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# Mg-O and Mg-$V_N$ defect complexes in cubic GaN

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Mg-O and Mg-$V_N$ defect complexes in cubic GaN are examined by means of *ab initio* calculations using a supercell approach in connection with the full-potential linear muffin-tin-orbital method. 32-atom supercells are used, and atomic relaxations are taken into account. The positions of the defect levels and formation energies are calculated and discussed in comparison with the results for individual defects. The calculations show, in agreement with experimental data, that both complexes, Mg-O and Mg-$V_N$, are energetically favorable in GaN, and should play an important role in the self-compensation mechanism. Both kinds of complexes introduce resonant states in the valence and conduction bands.

## I. INTRODUCTION

As-grown GaN is generally an *n*-type semiconductor. There are many suggestions that oxygen is the impurity primarily responsible for the *n*-type conductivity of GaN.[1,2] Secondary ion mass spectrometry (SIMS) measurements indicate that GaN can contain oxygen in concentrations at least in the range $10^{16}$–$10^{17}$ cm$^{-3}$.[3] Unintentionally doped bulk GaN,[4] especially, is known to contain a high concentration of oxygen, resulting in a high background electron concentration of $10^{18}$–$10^{19}$ cm$^{-3}$. Insulating or *p*-type-doped GaN is more difficult to grow. Currently, *p*-type doping in GaN is generally obtained by Mg compensation of the residual donors, and it appears that Mg is the only acceptor in GaN that at the present can generate, reproducibly, useful *p*-type conductivity. Typically, *p*-type GaN has a Mg concentration of the order of $10^{20}$ cm$^{-3}$, which results in a maximum hole carrier concentration of $10^{18}$ cm$^{-3}$. A high activation energy [about 0.16 eV for Mg (Ref. 5)] is one factor limiting the hole concentration, but also the growth technique and the thermodynamic parameters play important roles. Another serious factor limiting *p* conduction is self-compensation resulting from the occurrence of donor-acceptor pairs.[6] These can either be widely separated or created as nearest-neighbor complexes. Recent work indicates that donor-acceptor pairs in fact are bound in complexes. Here we consider two interesting aspects.

(1) Photoconductivity experiments performed by Pankove *et al.*[7] on bulk GaN crystals containing a high concentration of oxygen and magnesium have shown that the simultaneous presence of Mg and O in GaN makes GaN insulating. The fact that GaN is insulating implies almost indentical numbers of donors and acceptors, which most likely happens only when donors and acceptors are incorporated pairwise, so that they form molecular complexes. The authors[7] suggested that Mg would scavenge the residual donors and remove their donor levels from the band gap of GaN. To verify that Mg and O are forming complexes in GaN, ultraviolet reflection spectrometry was performed on the samples, and two peaks characteristic for MgO were found also in GaN:MgO.[7]

(2) Mg-$V_N$ is another complex that could be expected in *p*-type GaN. In *p*-type material the formation energy of the nitrogen vacancy becomes very small,[8] and the concentration of this defect type increases. It has been demonstrated that in Mg-doped GaN samples grown by metal-organic chemical vapor deposition (MOCVD) the concentration of $V_N$ at the growth temperature is practically the same as that of Mg (about $10^{19}$ cm$^{-3}$).[6] These impurities are oppositely charged and in analogy to the Mg-O case would tend to associate and form a nearest-neighbor complex. The blue Mg-induced 2.8 eV photoluminescence band in MOCVD-grown GaN, not observed in bulk samples, has been studied in a large number of crystals with varying Mg content. Some evidence for the distant donor-acceptor pair character of the 2.8 eV band was presented,[6] with suggestions that the acceptor could be isolated $Mg_{Ga}$, while the deep donor is a nearest-neighbor complex made out of a $Mg_{Ga}$ acceptor with a nitrogen vacancy, formed by self-compensation.[6] Since the GaN band gap in the wurtzite structure is 3.4 eV, and assuming that the Mg acceptor level is lying about 0.2 eV above the top of the valence band,[8] the estimated position of the deep donor level should be about 0.4 eV below the conduction band edge.

