

Stabilization Mechanism of Vacancies in Group-III Nitrides: Exchange Splitting and Electron Transfer

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We report first-principles calculations on mono-, di-, and tri-vacancies in group-III nitrides with clarifying two distinctive mechanisms in stabilization of the vacancy: Spin polarization due to exchange splitting of nitrogen-dangling bond states and electron transfer caused by breathing relaxation of cations. We also find that the significance of the two mechanisms strongly depends on the charge state of the vacancy and thus the Fermi-level position in the gap at which the charge state changes (the thermodynamic charge-state level) cannot be determined from single-electron levels at a certain charge state.

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Group IV elements such as Si and Ge are semiconductors in their condensed phases where the sp^3 hybridization forms a network of chemical bonds with the diamond structure. Pairs of group III and V elements are condensed to be compound semiconductors in an essentially identical manner. Defects such as the atomic vacancy strongly affect properties of host semiconductors by inducing deep levels in the energy gap. The deep level is generally localized in space, so that electron–electron interaction such as exchange interaction could be important. Yet experimental and theoretical efforts in the past^{1–3)} have clarified that covalency in those materials is significant determining material properties and rebonding of neighboring orbitals with symmetry lowering Jahn–Teller effect is a principal characteristic of the atomic vacancy.

Group-III nitride semiconductors are unique in the sense that the cation is much larger than the anion: Atomic radii of Al, Ga, and In are 1.43, 1.41, and 1.66 Å, respectively, whereas the radius of N is 0.75 Å. Then if a cation atom is removed, the remaining N dangling bonds hardly rebond with each other, which causes the spin polarization around vacancies, and unprecedented properties are expected. Due to direct energy gaps corresponding to a range from infrared to ultraviolet wavelengths, group-III nitrides are important in optoelectronics.⁴⁾ For microscopic identification of point defects, extensive calculations from first principles have been performed for GaN.^{5,6)} However, the possibility of the spin polarization of the cation vacancy explained above has been overlooked in those calculations. Although ferromagnetic behaviors in GaN doped with magnetic impurities have been reported^{7–10)} and a role of the cation monovacancy is examined in recent calculations,^{11–14)} it is certainly fair to say that our knowledge on defect spins is quite limited. In addition, doping procedures of magnetic impurities have been reported to introduce cation vacancies and their complexes.¹⁵⁾ At this stage, it is imperative to examine yet-to-be-discovered intrinsic spin-related properties of defects in nitride semiconductors.

Here, we report first-principles calculations that clarify the spin polarization and the lattice relaxation of mono- and

multi-vacancies (V_n) with various charge states in group-III nitrides. We demonstrate that nontrivial dependence of spin configurations on the charge state is attributed to novel interplay between the exchange splitting of N-originated states and the electron transfer from Ga to N dangling bonds associated with cation breathing relaxation. We ascribe these unusual properties to smallness of nitrogen atomic radius compared with cation radii. The spin polarization does not come from the wide band gap of GaN proposed previously.¹⁶⁾ We also find that the spin–lattice competition/cooperation and the resultant structural relaxation are sensitive to the charge state, so that the thermodynamic charge-state level is unable to be assessed from single-electron levels.

First-principles total-energy calculations were performed on the basis of density functional theory (DFT) within the generalized gradient approximation (GGA).^{17,18)} The ionic cores are represented by the projector-augmented wave potential¹⁹⁾ as implemented in the VASP code.^{20,21)} The closed-shell Ga $3d$ and In $4d$ states are explicitly calculated as valence states. Electronic wave functions are expanded using plane-wave basis sets with a cutoff energy of 400 eV. The wurtzite atomic structures are fully optimized using the $2\sqrt{3}\times 2\sqrt{3}\times 2$ supercell containing 96 sites. The k -point sampling is made using $4\times 4\times 4$ grids in the first Brillouin zone. The formation energy of the n -vacancy V_n^q with charge q ,

$$E_{\text{form}}[V_n^q] = E_{\text{total}}^q - (E_{\text{GaN}} - n_{\text{V}_{\text{Ga}}}\mu_{\text{Ga}} - n_{\text{V}_{\text{N}}}\mu_{\text{N}}) + q\varepsilon_{\text{F}},$$

is calculated as a function of the Fermi level ε_{F} . Here E_{total}^q and E_{GaN} are the total energies obtained in our supercell, $n_{\text{V}_{\text{Ga}}}$ and $n_{\text{V}_{\text{N}}}$ are the number of Ga and N vacant sites, and μ_{N} and μ_{Ga} are chemical potentials of N and Ga. The formation energies are used to calculate vacancy-dissociation energies for the reaction $V_n^q \rightarrow V_{n-1}^q + V_1^q$ through the following formula: $E_{\text{D}} = E_{\text{form}}[V_{n-1}^q] + E_{\text{form}}[V_1^q] - E_{\text{form}}[V_n^q]$.

