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Structures and electronic properties of vacancies at the interface of hybrid graphene/hexagonal boron nitride sheet

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ABSTRACT

As a novel two-dimensional material, hybrid graphene/*h*-BN has attracted a great deal of attention. Recently, vacancies were observed as main defects at the interface of such hybrids. In this work, the structural, electronic and magnetic properties of vacancies at the interface of hybrid graphene/*h*-BN sheet were studied using density functional theory. Calculated results showed that existence of vacancies at the interface of such hybrids slightly reduce the stability of the systems. The cohesive energy of the hybrid graphene/*h*-BN with a zigzag edge was comparable to that of the hybrid graphene/*h*-BN with an armchair edge. Graphene/*h*-BN hybrid systems with vacancies at a zigzag interface exhibit obvious metal properties. Some of the graphene/*h*-BN systems with vacancies at an armchair interface changes from an insulator to a metal property due to the effect of vacancies. These findings will contribute to the understanding of characteristics of the interface growth for the graphene-based composite material.

1. Introduction

Graphene and graphene-like materials have drawn extensive attention due to their unique electronic, mechanical and thermal properties [1–3]. As pristine graphene is a zero-gap semimetal, it is desirable to improve its bandgap for the applications such as electronic devises and plasmonics [1]. Many types of techniques have been developed out to achieve this purpose, such as chemical modification on graphene surface [4–7] and antidote lattices fabrication [8–10]. As a close analog of graphene, two-dimensional (2D) hexagonal boron nitride (*h*-BN) is a wide band gap III–V compound, which possesses remarkable physical and chemical properties [11–14]. Graphene/*h*-BN lateral heterostructure has been realized experimentally by Levendorf et al. [15]. It was reported as an effective way to control the electronic properties of graphene-based thin films [15–17]. The graphene/*h*-BN hybrids could be fabricated on a metal substrate by a one-step growth method, which usually leads to a randomly mixed graphene and BN domains. It could also be synthesized based on a two-step growth approach, for example "patterned re-growth" method by Levendorf and co-workers, which allows for the spatially controlled synthesis of lateral junctions between graphene and *h*-BN [16]. Device performance improvements using graphene/*h*-BN hybrid have also been proved by a number of experiments [18–21].

No matter which method is used, a large-scale seamless and defect-free interface between graphene and *h*-BN is expected for achieving excellent properties of the hybrid material. Recent experimental and theoretical studies have focused on the patterns and properties of the graphene/*h*-BN interface [22–26]. It was pointed out that a zigzag interface or an armchair interface might introduce different electronic properties on the graphene/*h*-BN surface [27,28].

However, due to the results of the lattice mismatch between graphene and *h*-BN, interfacial strain and uneven growth at the interface exist. Thus, discontinues such as fault lines and cracks may occur near and along the graphene/*h*-BN interface to reduce the elastic strain energy. Vacancies are one of the most popular point defects. In 2013, Loh et al. observed, using scanning tunneling microscopy (STM), discontinues and dislocations along the interface of a graphene/*h*-BN surface produced via a two-step sequential chemical vapor deposition (CVD) method [23]. As the atoms in the defects are not in perfect crystalline arrangement, the properties of this hybrid material may also be affected. In addition, pioneering experimental and theoretical works have pointed out that defects and dislocations have large impacts on the performance of the devices based on graphene or *h*-BN [29–34]. However, to the best of our knowledge, the effect of such defects on the structure and electronic properties of graphene/*h*-BN interface

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has not been reported. Two issues should be considered: (1) the stability of the point defects at the graphene/*h*-BN interface; and (2) the possible relationship between the electronic properties of graphene/*h*-BN and the defect parameters.

In this work, various typical types of point defects, located at the interface between graphene and *h*-BN, were studied by density functional theory (DFT). The interface structure, cohesive energy and electronic properties of the hybrid graphene/*h*-BN with and without defects were obtained and compared.

2. Computational details

The effect of vacancy defects on the structure and electronic properties of graphene/*h*-BN interface was investigated using DFT method. Generalized gradient approximation (GGA) with Per dew–Burke–Ernzerhof (PBE) function was chosen to describe the vacancy defects at graphene/*h*-BN interface [37]. The calculation was based on the double-numeric quality with a polarization functions (DNP) basis set. The periodic boundary condition was performed on the computational unit cell. For all of the defect models, a vacuum with a height of 20 Å was placed above the graphene/*h*-BN surface to minimize the influence between adjacent layers. In addition, the distance between adjacent interfaces was set as more than 15 Å to minimize the influence between them. Å $15 \times 15 \times 1$ k-point mesh was set up during the geometry equilibrium with all the atomic structure parameters fully relaxed. All calculations were realized using the DMol3 module (Accelrys Inc.).

3. Results and discussion

3.1. Vacancy defect models at the interface

As illustrated by previous experimental observations [17], the interface between graphene and *h*-BN may be via either a zigzag linking edge or an armchair linking edge. In the present work, both the zigzag edge interface (G-BN-zz) and armchair edge interface (G-BN-am) between graphene and *h*-BN were considered (as shown in Figs. 1 and 2). It is necessary to point out that due to the periodic conditions added to both the *x* and *y* directions of the simulation supercell, the G-BN-zz system contains two types of zigzag edges (see Fig. 1). That is, the left hand edge is a C-B zigzag shape, while the right hand edge possesses a C-N configuration.