In the present paper we report results of *ab initio* calculations of the electronic structure and formation energies of the MgO molecular impurity and the Mg-$V_N$ impurity complex in GaN, together with the calculations for the individual defects. Calculations of Mg and $V_N$ were published in Ref. 8, while results for oxygen are included in the present paper. Our results are compared with the conclusions deduced from the recent experimental data.[6,7] In the case of MgO molecular doping our results confirm the experimental conclusions,[7] that the states attributed to O appear in the conduction band while those of Mg appear in the valence band, i.e., the impurity levels found in the band gap for both of the isolated impurities disappear from the band gap when the complex is formed, leading to highly resistive material. The Mg-$V_N$ complex in GaN seems to be similar to the MgO complex. The Mg-related level, as in GaN:MgO, appears in the valence band, disappearing from the band gap, whereas the $V_N$ *p*-like state, like oxygen in the MgO complex, is moved high up into the conduction band and is not the source of electrons any longer.

## II. METHOD

GaN can crystallize in two phases, the cubic (zinc blende) and hexagonal (wurtzite) phases. We study here the cubic phase, believing that there is little difference in impurity level positions of the two phases. This is supported by the comparison of defects in hexagonal and cubic GaN made by Neugebauer and Van de Walle,[13] who found only minor differences in formation energy and atomic relaxations between these two hosts. Furthermore, the energy level positions were practically the same. The most distinct difference is a small splitting of the $t_2$ gap states related to the lower symmetry of the wurtzite structure compared to the cubic structure.

To study the lattice relaxation effects in the neighborhood of defects the full nonspherical shapes of potentials and charge distributions are taken into account. The calculations use the supercell approach with the linear muffin-tin-orbital (LMTO) method[9] in the full-potential version.[10] In the supercell approach, large but finite cells, each containing a defect, are repeated ad infinitum, leading to impurity bands with finite widths. In that case we can only estimate the impurity levels in the band gap as the center-of-gravity of the impurity band. This is determined by means of the density-of-states functions. Calculations are performed using 32-atom supercells, although previous tests have demonstrated that reliable relaxations can be obtained near point defects in GaN by using a cell with only 16 atoms. The main reason for choosing the larger cell is that this reduces the broadening of the impurity bands, making the identification of the impurity states easier. The band structure calculations used a basis set that includes partial waves of *s*, *p*, and *d* character on each atomic site, with three different decay constants for muffin-tin orbitals of *s* and *p* symmetry and two different decay constants for *d* orbitals, giving a total of 44 LMTO orbitals per GaN formula unit. The **k** space integrations used 1728 **k** points in the Brillouin zone. Additional ''empty spheres'' are introduced at the tetrahedral interstitial sites.[11] We chose all (nonoverlapping) muffin-tin spheres to have the same size. The local-density approximation[12] (LDA) to density functional theory is used, by which exchange and correlation effects are accounted for by a simple local potential. The fundamental gaps of semiconductors derived from the LDA band structures are generally too small. The calculated energy gap of GaN is 2.2 eV, while the experimental gap for the cubic phase is 3.25 eV. This has consequences for defect calculations, in particular for the energy level positions of bound states in the gap, which lie close to the conduction band minimum. This is another reason for using a rather large cell, and in that way obtaining narrow impurity bands. (We note that application of gradient-corrected density functionals does not repair this ''gap problem.'') For the relaxation and formation energy calculations, which are the major parts of this work, this problem is less important, though.

Performing the supercell calculations we concentrate in the present work on neutral states only. The energy levels as quoted in this paper are the eigenvalues of the self-consistent Kohn-Sham equations. A comparison to experiments should in fact rather be made by using calculated transition state energies (i.e., using half-integer occupation numbers). Often a good approximation to this is obtained by averaging eigenvalues for ''neighboring'' charge states.[14,15]

To check the stability of the defects created and their complexes we calculate the formation energies, defined as

$$E^f = E_{tot} - E_{host} + n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} + n_{\mathrm{N}}\mu_{\mathrm{N}} - \sum_i n_i\mu_i, \qquad (1)$$

where $E_{tot}$ is the total energy of the defect supercell, $E_{host}$ is the total energy of the ideal host supercell, $n_{\mathrm{Ga}}$, $n_{\mathrm{N}}$ are the numbers of Ga and N atoms substituted by the impurity, and $\mu_{\mathrm{Ga}}$, $\mu_{\mathrm{N}}$ their chemical potentials. Similarly, $n_i$ and $\mu_i$ are the number and chemical potential of impurity atoms of species *i*, respectively. The calculated formation energies for the defects considered here as well as their complexes are given in Table I, together with the chemical potentials used. For a detailed description and results for some defects and impurities in the III-V nitrides, see Ref. 8.