We begin with cation monovacancies in GaN, AlN, and $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$. Our structural optimization clearly indicates that small outward breathing relaxation (~ 0.2 Å) takes place and the spin polarization due to the exchange splitting is a principal factor in stabilizing the monovacancy. Figure 1 shows calculated densities of states for V_{Al} in AlN and V_{In} in $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$. In spin-unpolarized calculations, three defect states (or six states with spin) appear near the valence band

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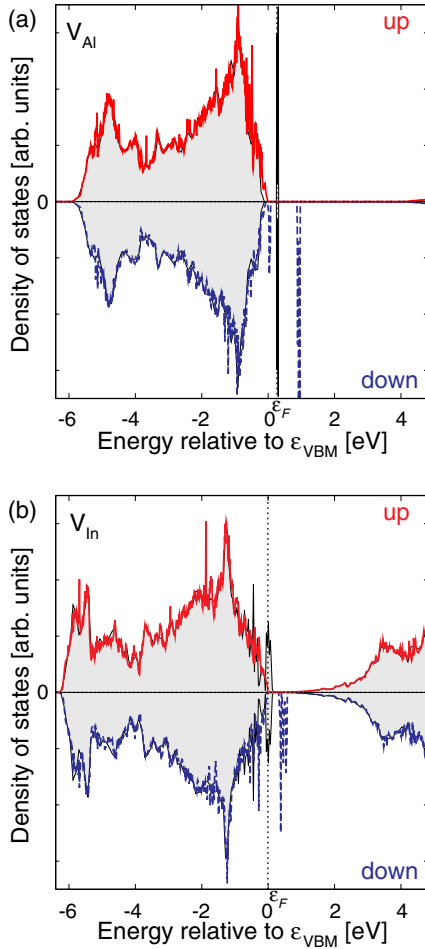


Fig. 1. (Color online) Calculated densities of states for majority and minority spins of (a) AlN with the Al vacancy and (b) $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ with the In vacancy. Results of our spin-unpolarized calculations are also shown with shades.

maximum (VBM) and almost degenerate for AlN. Three electrons are accommodated for the neutral case (Fig. 1, shaded). In addition, one filled defect state is resonant in the valence band for the spin-unpolarized configuration. Considering the spin-degrees of freedom, these three states exhibit the exchange splitting with the total-energy gain of 0.90, 0.69, and 0.58 eV for AlN, GaN, and $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$, respectively, making the majority spin states resonant in the valence bands (Fig. 1). Calculated magnetic moment for the neutral cation vacancy is $3\mu_B$ and decreases to 0 one by one by adding additional electrons, which is universal in all of three group-III nitrides examined. In previous calculations,¹⁶⁾ the spin polarization is attributed to wide gap-width. Yet it is irrelevant since our calculations clearly show the spin polarization in narrow-gap $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$. We argue that the imbalance between the cation and the anion in their atomic sizes induces the spin polarization, irrespective of the width of the band gap. The imbalance prevents N dangling bonds around the cation vacancy from rebonding with each other, suppresses Jahn–Teller-type symmetry lowering relaxation, and causes localization of the cation-vacancy-induced electron states. The localized electron states exhibit enhanced exchange-energy gain with the majority spin states being resonant in the valence bands and the minority spin states being empty in the energy gap.

