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Point defects engineering in graphene/h-BN bilayer: A first principle study

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ABSTRACT

Point defects engineering in a new type hetero bilayer consisting of graphene and hexagonal boron–nitrogen (h-BN) sheet, including vacancy, substitutional C/B/N doping and the possible combinations of the former two, was theoretically studied using first-principles calculations. The optimized geometry, formation energy, magnetic moment, and electronic property of these systems are discussed. It was found that N vacancy is more likely to form than B vacancy in graphene/h-BN bilayer and their electronic properties exhibit n-type and p-type conductivity, respectively. Divacancy of N and C in hetero bilayer shows high stability and induces direct band gap in up and down spin, respectively. Combined by N substitutional doping in graphene and B vacancy in h-BN layer, this substitution-vacancy combination shows low formation energy and changes the semiconductor property of pristine graphene/h-BN bilayer to metallic. In contrast, the graphene/h-BN bilayer with the combinated defect of C-substitution in B site and C vacancy in graphene shows half-metallic electronic property. The calculated magnetic moments are in reasonable agreement with the available theoretical analysis on atomic charge distribution. This work reveals that the electronic and magnetic properties of graphene/h-BN bilayer can be effectively tuned by above proposed point defects engineering.

1. Introduction

Graphene is a promising candidate among two dimensional materials for electronic application due to its unique Dirac electronic property [1]. In single layer graphene or graphene nanoribbons, it was found that vacancy can induce magnetism [2–5], as well as tune its energy gap [6]. Spin-polarized electronic current in graphene could be achieved by substitutional doping with boron and nitrogen atoms [7]. Because of the structural similarity, single layer hexagonal boron nitrogen (h-BN) is an analog to graphene. In h-BN sheet, significant spin polarization can be induced by vacancy defects [8]. However, B—N pair vacancies in h-BN sheet make it polarize by non-spin polarization [9]. Density functional study [10] showed that the electronic properties of a single layer hybrid h-BN and C sheet are related to both geometrical confinement and bonding character at the h-BN/C interface. In graphene and single layer h-BN sheet, point defects such as vacancies or substitutional dopants have significant influence on their electronic and magnetic properties.

Besides single layer atomic crystal, a new type of two-dimensional hetero-bilayer, called graphene/h-BN, was successfully prepared in experiments [11,12]. For this hybrid nanostructure which was combined by graphene and h-BN sheet, a minor energy gap was found because of interplanar interaction [13]. This energy gap is originated from the symmetry breaking of sublattice, which is similar with the case of graphene on h-BN substrate [14,15]. In Dirac nanoelectronics, energy gap opening at K point is particular important for achieving on/off current ratios. Raman experiments [16] and HRTEM imaging [17] proved that graphene/h-BN ultra-thin film posses significant carrier mobility. Moreover, using strain [13] and electric field [18] could effectively tune its band gap. Strain engineering on graphene/h-BN hetero-bilayer was also found interesting for sensor application [19]. The

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Table 1
Summary of results in graphene/h-BN hetero-bilayer with vacancy defects. The bond length in angstrom, the magnetic moment in μB, the electron number N_{up} and N_{dn} in up and down spin on nearby atoms around vacancies, the spin polarization $P(E_f)$ and Gibbs formation energy G_f in eV are indicated. "+" and "−" means the moving of Fermi level upward and downward respect to the Fermi level in pristine graphene/h-BN hetero-bilayer, respectively. M and SC represent for metal and semiconductor properties deduced from band structures.

Configurations	Bond (Å)		Magnetic moment (μB)				Atomic charge distribution (e)			$P(E_f)$ (%)	G_f (eV)	Gap (eV)	
	C—C	B—N				Tot	N_{up}	N_{dn}	$N_{up} - N_{dn}$			Majority	Minority
$B_{15}N_{16}/C_{32}$	1.42	1.41	0.28 (N)	0.59 (N)	0.59 (N)	1.79	2.28 (N)	1.68 (N)	0.60 (N)	10	0.146	−0.04 (M)	−0.05 (M)
$B_{16}N_{16}/C_{31}$	1.43	1.42	0.46 (C)	0.46 (C)	0	1.22	1.43 (C)	1.03 (C)	0.40 (C)	12	0.115	−0.17 (M)	−0.15 (M)
$B_{16}N_{15}/C_{32}$	1.42	1.43	0	0	0	0.51	0	0	0	72	0.105	+0.13 (M)	+0.16 (M)
$B_{15}N_{16}/C_{31}$	1.42	1.41	0.28 (C) 0.52 (N)	0.28 (C) 0.52 (N)	0.28 (C) 0.52 (N)	3.03	1.34 (C) 2.16 (N)	1.10 (C) 1.60 (N)	0.24 (C) 0.56 (N)	6	0.265	−0.47 (M)	−0.19 (M)
$B_{16}N_{15}/C_{31}$	1.43	1.42	0.77 (C)	0	0	1.00	1.62 (C)	1.00 (C)	0.62 (C)	0	0.207	0.14 (SC)	0.07 (SC)

open question arises such as whether vacancies or substitutional dopants of B, C and N in graphene/h-BN hetero-bilayer have impact on its electronic and magnetic properties? In this paper, we perform first-principles calculations to study the structural, electronic and magnetic properties of graphene/h-BN hetero-bilayer under three kinds of defect engineering: vacancy, anti-site substitution, and the possible combinations of the former two. We found that the electronic and magnetic properties of graphene/h-BN hetero-bilayer can be effectively tuned by the engineering of above mentioned point defects.

