

A first-principles approach to investigating the effects of Be, Mg and Zn on intrinsic *n*-type GaN systems

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The effects of *p*-type dopants on the structural and electronic properties of *n*-type intrinsic GaN systems were investigated using a first-principles approach. Nitrogen vacancies and oxygen substitutions were intentionally used to obtain an *n*-type intrinsic GaN system. The formation energy of the Be-doped *n*-type intrinsic GaN system based on nitrogen vacancies depended strongly on concentration, with a maximum energy difference of 4.87 eV. The incorporation of metallic cations (Be, Mg, and Zn) led to the formation of a *p*-type GaN system with desirable electronic properties that were attributed to charge transfer from partially occupied Ga-, N-, and O-s states to the *p* states of the metallic cations.

Key word: First-principles, GaN, LED, Be doping, Mg doping, Zn doping.

Introduction

GaN has been widely used as a base material in optoelectronic devices such as light-emitting diodes (LED), [1-3] laser diodes (LD), [4, 5] and UV photodetectors, [6] due to its wide optical spectrum. [7-13] Since after-grown GaN crystals have *n*-type characteristics because of intrinsic defects originating from the difficulty of controlling complicated fabrication processes such as thermal annealing [14, 15] and ion implantation, [16, 17] it is difficult to obtain *p*-type GaN. Recently, several experiments on the doping effects of Be, Mg, and Zn ions in the intrinsic *n*-type GaN system were reported, and showed that this type of doping could be a source of *p*-type characteristics in GaN systems. However, theoretical studies using first-principles calculations have been made only on perfect GaN crystal systems. [18-26] In this paper, using the first-principles method, we intensively investigated the structural and electronic structural properties of intrinsic *n*-type GaN systems after substitutions of Be, Mg, or Zn ions onto Ga atom sites (Be_{Ga}, Mg_{Ga}, and Zn_{Ga}), which included the intrinsic point defects such as nitrogen vacancies (V_N) and oxygen atoms substituted at nitrogen sites (O_N).

Computational Details

The results of this study were obtained by a first-principles calculation using projector-augmented-wave (PAW) [27] potentials based on the density functional theory (DFT)

within the generalized gradient approximation (GGA) scheme [28] as implemented in VASP code. [29] The equilibrium lattice parameters were identified by minimizing the total energy of the GaN unit cell, which is fully relaxed until all forces are reduced below a threshold level of 0.02 eV/Å. The calculated equilibrium lattice constants *a*, *c/a*, and *u* in Wurtzite GaN were 3.215 Å, 1.630, and 0.377, respectively. The Ga-3*d* electrons were treated as valence electrons since Ga-3*d* electrons are not chemically inert but play a significant role in chemical bonding. Integration over the Brillouin zone was performed using a gamma-centered 8 × 8 × 4 *k*-points mesh, and the corresponding wave functions were expanded on a plane wave basis with a cutoff energy of 800 eV. To reduce interactions between dopants in neighboring cells, a 3 × 3 × 3 GaN supercell (corresponding to 108 atoms, Ga₅₄N₅₄) was employed, and the distances between the doped atoms (Be_{Ga}, Mg_{Ga}, and Zn_{Ga}) and the defects (V_N and O_N) were maintained at 6.389 as shown in Fig. 1. To understand the effects of doping concentration, pairs of atoms of Be, Mg, and Zn substituted into the *n*-type intrinsic GaN system were also considered.

Results and Discussion

The formation energies of Be_{Ga}, Mg_{Ga}, and Zn_{Ga} were calculated on the basis of the intrinsic *n*-type GaN systems and defined as:

$$E_f = E_{\text{tot}}[\text{GaN}|n_i X_{\text{Ga}} : Y_{\text{N}}] - E_{\text{tot}}[\text{GaN}|Y_{\text{N}}] - \sum n_i \mu_i \quad (1)$$

where $E_{\text{tot}}[\text{GaN}|n_i X_{\text{Ga}} : Y_{\text{N}}]$ is the total energy of the metallic cation (Be, Mg, or Zn) doped at a Ga site in GaN systems that included a V_N or O_N defect, and $E_{\text{tot}}[\text{GaN}|Y_{\text{N}}]$ is the

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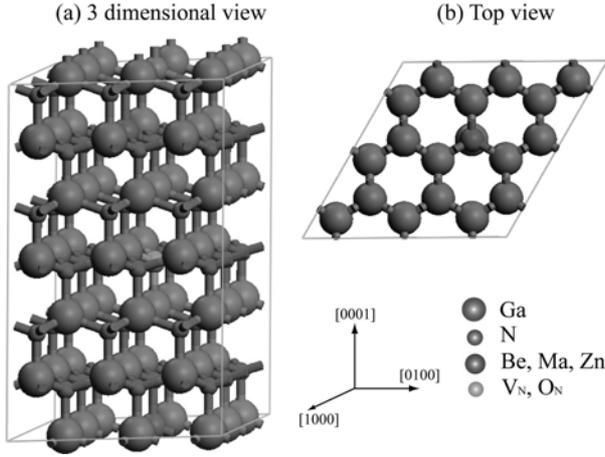


Fig. 1. Schematic illustration of a 108-atom GaN supercell doped by Be, Mg, and Zn in intrinsic n -type GaN systems: (a) three-dimensional view; (b) top view.

