Passivation of beryllium acceptor in GaN and a possible route for *p*-type doping

D. O. Demchenko, M. A. Reshchikov

Department of Physics, Virginia Commonwealth University, Richmond, VA 23220, USA

Using theory and experiment, we address a possible *p*-type doping route of GaN using Be acceptor. Hybrid functional calculations suggest that straightforward incorporation of Be in GaN will likely lead to compensated high resistivity samples. In this case, beryllium interstitial and nitrogen vacancy are the most likely compensating donors. However, calculations also show that simultaneous incorporation of beryllium and hydrogen in the nitrogen-rich growth regime is likely to lead to the formation of neutral Be_{Ga}-H_i complexes. These complexes are energetically favorable and do not exhibit any transition levels in the bandgap. Subsequent annealing in hydrogen-free or nitrogen ambient will dissociate these complexes and activate *p*-type conductivity in GaN. Experimental measurements, where an ultraviolet photoluminescence band related to the shallow Be_{Ga} acceptor emerges after annealing the Be-doped GaN, confirm these findings.

Hydrogen plays a significant role in the properties of semiconductors.[1,2] In particular, it passivates defects and impurities, which can be beneficial for device design. A vivid example is the development of *p*-type GaN, which ended with a breakthrough in the fabrication of bright blue LEDs and various solid-state lighting applications.[3] Mg-doped GaN is high-resistivity due to compensation by parasitic donors, as well as passivation of Mg acceptor with H, if it is grown by techniques involving hydrogen, such as metalorganic chemical vapor deposition (MOCVD). Thermal annealing at $T \approx 800$ ºC in a hydrogen-free ambient activates Mg acceptors and results in a conductive *p*-type material.[4,5] In Mg-doped GaN grown by MOCVD, hydrogen from the source

gas incorporates in GaN in amounts approximately equal to that of Mg over the wide range of Mg doping (between 6×10^{16} and 3×10^{19} cm^{-3}), which suggests the formation of the Mg_{Ga}-H complexes.[6] Illumination with ultraviolet (UV) light helps dissociate the Mg_{Ga}-H complexes, and the annealing temperature can be reduced to 500 ºC.[7] The presence of the Mg_{Ga}-H complexes and hydrogen removal by thermal annealing was also confirmed by observing the Mg_{Ga}-H local vibrational mode at 3125 cm^{-1}.[8] Upon annealing of GaN:Mg samples at T = 850 ºC, all Mg_{Ga}-H complexes dissociate, and the concentration of electrically active Mg_{Ga} acceptors approaches the total concentration of Mg.[6] Note that for high concentrations of Mg (more than 10^{19} cm^{-3}), two types of Mg-H complexes are proposed: a metastable one that leads to activation of Mg_{Ga} acceptors after annealing and a stable one (electrically inactive), which remains after the annealing in samples with a high concentration of Mg.[9] The lowest resistivity of Mg-doped GaN is about 0.2 Ω cm, achieved with the concentration of holes $2\text{-}3\times10^{18}$ cm^{-3} and the hole mobility 9-19 cm^2/Vs.[10,11,12] The highest room-temperature mobility of 43 cm^2/Vs was demonstrated for two-dimensional hole gas in GaN-based heterostructures.[13]

While the experimental results indicate that Mg_{Ga}-H complexes are formed in MOCVD-grown GaN:Mg, the question of whether they are electrically active is still not clear. Calculations by Lyons *et al*.[14] predict that the Mg_{Ga}-H complexes are electrically active, with the 0/+ transition level at 0.13 eV above the valence band maximum (VBM). According to these calculations, the UVL band with a maximum at 3.27 eV in the photoluminescence (PL) spectrum from undoped or Mg-doped GaN is caused by transitions from the conduction band to this donor level of the Mg_{Ga}-H complex. However, this attribution of the UVL band in GaN is inconsistent with a very high hole-capture coefficient (1×10^{-6} cm^3/s) for the related defect,[15,16] and the fact that the UVL band

is the main PL band in hydrogen-free GaN grown by molecular beam epitaxy (MBE) and doped with Mg with concentrations between 10^{17} and 10^{20} cm^{-3}.[17]