TABLE I. Calculated formation energies, in eV, for defects and complexes in GaN. Also listed are the chemical potentials of the atoms, likewise in eV. Both Ga-rich and N-rich growth conditions are considered. The calculated formation energy for bulk GaN is 1.9 eV.

| | Ga-rich | N-rich |
|---|---|---|
| $\mu_{\mathrm{Ga}}$ | −3.5 | −5.5 |
| $\mu_{\mathrm{N}}$ | −10.2 | −8.3 |
| $\mu_{\mathrm{O}}$ | −4.7 | −4.7 |
| $\mu_{\mathrm{Mg}}$ | −1.7 | −3.2 |
| $V_{\mathrm{N}}$ | 2.7 | 4.6 |
| $\mathrm{O_N}$ | −2.6 | −0.7 |
| $\mathrm{Mg_{Ga}}$ | 1.0 | 0.6 |
| MgO | −4.9 | −3.5 |
| Mg-$V_{\mathrm{N}}$ | 0.9 | 2.3 |
| Mg(i)-$V_{\mathrm{N}}$ | 7.0 | 10.4 |

## III. MG-O COMPLEX

Native defects and some impurities in cubic GaN and AlN were considered in Ref. 8, where it was found that substitutional Mg on a cation site forms shallow acceptor states. The neutral state is occupied by one hole and five electrons. This level was estimated to lie 0.15 eV above the valence band edge. From total energy calculations we found symmetrical outward relaxations around the defect. The displacements of the surrounding atoms are rather small, 4% of the bond length. The formation energy is very low under both Ga-rich (1.0 eV) and N-rich (0.6 eV) conditions, indicating that Mg atoms can readily replace Ga under any conditions (see Table I).

The defect level connected with substitutional oxygen on a N site is found to be degenerate with the conduction band minimum. The finite size of the supercell leads to a wide impurity band, which is centered at ~0.4 eV above the conduction band edge. For the neutral state one electron is bound in a shallow donor level, i.e., the oxygen acts as a single donor. Symmetrical outward relaxations (4% of the bond length) are found around the defect. The calculated formation energies for the neutral charge state are negative for both Ga-rich and N-rich conditions, as shown in Table I. Consequently, oxygen is readily dissolved in GaN.

To study the Mg-O complex, magnesium is placed on the Ga site and oxygen on the N site. The calculated formation energy for this complex is negative under any conditions (see

Table I). Furthermore, the complex is seen to be bound by 3.3 eV with respect to the isolated $\mathrm{Mg}_{\mathrm{Ga}}$ and $O_{\mathrm{N}}$ impurities, thus confirming the hypothesis that these two impurities do compensate. Our calculations also show that the opposite configuration (Mg on the N site, O on the Ga site) has much higher (by about 20 eV!) formation energy and is very unlikely to be created. Considering the lattice relaxation around the Mg and O atoms we find that the position of Mg is almost ideally substitutional, whereas the nearest neighbors, including oxygen, relax outward nearly symmetrically. This relaxation is 3% of the bond length. The Ga atoms that are the nearest neighbors of oxygen relax outward by approximately the same amount (i.e., 3% of the bond length).

The positions of the impurity band centers are estimated from the density-of-states functions for each of the cases considered. In Fig. 1(a), the total density of states for pure GaN is shown, while Figs. 1(b)–(d) show the total densities of states for the cases of GaN:Mg, GaN:O, and GaN:MgO, respectively. Comparing the defect levels of the Mg-O complex we find that the Mg acceptor level, which is lying about 0.15 eV above the valence band maximum in the case of GaN:Mg, moves down to about 0.6 eV below the valence band maximum. On the other hand, the oxygen-originated level appears to be high up in the conduction band, about 1.0 eV above the conduction band minimum. Thus, going from the individual impurity cases (GaN:Mg and GaN:O) to the GaN:MgO complex we find a downward shift of the Mg-related impurity level by about 0.7 eV, and an upward shift of $\sim 1$ eV of the O-related impurity level. This is schematically shown in Fig. 2.