Table 1. The calculated enthalpies and chemical potentials of metallic nitride compounds

Species	$r_{M,cov}$ (M = Be, Mg, Zn)	μ_M	ΔH_f (eV)
Be_3N_2	0.89	-4.63	-7.64
Mg_3N_2	1.36	-3.36	-6.40
Zn_3N_2	1.25	-1.38	-0.73

total energy of a GaN system including V_N or O_N , n_i indicates the number of doped cations that have been implanted into intrinsic n -type GaN systems, and μ_i is the corresponding chemical potential of the doped cations obtained by the metallic bulk.

Chemical potentials in the equilibrium states of these compounds can be expressed as:

$$\begin{aligned} \mu[\text{M}_3\text{N}_2] &= 3\mu_M + 2\mu_N \\ &= 3\mu_{M[\text{bulk}]} + 2\mu_{N[\text{N}_2]} + \Delta H_f[\text{M}_3\text{N}_2] \end{aligned} \quad (2)$$

in which $\Delta H_f[\text{M}_3\text{N}_2]$ is the formation enthalpy of the metallic nitride compound, *i.e.* Be_3N_2 , Mg_3N_2 , or Zn_3N_2 . The calculated formation enthalpies of the metallic nitride compounds were -7.64 eV, -6.40 eV, and -0.73 eV for Be_3N_2 , Mg_3N_2 , and Zn_3N_2 , respectively (see Table 1). Since the formation enthalpy of Be_3N_2 was the smallest, we see that Be_{Ga} was more favorable than Zn_{Ga} in the GaN system, despite the large difference in covalent radii between Ga (1.25 Å) and Be (0.89 Å).

Table 2 shows the formation energies of metallic cation-doped GaN systems. It was found that single cation doping ($\text{GaN}|X_{\text{Ga}} : Y_N$) yielded more stable results than double cation doping ($\text{GaN}|2X_{\text{Ga}} : Y_N$) in all cases. This indicates the difficulty of metallic cation heavy doping in GaN systems containing n -type intrinsic point defects. In a $\text{GaN}|nX_{\text{Ga}} : V_N$ system (n -type GaN system containing a nitrogen vacancy), a single Be substitution showed the smallest formation energy of -1.81 eV. However, the largest formation energy was obtained with double Be doping, with a large energy difference of 4.87 eV occurring between the single and double substitution of Be at the Ga sites. In the $\text{GaN}|nX_{\text{Ga}} :$

Table 2. The formation energies with concentrations of metallic atoms doped in different intrinsic n -type GaN systems

n -type	Dopants	Species	E_f (eV)
V_N	Be	$\text{Ga}_{53}\text{Be}_1\text{N}_{53}$	-1.81
		$\text{Ga}_{52}\text{Be}_2\text{N}_{53}$	3.06
	Mg	$\text{Ga}_{53}\text{Mg}_1\text{N}_{53}$	-0.26
		$\text{Ga}_{52}\text{Mg}_2\text{N}_{53}$	1.45
		Zn	$\text{Ga}_{53}\text{Zn}_1\text{N}_{53}$
O_N	Be	$\text{Ga}_{53}\text{Be}_1\text{O}_1\text{N}_{53}$	0.30
		$\text{Ga}_{52}\text{Be}_2\text{O}_1\text{N}_{53}$	2.86
	Mg	$\text{Ga}_{53}\text{Mg}_1\text{O}_1\text{N}_{53}$	-0.46
		$\text{Ga}_{52}\text{Mg}_2\text{O}_1\text{N}_{53}$	1.25
		Zn	$\text{Ga}_{53}\text{Zn}_1\text{O}_1\text{N}_{53}$
		$\text{Ga}_{52}\text{Zn}_2\text{O}_1\text{N}_{53}$	1.00

O_N system (an oxygen atom substituted into n -type GaN), single Be atom doping was not favorable, leading to a positive formation energy of 0.30 eV. Only single Mg and Zn doping were favored energetically in $\text{GaN}|O_N$ systems, having small formation energies of -0.46 eV and -0.47 eV, respectively.

To investigate the electronic structures of Be, Mg, and Zn-incorporated n -type GaN systems, we performed partial density of states (PDOS) calculations. Fig. 2 illustrates the electronic structures of Be-, Mg-, and Zn-doped n -type GaN systems, including perfect GaN and intrinsic n -type GaN. In the PDOS calculations, the Fermi level was determined by the position of the valence maximum in a perfect GaN system. The Fermi level positions in both the $\text{GaN}|V_N$ and $\text{GaN}|O_N$ systems were shifted towards the conduction band minimum by as much as 1.79 eV and 2.54 eV respectively, which was due to the intrinsic point defects (V_N and O_N), and indicates that the $\text{GaN}|Y_N$ systems possess n -type GaN characteristics.

