Research on monolayer h-BN cell strain effect vacancy stability

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Abstract. This article presents a research on Hexagonal Boron Nitride (h-BN) monolayer cell strain effect 2 % and 4 %. Structure of h-BN with nitrogen vacancy, with boron vacancy and with divacancy was considered for this. The calculations were carried out within framework of the density functional formalism with gradient corrections and using the VASP package. Vanderbilt Ultra-Soft Pseudopotential was used in the course of the calculations. It is possible to conclude that nitrogen vacancies are the most stable, regardless of monolayer deformation on the results obtained. Understanding of atomic scale stability and dynamics of defects in such systems is crucial for predicting their properties and applications in electronics.

1. Introduction

Scientists have had an increased focus on flat, curved, and wrapped nanoscale structures, such as graphene, fullerenes, and nanotubes [1]. Those nanoscale structures have attracted strong technological interest due to their structural, electronic, and mechanical properties for the recent decade. For example, carbon nanotubes (CNTs) can be considered as an ideal sheet, which is wrapped in a cylinder, and fullerene is a three-dimensional array of five hexagons with carbon atoms in angles, rolled up like a soccer ball. However, the presence of defects may lead to significant changes in such perfect structures causing corresponding changes in physical properties.

Graphene has zero band gap with high carrier mobility, h-BN has wide band gap of insulating material with potential use for hydrogen and UV light source storage [2]. Graphene and h-BN consist of individual sheets with sp²-bonded atoms, forming the structure of honeycomb. They, however, have different atomic packages. Boron atoms are superimposed.

N. Alem and others [3] successfully isolated one monolayer h-BN and uniquely determined boron and nitrogen atoms in primitive cell using a transmission electron microscope in the research. It was found that the defects in monolayer h-BN are formed as a result of boron atoms ejection from the lattice; the edges have a zigzag shape and consist of nitrogen atoms.

Atomic thin 2D crystals, such as graphene and hexagonal boron nitride (h-BN), are considered as new materials with potential use in the sensory and electronic industries [4]. The electrical, thermal, chemical, and mechanical properties of such crystals strongly depend on their atomic structure. Thus, an understanding of atomic-scale stability and the dynamics of defects (vacancies and adatoms) in such systems it is crucial for predicting their properties, and as a result, potential applications.
2. Objects and research methods

The calculations were carried out within the framework of Density Functional Theory (DFT) [5] with gradient corrections (The Perdew-Burke-Ernzerhof (PBE) functional) using the VASP package (Vienna Ab-initio Simulation Package) [6]. The Vanderbilt Ultra-0Soft Pseudopotential [7] was used in the course of calculations.

The reciprocal lattice in the first Brillouin zone was automatically divided into the Monkhorst-Pack grid [8] in the course of geometry optimization, the number of k-points along each of direction was 2 x 2 x 1. The number of k-points was 6 x 6 x 1 when calculating the density of states. All calculations in work were carried out with maximum plane wave energy value of 348.1 eV. The minimum value of the energy was 0.01 eV / Å when optimizing the geometry.

Hexagonal cell was used to construct the band structure of monolayer h-BN without vacancies and deformation. A rectangular cell was used in all other cases. The monolayer h-BN in form of a supercell containing 5 x 3 x 1 rectangular cells (60 atoms; 12.3 x 11.2 Å) was modeled to study the effect of deformation and vacancies on the electronic structure and magnetic properties. The supercell consisted of 5 translation vectors of the rectangular cell along the A direction, and along B - 3.

The monolayer h-BN in the form of supercell containing 5 x 5 x 1 rectangular cells (100 atoms; 11.2 x 18.1 Å) was modelled to calculate the monolayer h-BN vacancy energy without deformation and in the presence of uniaxial stress (2% and 4%). Similar parameters were chosen to eliminate interaction of simulated defects located in different supercells. Since the program in which the calculations were carried out, works using periodic conditions, then to separate the monolayer, along the C direction (the direction normal to the monolayer h-BN surface), a vacuum interval was introduced. The value of the vacuum interval was chosen on the assumption that at this distance the h-BN layers located in the adjacent supercells would not affect each other. Preliminary calculations were carried out to find the optimal interval between the layers; it was found that the vacuum interval of 15 Å is optimal.

3. Results and Discussion

The effect of deformation on the thermodynamic stability of vacancies was studied in the course of research. For this, the monolayer h-BN structures with boron vacancy, with nitrogen vacancy and with divacancy (boron and nitrogen vacancies simultaneously) were considered. The deformation was simulated by reducing or increasing the translation vector along one of the axes by 2% and by 4%. The calculation of the energy of the vacancies formation for boron was carried out according to the formula:

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

where $E(B)$ is the energy of vacancies formation according to B (N), $E(B_{50}N_{50})$ – is the total energy of the monolayer h-BN with vacancy B (N), $E(B_{50}N_{50})$ is the total energy of the monolayer h-BN, $\mu(B)$ is chemical potential of atom B in hexagonal boron nitride. In turn, the value of chemical potential $\mu$ was defined as:

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

where $E(BN)$ is the energy of the primitive cell h-BN, and $E(N_2)$ is the energy of molecular nitrogen.

A similar method of calculating a single vacancy in a binary compound was described in work [9]. The calculation of the vacancy energy for nitrogen was made according to the formula similar to (1), except that the calculated value of nitrogen chemical potential in h-BN was used.