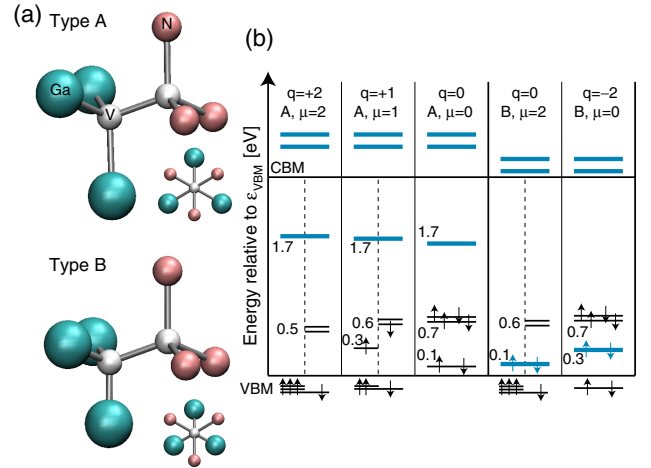


Fig. 2. (Color online) (a) Configurations of nearest-neighbor atoms of the neutral divacancy V_2^0 . (b) Single-electron energy levels induced by V_2^q for all the possible charge states. Thicker cyan lines and thinner black lines depict the states with the Ga- and N-dangling bond characters, respectively, where the level position relative to the VBM is given in eV. Arrows below the VBM indicates spins occupying the defect levels resonant in the valence bands. Defect states above the conduction band minimum (CBM) are also shown schematically.

We next focus attention on the divacancy $V_2 \equiv V_{\text{Ga}} - V_{\text{N}}$ in GaN. We have found two stable atomic configurations A and B with qualitatively different electronic structures. Figure 2(a) shows the two atomic configurations for the nearest neighbor atoms. The most significant difference between the type A and type B structures is the position of Ga atoms: In the type A structure, the nearest-neighbor Ga atoms show a large outward-breathing displacement of $\sim 0.4 \text{ \AA}$, whereas the displacement is only $\sim 0.1 \text{ \AA}$ inward in the type B structure.

The divacancy in GaN induces six defect states which are roughly classified into three N-dangling bond states and the other three Ga-dangling bond states, although sizable hybridization between N- and Ga-dangling bond states and with host orbitals has been indeed observed in our calculations. We have found that the N-dangling bond states [thinner black lines in Fig. 2(b)] are more localized compared to the Ga-dangling bond states (thicker cyan lines). The outward relaxation in the type A structure modifies the character of Ga dangling bonds to be more *p*-like making its energy higher than that in the case without outward relaxation by $\sim 1.6 \text{ eV}$ [Fig. 2(b)]. This causes additional electron transfer from the Ga dangling bonds to the lower-energy N dangling bonds. As a consequence of this electron transfer, the outward-breathing displacement becomes stabilized due to ionic repulsion among Ga atoms charged more positively, in which the Ga-dangling bond states are unoccupied. The defect levels with the N-dangling bond character which are located near the VBM accept the transferred electrons. Then the levels exhibit the exchange splitting as in the cation monovacancy depending on the occupancy. This situation is clearly seen in the level structures shown in Fig. 2(b): For the neutral and positive charge states ($q = +2, +1$, and 0), the type A structure is most stable in which the magnetic moment μ is finite for $q = +2$ and $+1$ with the partially-occupied N-dangling bond states, whereas it vanishes for $q =$

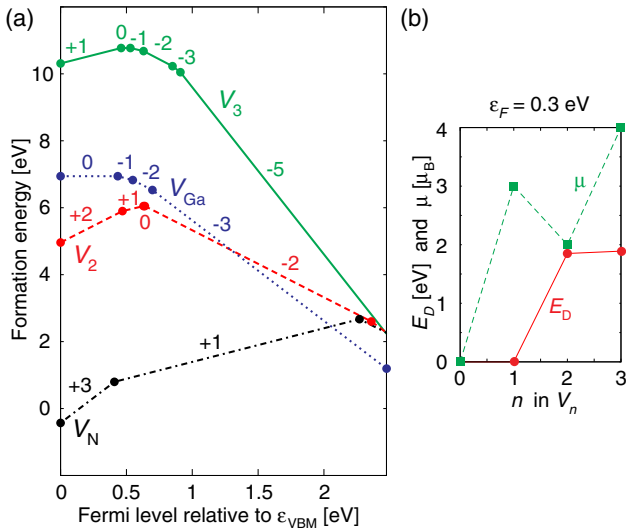


Fig. 3. (Color online) (a) Formation energies $E_{\text{form}}[V_n^q]$ for V_2 and V_3 as well as V_{Ga} and V_{N} in GaN as a function of ε_{F} , where the vacancy-charge state q is also shown. (b) Vacancy-dissociation energies E_{D} for the reaction $V_n^q \rightarrow V_{n-1}^q + V_1^q$ and magnetic moments μ of V_{Ga} , V_2 , and V_3 with $\varepsilon_{\text{F}} = 0.3$ eV.

0 with the fully occupied N states. Stabilization of the type A structure is thus the consequence of the electron transfer due to the outward relaxation and the exchange splitting in positively charged cases.