Recently, we showed that beryllium (Be) in GaN exhibits a shallow acceptor state at 113±5 meV above the VBM, which is responsible for a PL band labeled UVL_{Be} with a sharp peak at 3.38 eV followed by a series of LO phonon replicas.[18] Be-doped GaN is commonly grown by MBE,[19] where the UVL_{Be} band is the dominant feature in the PL spectrum,[20,21,22] yet reports on *p*-type conductivity in such material are rare.[23] The UVL_{Be} band was also observed in bulk GaN:Be grown by the high-pressure method.[24] However, usually only the broad yellow band with a maximum at 2.2 eV, labeled the YL_{Be} band hereafter, is observed from such samples. This YL_{Be} band was previously attributed to the Be_{Ga}-O_N complex.[25] We are aware of only one publication where Be-doped GaN was grown by the MOCVD technique.[26,27] In that work, the as-grown GaN:Be was highly resistive, while rapid thermal annealing at 920 ºC for 12 seconds in N_2 ambient converted the material into a conductive *p*-type with the room-temperature concentration of free holes 1.7×10^{18} cm^{-3} and the acceptor activation energy of 118±4 meV. The UVL_{Be} band was also observed in these samples. However, the passivation mechanism and the activation of the Be_{Ga} acceptor is currently not well understood. In this Letter, we use first-principles calculations and experimental PL measurements to elucidate this question.

Theoretical calculations were performed using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional.[28] The HSE functional was tuned to fulfill the generalized Koopmans condition for the Mg_{Ga} acceptor in GaN (fraction of exact exchange of 0.25, the range separation parameter of 0.161 $Å^{-1}$).[29] All calculations were performed in 300-atom hexagonal supercells at the **Γ**-point, with plane-wave energy cutoffs of 500 eV. All atoms were relaxed within HSE to minimize forces to 0.05 eV/Å or less. The formation energies of a defect *X* in a charge state *q* were calculated as:

$$E_{form} = E_{tot}(X^q) - E_{tot}(\mathrm{GaN}) - \sum_{\alpha} n_\alpha \mu_\alpha + q(E_V + E_F) + \Delta E^q_{corr}, \qquad (1)$$

where $E_{tot}(X^q)$ is the total energy of the supercell containing the defect and $E_{tot}(\mathrm{GaN})$ is that without the defect, n_α is the number of atoms of an element α with the elemental chemical potential μ_α added to or removed from the supercell, E_V is the energy of the VBM, E_F is the Fermi energy relative to the VBM, and ΔE^q_{corr} is the correction for spurious electrostatic interactions in periodic supercells.[30] Chemical potentials, which determine the relative abundance of chemical elements during the growth process, depend on the phases competing with the GaN growth. Depending on the experimental growth conditions, chemical potentials vary between the bounds set by these competing phases, here assumed to be metallic Ga and N_2 molecule. Therefore, the formation of GaN is determined by the following thermodynamic condition

$$\mu_{\mathrm{GaN}} = \mu_{\mathrm{Ga}}(\text{Ga metal}) + \mu_{\mathrm{N}}(\mathrm{N_2}) + \Delta H_{\mathrm{f}}(\mathrm{GaN}), \qquad (2)$$

where $\Delta H_{\mathrm{f}}(\mathrm{GaN})$ is the formation enthalpy of GaN. In the limiting case of N-rich growth, the chemical potential of nitrogen is set to $\mu_{\mathrm{N}}(\mathrm{N_2})$, while that of gallium is set to $\mu_{\mathrm{Ga}}(\text{Ga metal}) + \Delta H_{\mathrm{f}}(\mathrm{GaN})$. In the case of Ga-rich growth, $\mu_{\mathrm{N}} = \mu_{\mathrm{N}}(\mathrm{N_2}) + \Delta H_{\mathrm{f}}(\mathrm{GaN})$ and $\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga}}(\text{Ga metal})$. In the presence of oxygen, the formation of beryllium defects is assumed to be limited by the growth of beryllium oxide BeO: $\mu_{\mathrm{Be}} + \mu_{\mathrm{O}} = \mu_{\mathrm{BeO}}$. In turn, the chemical potential of oxygen is assumed to be limited by the formation of gallium oxide Ga_2O_3: $2\mu_{\mathrm{Ga}} + 3\mu_{\mathrm{O}} = \mu_{\mathrm{Ga_2O_3}}$. Finally, two possibilities were considered for the chemical potential of hydrogen: the formation of a hydrogen molecule, $\mu_{\mathrm{H}} = \mu_{\mathrm{H}}(\mathrm{H_2})$, or ammonia, $\mu_{\mathrm{N}} + 3\mu_{\mathrm{H}} = \mu_{\mathrm{NH_3}}$.

