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Research Article

Influence of Vacancy Defect on Surface Feature and Adsorption of Cs on GaN(0001) Surface

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The effects of Ga and N vacancy defect on the change in surface feature, work function, and characteristic of Cs adsorption on a (2×2) GaN(0001) surface have been investigated using density functional theory with a plane-wave ultrasoft pseudopotential method based on first-principles calculations. The covalent bonds gain strength for Ga vacancy defect, whereas they grow weak for N vacancy defect. The lower work function is achieved for Ga and N vacancy defect surfaces than intact surface. The most stable position of Cs adatom on Ga vacancy defect surface is at T_1 site, whereas it is at B_{Ga} site on N vacancy defect surface. The E_{ads} of Cs on GaN(0001) vacancy defect surface increases compared with that of intact surface; this illustrates that the adsorption of Cs on intact surface is more stable.

1. Introduction

Due to its important characteristics such as wide band gap, high thermal conductivity, high breakdown voltage, high melting point, and chemical stability, among others, GaN and its compounds such as GaN_xAs_{1-x} [1–3] have emerged as a new type material for the fabrication of optoelectronic devices in the blue and ultraviolet spectral region [4–10]. Most research has focused on its physical properties, growth mechanisms, and surface structures [11–15]. The (0001) surface of Wurtzite GaN has good surface state and simple production process [16], the surface size of GaN(0001) is different, and the reconstruction is different in atomic structure [17, 18]. The 2×2 surface is considered the most stable surface [19], while a 2×2 Ga adatom model is thermodynamically favored under moderately Ga-rich conditions [20]. The surface stability and conductivity properties of GaN(0001) are superior to that of $(000\bar{1})$ [13, 21]. GaN(0001) surface becomes the focus of attention of optoelectronics community. The effective negative electron affinity has been demonstrated for p-GaN(0001) surfaces after Cs adsorption or Cs and O activating [22–27]; this is important for vacuum-type optoelectronic devices.

Defects may be produced in GaN materials growth process and interact with carriers. The existence of defects will affect the adsorption of Cs on GaN surface and then affect the performances of photoelectric devices. Theoretical studies of the eigen defects of GaN have been reported [28–30]; however, the influence of such defects on the adsorption of Cs on GaN surface has not been determined. In this paper, we employ plane-wave with ultrasoft pseudopotential method to study the influence of Ga and N vacancy defects on the surface feature and adsorption of Cs on GaN(0001) surface based on the first-principle density functional theory (DFT).

2. Computational Methods

The parameters for the optimized bulk wurtzite GaN structures are $a = b = 0.3189$ nm and $c = 0.5185$ nm [31]. All calculations were performed with the quantum mechanics

program Cambridge Serial Total Energy Package [32] based on density functional theory (DFT). The Broyden-Fletcher-Goldfarb-Shanno algorithm was used to relax the structure of the crystal model. The convergence precision was set to an energy change $< 2 \times 10^{-6}$ eV/atom, force < 0.005 eV/nm, convergence tolerance of a single atomic energy $< 1 \times 10^{-5}$ eV/atom, stress < 0.05 GPa, and change in displacement < 0.0001 nm in an iterative process. The surface slab was modeled with six GaN(0001) bilayers of which the lower three bilayers were fixed in the bulk configurations and a vacuum region equivalent to six GaN bilayers with overall approximate length of 1.3 nm was required. The bottom side of the slab was saturated with pseudohydrogen atoms to prevent transfer of surface charges (shown in Figure 1). Wave functions were expanded in a plane-wave basis set up to an energy cutoff of 400 eV and integrations over the Brillouin zone were performed using a $4 \times 4 \times 1$ Monkhorst-Pack set sampling-point scheme for the surface supercell. The electron exchange and correlation were treated by using the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) [33].

