Theoretical Study of Vacancies and Adatoms in White Graphene

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The stability of the B and N atomic vacancies and divacancies in an h-BN monolayer deformed by 2 and 4% along one of the axes has been investigated. It has been established that the N atomic vacancies are most stable; their concentration is insignificant and does not affect the properties of white graphene. The number of vacancies depends on the mobility of N and B atoms on the layer surface; therefore, the probability of recombination with the vacancies has been estimated. It has been revealed that the energy barrier for the migration of the B and N adatoms is about 0.23 and 1.23 eV, respectively. In view of such a low barrier for the B adatom, this type of adatoms will quite rapidly move over the surface and recombine with vacancies, in contrast to the N adatoms. Therefore, only nitrogen atom vacancies can exist in the h-BN monolayer grown by the methods, where the adatoms could possibly appear on the surface.

1. INTRODUCTION

Hexagonal boron nitride (h-BN) is a layered structure similar to graphite and is its isoelectric analog [1, 2]. The atoms alternate in the hexagonal lattice hexagons, and a B atom is bonded to three N atoms (and vice versa) adjacent to it in one plane. Each of the neighboring N and B atoms are in this case bonded to each other by a covalent bond with the partial displacement of the electron density to an N atom [3]. The interplanar bond in the crystal is rather weak, although, in contrast to graphite, the interlayer van der Waals attraction is supplemented by the interaction between the oppositely charged N and B atoms in the neighboring planes [4]. However, this contribution is insignificant, and the parameters of the h-BN lattice are close to those in graphite [5].

One of the possible applications of this material is explained by its high strength. For example, Ooi et al. [6] presented the bulk moduli for h-BN that are one or two orders of magnitude higher than those in other similar (III−V) materials.

Owing to the features of the synthesis of h-BN crystal samples [7], it is difficult to measure their elastic properties by the powder [8] and indirect methods (Brillouin light scattering [9] and Raman scattering [10]) applied for thin films [11]. Therefore, alongside the experimental methods to determine the bulk modulus, it is reasonable to use the calculation methods that provide good agreement with the experimental data [8, 12−14].

Like carbon, the h-BN compound can exist in the form of separate planes, the so-called white graphene [15−21]. The synthesis of these monolayers can be accompanied by the formation of vacancies in the structure, which, at high concentrations, can considerably change the material properties [12, 22]. By chemical deposition from the gas phase, the authors of [12] synthesized the h-BN films (from two to five atomic layers) and modeled the behavior of the shear modulus E^{2D} of the h-BN monolayer at the vacancy concentration of 1−10%. They established that the E^{2D} value decreases linearly from 292.1 N/m (for the defect-free h-BN monolayer) to 115.4 N/m (10% of the vacancies) as the vacancy concentration increases. Presently, it is impossible to estimate the actual vacancy concentration, because no detailed information on their stability is available. There are many works where vacancies in the BN nanotubes were calculated [23−27]. However, the experience on the nanostructures suggests that the properties of the nanotubes and similar planes can differ considerably. Therefore, it is unreasonable to use the data on the defect stability in the BN nanotubes to estimate the vacancy concentration in a plane monolayer. There are also works where the defects in the h-BN monolayer were theoretically studied [28]. The authors
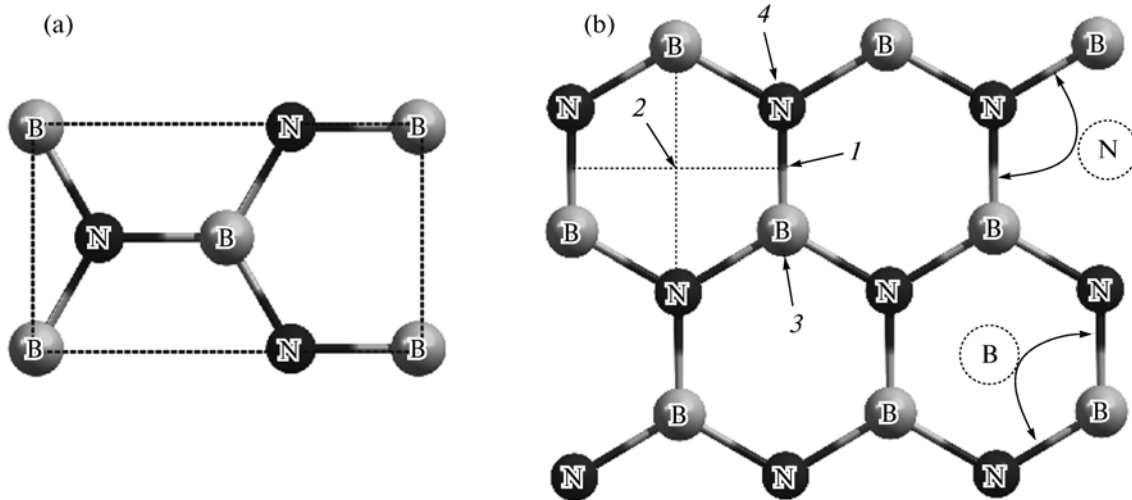
Fig. 1. (a) The rectangular unit cell of the h-BN monolayer. (b) The possible sites of the B and N adatoms and conditional paths of the B and N adatoms over the surface of the h-BN monolayer: (*1*) the B(N) adatom locates along the B−N bond, (*2*) the B(N) adatom locates in the BN hexagon center, (*3*) the N adatom locates above the B atom of the h-BN monolayer, and (*4*) the B adatom locates above the N atom of the h-BN monolayer.