## IV. Mg-$V_{\mathrm{N}}$ COMPLEX

The $a_1$ ($s$-like) state of the nitrogen vacancy, $V_{\mathrm{N}}$, forms a resonance 0.1 eV below the valence band maximum, whereas the $t_2$ ($p$-like) state appears as a resonance in the conduction band. The approximate position of the $t_2$ resonance is at 0.5 eV above the conduction band minimum according to our previous calculation.[8] In analogy with oxygen, for the neutral charge state one electron is bound in a shallow donor level, i.e., the nitrogen vacancy acts as a single donor. Lattice relaxations are small near the nitrogen vacancy. We find that the nearest-neighbor Ga atoms move inward by 2% of the bond length. The formation energies are 2.7 eV and 4.6 eV for Ga-rich and N-rich conditions, respectively. In $p$-type GaN grown under Ga-rich conditions the $V_{\mathrm{N}}^{+}$ defect will dominate.

Considering the Mg-$V_{\mathrm{N}}$ complex with Mg replacing a Ga neighbor of $V_{\mathrm{N}}$ we find that the $a_1$ defect level connected with the nitrogen vacancy $V_{\mathrm{N}}$ is now in the band gap—about 0.1 eV above the valence band top, whereas the $t_2$ ($p$-like) state appears about 0.7 eV above the conduction band edge. The defect level connected with magnesium lies about 0.6 eV below the valence band edge, as in the Mg-O case.

The total energy calculations show that the magnesium atom is moved out of the ideal position by about 3% and the neighboring nitrogen atoms relax outward nearly symmetrically, also by about 3% of the bond length. One observes from Table I that the calculated formation energies of Mg-$V_{\mathrm{N}}$ are significantly lower than the sum of the formation energies of the $\mathrm{Mg}_{\mathrm{Ga}}$ and $V_{\mathrm{N}}$ single defects, so that $\mathrm{Mg}_{\mathrm{Ga}}$ and $V_{\mathrm{N}}$ bind by 2.8 eV, demonstrating that these defects also will have a strong tendency to compensate.