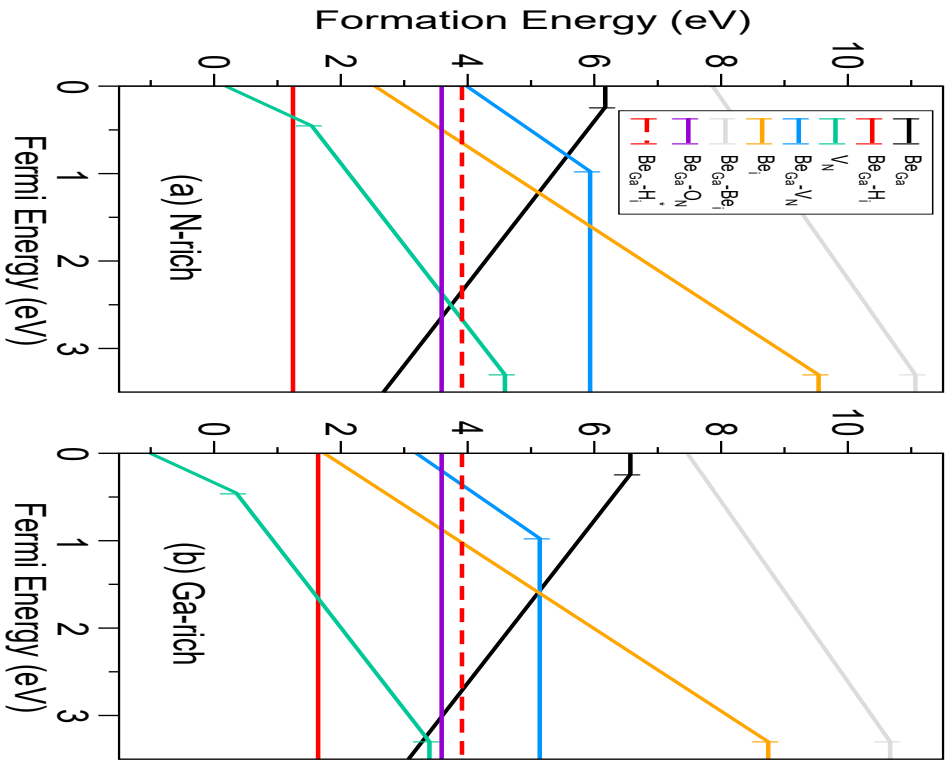

FIG. 1. Calculated formation energies of Be-related defects in GaN: the shallow Be_{Ga} acceptor, Be_{Ga}-H_i complex (for μ_H from H_2 and NH_3, the latter is labeled Be_{Ga}-H_i^*), nitrogen vacancy V_N, Be_{Ga}-V_N complex, Be interstitial Be_i, Be_{Ga}-Be_i complex, Be_{Ga}-O_N complex. (a) Nitrogen-rich conditions. (b) Gallium-rich conditions.

HSE calculations predict that the Be_{Ga} is a dual nature acceptor, possessing both deep and shallow acceptor states. The deep acceptor state is a small polaron with the transition level calculated at 0.58 eV above the VBM, in agreement with recent HSE calculations.[31,32] However, similar to other Koopmans corrected calculations,[33] we also predict the shallow acceptor state with an acceptor level at about 0.2 eV, a value overestimated by about 0.1 eV due to the supercell approach.[18] The interplay between the deep and shallow states of Be acceptor is analyzed in detail

in Ref. [18]. However, the deep state has not yet been observed experimentally, and PL experiments reveal only the shallow transition level.

The results of the formation energy calculations are presented in Fig. 1. Although this acceptor exhibits a shallow transition level that is the lowest of all known acceptors in GaN to date, producing a *p*-type Be-doped GaN faces challenges due to several compensating defects. First of all, even in an ideal impurity-free growth situation, self-compensation of the *p*-type material would present a serious obstacle. Beryllium interstitial defect (Be_i) has lower formation energy in *p*-type material by about 2 eV. This suggests that if the initial stages of growth produce *p*-type material due to the formation of Be_{Ga} acceptors, pushing the Fermi level towards the valence band will lead to an overwhelming fraction of Be atoms going to the interstitial sites, rather than substituting for Ga. In addition, since Be_i is a double donor, each Be_i defect would compensate two Be_{Ga} acceptors. The high formation energy of the Be_{Ga}-Be_i complex suggests that it does not play a substantial role in the compensation mechanism.