present the defect formation energies of 8.91 and 11.22 eV for the N and B atoms, respectively. In this case, the optimal geometry was sought using the density functional based tight binding (DFTB) method, while the subsequent more accurate energy value was obtained using the density functional theory in the local density approximation (DFT−LDA). All the calculations in that work were performed only for the Γ point of the reciprocal space. Since the LDA method for the systems with strong covalent bonds can give a rather large error and the results of periodic calculations strongly depend on the number of the points of the reciprocal space, the vacancy formation energies presented in that work should be refined. Moreover, the h-BN monolayer is grown on a substrate of another material, and this can deform the monolayer lattice. Due to this, the vacancy thermodynamic stability can change. Possible recombination of the vacancies with the B and N atoms can also considerably affect their concentration. In this case, an important factor is the velocity of the adatom motion over the monolayer surface.

In this work, we calculate the energy of the vacancies of the h-BN monolayer in the absence and presence of uniaxial strain (2 and 4%), as well as investigate the parameters of the B and N adatom migration over its surface.

2. SUBJECTS OF INVESTIGATION AND CALCULATION METHOD

The calculations were performed within the density functional theory (DFT) [29] with the gradient corrections (PBE) using the Vienna ab initio simulation package (VASP) [30−32]. The Vanderbilt ultrasoft

pseudopotential was used in the calculations [33]. The h-BN monolayer was modeled as a supercell containing $5 \times 5 \times 1$ rectangular cells (100 atoms; 11.2 × 18.1 Å). This supercell is presented in Fig. 1. Such parameters were chosen to eliminate the interaction between the defects under study located in different supercells. The program used in the calculations requires periodic conditions; for this reason, a vacuum gap of 15 Å was specified to model the monolayer along the normal to its plane. The vacuum gap was determined under the assumption that the h-BN layers located in the neighboring supercells at this distance will not affect each other. The reciprocal space in the fundamental Brillouin zone was automatically subdivided on a grid by the Monkhorst−Pack scheme [34], the numbers of the *k* points along three directions were $2 \times 2 \times 1$. All the calculations were performed at the maximum energy of plane waves of 348.1 eV. In the geometry optimization in this study, the minimum force was 0.01 eV/atom.

3. RESULTS AND DISCUSSION

At the initial stage, we modeled the h-BN layer without vacancies and strains. Then, we studied the effect of strain on the stability of defects. To this end, we simultaneously considered the structures of h-BN monolayers with a B vacancy, an N vacancy, and a B−N divacancy. The strain was modeled using either a decrease or an increase by 2 and 4% in the translation vector along one of the axes. The formation energy of boron vacancy was calculated by the formula

$$E_{vac}(B) = E(B_{49}N_{50}) - E(B_{50}N_{50}) + \mu(B), \quad (1)$$

where $E_{vac}(B)$ is the formation energy of B vacancy, $E(B_{49}N_{50})$ is the total energy of the h-BN monolayer with the B vacancy, $E(B_{50}N_{50})$ is the total energy of the h-BN monolayer, and $\mu(B)$ is the chemical potential of the B atom in the hexagonal boron nitride. In turn, the chemical potential was determined as

$$\mu(B) = E(BN) - \frac{E(N_2)}{2}, \qquad (2)$$

where $E(BN)$ is the energy of the h-BN unit cell, and $E(N_2)$ is the energy of the nitrogen molecule. A similar calculation method for a single vacancy in a binary compound was presented in [35]. The nitrogen vacancy energy was calculated by a formula similar to Eq. (1), but with the calculated chemical potential of nitrogen in h-BN,

$$\mu(N) = E(BN) - \frac{E(B_{12})}{12}, \qquad (3)$$

where $E(BN)$ is the h-BN unit cell energy and $E(B_{12})$ is the unit cell energy for the most stable boron phase.