One Ga atom or one N atom on the outmost layer of 2×2 GaN(0001) surface was removed in researching vacancy defect surface, respectively (shown in Figure 1). Figure 1(a) shows the side view of Ga vacancy defect surface and (c) is the top view. Figure 1(b) shows the side view of N vacancy defect surface and (d) is the top view. For a Cs adsorption on GaN(0001) surface, five typical adsorption models including sites of T_1 (Ga top), H_3 (hollow site), T_4 (N top), B_{Ga} (Ga bridge), and B_N (N bridge) were chosen [34, 35]. In this paper, these five typical adsorption sites are adopted to study the influence of Ga and N vacancy defects on the adsorption of Cs on GaN(0001) surface. Figure 2 shows the top view of Cs at T_1, H_3, T_4, B_{Ga}, and B_N sites on GaN(0001) defect surface. Figure 2(a) shows the top view of Cs on Ga vacancy defect surface and Figure 2(b) is Cs on N vacancy defect surface.

3. Deficient Surface

Based on the mean of atoms coordinates, the thickness of the first bilayer is calculated; it is 0.0272 nm for Ga vacancy defect surface, whereas it is 0.0436 nm for N vacancy defect surface and 0.0653 nm for intact surface, compared with an ideal value 0.0647 nm. It has the biggest change in surface feature for Ga vacancy defect surface after relaxation. To study the reason for the change of surface feature, the charges of atoms in the outmost layer are shown in Table 1; the overlap populations and bond lengths between Ga and N atoms in the outmost layer of intact, Ga vacancy defect, and N vacancy defect surfaces are shown in Table 2.

The overlap population increases, the bond length decreases, and the covalent bond between Ga and N gains strength for Ga vacancy defect surface as shown in Table 2 caused mainly by the increase of charges of every Ga atom (see Table 1) compared with that of intact surface.

The overlap population decreases, covalent bond is weakened, and bond length between Ga and N increases for N vacancy defect surface as shown in Table 2 caused mainly by the decrease of charges of N and Ga atoms (see Table 1) compared with that of intact surface.

The main reason for the change of surface feature is the break of atoms bonds in the outmost surface layer, there are uncompensated electrons, and dipole moment directing to outside is formed. Compared with the intact surface, the charges of every Ga atom in Ga vacancy defect surface increases, while the total charges of Ga atoms in the outmost layer decrease, so the dipole moment increases. The thickness of the first bilayer is compacted by means of strong dipole moment and covalent bond. There is a preponderance of uncompensated electrons for N vacancy defect surface; the dipole moment is the max, but the change in the first layer thickness is less than that of Ga vacancy defect surface by means of the weak covalent bond.

For semiconductors, the work function is the minimum energy needed by electrons at the bottom of the semiconductor to escape externally. The easier the escape is, the larger dipole moment directing to outside is formed, the lower work function is. The size of the dipole moment among three surfaces is intact surface < Ga vacancy defect surface < N vacancy defect surface. Work functions of three surfaces are 4.20 eV (in agreement with Re.18), 4.054 eV, and 4.052 eV, respectively (shown in Table 3). Calculations show that the defect favors the escape of electrons but can induce bigger change in surface feature.

The charge density difference in the (0001) plane of the surface atoms is shown in Figure 3 to indicate the influence of Ga, N defect on the interaction between atoms visually, in which the bond length is also given. The electron cloud of the N atoms is uniformly distributed in three directions, joining to Ga atoms in the (0001) plane for intact surface, as shown in Figure 3(a). The degree of electron aggregation enlarges after Ga defect (Figure 3(b)), the overlap population increases, the covalent bond of Ga-N is stronger and the bond length of Ga-N is shorter than that of intact surface. The overlap population between the Ga and N atoms gets its minimum after N defect (Figure 3(b)); the bond length of Ga-N increases.

4. Cs Adsorption on GaN(0001) Deficient Surface

To study the effect of defect on the adsorption of Cs on GaN(0001) surface, first, a Cs was placed at H_3 site on Ga and N vacancy defect surfaces above surface 0.1 nm moving freely in relaxation process and, then, was fixed at five high symmetry sites moving only in Z direction.