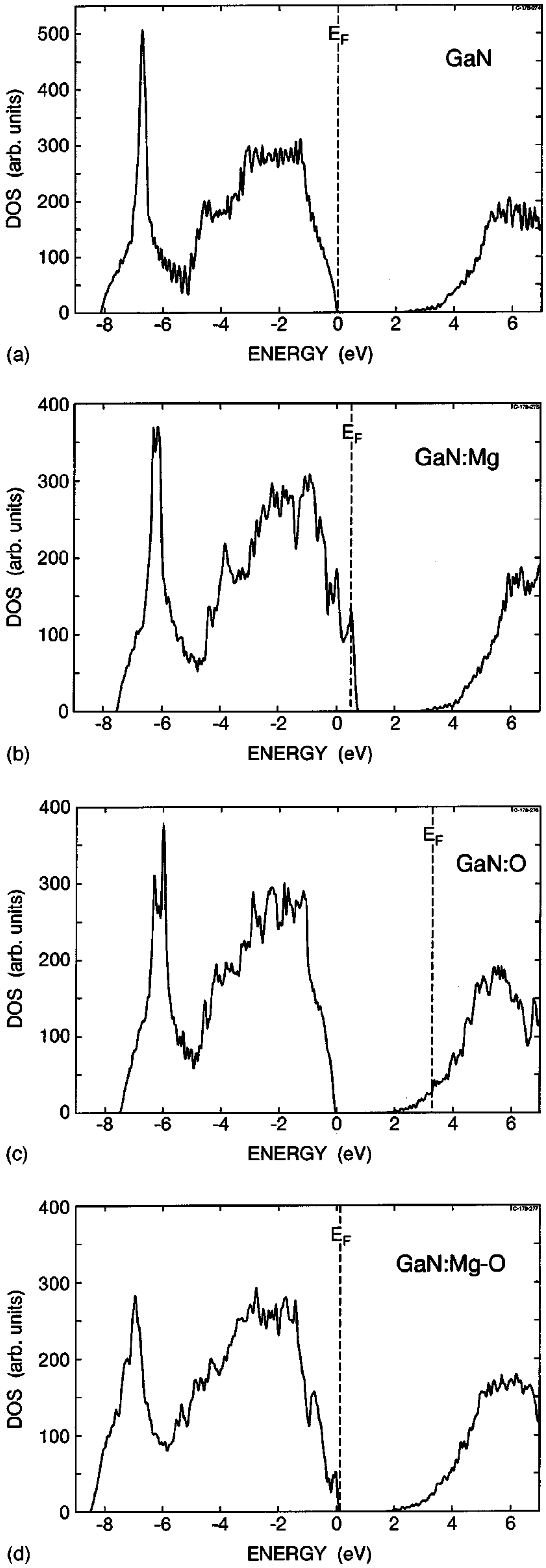

FIG. 1. The total density of states for (a) GaN, (b) GaN:Mg, (c) GaN:O, and (d) GaN:MgO.

The density-of-states functions for GaN:$V_{\mathrm{N}}$ and for GaN:Mg-$V_{\mathrm{N}}$ are shown in Figs. 3(a) and 3(b), respectively.

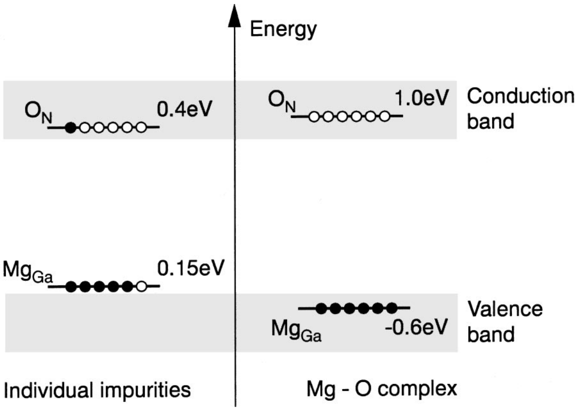

FIG. 2. Schematic diagram of the defect level positions in the case of individual dopants and the MgO complex.

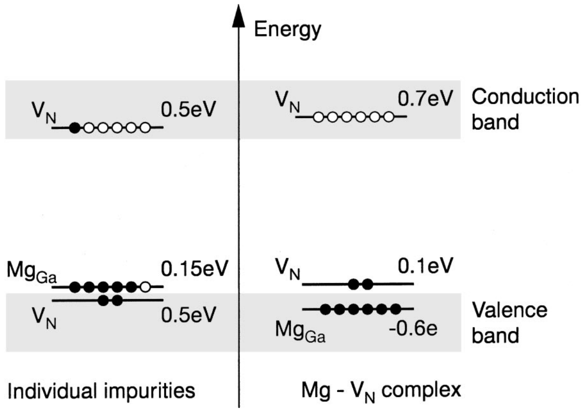

FIG. 4. Schematic diagram of the defect level positions in the case of individual defects and Mg-$V_N$ complex.

A comparison of the defect level positions for individual defects and for the case of the Mg-$V_N$ complex is schematically shown in Fig. 4. In that context, note that the hypothesis that the $Mg_{Ga}$ acceptor when forming a complex with the $V_N$ donor creates a deep donor level about 0.4 eV below the conduction band minimum is not supported, and it seems that the blue photoluminescence cannot be explained by transitions between deep donor states arising from the Mg-$V_N$ complex and acceptor levels assigned to isolated $Mg_{Ga}$.

