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Band gap engineering of graphene with inter-layer embedded BN: From first principles calculations

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ABSTRACT

Graphene is a promising material for the next generation electronics. However, its zero band gap limits its applications on electronic devices. Robust methods that modify graphene electrical properties by chemical doping are in great demand due to the potential applications of graphene on electronic devices. In this work, we explore BN doping behaviors with three different concentrations in graphene matrix by using first principles calculations. We calculate the band structure and find that the band gap opens up from zero in pristine graphene to 51, 78 and 93 meV in 1%, 2% and 3% BN embedded graphene, respectively. The results of calculated band gap reveal that BN doped graphene exhibits an intrinsic semiconductor band structure characteristic, in which the Fermi level lies in the center of the forbidden gap. The normalized formation energy of BN as a function of BN concentration in graphene reveals that BN would prefer accumulating a big domain rather than a small domain in graphene.

1. Introduction

Graphene has recently emerged as a serious contender for the post silicon era and been attracting more attention due to its intriguing physical, chemical and mechanical properties originating from its novel electronic band structures. The remarkable feature of graphene is its high electron mobility, making it a promising material for high performance electronics. The excellent tunable electronic and optical properties make graphene having great potential for wide nano- and optoelectronic applications [1]. Beyond its electronic properties, graphene has many superlative physical properties and so has been employed in corrosion inhibitors [2], photovoltaic cell as transparent electrode [3] and electrochemical energy devices (fuel cells, metal–air batteries) and biosensors [4].

Graphene is a basic building block for graphitic materials of all other dimensionalities (0D fullerenes, 1D nanotubes, and 3D graphite), and studying doped graphene is expected to provide fundamental insight into doped carbon materials [5]. However, such promising application in electronics has been hampered by its zero band gap, which results a transistor made from graphene having no “off” state. Hence, the opening of a band gap is thus essential from electronics point of view for graphene-based devices. Chemical doping is one of the efficient ways to tailor the electronic properties and which has been widely used in semiconductor industries.

Hexagonal boron nitride (*h*-BN) turns to be the perfect dopant for graphene for tuning band gap. *h*-BN can be considered to be a graphene with carbon atoms replaced by boron and nitrogen resulting in the same honeycomb lattice 2D structure, and has nearly perfect lattice constant that matches to graphene. *h*-BN is an insulator with an extremely wide band gap (~5.5 eV). Hence, *h*-BN is considered one of the best candidates for opening graphene band gap. One of the widely used methods for tuning band gap is van der Waals heterostructures consisting of *h*-BN and graphene layers. Stacked graphene/*h*-BN structures have also been intensively investigated and reported as a measurable band gap [6–11]. Moreover, theoretical results also predicted that AB stacked graphene and *h*-BN heterostructures would generate a tunable band gap [12]. However, the misorientation of the two 2D layers was very difficult to control in a real fabrication process using a direct transfer technology, and it was reported that the tunable band gap was a function of the twist angles. Such as, the measure band gap was varied between 16.8 and 27.8 meV corresponding to the twist angles of 0.5° to 5° [6]. And the random stacking always leads to the uncertainty in the electronic properties of graphene/*h*-BN structures. Controllable synthesis of well-aligned graphene/*h*-BN heterojunctions is a big challenge and thus highly demanding.

Chemical functionalization such as hydrogen adsorption would yield a measurable band gap in graphene, however, it is very difficult to control the adatoms distribution and the results have poor reproducibilities [13]. Based on the comparison on electrical and physical properties between graphene and *h*-BN, inter-layer hybridized graphene and BN would be an alternative solution for opening up graphene band gap. Despite the enormous interest in *h*-BN/graphene hybridized inter-layer structures, there has been limited experimental success in achieving

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these structures. It was demonstrated that planar graphene/*h*-BN heterostructures could be formed by growing graphene in lithographically patterned *h*-BN atomic layers [14]. Ci and co-authors reported the synthesis and characterization of large-area atomic layers of *h*-BNC material, consisting of hybridized, randomly distributed domains of *h*-BN and C phases with compositions ranging from pure BN to pure graphene, and their structural features and band gap were distinct from those of graphene, doped graphene and *h*-BN [15]. Nevertheless, it is very difficult to control the arrangement of B, C and N atoms in these structures and ensure a uniform crystal structure [15]. The interfacial energies of graphene domains with different shapes embedded in BN were studied by using the first principles calculations and it was suggested that BNC mixtures should separate into immiscible BN and C [16].

Numerous interesting graphene/*h*-BN inter-layer hybridized structures have been proposed but their implementation has been very limited [15,17,18]. It should be noted that the use of density functional theory (DFT) has always played an instrumental role in understanding and predicting the properties of materials, especially on electrical properties, often in a quantitative way. To the best of our knowledge, so far, there are no systemically theoretical studies on the concentration of *h*-BN dopant dependence of graphene band gap. Hence, more theoretical and experimental works are still highly demanding to explore *h*-BN configurations within the graphene sheets and sub-lattices. A microscopic understanding of the different bond types and their diverse effects on electrical properties in BN doped graphene are therefore highly desirable. In this study, we mainly focus on the electrical properties of *h*-BN embedded graphene by using the first principles calculations.