Adsorption energy E_{ads} was calculated as the difference between the total energy of the GaN(0001) slab with adsorbed Cs and the sum of the total energies of the clean surface and isolated Cs atom [25]. The E_{ads} of a Cs at these six sites on Ga vacancy defect surface is shown in Table 3. The results show that E_{ads} is negative no matter Cs is at the five high symmetry sites or moves freely; it means that the absorption process is an exothermic chemical process and is stable. The final convergence position of Cs is above the Ga vacancy when it moves freely on Ga vacancy defect surface. The E_{ads} of every

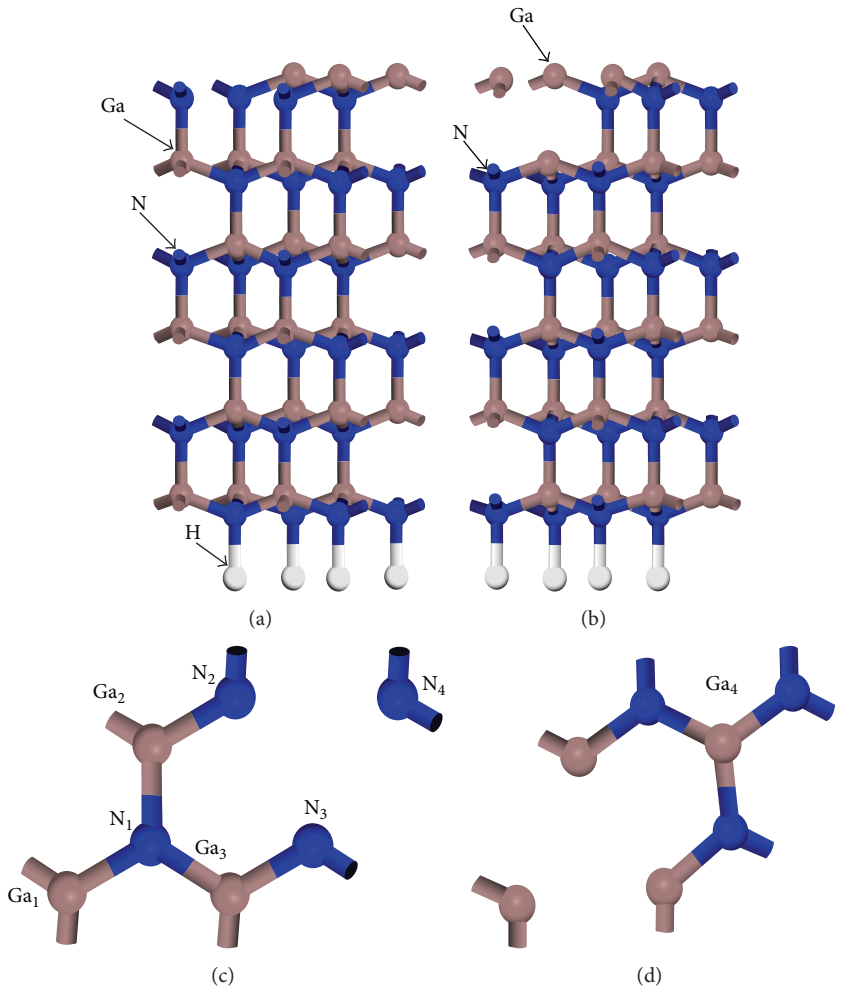

Figure 1: 2 × 2 GaN(0001) surface: (a) side view of Ga vacancy defect surface, (b) side view of N vacancy defect surface, (c) top view of Ga vacancy defect surface, and (d) top view of N vacancy defect surface. Ga and N atoms are marked.

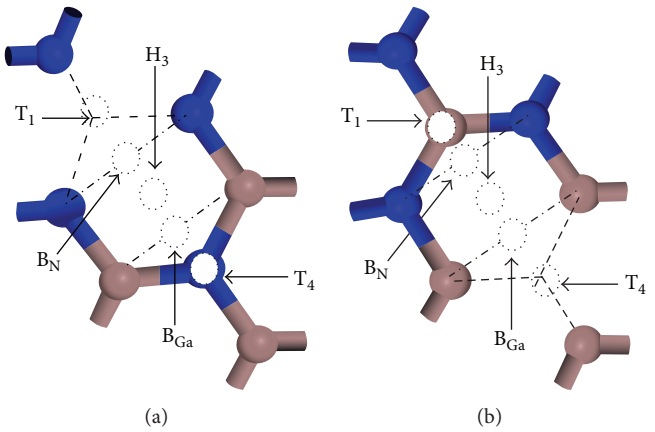

Figure 2: Top view of various possible adsorption sites of Cs on 2 × 2 GaN(0001) defect surface: (a) Cs on Ga defect surface, (b) Cs on N defect surface.