A new model of the origin of the blue photoluminescence in GaN was proposed recently by Lee and Chang,[16] who performed first-principles pseudopotential calculations of the defect complex composed of the N vacancy and the Mg interstitial at a nearby empty site in wurtzite GaN. They found that this complex gives rise to optical transition levels around 2.8 eV above the valence band maximum and could be responsible for the blue photoluminescence. Investigating the Mg(i)-$V_N$ complex in cubic GaN by our LMTO method, we obtain similar results. At first, quite remarkable lattice relaxation effects have been found: (i) Mg is moved toward the vacancy reducing the distance by about 5%; (ii) the bond length between one of the Ga atoms neighboring Mg and $V_N$, and the other Ga atom, neighboring $V_N$ but not Mg, is reduced by 4% to 12%, depending on the charge state of the complex (+1, 0, or −1); (iii) all the remaining Ga neighbors of magnesium relax outward by about 6%. The energy gain due to the relaxation is about 2 eV. Moreover, we find that, in contrast to the complex with substitutional magnesium, self-compensation does not occur in this case. The singly occupied donor level is lying in the conduction band in the nonrelaxed case, but moves down to the conduction band edge when lattice relaxation is included. More detailed calculations might support the idea that this donor level is responsible for deep-donor to valence-band (or shallow-acceptor) transitions leading to the blue luminescence. However, the calculated formation energies of the Mg(i)-$V_N$ complex are so high (see Table I), that it seems unlikely that this defect can form. Those calculated in Ref. 16 for the wurtzite structure are even higher (8.9 eV and 10.9 eV, for Ga- and N-rich conditions, respectively). To explain the formation of the Mg(i)-$V_N$ complex the authors[16] assume that the complex can be stabilized by hydrogen passivation. They found that the most stable geometry obtained is when three H atoms and the Mg interstitial are directly bonded to the four vacancy-neighboring Ga atoms. This disagrees with the conclusion from calculations by Van de Walle,[17] who pointed out that a typical Ga-H bond distance is too large for more than one H to fit inside the nitrogen vacancy. Also, adding more than one H atom to this region results in large repulsion and a high energy.[17]

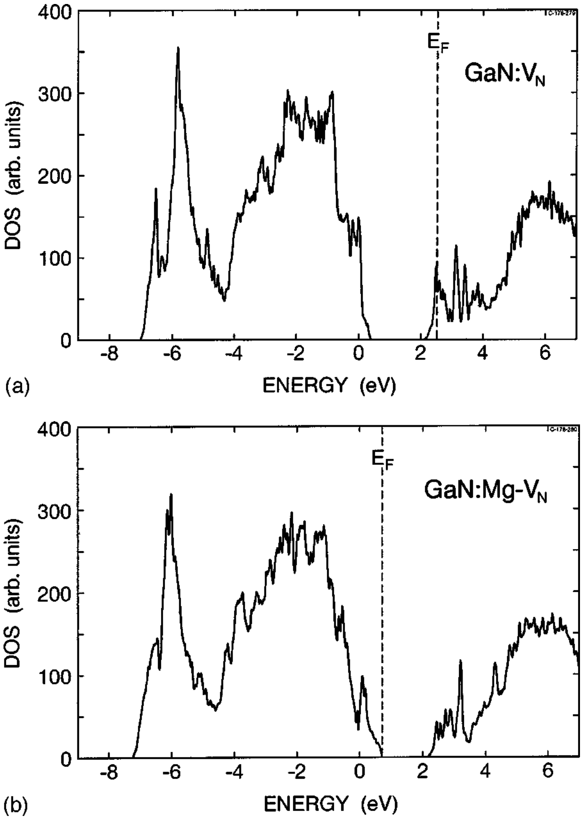

FIG. 3. The total density of states for (a) GaN:$V_N$ and (b) GaN:Mg-$V_N$.

Therefore, the discussion about the possible sources of the blue luminescence in GaN seems to be still open.

## V. SUMMARY

The suggestions based on experimental data for the Mg-O complex in GaN (Ref. 7) are fully confirmed by our calculations. The calculated formation energy of the MgO molecule in GaN is significantly lower than for the individual dopants, showing that the MgO complex will be abundant. The states attributed to O appear in the conduction band while those of Mg appear in the valence band, i.e., both disappear from the band gap, which leads to high resistivity.

The case of the Mg-$V_N$ complex appears to be quite similar. The calculated formation energy of the Mg-$V_N$ complex is also significantly lower than that for the individual $V_N$ and Mg defects. The $V_N$ defect is analogous to oxygen as a single defect, since both have shallow donor levels and are sources of electrons, leading to $n$-type GaN. In the Mg-$V_N$ complex this shallow level moves well into the conduction band, similarly to the oxygen donor level in GaN:MgO. The $a_1$ acceptor level of $V_N$, which is resonant with the valence band in the case of the isolated impurity, moves, when the Mg-$V_N$ complex is formed, into the energy gap, creating a shallow acceptor level. On the other hand, the Mg-originated level disappears from the energy gap and becomes resonant with the valence band, exactly as in the GaN:MgO case.

Our calculations do not support the model in which the blue photoluminescence is explained by transitions between deep donor states arising from the Mg-$V_N$ complex and acceptor states assigned to isolated $Mg_{Ga}$.

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