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Structural characteristics and electronic properties of GaN with N_V, O_N, and N_V-O_N: first-principles calculations

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Abstract Structural and electronic properties of bulk GaN with nitrogen vacancy (V_N), oxygen substitution on nitrogen site (O_N), and complex of nitrogen vacancy and oxygen substitution on nitrogen site (V_N-O_N) were investigated using the first principle calculations. It was found that stability of defect formation is dependent on the epilayer growth conditions. The complex of V_N-O_N is energetically the most favorable state in a condition of Ga-rich, however, oxygen substitution in nitrogen site is the most favorable state in N-rich condition. The electronic property of complex with negative charge states at Γ point was changed from semiconductor to metal. On the contrary, the properties of nitrogen vacancy except for neutral charge state have shown the semiconductor characteristics at Γ point. In the oxygen substitution on nitrogen site, the energy differences between conduction band minimum and Fermi level were smaller than that of defect-free GaN.

Key words *ab initio*, GaN, Nitrogen vacancy, Oxygen, Γ point

1. Introduction

The semiconductors based on GaN system have a significant potential for application in high-power, high-temperature, and high-frequency electronics. In particular, GaN system has been widely applied for optoelectronic devices such as light-emitting diodes (LED), laser diodes (LD), and UV photodetectors due to a wide bandgap that work in visible to UV wavelength [1].

The intrinsic defects and extrinsic impurities, which can be employed by growth conditions, have a significant influence on the electronic structure of GaN. However, the real experiment could be restricted in the parts of atomic-scale studies. Therefore, the research using first-principles calculations [2] for GaN system can make up for the restrictions of real experiments, because first-principles calculations enable us to approach atomic-scale research. Indeed, the investigation of intrinsic point defects for GaN system using first-principles calculations was carried out by several groups [3, 4]. Therefore, first-principles calculations play an important role in understanding the formations and configurations of intrinsic defects and extrinsic impurities with atomic-scale.

Among the intrinsic points defects, nitrogen vacancy has the lowest energy in GaN, compared to other types of intrinsic defect such as self-interstitial and antisite defects, and can play an important role as compensating centers [5]. However, nitrogen vacancy cannot explain the observed n-type conductivity of GaN completely because nitrogen vacancy has high formation energy in n-GaN. Therefore, it is essential to investigate the behavior of extrinsic impurities in order to understand the structural and electronic properties of GaN.

In this paper, First-principles calculations of bulk GaN, which consists of V_N, O_N and V_N-O_N, were performed using projector-augmented-wave (PAW) [6] and Perdew, Burke, and Ernzerhof (PBE) [7] potentials based on the density functional theory (DFT) within the generalized gradient approximation (GGA) scheme [8] as implemented in the VASP code [9].

2. Experiments

Two types of valence electron configurations for Ga atom, which are $3d^{10}$ $4s^2$ $4p^1$ and $4s^2$ $4p^1$, were chosen to find the effects of *d* electrons which are difficult to handle in conventional plane-wave pseudo-potential calculations [10]. Atomic relaxations were continuously performed until all forces were reduced below threshold level of 0.02 eV/Å. After that, equilibrium lattice parameters and cohesive energies for each type of GaN were determined in the lowest total energy. The results were shown in the Table 1.

PAW method and $3d^{10}$ $4s^2$ $4p^1$ configuration for Ga

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Table 1
The lattice constant a_0, c/a ratio, internal parameter u, and cohesive energy E_{coh} for α-GaN were calculated. A comparison with experimental data is also provided

	a_0 (Å)	c/a	u	$E_{coh.}$ (eV)
PAW13[a]	3.215	1.629	0.377	−12.27
PAW3[b]	3.246	1.623	0.377	−12.28
PBE13[c]	3.215	1.631	0.376	−12.32
Expt.[10]	3.189	1.624	0.375	−9.06

[a]$[Ar]3d^{10}4s^24p^1$ configuration for Ga
[b]$[Ar]4s^24p^1$ configuration for Ga
[c]$[Ar]3d^{10}4s^24p^1$ configuration for Ga

atom has been chosen for the 442 supercell (128-atom) calculations, because the obtained volume of unit cell from PAW method and $3d^{10}$ $4s^2$ $4p^1$ configuration for Ga atom was in the closest to that of experiment. The 2 × 2 × 2 mesh as a k-point sampling was used for total energy calculations of Ga atom, N_2 molecule, O_2 molecule and GaN bulk. In particular, the calculations of N_2 and O_2 molecule were carried out in the cubic cell with the length of 11 Å. The electron wave function calculations for the 128-atom were expanded in a plane wave basis set using cut-off energy of 800 eV. The Gamma Monkhorst-Pack scheme was used to generate the special k-points in the irreducible brillouin zone (IBZ).