Table 1: Charges of atoms in the outmost layer of intact, Ga vacancy defect, and N vacancy defect surfaces.

Surface	Atoms and its charges/e							
	Ga_1	Ga_2	Ga_3	Ga_4	N_1	N_2	N_3	N_4
Intact	0.75	0.75	0.75	0.75	−0.98	−0.98	−0.98	−0.98
Ga vacancy defect		0.88	0.88	0.88	−1.04	−0.97	−0.98	−0.97
N vacancy defect	0.79	0.35	0.35	0.27		−0.94	−0.94	−0.95

Table 2: N–Ga bond lengths and overlap populations of intact, Ga vacancy defect, and N vacancy defect surfaces.

Bonds	Intact surface		Ga vacancy defect surface		N vacancy defect surface		
	Overlap population	Bond length/nm	Overlap population	Bond length/nm	Bonds	Overlap population	Bond length/nm
N_1–Ga_1	0.56	0.1974	0.73	0.1868	N_2–Ga_4	0.47	0.2053
N_1–Ga_2	0.55	0.1972	0.73	0.1868	N_3–Ga_4	0.47	0.2053
N_1–Ga_3	0.58	0.1967	0.65	0.1970	N_4–Ga_4	0.53	0.2012

Table 3: E_{ads} and work functions of Cs on GaN(0001) intact, Ga vacancy defect, and N vacancy defect surfaces.

Adsorption site	Intact surface		Ga vacancy defect		N vacancy defect	
	E_{ads}/eV	Work function/eV	E_{ads}/eV	Work function/eV	E_{ads}/eV	Work function/eV
H_3	−2.02	2.16	−1.15	2.46		Misconvergence
T_1	−1.89	2.30	−1.89	2.28	−1.55	2.30
T_4	−1.96	2.37	−0.80	2.28	−1.48	2.23
B_{Ga}	−1.98	2.36	−0.84	2.22	−1.57	2.20
B_N	−2.04	2.36	−0.84	2.33	−1.54	2.12
Freedom	−2.04	2.42	−1.99	2.67	−1.53	2.19

symmetry site decreases compared with that of Cs on intact surface. The most stable adsorption site is T_1 site (top of Ga vacancy), no longer the B_N and H_3 sites for intact surface [26]; the most unstable adsorption site is T_4 site. The lack of Ga atom makes the repulsive interaction of Ga to Cs nonexistent and Cs be attracted only by three N atoms, so the stable adsorption site changes compared with that of intact surface. Since the increase of uncomplexed electrons after Ga absence leads to the increasing of dipole moment; work functions of Ga vacancy defect surface with Cs at different high symmetry sites decline slightly compared with that of intact surface.

The E_{ads} is negative no matter a Cs is at the five high symmetry sites or moves freely on N vacancy defect surface (shown in Table 3); it means that the absorption process is also stable. The results show that E_{ads} of every symmetry site decreases compared with that of Cs on intact surface, while it is bigger than that of Cs on Ga vacancy defect surface. B_{Ga} is the most stable adsorption site in agreement with the case when Cs moves freely on N vacancy defect surface; H_3 is not convergence different from the case of intact surface. Since the increase of uncomplexed electrons after N absence leads to the increasing of dipole moment, work functions of N vacancy defect surface in different high symmetry sites decline slightly compared with that of intact surface.

Comparing the E_{ads} of Cs on Ga and N vacancy defect surfaces, it can be seen that the adsorption of Cs on N vacancy defect surface is more stable than on Ga vacancy defect surface. The lower work function is achieved for Ga and N vacancy defects surfaces than intact surface in agreement with the analysis of dipole moments before.

