

# Theoretical Study of Multiatomic Vacancies in Hexagonal Boron Nitride

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## Abstract

**Electronic structures of multiatomic vacancies in a two-dimensional hexagonal boron nitride are investigated by the first-principles calculations. It is found that the origin of the large N-edge vacancies observed in experiments can be explained by the excess electron injection.**

## 1. Introduction

Hexagonal boron nitride (h-BN) consists of boron (B) and nitrogen (N) atoms, and is a two-dimensional monolayer semiconductor [1]. The h-BN is expected as an excellent substrate of the graphene devices [2]. It is also expected as a high-quality gate insulator of the graphene field effect transistors [3]. Moreover, the h-BN is expected as a high-performance tunneling barrier of the graphene resonant tunneling transistors [4]. In these applications, the h-BN is required to have superior crystallinity. However, experiments have shown that many large multiatomic vacancies are formed in the h-BN by the charging effect when the electron beam is injected [5]. This means that the applied electric field has a potential to form vacancies in h-BN, when the h-BN is used for the device material. Therefore, it is important to clarify the mechanism of the vacancy formation in the h-BN. In this work, we focus on such a mechanism and investigate optimized atomic structures of multiatomic vacancies by the first-principles calculations with extending previous theoretical studies [6]. Based on the results, we discuss the charging effect on the formation energies and the electronic states.

## 2. Calculation method

Our calculations are performed using a first-principles electronic structure calculation program, PHASE [7]. The exchange-correlation interaction is considered within GGAPBE. Ultrasoft pseudopotentials are used for B and N. The energy cut off for the plane-wave expansion is 12.5 HR.

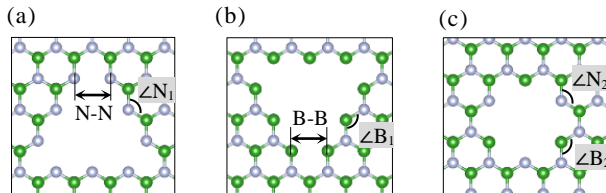


Fig. 1 Initial atomic structures of vacancies of (a)  $V_{B6N3}$ , (b)  $V_{B3N6}$ , and (c)  $V_{B3N3}$ . Green and grey circles denote B and N atoms, respectively [8]. The atoms in these figures are located at ideal positions.

The Brillouin zone sampling is performed with the Monkhorst-Pack special k point meshes. For the primitive hexagonal unit cell, a grid of  $16 \times 16 \times 1$  is used, and is scaled with respect to the supercell size. All atoms are allowed to relax until the calculated force on each atom is smaller than 0.001 HR/bohr. The formation energies  $E_f$  of various vacancies as the function of the electronic chemical potential  $\mu_e$  are calculated as

$$E_f = E_t - n_B \mu_B - n_N \mu_N + q(\mu_e + \varepsilon_v),$$

where  $n_B$  and  $n_N$  are the numbers of B and N atoms in supercell, respectively [6].  $E_t$  is the total energy and  $\varepsilon_v$  is the energy of the valence band maximum.  $\mu_e$ ,  $\mu_B$ , and  $\mu_N$  are the chemical potentials of the electron, B, and N, respectively.  $q$  is the charge state of the vacancy. The multiatomic vacancies shown in Fig. 1 are studied in this work. Other multiatomic vacancies are also studied for the comparison. The supercell size is  $8 \times 8 \times 1$  of the primitive cell.

## 3. Results and Discussion

First we calculate formation energies  $E_f$  of various vacancies as the functions of the electronic chemical potential  $\mu_e$ . Figure 2 shows the results under the N-rich condition. In our study,  $\mu_N$  under the N-rich condition is calculated from a  $N_2$  molecule, and  $\mu_B$  is calculated by assuming the equilibrium with the perfect h-BN. It is shown that N-edge vacancies such as  $V_B$ ,  $V_{B3N}$ , and  $V_{B6N3}$  are stable when the  $\mu_e$  is close to the conduction band minimum. On the other hand, the B-edge vacancies such as  $V_N$ ,  $V_{BN3}$ , and  $V_{B3N6}$  are

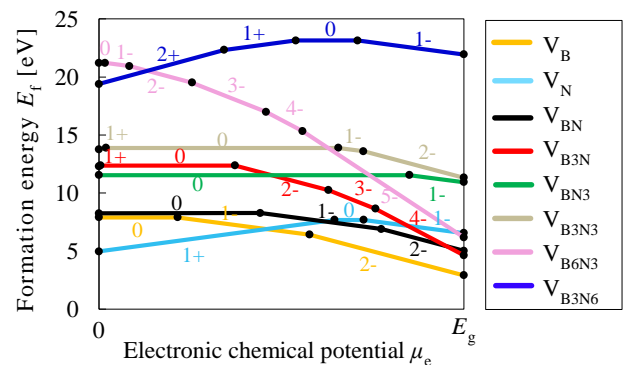


Fig. 2 Formation energies of various vacancies as the functions of the electronic chemical potential under the N-rich condition. Numbers denote the charge states  $q$  of vacancies. Electronic chemical potential  $\mu_e$  ranges  $\varepsilon_v + 0 \leq \mu_e \leq \varepsilon_v + E_g$ , where  $E_g$  is the bandgap of 4.14 eV according to our calculation.