3. Results and Discussion

Each chemical potential comprising GaN bulk is restricted to be in some range below its respective bulk value. Namely, chemical potential could be varied depending on the specific growth conditions assuming thermodynamic equilibrium. If the system consists of metallic Ga atom and gas phase N molecule, the relationship of $\mu_{GaN} = \mu_{Ga} + \mu_N$ holds and μ_{Ga} and μ_N are independent. The extreme conditions are called Ga-rich or N-rich and the corresponding equations have to be obeyed $\mu_{Ga} = \mu_{Ga\ [bulk]}$ for Ga-rich case (upper limit on μ_{Ga}) and $\mu_N = \mu_{N2\ [molecule]}$ for N-rich case (upper limit on μ_N). Therefore, the thermodynamically allowed chemical potential for Ga and N could be calculated. From the calculated chemical potentials of atomic constituents in GaN, the enthalpy of formation could be written as

$$E_{tot}\,[GaN] = \mu_{Ga}\,[bulk] + \mu_N\,[N_2] + \Delta H_f\,[GaN] \quad (1)$$

ΔH_f [GaN] is always negative for stable compounds. The calculated formation enthalpy is −1.39 eV for GaN bulk including the spin-polarization correction of 0.65 eV for N_2 molecule, which is in good agreement with the experimental value of −1.17 eV [11].

The formation energy for the neutral charge GaN system with defects and impurities could be induced using the definition of formation energy [12].

$$E^f\,[V_N^0] = E_{tot}\,[V_N^0] - E_{tot}\,[GaN, bulk] + \mu_N - E_{corr} \quad (2)$$

$$E^f\,[O_N^0] = E_{tot}\,[O_N^0] - E_{tot}\,[GaN, bulk] + \mu_N - \mu_O - E_{corr} \quad (3)$$

$$E^f\,[(V_N - O_N)^0] = E_{tot}\,[(V_N - O_N)^0] - E_{tot}\,[GaN, bulk] + 2\mu_N - \mu_O - E_{corr} \quad (4)$$

The correction term (E_{corr}) could be obtained from the energy difference between the highest occupied state at the Γ point and the highest special k-points in the finite supercells, and has been defined as positive numbers [13]. The calculated correction energies for $[V_N]^0$, $[O_N]^0$, and $[V_N - O_N]^0$ in the 128-atom were 0.052 eV, 0.054 eV, and 0.062 eV, respectively. The reported correction energies have a range of ~0.2 eV in the 96-atom to ~0.5 eV in the 32-atom [13]. Formation energies for the defects in the neutral charge state were dependent on the environmental conditions such as Ga-rich conditions or N-rich conditions. The formation energies obtained from first-principle calculations have shown in Table 2.

Ga-rich conditions are energetically more favorable than N-rich conditions for formation of V_N, O_N and $V_N - O_N$ during the growth. The result is in agreement with the previous reports, which is more favorable in Ga-rich conditions for GaN growth using molecular beam epitaxy (MBE) [14, 15].

Comparing the total energy of nitrogen vacancy and oxygen substitution on nitrogen site, it could be expected that the formation of nitrogen vacancy during the growth has lower possibility than that of oxygen substitution on nitrogen site without regard to Ga-rich or N-rich condition. The result could been associated with that oxygen instead of nitrogen vacancy is responsible for n-type conductivity in GaN system [16]. However, the complex with formation energy of 0.14 eV in a con-

Table 2
The formation energies according to the growth conditions and correction energies for each different defect were shown. Energy is in eV

	Ga-rich	N-rich	E_{corr}
$(V_N)^0$	2.2493	3.6266	0.052
$(O_N)^0$	0.2752	1.6525	0.054
$(V_N - O_N)^0$	0.1381	2.8927	0.062

Table 3
The obtained energy difference by subtracting Fermi level from conduction band minimum according to the charge states at Γ point were listed. The parentheses indicate charge states of nitrogen vacancy. The negative values indicate conduction band minimum is located below the Fermi level. Energy is in eV

	0 (0)	−1 (1)	−2 (2)	−3 (3)
V_N	(−0.23)	(1.51)	(1.83)	(1.57)
$(V_N$-$O_N)$	0.11	−0.28	−0.45	−0.58

dition of Ga-rich is the most favorable configuration comparing to that of nitrogen vacancy or oxygen substitution on nitrogen site.