In the type B structure, the upward shift of the Ga-dangling bond state is absent, so that the electron transfer is the usual cation-anion transfer corresponding to the level structures shown in Fig. 2(b) (right side): For V_2^0 , the Ga-dangling bond state is located at 0.1 eV above the VBM. Hence the electrons accommodated at the N-dangling bond states at 0.7 eV above the VBM in the type A structure are back to this Ga-dangling bond state. For the neutral V_2 , the most stable structure is type A which is lower in the total energy by 0.21 eV than type B, even though the type A structure cannot have the spin polarization due to the full occupancy of N-dangling bond states: The charge-transfer stabilization is more favorable than the exchange splitting, when they compete with each other.

Yet the type B structure is favorable for negatively charged V_2 . When an electron is added to V_2^0 with the type A structure, it should be accommodated in the Ga-dangling bond state at 1.7 eV. The outward breathing in type A becomes unfavorable in this case and type B emerges. Again, the energy gain due to the exchange splitting is effective, leading to the magnetic moment of $2\mu_{\text{B}}$ for $q = 0$ and $1\mu_{\text{B}}$ for $q = -1$ (not shown).²²⁾

Figure 3(a) shows vacancy-formation energies $E_{\text{form}}[V_n^q]$ for V_2 and $V_3 \equiv V_{\text{Ga}} - V_{\text{N}} - V_{\text{Ga}}$ as well as for V_{Ga} and V_{N} . To avoid the DFT-gap problem, we use the thermodynamic charge-state level $\varepsilon(-3/-4)$ for V_{Ga} as the upper bound for the Fermi-level position. This is based on our finding that the V_{Ga} -related levels in the gap accommodates at most three electrons. The formation energies shown in Fig. 3 are for the cation-rich condition. In the anion-rich condition, the values change by ~ 1 eV: The values for V_{Ga} and V_3 decrease whereas the value for V_{N} increases, compared with the corresponding formation energies in the

cation-rich condition. It is noteworthy that the formation energies for V_2 and V_3 in n -type GaN are comparable with the ones for V_{Ga} and V_{N} , indicating their importance.

We have found that V_2^{-1} is always metastable for any position of ε_{F} [Fig. 3(a)]. This indicates that V_2 has a negative U character. Adding electrons to V_2^0 causes drastic change in both the atomic structure (from A to B) and in the single-electron level structure [Fig. 2(b)]. Due to this drastic change, the thermodynamic charge-state level lies at $\varepsilon(0/-2) = 0.7$ eV that is much lower than the position of the Ga-dangling bond state for the neutral charge state, $\varepsilon = 1.7$ eV. It is now clear that the thermodynamic level is unable to be assessed from single-electron levels of any particular charge state.

The magnetic moment μ and the dissociation energy E_{D} for $\varepsilon_{\text{F}} = 0.3$ eV are shown in Fig. 3(b) for V_{Ga} , V_2 , and V_3 . It is clear that all of V_{Ga}^0 , V_2^{+2} , and V_3^{+1} are spin polarized for p -type GaN. Dissociation energies for V_2^{+2} and V_3^{+1} are large enough for their stable existence. It should be noted that, although $E_{\text{form}}[V_3^{+1}]$ is more than 10 eV, the formation energy per vacant site is as low as ~ 3 eV, which means in consistency with the sign of E_{D} that single trivacancy exists more stably than isolated three monovacancies.²³⁾ For n -type doped GaN, E_{D} is somewhat smaller: At $\varepsilon_{\text{F}} \simeq 0.9$ – 2.2 eV, we obtain $E_{\text{D}}[V_2^{-2}] = 1.69$ eV and $E_{\text{D}}[V_3^{-5}] = 1.33$ eV. Judging from the stable existence of di- and tri-vacancies, it is plausible that larger vacancy complexes, e.g., hexavacancy, can be found as have been done for Si.