Since Be acceptor substitutes for the gallium atom, *p*-type doping is more favorable in the N-rich regime, where Ga vacancies are likely to be filled with Be atoms. Note that the nitrogen vacancy, which is a donor, exhibits low formation energy even in this growth regime. The formation of the Be_{Ga}-V_N complexes is also about as likely as the formation of the isolate Be_{Ga}. In addition, since oxygen is commonly present in GaN samples grown by various techniques, the formation of the Be_{Ga}-O_N complex is also likely due to its relatively low formation energy. In our calculations, the Be_{Ga}-O_N complex is stable and electrically neutral, with a binding energy of 1.8 eV. It does not exhibit any transition levels in the bandgap, suggesting that the attribution of YL_{Be} band to this complex is unlikely. Overall, based on these results, it is difficult to expect efficient *p*-type by using straightforward hot growth of Be-doped GaN. Most likely, high levels of

compensation will occur, with the Fermi level pinned near the middle of the bandgap, producing a high resistivity material.

However, our calculations show that it is possible to circumvent the compensation issues in a way similar to that used to produce Mg-doped *p*-type GaN. Namely, positively charged hydrogen is expected to efficiently bind with the negatively charged Be_{Ga} acceptors to form the Be_{Ga}-H_i complex. The most stable configuration of this complex with calculated binding energy varying between 1.8 and 2.0 eV (depending on the Fermi energy) is hydrogen occupying a bond-center site between Be_{Ga} and nearest N neighbors, which pushes Be from the Ga site along the Be-N bond by 0.6 Å. The formation energy of this complex is the lowest among all considered defects, with the only exception of the nitrogen vacancy for the Fermi level close to the valence band. Furthermore, the Be_{Ga}-H_i complex is electrically neutral at any Fermi energies; i.e., it does not have transition levels in the bandgap. For the chemical potentials of hydrogen determined by the formation of ammonia, the formation energy of the Be_{Ga}-H_i complex is significantly higher. However, even in this case for N-rich growth, the formation of this complex is still energetically most favorable among Be-related defects for the Fermi energies from 0.65 to 2.35 eV above the VBM (while for E_F>2.65 eV, Be_{Ga} acceptor is the lowest energy defect). This offers an opportunity to grow Be-doped *n*-type GaN in the presence of hydrogen, where the Fermi level is pushed closer to the conduction band by natural shallow donors, such as O_N. In this case, Be atoms will predominantly occupy the gallium sites (since Be_i interstitials will be extremely energetically unfavorable) and form complexes with mobile interstitial hydrogen. Subsequent annealing in nitrogen ambient will out-diffuse and evaporate hydrogen, leaving the Be_{Ga} acceptors uncompensated and producing a *p*-type GaN. A very shallow transition level of the Be_{Ga} suggests

that this growth route can potentially produce a *p*-type GaN with significantly higher hole concentrations compared to that produced by Mg-doping.

In addition to the reported successful activation of the shallow Be acceptor in MOCVD-grown GaN,[26] attempts to activate it in Be-doped MBE GaN led to an increase of the UVL_{Be} intensity, yet the samples remained semi-insulating.[22,34] We studied PL from Be-doped, Ga-polar GaN samples grown on sapphire substrates by RF-plasma-assisted MBE at WVU.[22,34] The Ga-polar 1 μm-thick GaN layers with the concentration of Be between 5×10^{17} and 1×10^{20} cm^{-3} were grown on top of the ~0.1 μm-thick undoped GaN on sapphire substrates. Three GaN:Be samples were grown in the presence of atomic hydrogen. The presence of H enhanced the incorporation of Be at low Be fluxes.[35] In most cases, the Be_{Ga}-related UVL_{Be} intensity greatly increased after annealing samples at T = 900 ºC for two hours in N_2 ambient, yet we could not find a clear correlation between the intensity UVL_{Be} band and growth conditions such as the concentration of Be, co-doping, or sample polarity. Note that no conductive *p*-type was obtained; the samples remained semi-insulating after the annealing.