For this hybrid material, there are many types of vacancy defects at the interface. However, due to the periodical arrangement of carbon, boron and nitrogen atoms, some vacancy defects may possess similar atom distribution around the vacancy. For example, when a nitrogen vacancy exists at the C-N zigzag interface, one dangling carbon atom and two dangling boron atoms will form. This structure (around the vacancy) is similar to the nitrogen vacancy at the graphene/*h*-BN armchair interface. Thus, in the present work, only five typical point defects for a C-B zigzag interface and a BN armchair interface were selected as probes for discussion. The five point defects are four types of single vacancy defects (SV) and a double vacancy defect (DV). To cover more types of vacancy defects, carbon and boron vacancies were considered at the C-B zigzag interface, while carbon and nitrogen vacancies were considered at the BN armchair interface.

The nomenclature and structure of the defect models are shown in Fig. 1 (with zigzag interface) and Fig. 2 (with armchair interface). As an illustration on the nomenclature used in this work, a single vacancy defect with a carbon atom lost at the graphene/*h*-BN zigzag interface is named as zz-SV-C (with three dangling atoms) or zz-SV-C-5566 (with two five-member rings and two six-member rings).

3.2. Structures of the graphene/*h*-BN systems

As shown in Figs. 1 and 2, due to the energy release all the graphene/*h*-BN surfaces with defects exhibit three-dimensional (3D) warping. To reflect the structural changes of graphene/*h*-BN interface due to the vacancies, inflection angle and misorientation angle, which are defined in Supporting Information Fig. S1, were introduced. These two structural parameters of all graphene/*h*-BN systems considered in this work, as well as the pristine graphene and *h*-BN, are shown in Table 1. Due to the mismatch between the lattices of graphene and *h*-BN, the inflection angle of the G-BN-zz system came to 8 degree and its misorientation angle was 58.5°, these indicated a deviation of the graphene/*h*-BN surface from the pristine graphene or *h*-BN surface. The inflection angles of the five defect models with a zigzag edge ranged from 6° to 25°, and the misorientation angles of these systems changed from 59.0° to 62.0°. These values basically indicated that comparing to the G-BN-zz system without defect, the vacancy defects enhanced the degree of the buckling and mismatching of the graphene/*h*-BN surface.

To further examine the in-plane strain profile around the vacancy defect, the changes of the *h*-BN lattice parameters were studied. The average strain of each BN line was analyzed with respect to the vertical distance between the BN line and the interface (see Supporting Information Eq. (S1) for the detailed procedures of strain calculation). The strain profile (Fig. 3(a)) revealed that for the G-BN-zz system, the strain of the BN line increased in the first three atomic rows and reached a maximum at the third row. Then it decreased to a relatively constant level (at about 1.2%). As shown in Fig. 3(a), most of the defective models with zigzag edge (except the zz-DV system) started with strain level from 0.6% to 2.3% at the first BN line, and gradually became stable to the balance strain level of the surface. The zz-DV system started from a higher strain of 3.6%, and stabilized at about 1.8%, which is also higher than those of the other graphene/*h*-BN systems with defects. It might be caused by the formation of the two five-member rings in this model. Due to the deviation of the structure caused by the defects, the bond lengths and angles around the vacancies changed accordingly. The detailed information of these structural parameters for the G-BN-zz system and the defective models with a zigzag edge was listed in Table S1. Comparing the G-BN-zz system to the pristine graphene or *h*-BN, just slight changes for the C–C–C angles, B–N–B angles, C–C bonds and B–N bonds were observed. For the defective models with a zigzag edge, the maximum elongation (7.6%) of B–N bond occurred at the vacancy of the zz-SV-C-5566 system; while the maximum change (4.2%) of C–C bond was found at the interface of the zz-SV-C system. The changes of the angles around the vacancies for these systems ranged from 0.8% to 5.8%. As shown in Fig. 1, the N atom around the vacancy on the surface of zz-SV-B-5566 system exhibited a slight elevation (0.58 Å) from the 2D surface.

For the graphene/*h*-BN systems with an armchair edge, as shown in Table 1, the inflection angles for the single vacancy defects ranged from 10° to 20°, and the misorientation angles of these four defective systems changed from 1.2° to 4.0°. These values are comparable with those of the G-BN-am system. However, the structure of the am-DV system exhibited an obvious deviation from the G-BN-am system. That is the inflection angle and misorientation angle of the am-DV system were 53° and 18.0°, respectively. The in-plane strain distribution of these defective systems with an armchair edge can be found in Fig. 3(b). The strains of systems of am-SV-C (2.5%), am-SV-C-5566 (1.8%) and am-DV (2.5%) are higher than that of the G-BN-am system (1.48%) at the first BN line. Then the strain of these three defective systems decreased rapidly. Systems of am-SV-C-N (0.69–1.02%) and am-SV-N-5566 (0.51–0.74%) always showed lower strains than that of the