74**, 1854–1856 (1999).

[26]D. D. Koleske, A. E. Wickenden, R. L. Henry, J. C. Culbertson, and M. E. Twigg, "GaN decomposition in H_2 and N_2 at MOVPE temperatures and pressures," J. Cryst. Growth **223**, 466–483 (2001).

[27]C. G. Van de Walle and J. Neugebauer, "First-principles calculations for defects and impurities: Applications to III-nitrides," J. Appl. Phys. **95**, 3851–3879 (2004).

[28]H. Ding, J. Wang, C. Li, J. Nie, and X. Liu, "Study of the surface segregation of carbon vacancies in TiCx," Solid State Commun. **152**, 185–188 (2012).

[29]J. Neugebauer and C. G. Van de Walle, "Gallium vacancies and the yellow luminescence in GaN," Appl. Phys. Lett. **69**, 503–505 (1996).

[30]Y. Tokuda, Y. Matsuoka, H. Ueda, O. Ishiguro, N. Soejima, and T. Kachi, "DLTS study of n-type GaN grown by MOCVD on GaN substrates," Superlattices Microstruct. **40**, 268–273 (2006).

[31]J. L. Lyons and C. G. Van de Walle, "Computationally predicted energies and properties of defects in GaN," npj Comput. Mater. **3**, 12 (2017).

[32]Z. Xie, Y. Sui, J. Buckeridge, C. R. A. Catlow, T. W. Keal, P. Sherwood, A. Walsh, M. R. Farrow, D. O. Scanlon, S. M. Woodley, and A. A. Sokol, "Donor and acceptor characteristics of native point defects in GaN," e-print arXiv:1803.06273 [cond-mat].

[33]M. S. Daw and D. L. Smith, "Vacancies near semiconductor surfaces," Phys. Rev. B **20**, 5150 (1979).

[34]K. Rapcewicz, M. Buongiorno Nardelli, and J. Bernholc, "Theory of surface morphology of wurtzite GaN (0001) surfaces," Phys. Rev. B **56**, R12725–R12728 (1997).

[35]M. E. Bartram and J. R. Creighton, "GaN CVD reactions: Hydrogen and ammonia decomposition and the desorption of gallium," MRS Internet J. Nitride Semicond. Res. **4**, 369–374, (1999).

[36]S. Nakamura, Y. Harada, and M. Seno, "Novel metalorganic chemical vapor deposition system for GaN growth," Appl. Phys. Lett. **58**, 2021–2023 (1991).

[37]S. Limpijumnong and C. Van de Walle, "Diffusivity of native defects in GaN," Phys. Rev. B **69**, 035207 (2004).

[38]T. V. Bezyazychnaya, D. M. Kabanau, V. V. Kabanov, Y. V. Lebiadok, A. G. Ryabtsev, G. I. Ryabtsev, V. M. Zelenkovskii, and S. K. Mehta, "Influence of vacancies on indium atom distribution in InGaAs and InGaN compounds," Lith. J. Phys. **55**, 10–16 (2015).

[39]A. Uedono, T. Watanabe, S. Kimura, Y. Zhang, M. Lozac'h, L. Sang, S. Ishibashi, N. Oshima, R. Suzuki, and M. Sumiya, "Vacancy-type defects in $In_xGa_{1-x}N$ grown on GaN templates probed using monoenergetic positron beams," J. Appl. Phys. **114**, 184504 (2013).

[40]A. Terentjevs, A. Catellani, and G. Cicero, "Nitrogen vacancies at InN (1100) surfaces: A theoretical study," Appl. Phys. Lett. **96**, 171901 (2010).

[41]P. Kessler, K. Lorenz, S. M. C. Miranda, J. G. Correia, K. Johnston, and R. Vianden, "An In-defect complex as a possible explanation for high luminous efficacy of InGaN and AlInN based devices," Hyperfine Interact. **197**, 187–191 (2010).

[42]S. F. Chichibu, A. Uedono, K. Kojima, H. Ikeda, K. Fujito, S. Takashima, M. Edo, K. Ueno, and S. Ishibashi, "The origins and properties of intrinsic nonradiative recombination centers in wide bandgap GaN and AlGaN," J. Appl. Phys. **123**, 161413 (2018).