5. Discussion and Conclusions

The change of surface feature has been compared between GaN(0001) vacancy defect and intact surfaces. Adsorption characteristic and change in work function of a Cs atom on GaN(0001) (2 × 2) vacancy defect surface have been investigated using DFT with a plane-wave ultrasoft pseudopotential method based on first-principles calculations, compared with that of intact surface. Results show that Ga and N vacancy defects may cause contraction of the first bilayer and decrease of surface work function for the increase of dipole moment. The most stable adsorption site is T_1 site (top of Ga vacancy) for Ga vacancy defect surface, while it is B_{Ga} site for N vacancy defect surface. When the Cs was adsorbed on the vacancy defect surfaces, work functions for different high symmetry sites decline slightly compared with that of intact surface, but E_{ads} increases, this illustrates that the adsorption of Cs on intact surface is more stable.

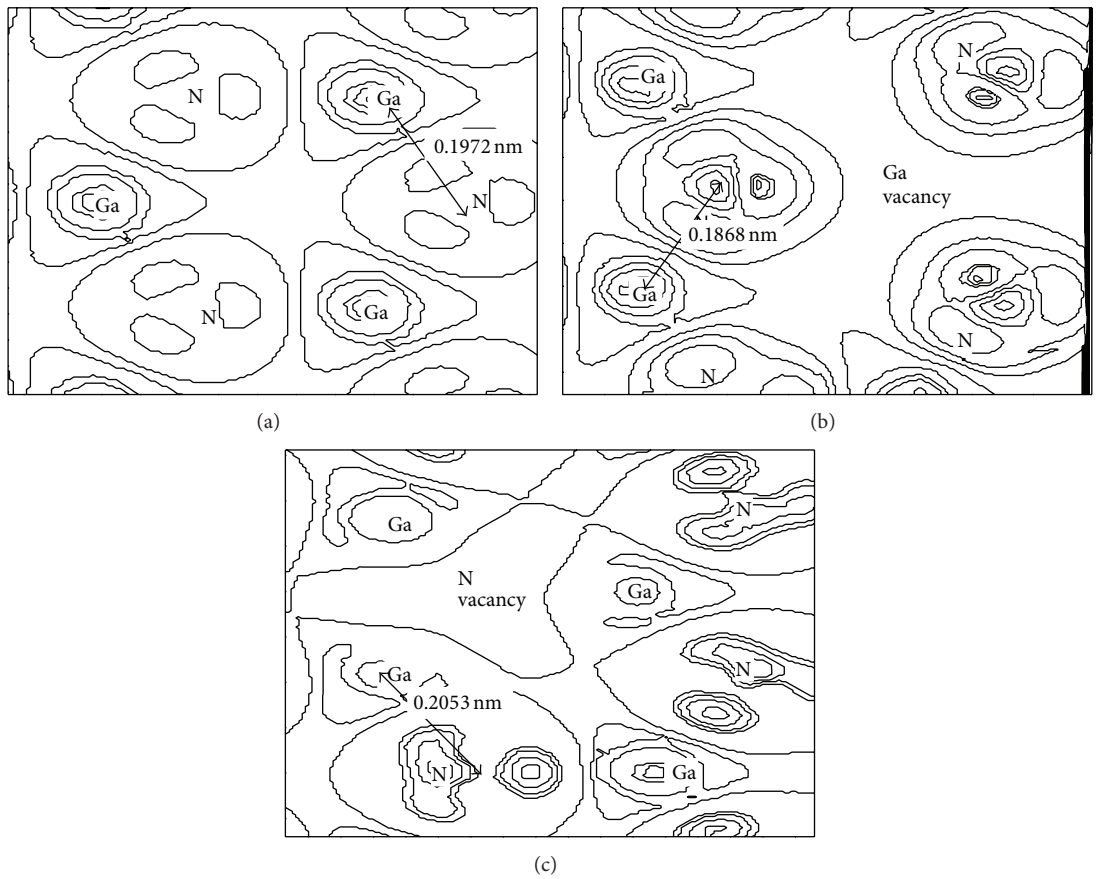

Figure 3: Electron density difference in the (0001) plane of the surface atoms: (a) intact surface, (b) Ga vacancy defect surface, and (c) N vacancy defect surface.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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