2. Methods

h-BN is adopted as possible dopant for opening the graphene band gap. In order to explore the effect of BN concentration on the graphene band gap, we consider three different BN pairs substituted at C sites: one BN pair substituted at two carbon atoms, two BN pairs substituted at four carbon atoms, and three BN pairs substituted at six carbon atoms in graphene matrix within one hexagonal ring. The calculations were carried out using DFT with the generalized gradient approximation (GGA) [19] and projector augmented wave (PAW) method [20], as implemented in the VASP code [21], in which 2 s^2 2 p^2, 2 s^2 2 p^1 and 2 s^2 2 p^3 are treated as valence electrons for C, B and N atoms, respectively. For the hybridize system calculations, we create $10 \times 10 \times 1$ supercells containing 200 C atoms. The large size of the supercell separates the periodic embedded BN images by more than 20 Å and dilutes dopant concentration. In this study, the BN concentration is 1%, 2% and 3% corresponding to one BN, two BN and three BN pairs, respectively. We fix the supercell lattice constants and relax all atomic coordinates until atomic forces are less than 0.01 eV/Å. For each system, the total energy convergence is tested with respect to Brillouin zone sampling with a range of *k*-point numbers between 1 and 12. Energy convergence with respect to the plane wave cutoff is tested by varying this parameter between 300 and 600 eV. Convergence to within 10 meV is achieved with 8-*k* points and cutoff energy of 400 eV for pristine graphene and BN embedded graphene supercells.

3. Results and discussion

First, we examine the atomic structures of 2D graphene and *h*-BN unit cells, as shown in Fig. 1. There are two atoms in each unit cell. The optimized lattice constants *a* are 2.47 Å and 2.53 Å for graphene and *h*-BN, and relative lattice constant results the bond length of $d_{\mathrm{C-C}} = 1.426$ Å and $d_{\mathrm{B-N}} = 1.461$ Å, respectively. The results show a good agreement between the theoretical and experimental values of 2.46 and 2.51 Å, therefore we consider that our computational results are reliable. We expand the optimized graphene unit cell to 200-atom supercells for doping calculations. The optimized B–N bond length is only 2.4% (experimental value of 2.0%) larger than the C–C bond, which makes them perfect for doping with minimal internal stress.

For the case of the two BN pairs substituted at four carbon atoms, firstly, we find the most energetic configuration among all possible distributions. The possible configurations of the two BN pairs in graphene matrix and the calculated ground state energy as a function of the configurations of the two BN pairs embedded graphene are shown in Fig. 2, in which, we find that the two neighboring BN pairs in the same hexagonal ring have the lowest ground state energy in contrast to other possible distributions. When the two neighboring BN pairs embedded in graphene matrix within the same hexagonal ring, the total 9 C–C bonds would be broken to form B–C, N–C and B–N bonds. However, for the rest of possible configurations, the total 10 C–C bonds need to be broken for embedding two BN pairs in graphene matrix. Our results are in consistent with the order of bonding strength. The bonding strength of C–C is much higher than that of B–N, 607 kJ/mol vs. 389 kJ/mol. More external energy would be required for forming separately small domains in which more C–C bonds should be broken. Hence, for the case of the two BN pairs substituted at four carbon atoms, we only consider the neighboring BN pairs configuration for calculating electrical properties. The local defect model configurations for this study are shown in Fig. 1(c)–(e).

Next, we investigate the formation energy of BN pair in graphene matrix. In general, the formation energy of BN pair E_f in graphene is defined as:

$$E_f = E^{def} - \sum H_C \mu_C - \sum D_{BN} \mu_{BN} \tag{1}$$

where E^{def} is the total energy of BN embedded graphene supercell, $\sum H_C \mu_C$ and $\sum D_{BN} \mu_{BN}$ are the sum of host C atoms H_C and dopant atoms D_{BN} multiplied by their respective chemical potentials μ_C and μ_{BN}, which are calculated from the chemical potential C in graphene and BN pair in (*h*-BN), respectively. In order to explore the relationship between the formation energy of BN in graphene and BN concentrations, we further define the normalize formation of BN in graphene, which is given by:

$$E_f^N = \left(E^{def} - \sum H_C \mu_C - \sum D_{BN} \mu_{BN}\right) / D_{BN}. \tag{2}$$

The normalized formation energies of substitutional BN pair as a function of BN concentration in graphene are shown in Fig. 3. We find that the normalized formation energy is decreased with the BN pair concentration increase. According to our theoretical results as shown in Fig. 3, we suggest that BN would be energetically form big *h*-BN domains in graphene matrix. Our prediction has a good agreement with the experimental result which reported that *h*-BN in graphene is likely to accumulate a big domain rather than separately small domains [15].

In order to explore the contribution of BN doping in electrical properties, we further calculate the band structures of BN embedded graphene with three different doping concentrations and the results are shown in Fig. 4. As a benchmark, the calculated band structure of pristine graphene is shown in Fig. 4(a). The results of the partial density of states (PDOS) (not shown in this work) show that the p_z orbitals of C form bonding orbital (π) and anti-bonding orbitals (π*) below and above the Fermi energy level. π-Orbital and π*-orbital contact at one point in the momentum space just at the Fermi energy, which results graphene having a zero band gap. In view of the result on the graphene band structure calculation, it seems that DFT-GGA succeeds to describe the band structure of graphene.

The calculated band structures of BN embedded graphene systems are shown in Fig. 4(b)–(c), the band gap of one BN pair embedded graphene opens up to 51 meV (~394 K). When more BN pairs are embedded in graphene, the band gap further increases to 78 meV (~901 K) for four C replaced by two BN pairs and 93 meV (~1075 K) for six C replaced by three BN pairs. Embedded BN pairs in graphene