The electronic structures in various charge states were also investigated by calculating the magnitude of relative shifts between conduction band minimum and Fermi level at Γ point. Table 3 has shown the electronic properties of the complex and nitrogen vacancy.

The property of the complex with negative charge states was changed from semiconductor to metal. Semiconductor property was shown in neutral charge state. Namely, electronic property in the negative charge states indicates that conduction band minimum was below the Fermi level. In the case of nitrogen vacancy, positive charge states except for neutral charge state have shown the semiconductor characteristics. In particular, double-positive charge state shows a high energy difference corresponding to 1.83 eV unlike to other cases. The results could be estimated with relationship between the formation energy and Fermi level of defect generation in different charged states. Indeed, it was reported that single-positive charged state is more stable in the n-doped GaN and triple-positive charge state in the p-doped GaN, indicating double-positive charge state is never stable [5, 17].

The electronic structures of oxygen substituting nitrogen site were shown in Fig. 1. The defect level due to oxygen substitution in nitrogen site was introduced in the band structure. The defect level was shifted away from the Fermi level by transition from the neutral charge state to single-negative charge state. The energy difference between conduction band minimum and Fermi level of defect GaN was smaller than that of defect-free GaN. The result seems to be related with that oxygen has play an important role in n-type conductivity during growth due to the shift of Fermi level toward conduction band minimum.

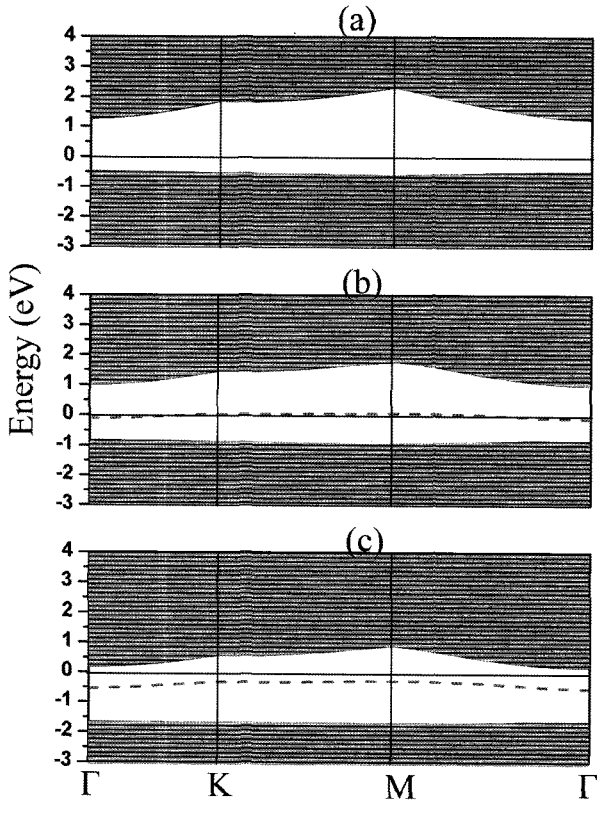

Fig. 1. The electronic band structure of GaN with (a) defect-free, (b) O_N, and (c) O_N^{-1}. Solid lines indicate the positions of the Fermi level and dashed lines indicate the positions of defect level caused by oxygen.

4. Conclusions

First-principles calculations for bulk GaN with nitrogen vacancy, oxygen substitution in nitrogen site, and a complex were performed. It was found that nitrogen vacancy has the highest formation energy indicating the most unfavorable type of three different cases. Complex is more favorable than the case of nitrogen vacancy or oxygen substitution in nitrogen site.

The electronic structures of the complex have shown semiconductor property in the neutral charge state, and were changed from semiconductor to metal in the negative charge states. Semiconductor characteristics were also shown in nitrogen vacancy with positive charge states, except for the neutral charge state. In particular, double-positive charge state had a relatively high energy difference between conduction minimum and Fermi level. The results could be estimated with relationship between the formation energy and Fermi level of defect generation in different charge states. In the oxygen substitution in nitrogen site, the energy gap between conduction band minimum and Fermi level was smaller than that of defect-free GaN. It can be estimated from the results that oxygen atom plays an important role in n-type conductivity during growth.

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