2. Computational method and model

Our calculations are performed based on density functional theory (DFT) [20] and plane-wave method as implemented in Vienna ab initio software package (VASP) [21]. The exchange correlation potential is treated within the local density approximation (LDA) as implemented by PAW function [22]. The cut-off energy of 450 eV was used and is found sufficient for the convergence in total energy. A vacuum space of 20 Å above the hetero-bilayer is used to eliminate the neighboring interaction between the supercells. A Monkhorst–Pack $13 \times 13 \times 1$ k-mesh for unit cell and $7 \times 7 \times 1$ k-mesh for 4×4 supercell in Brillouin zone are employed. Spin polarization calculations are taken into account with a criterion of maximum force on each atom to be smaller than 0.01 eV/Å. Due to the importance of van-der-Waals (VDW) interactions [23–25] between the interlayers, VDW interaction has been accounted in our total energy calculations. Additionally, the dipole moment [26,27] is corrected along the direction perpendicular to the hetero-bilayer.

The stability can be evaluated by Gibbs formation energy G_f, which was calculated as the difference in total energy [28]

$$G_f(X) = E_{tot} - \chi_B\mu_B - \chi_C\mu_C - \chi_N\mu_N \quad (1)$$

where E_{tot} is the average cohesive energy per atom of the optimized graphene/h-BN hetero-bilayer with point defects, χ_i denotes the molar fraction of atom i (i = B, C, N) in the studied configurations satisfying

$$\chi_B + \chi_C + \chi_N = 1 \quad (2)$$

and μ_X is the chemical potential of a single atom X (X = B, C, N). For h-BN monolayer, the chemical potentials of B and N atoms satisfy

$$\mu_{BN} = \mu_B + \mu_N \quad (3)$$

where μ_N is the energy of a single N atom obtained from a N_2 molecule [29], and μ_C is the energy of a C atom obtained from pristine bilayer graphene [30]. The spin polarization $P(E_f)$ at Fermi level can be expressed as

$$P(E_f) = \frac{D(E_{(f)\uparrow}) - D(E_{(f)\downarrow})}{D(E_{(f)\uparrow}) + D(E_{(f)\downarrow})} \quad (4)$$

where $D(E_{(f)\uparrow})$ and $D(E_{(f)\downarrow})$ is the value of DOS in majority and minority spin at the Fermi level, respectively [1]. The difference

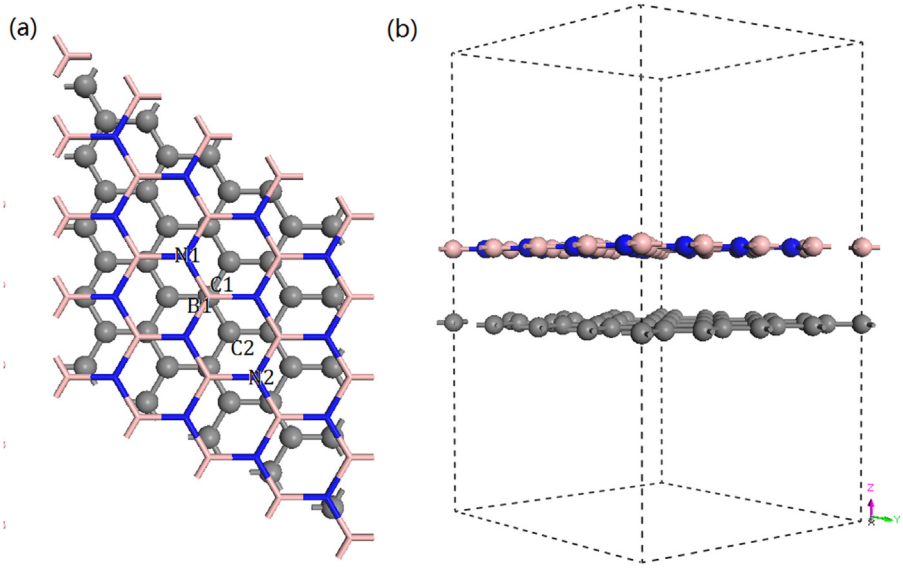

Fig. 1. Relaxed configuration of pure graphene/h-BN bilayer, (a) top view and (b) side view. Boron, nitrogen, and carbon atoms are indicated in pink, blue and gray, respectively. In (a), C1, C2, B1, N1, N2 denote the sites where vacancy or substitution may be occur. Graphene layer is schematic indicated by ball-stick model and h-BN layer is depicted by stick model. In (b), the dashed line indicates the 4×4 supercell used in our study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)