The divacancy energy was calculated by the formula

$$E_{divac} = E(B_{49}N_{49}) - E(B_{50}N_{50}) + E(BN), \qquad (4)$$

where E_{divac} is the divacancy formation energy, $E(B_{49}N_{49})$ is the total energy of the h-BN monolayer with a divacancy, $E(B_{50}N_{50})$ is the total energy of the h-BN monolayer, and $E(BN)$ is the h-BN unit cell energy. The results are presented in Fig. 2.

The dependences obtained imply that the N vacancies are most stable. In this case, we can estimate the vacancy concentration

$$n_{vac} = \exp\left(-\frac{E_{vac}}{kT}\right). \qquad (5)$$

For example, the concentration of the N vacancies with the minimum formation energy is 2.00×10^{-76} at a standard temperature of 298 K. The concentration of the B atom vacancies and divacancies will be considerably lower, because they have much higher formation energies. At the temperature of about 900 K of the chemical vapor deposition (CVD) synthesis, the concentration of the N atom vacancies will be 8.61×10^{-26}. This low equilibrium concentration of the vacancies even at this temperature will scarcely affect the properties of white graphene. Therefore, the calculations performed in [12], where the authors assumed that a similar structure can contain up to 10% of the vacancies, can describe the properties of this structure only when the system during growth does not pass to a more thermodynamically favorable state.

Therefore, the thermodynamic consideration allows us to conclude that the number of the vacancies in the h-BN monolayer will be rather small, and the N atom vacancies are most stable. However, along with
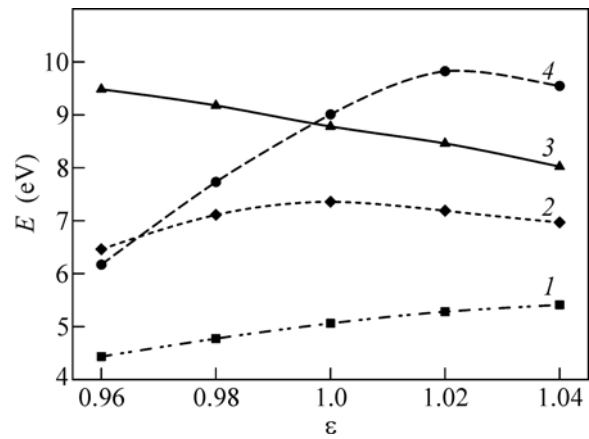
Fig. 2. Vacancy formation energy versus the strain for the h-BN monolayer with the (*1*) N vacancy, (*2*) B vacancy, (*3*) divacancy under compression normal to the vacancy direction, and (*4*) the divacancy under compression along the vacancy direction.

the aforementioned, the number of the vacancies will be affected by the mobilities of N and B adatoms on the monolayer surface, and, as a consequence, the possibility of their recombination with the vacancies. To estimate the probability of these processes, we modeled the adatom motion in order to calculate the kinetic parameters of the hop over the surface of the h-BN monolayer.

The parameters of the migration of B and N adatoms over the surface of the h-BN monolayer were calculated in two stages. At the first stage, the most favorable positions of the adatoms on the surface were found. To this end, we considered four different sites of the possible localization of a B(N) adatom (see Fig. 1b). The results are presented in the table where the adsorption energy in the other positions was measured from the energy of the most favorable position.

At the second stage, we studied the possibility of the motion of the adatom (both N and B) over the surface of the h-BN monolayer. For this purpose, we modeled

Table

Adatom position (Fig. 1b)	Relative adsorption energy of the B atom ($E_{ads}(B)$), eV	Relative adsorption energy of the N atom ($E_{ads}(N)$), eV
1	0.00[1]	0.00[1]
2	0.17[2]	0.34
3	0.46	0.35
4	1.36	0.41

[1] In the optimization process, the adatom arrangement was not symmetric with respect to the B–N bond, but the B atom was displaced toward the N atom, and the N atom toward the B atom.

[2] The B adatom position in the hexagon center after optimization was displaced toward the N atom being in the h-BN plane.

the process of the transition of the adatom between the most favorable positions (see Fig. 1b). The calculation yielded the energy barriers. They are about 0.23 and 1.23 eV for the B and N adatoms, respectively. Such a low barrier for the B adatom indicates that this type of adatom will quite rapidly move over the surface in contrast to the N adatoms. Hence, the methods of the growth of the h-BN monolayer where the adatoms can appear on the surface (e.g., chemical vapor deposition (CVD)) will produce a structure where only the N vacancies can exist.

4. CONCLUSIONS

The theoretical studies have demonstrated that, in terms of thermodynamics, the vacancy concentration in white graphene will be sufficiently low, and it should not affect the properties of the material. In the case of their formation, the N adatom vacancies will prevail, because they have the minimum formation energy. Moreover, the concentration of B vacancies will decrease due to their recombination with the B adatoms, which can move quite freely over the monolayer surface.

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