As for the trivacancy V_3 , we have found that V_3 exhibits a variety of charge states, $+1$, 0 , -1 , -2 , -3 , and -5 , as shown in Fig. 3(a). For $q = 0$, four defect states with the N-dangling bond character appear at $\varepsilon \simeq 0.6$ eV for the minority spin, one of which is occupied and visualized in Fig. 4(a). Due to the spin polarization of these N-dangling bond states, V_3^0 has the magnetic moment of $\mu = 3\mu_{\text{B}}$. This spin-polarized electronic configuration is more stable than the spin-unpolarized one by 0.44 eV. We have also obtained the same feature for $V_3 \equiv V_{\text{Al}} - V_{\text{N}} - V_{\text{Al}}$ in AlN and $V_3 \equiv V_{\text{In}} - V_{\text{N}} - V_{\text{Ga}}$ in $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ with the energy differences of 0.60 and 0.42 eV, respectively. The four N-dangling bond states are also responsible to the charge-state change of V_3 from $+1$ to -3 . In contrast, the vacancy state at $\varepsilon \simeq 2$ eV consists mainly of Ga dangling bonds as shown in Fig. 4(b). Upon adding further electrons to V_3^{-3} , this Ga-dangling bond state reduces its energy with removing Ga outward-breathing displacement in essentially the same fashion demonstrated for V_2 (the structural change from type A to B). Consequently, $\varepsilon(-3/-5)$ of ~ 0.9 eV is much lower than the corresponding single-electron level in V_3^{-3} , $\varepsilon \simeq 2$ eV, leaving V_3^{-4} metastable at any position of ε_{F} .

In group-III nitrides, the Jahn–Teller structure relaxation to eliminate the dangling bonds is suppressed, which is attributed to the size difference between the anion and the cations as discussed above. This situation remains valid even if one considers another kind of symmetry-breaking relaxation without the rebond formation due to possible strong electron localization obtained by atomic-orbital-based approximate self-interaction correction (ASIC) scheme.²⁴⁾ Indeed, these two symmetry-breaking relaxations have opposite effects: the rebond formation removes the spin

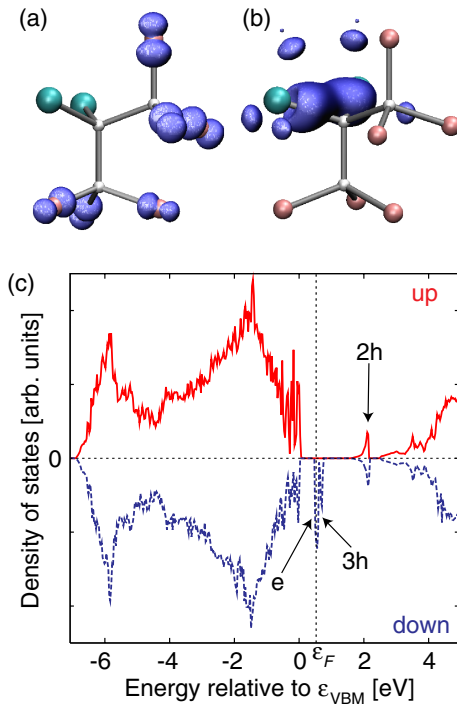


Fig. 4. (Color online) (a) Atomic configuration of nearest-neighbor atoms of the neutral trivacancy V_3^0 together with the electron density distribution for the electron state indicated by “e” in (c). (b) Same as (a) but for the state indicated by “2h” in (c). (c) Density of states for GaN with V_3^0 .

polarization, whereas the strong localization promotes it. Particularly, magnetic moments obtained by standard DFT agree with ASIC results. Thus, even though DFT-GGA is in general not sufficient to describe electron correlation among localized electron states, the stabilization mechanism we have found is successfully described within DFT-GGA. There are a few attempts such as ref. 24 to determine the position of the transition levels more precisely. However, it is fair to say that we are not yet in a position to calculate the defect-level position in a conclusive manner from first principles.

In conclusion, we have performed first-principles calculations for the vacancy in GaN as well as in AlN and $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ with various charge states. We have identified two stabilization mechanisms: the exchange splitting and the electron transfer from Ga to N associated with the breathing relaxation. We have also found that the thermodynamic charge-state levels differ qualitatively from corresponding single-electron levels since the competition and cooperation between the exchange splitting and the electron transfer strongly depend on the defect-charge state.

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- 22) Note that the occupancy of the defect levels within the band gap and the magnetic moment depend on the number of electrons for the N dangling bonds resonant in the valence bands as shown in Fig. 2(b).
- 23) Indeed, in the case of silicon where the defect properties are well identified, large multivacancies, e.g., hexavacancy, have been observed by positron annihilation. In semiconductor device fabrications, thermal annealing enhances diffusion of monovacancies, which can result in the formation of multivacancy. Even though the formation energy of n -vacancy is large, it emerges if energetically favorable than the presence of isolated n monovacancies. Therefore, the comparison should be made for three monovacancies with single trivacancy.
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