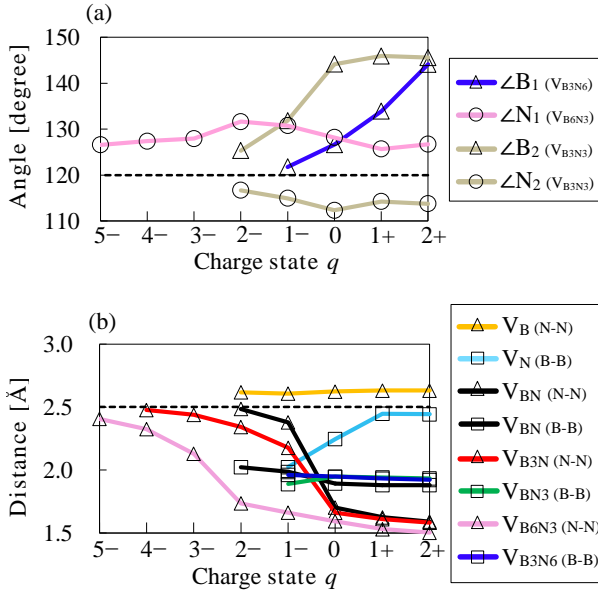


Fig. 3 Transformation of bond angles and bond distances as the function of the charge state: (a) bond angles at the midpoints of the edges, and (b) bond distances of B-B and N-N pairs. The broken lines indicate ideal ones.

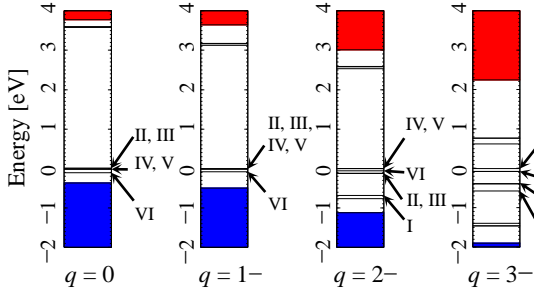


Fig. 4 Energy positions of the electronic states in the bandgap at the  $\Gamma$  point in  $V_{B6N3}$ . Red and blue regions are the conduction and the valance bands, respectively.

much less stable. The experiments with the electron beam injection dominantly observed N-edge vacancies. This means that the charging effect induced by the electron beam injection causes the formation of the N-edge vacancies. Our results also suggest that B-edge vacancies might be formed by the removal of electrons.

We also found that atomic structures of vacancies change with the addition or the removal of electrons. Figure 3(a) shows the optimized bond angles at the midpoints of the edges in  $V_{B3N6}$ ,  $V_{B6N3}$ , and  $V_{B3N3}$  as the functions of the charge states of vacancies. The angle of  $\angle B_1$  in  $V_{B3N6}$  (Fig. 1(b)) significantly decreases with the addition of electrons. On the other hand, the angle of  $\angle N_1$  in  $V_{B6N3}$  (Fig. 1(a)) does not significantly change with the addition or the removal of electrons. In  $V_{B3N3}$ , the angle of  $\angle B_2$  (Fig. 1(c)) significantly decreases with the addition of electrons, while that of  $\angle N_2$  (Fig. 1(c)) does not significantly change.

Figure 3(b) shows the optimized interatomic distances of B-B and N-N pairs at the vacancy corners as the functions of the charge states of vacancies. In  $V_{B3N6}$ , the dis-

tances of B-B pairs remain around 2.0 Å being independent of the addition of electrons. On the other hand, in  $V_{B6N3}$ , the distances of N-N pairs approach to the ideal distance of 2.5 Å with the addition of electrons.

The transformation of the bond distances is closely related to the changes of the electronic states. Figure 4 shows the energy positions of the electronic states in the bandgap at the  $\Gamma$  point in  $V_{B6N3}$ . According to our analyses, IV, V, and VI consist of in-plane atomic orbitals, and I, II, and III consist of  $p_z$  orbitals. I, II, and III are antibonding states for the N-N pairs, while IV, V, and VI have weak character of antibonding states for the N-N pair. In case of  $q = 0$ , II, III, IV, and V are almost four times degenerated, and five eighths of them are occupied by the electrons. Therefore, when  $q$  approaches 3- from 0, the antibonding states for the N-N pair are occupied sequentially. This is the reason why the bond distance of the N-N pair increases. In  $q = 0$ , a covalent bond is formed between the N-N pair, but the bond is broken by the enhancement of the antibonding feature.

The variation of the formation energies is also closely related to the changes of the electronic states. In  $V_{B6N3}$ , II, III, IV, and V are almost four times degenerated and partially occupied. Therefore, it is easy to add electrons to  $V_{B6N3}$ . This is consistent with the variation of the formation energies shown in Fig. 2. On the other hand, II, III, IV, and V are so close to the valence band maximum. Therefore, no positive charge state is realized for  $V_{B6N3}$ . This is also consistent with Fig. 2.

Therefore, in  $V_{B6N3}$ , both the transformation of the bond distance and the variation of the formation energy are related with the property of the electronic states. It is also confirmed that similar relations are also held in  $V_{B3N6}$ , while the detail behaviors of the formation energy and the bond distance are different.

#### 4. Conclusion

We found that the N-edge multiatomic vacancies are stable with the addition of electrons under the N-rich condition. This means that the electron injection is the key for the formation of the experimentally observed N-edge multiatomic vacancies with the triangle shape.

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