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

where $E(BN)$ is the energy of the primitive cell h-BN, and $E(N_{12})$ is the energy of primitive cell for the most stable phase of boron (the primitive cell contains 12 boron atoms in this case).

The following formula was used to calculate the energy of divacancy formation:

$$E_{\text{divacancy}} = E(B_{49}N_{49}) - E(B_{50}N_{50}) + E(BN),$$

where $E_{\text{divacancy}}$ is the energy of divacancy formation, $E(B_{49}N_{49})$ is the total energy of the monolayer h-BN with divacancy, $E(B_{50}N_{50})$ is the total energy of the monolayer h-BN, $E(BN)$ is the energy of primitive cell h-BN. Two directions of divacancy deformation with deformation vector along and
perpendicular to the vacancy were described. The received results are shown in the Table 1 and in the Figure 1.

![Figure 1](image)

**Figure 1.** The dependency graph of the formation energy of vacancies on the relative deformation of monolayer h-BN: 1 – with nitrogen vacancy; 2 – with boron vacancy; 3 – with divacancy at compression perpendicular to the direction of the vacancy; 4 – with divacancy in compression along the vacancy direction

| Cell Deformation, % | Energy of boron vacancies formation (E(B)), eV | Energy of nitrogen vacancies formation (E(B)), eV | Energy of divacancy formation (E_{divacancy}), eV |
|---------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
|                     | Deformation along the divacancy direction     | Deformation perpendicular to the divacancy direction |
| -4                  | 6.46                                          | 4.43                                          | 6.17                                          | 9.48                                          |
| -2                  | 7.11                                          | 4.77                                          | 7.73                                          | 9.18                                          |
| 0                   | 7.36                                          | 5.06                                          | 9.01                                          | 8.78                                          |
| 2                   | 7.19                                          | 5.28                                          | 9.82                                          | 8.46                                          |
| 4                   | 6.97                                          | 5.41                                          | 9.54                                          | 8.02                                          |

It is possible to make a conclusion that nitrogen vacancies are the most stable vacancies. This is consistent with the data obtained in the work [10]. Formula (5) was used to estimate the concentration of vacancies. The results of the concentrations calculation are shown in Table 2 for temperature 298 K and 900 K:

\[
n_{\text{vac}} = \exp\left(-\frac{E_{\text{vac}}}{kT}\right), \tag{5}\n\]

where \(n_{\text{vac}}\) is the concentration of vacancies in monolayer h-BN; \(E_{\text{vac}}\) is the energy of vacancies formation B (N) in monolayer h-BN; \(k\) is the Boltzmann constant (8.617 · 10^{-5} eV / K); \(T\) is temperature (K).

Thus, the concentration of nitrogen vacancies with the minimum energy of formation is \(1 \cdot 10^{-75}\), at a standard temperature of 298 K. The concentration of boron atoms vacancies and divacancies is significantly lower, since they have a much higher energy of formation. At CVD method synthesis temperature, which is \(\sim 900\) K, the concentration of nitrogen atom vacancies will be \(1 \cdot 10^{-25}\). Such insignificant concentration of vacancies, even at such temperature, will have almost no effect on the properties of the white graphene.
Table 2. Values of vacancies concentration in monolayer h-BN at temperatures 298 K and 900 K

| Cell Deformation, % | Concentration of boron vacancies | Concentration of nitrogen vacancies | Concentration of divacancies along the defect (X) | Concentration of divacancies perpendicular to the defect (Y) |
|---------------------|----------------------------------|-------------------------------------|--------------------------------------------------|----------------------------------------------------------|
|                     | 298 K                            | 900 K                               | 298 K                                            | 900 K                                                    |
|                     | 298 K                            | 900 K                               | 298 K                                            | 900 K                                                    |
|                     | 298 K                            | 900 K                               | 298 K                                            | 900 K                                                    |
|                     | 298 K                            | 900 K                               | 298 K                                            | 900 K                                                    |
| -4                  | 5·10⁻¹¹⁰                        | 6·10⁻³⁷                            | 1·10⁻⁷⁵                                         | 1·10⁻⁵⁵                                                  |
| -2                  | 5·10⁻¹²¹                        | 1·10⁻⁴⁰                            | 2·10⁻⁸¹                                         | 2·10⁻²⁷                                                  |
| 0                   | 4·10⁻¹²⁵                        | 6·10⁻⁴²                            | 2·10⁻⁸⁶                                         | 4·10⁻²⁹                                                  |
| 2                   | 2·10⁻¹²²                        | 5·10⁻⁴¹                            | 5·10⁻⁹⁰                                         | 3·10⁻³⁰                                                  |
| 4                   | 1·10⁻¹¹⁸                        | 9·10⁻⁴⁰                            | 3·10⁻⁹²                                         | 5·10⁻³¹                                                  |

4. Conclusion

Thus, the calculations carried out in the work [11] in which the authors proceeded from the assumption that such structure might contain up to 10% of vacancies, and they can describe the properties of this structure only if the methods of growth are used, in which the system does not have time to go to the more favorable state in respect to thermodynamics.

As a result of modeling the monolayer of hexagonal boron nitride (h-BN) with the vacancy (boron, nitrogen and divacancy) and research on the effect of monolayer deformation by 2 % or 4 %, it was found that vacancies of nitrogen atoms are the most thermodynamically stable independently of the monolayer deformation. Therefore, vacancies of this type will dominate in the material.

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