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.

KEYWORDS: first-principles calculations, vacancy, spin polarization, group-III nitrides

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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 form 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,$^{1–3,11–14}$ it is certainly fair to say that our knowledge on defect spins is quite limited. In 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 potential$^{19}$ 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 $\sqrt{3} \times \sqrt{3} \times 2$ supercell containing 96 sites. The $k$-point sampling is made using 4×4×4 grids in the first Brillouin zone. The formation energy of the $n$-vacancy $V_n^q$ with charge $q$, $E_{\text{form}}[V_n^q] = E^q_{\text{total}} - (E_{\text{GaN}} - n\nu_{\text{Ga}}\mu_{\text{Ga}} - n\nu_{\text{N}}\mu_{\text{N}}) + q\epsilon_F$, is calculated as a function of the Fermi level $\epsilon_F$. Here $E^q_{\text{total}}$ and $E_{\text{GaN}}$ are the total energies obtained in our supercell, $n\nu_{\text{Ga}}$ and $n\nu_{\text{N}}$ are the number of Ga and N vacant sites, and $\mu_{\text{N}}$ and $\mu_{\text{Ga}}$ are chemical potentials of N and Ga. The formation energies are used to calculate vacancy-dissociation energies for the reaction $V_n^q \rightarrow V_n^{q'} + V_n^{q''}$ through the following formula: $E_D = E_{\text{form}}[V_n^{q''}] + E_{\text{form}}[V_n^{q'}] - E_{\text{form}}[V_n^q]$.

We begin with cation monovacancies in GaN, AlN, and In$_{0.5}$Ga$_{0.5}$N. Our structural optimization clearly indicates that small outward breathing relaxation ($\approx$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 $V_{\text{Al}}$ in AlN and $V_{\text{In}}$ in In$_{0.5}$Ga$_{0.5}$N. In spin-unpolarized calculations, three defect states (or six states with spin) appear near the valence band.
width. Yet it is irrelevant since our calculations clearly show
0.90, 0.69, and 0.58 eV for AlN, GaN, and In
exhibit the exchange splitting with the total-energy gain of
Considering the spin-degrees of freedom, these three states
the valence band for the spin-unpolarized configuration.
shaded). In addition, one filled defect state is resonant in
electrons are accommodated for the neutral case (Fig. 1,
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 In$_{0.5}$Ga$_{0.5}$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,\textsuperscript{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 In$_{0.5}$Ga$_{0.5}$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 re-
laxation, and causes localization of the cation-vacancy-
duced 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. 1. (Color online) Calculated densities of states for majority and
minority spins of (a) AlN with the Al vacancy and (b) In$_{0.5}$Ga$_{0.5}$N with
the In vacancy. Results of our spin-unpolarized calculations are also
shown with shades.

We next focus attention on the divacancy $V_2 \equiv V_{Ga} - V_{N}$
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
$\sim 0.4 \text{Å}$, whereas the displacement is only $\sim 0.1 \text{Å}$ 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 hybrid-
ization 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 $\mu$ is finite for $q = +2$ and $+1$ with the partially-
occupied N-dangling bond states, whereas it vanishes for $q =$
and V\textsubscript{dangling bond state} is absent, so that the electron transfer is 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\textsubscript{GaN}\textsuperscript{2-}, 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\textsubscript{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\textsubscript{2}. When an electron is added to V\textsubscript{2} 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\textsubscript{B} for q = 0 and 1\mu\textsubscript{B} for q = -1 (not shown).\textsuperscript{21}

Figure 3(a) shows vacancy-formation energies \(E_{\text{form}}[V\textsubscript{N}^q]\) for V\textsubscript{2} and V\textsubscript{3} as well as V\textsubscript{Ga} and V\textsubscript{N} in GaN as a function of \(E\text{\textsubscript{F}}\), where the vacancy-charge state q is also shown. (b) Vacancy-dissociation energies \(E_D\) for the reaction \(V\textsubscript{Ga}^{q-} + V\textsubscript{N}^{q+}\) and magnetic moments \(\mu\) of V\textsubscript{Ga}, V\textsubscript{2}, and V\textsubscript{3} with \(E\text{\textsubscript{F}} = 0.3\text{ eV}\).

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.

The magnetic moment \(\mu\) and the dissociation energy \(E_D\) for \(E\text{\textsubscript{F}} = 0.3\text{ eV}\) are shown in Fig. 3(b) for V\textsubscript{Ga}, V\textsubscript{2}, and V\textsubscript{3}. It is clear that all of V\textsubscript{0}, V\textsubscript{2} and V\textsubscript{3} are spin polarized for p-type GaN. Dissociation energies for V\textsubscript{Ga} are large enough for their stable existence. It should be noted that, although \(E_{\text{form}}[V\textsubscript{Ga}^{2-}]\) is more than 10 eV, the formation energy per vacant site is as low as \(\approx 3\text{ eV}\), which means in consistency with the sign of \(E_D\) that single trivacancy exists more stably than isolated three monovacancies.\textsuperscript{23} For n-type doped GaN, \(E_D\) is somewhat smaller: At \(E\text{\textsubscript{F}} \approx 0.9\text{ eV}\), we obtain \(E\text{\textsubscript{D}}[V\textsubscript{2}^{-2}] = 1.69\text{ eV}\) and \(E\text{\textsubscript{D}}[V\textsubscript{3}^{-3}] = 1.33\text{ eV}\). 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\textsubscript{3}, we have found that V\textsubscript{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 \(\varepsilon \approx 0.6\text{ eV}\) 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\textsubscript{3} 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\textsubscript{3} = V\textsubscript{Al} = V\textsubscript{N} − V\textsubscript{Al} in AlN and V\textsubscript{3} = V\textsubscript{In} = V\textsubscript{N} − V\textsubscript{Ga} in In\textsubscript{N}Ga\textsubscript{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\textsubscript{3} from +1 to −3. In contrast, the vacancy state at \(\varepsilon \approx 2\text{ eV}\) consists mainly of Ga dangling bonds as shown in Fig. 4(b). Upon adding further electrons to V\textsubscript{3} −, this Ga-dangling bond state reduces its energy with removing Ga outward-breathing displacement in essentially the same fashion demonstrated for V\textsubscript{2} (the structural change from type A to B). Consequently, \(\varepsilon(-3/5)\) of \(\approx 0.9\text{ eV}\) is much lower than the corresponding single-electron level in V\textsubscript{3} −, \(\varepsilon \approx 2\text{ eV}\), leaving V\textsubscript{3} metastable at any position of \(E\text{\textsubscript{F}}\).

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.\textsuperscript{24} Indeed, these two symmetry-breaking relaxations have opposite effects: the rebond formation removes the spin...
In conclusion, we have performed first-principles calculations for the vacancy in GaN as well as in AlN and In_{0.5}Ga_{0.5}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.