To find the best dopant for improving p -type characteristics in n -type intrinsic GaN systems, the formation energy and electronic structure of the $\text{GaN}|nX_{\text{Ga}} : Y_N$ systems should be considered simultaneously. Therefore, we determined that $\text{GaN}|Be_{\text{Ga}} : V_N$ systems had the best formation energies and that the Fermi level was shifted up to the valence band maximum in these systems, which indicates p -type electronic properties. Since the Ga-s and N-s states are dominant in the conduction band minimum of intrinsic n -type GaN systems, the Fermi level shift was attributed to charge transfer from the Ga- and N-s state to the Be-p states. Similarly, it can also be determined that the performance of p -type GaN with Mg and Zn is due to the charge transfer from the partially-occupied Ga-s and N-s states to the Mg- or Zn-p states as shown in Fig. 2.

In summary, we investigated p -type doping effects on intrinsic n -type GaN systems using first-principles calculations. The formation energies and partial densities of states were evaluated for metallic cation-doped intrinsic

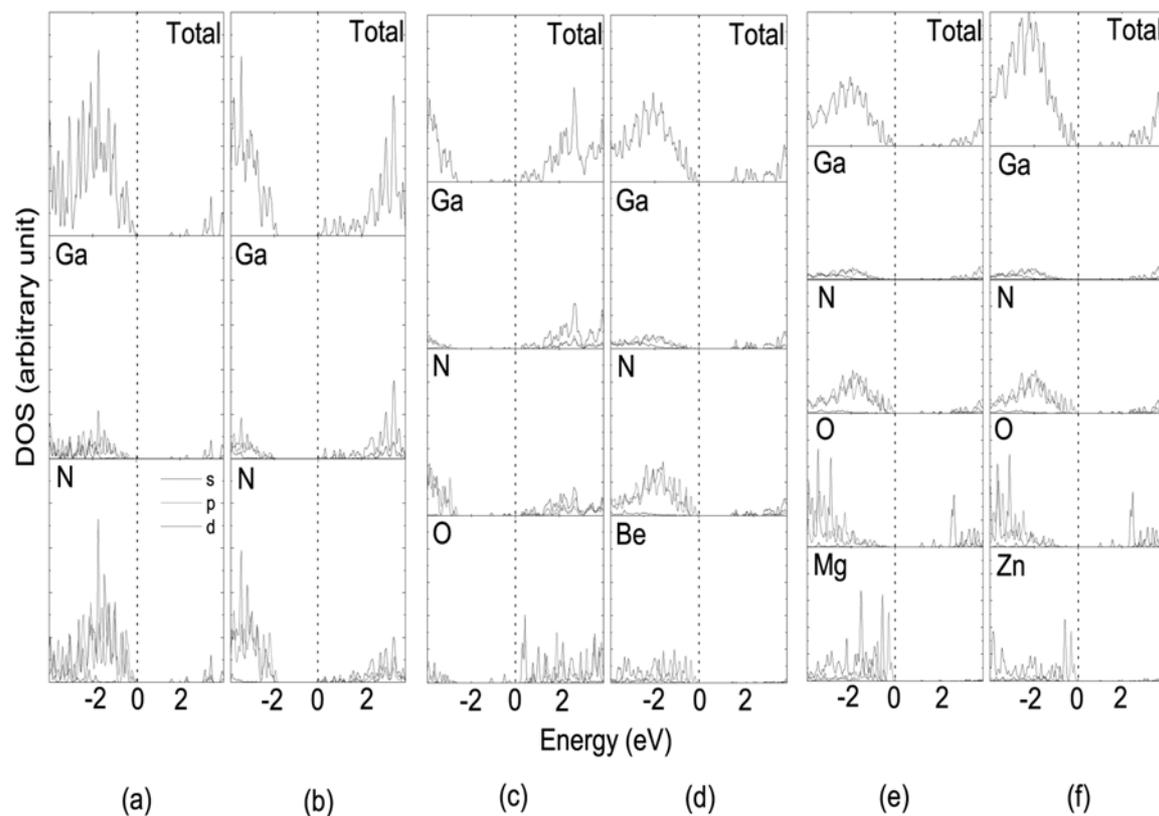


Fig. 2. Partial density of states of perfect-GaN (a), GaN|V_N (b), GaN|O_N (c), GaN|Be_{Ga} : V_N (d), GaN|Mg_{Ga} : O_N (e), and GaN|Zn_{Ga}:O_N (f). The Fermi level is set to zero.

n-type GaN systems. Single atom-doping of Mg or Zn was favored in both GaN|V_N and GaN|O_N systems, due to the small formation energies required. Metallic cation doping was not energetically stable in systems with double-atom doping. When using Be as the dopant, it was possible to dope only a single atom into a GaN|V_N system, which led to the smallest recorded formation energy of -1.81 eV. Through the PDOS results, we confirmed that doping of Be, Mg, and Zn accomplished *p*-type electronic properties in intrinsic *n*-type GaN systems. The *p*-type characteristics of the GaN|X_{Ga} : Y_N system originated in charge transfer from the partially-occupied Ga-, N-, and O-s states to the Be-, Mg-, and Zn-p states, which led to a Fermi level shift up to the valence band maximum.

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