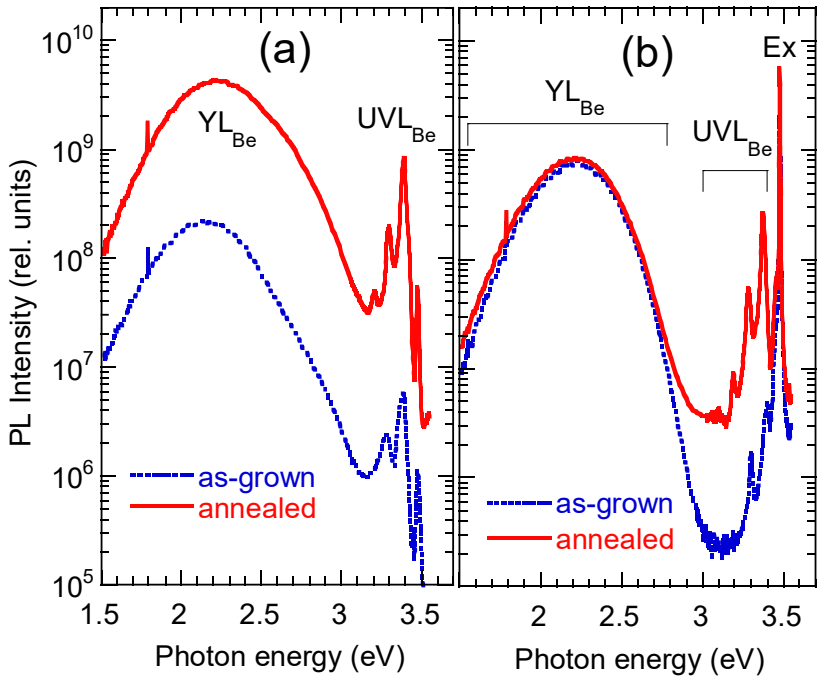

FIG. 2. PL spectra from GaN:Be before and after annealing at 900 ºC for two hours in N_2 ambient. (a) GaN:Be,H samples 0414a,b with [Be] = 1×10^{19} cm^{-3}, (b) GaN:Be samples 0408a,b with [Be] = 5×10^{17} cm^{-3}. The excitation intensity is 0.13 W/cm^2 and T = 20 K. The PL spectra are measured in identical conditions. The exciton line at 3.478 eV is labeled "Ex".

Fig. 2 shows examples of PL spectra for two GaN:Be samples before and after annealing at 900 ºC for two hours in N_2 ambient. Sample 0408 with the concentration of Be 5×10^{17} cm^{-3} was grown without additional hydrogen, while sample 0414 with [Be] = 10^{19} cm^{-3} contained a high concentration of H.[34] The intensity of the broad YL$_{Be}$ band at 2.2 eV remained the same after the annealing for sample 0408 and increased by a factor of 20 for sample 0414. This indicates that the origin of the YL$_{Be}$ is likely unrelated to the Be$_{Ga}$-O$_N$ complex, which is expected to dissociate at 900 ºC. Therefore, the attribution of the YL$_{Be}$ to a specific defect is currently uncertain and beyond

the scope of this work. The zero-phonon line of the UVL_{Be} band originating from the shallow state of the Be_{Ga} acceptor is located at 3.37-3.38 eV, accompanied by weaker LO phonon replicas. Remarkably, the UVL_{Be} band with relatively high intensity emerges only after the annealing in sample 0408 and increased by a factor of 100 in sample 0414, indicating a significant increase in the number of the Be_{Ga} acceptors in these samples. The significant rise of PL intensity after annealing for sample 0414 containing a high concentration of H suggests that a significant part of the Be_{Ga} defects could be passivated with H, and the annealing activated these acceptors by dissociating the Be_{Ga}-H_i complexes. However, no significant concentration of H is expected in Be-doped GaN grown by RF-plasma-assisted MBE without H, and the emergence of the UVL_{Be} band in sample 0408 after annealing is surprising. HSE calculations (Fig. 1) suggest that in this case Be_{Ga} acceptors could be passivated by oxygen, forming the Be_{Ga}-O_N complexes. Both the Be_{Ga}-H_i and Be_{Ga}-O_N complexes are predicted to be electrically neutral, energetically favorable, with similar binding energies of ~1.8 eV, indicating that either complex would convert into an isolated Be_{Ga} acceptor upon annealing at 900 ºC (Fig. 2). However, since hydrogen is easier to out-diffuse, co-doping with hydrogen during growth would be advantageous for Be activation.

In conclusion, our results suggest a possible route for *p*-type Be doping of GaN. Nitrogen-rich growth of GaN doped with Be in the presence of hydrogen will lead to the preferential formation of the Be_{Ga}-H_i complexes, which are electrically neutral and do not exhibit any transition levels in the bandgap. The formation energy of the complex is independent of the Fermi energy and remains low during growth. Therefore, *n*-type GaN can be initially grown, containing a large number of neutral Be_{Ga}-H_i complexes. Subsequent annealing can dissociate these complexes, removing hydrogen atoms and activating the *p*-type conductivity of GaN.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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