Comment on “Determination of the Nitrogen Vacancy as a Shallow Compensating Center in GaN Doped with Divalent Metals”

In a recent paper [1], the authors reported on the calculated defect formation and ionization energies for a number of defects in GaN, claiming excellent agreement with photoluminescence (PL) experiments for the nitrogen vacancy (V_N), the $\mathrm{Mg_{Ga}}$ defect, and several other divalent metals. A crucial assumption was made that the energy of the emitted photons is equal to the excitation energy: “Such [ionization energies] correspond to emission energies of photoexcited electrons recombining with these defect levels, as would be observed in PL experiments, where, after excitation, atoms typically do not have adequate time to fully relax.” The purpose of this Comment is to point out that this assumption is invalid for defects in GaN, which calls into question the interpretation of the results.

Figure 1 shows a one-dimensional configuration coordinate (CC) diagram for a defect in GaN ($E_g = 3.50$ eV). The lowest (highest) parabola is the total energy versus the generalized atomic coordinate of the defect in charge state q (defect q plus an electron in the conduction band). The middle parabola corresponds to charge state $q+1$. E_0 is the zero-phonon line, and E_A is the energy difference between the $q/q+1$ transition level and the valence band maximum. Following Ref. [1], we call the electron photoexcitation from the defect to the conduction band (transition $a \rightarrow b$) the *vertical ionization energy* (IE). After the photoexcitation, the defect system emits several phonons and relaxes into its equilibrium geometry (transition $b \rightarrow c$). The above model explains the observed PL emission and absorption peaks, the zero-phonon lines, and the line shapes for defects in GaN [2–4].

It is well established that the vibrational relaxation time ($\tau_V = 10^{-12} - 10^{-11}$ s) is several orders of magnitude shorter than the PL lifetime (τ) [5,6]. For the majority of defects in GaN, $\tau = 10^{-6} - 10^{-3}$ s [2]. In particular, $\tau = 0.3$ ms for the V_N-related green (2.35 eV) band [3] and $\tau \approx 1\ \mu$s for the blue (2.8 eV) band in Mg-doped GaN [7]. The shortest defect-related PL lifetime of 0.6 ns, reported for the 3.21 eV band in p-type GaN [8] is still 2–3 orders of magnitude longer than τ_V [9]. In agreement with the current understanding of defect-related PL, bands with energies equal to the IE have not been observed in GaN.

In Ref. [1], the assumption that the PL band is observed at the same photon energy as the IE leads to an erroneous interpretation of the results. For example, the calculated parameters for the $+/2+$ (and $2+/3+$) level of the V_N are IE ≈ 2.9 eV and $E_A \approx 1.9$ eV [1]. Applying these numbers to the CC diagram (Fig. 1) yields the corresponding PL band maximum in the *infrared* ($\hbar\omega_m < 1.6$ eV), not in the blue region. For the $-/0$ transition level of $\mathrm{Mg_{Ga}}$, the calculated parameters are $E_A = 1.404$ and IE $= 2.752$ eV [1], and the PL should be observed in the red or infrared, not the blue, region.

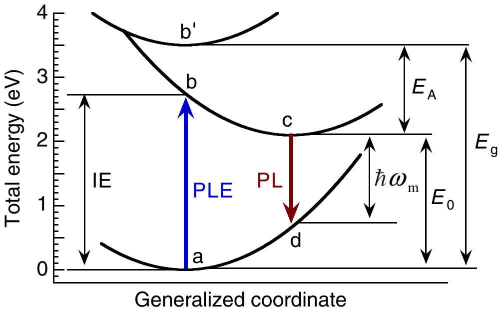

FIG. 1 (color online). Schematic CC diagram for a defect in GaN.

There are also several questionable statements in Ref. [1]. In particular, the 3.466 eV PL peak in GaN is reliably attributed to acceptor-bound excitons, and there is no experimental evidence that it could be due to electron transitions via the $0/+$ level of the V_N [2]. In addition, the V_N is unlikely to be present with any significant concentration in n-type GaN [2,10]. The calculated thermodynamic $0/-$ transition level of the $\mathrm{Mg_{Ga}}$ acceptor at $\sim$1.4 eV, along with the claim that $\mathrm{Mg_{Ga}}$ does not lead to p-type conductivity in GaN, also contradicts the experiment [2,10].

In conclusion, the invalid assumption that the PL process is faster than the vibrational relaxation calls into question the validity of the calculations as well as the interpretation of the results in connection with the experiment discussed in Ref. [1].

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D. O. Demchenko and M. A. Reshchikov
Department of Physics
Virginia Commonwealth University
Richmond, Virginia 23284, USA

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