Investigating the effect of Vacancy Defect on Graphene/Hexagonal Boron Nitride In-plane Heterostructure

Habibu Aminu Hussain, İzmir Katip Çelebi Univ., Graduate School of Natural and Applied Sciences, Nanotechnology, Çiğli Main Campus, İzmir, Türkiye*
Cem Özdoğan, Department of Engineering Science, İzmir Katip Çelebi Univ. Çiğli Main Campus, İzmir, Türkiye
Nurten Akman, Department of Physics, Mersin University, 33343 I¸cel, Turkey
**Corresponding author: habaminu@gmail.com*

Keywords: graphene, h-BN, defect
Discipline: Physics

Abstract

In this study we have successfully investigated the effect of mono vacancy on structural, electronic and magnetic properties of an in-plane (GBN) nanosheet structure. We create the in-plane GBN structure by implanting graphene island on hexagonal boron nitride substrate. We create vacancy defect at different location on the hybrids, by removing one atom of either C, B or N. The effect of these vacancies and their positions on electronic, magnetic, and physical properties of the hybrids were fully investigated.

Introduction

The extraction of single-atom-thick graphene from bulk graphite in 2004 has led to the massive interest in other single layer materials, with or without honeycomb structure by the scientific community [1]. One of the stable one similar to graphene is the boron nitride in hexagonal form (h-BN) [2]. The ideal lattice match between graphene and h-BN make it practicable to create graphene/h-BN in-plane hybrids (GBN) structure. The honeycomb lattice of carbon atoms makes it an attractive structure in fundamental physics and electronic devices, such as capacitors and field effect transistors (FETs) [3]. Moreover, tuning it's band gap might further increase its application in optoelectronics and nanoelectronics devices. Several techniques have been suggested to open an energy gap between the valence and conduction band. One basic approach involves chemical modification such as chemical doping of graphene with foreign atoms [4]. Using liquid precursor based chemical vapor deposition (CVD) techniques, nitrogen-doped graphene was grown directly on Cu current collector and studied for its reversible Li-ion intercalation properties by Reddy [5]. The properties of purest graphene are outstanding. Being the strongest material ever tested, conduct heat and electricity efficiently and nearly transparent. Graphene is one of the favorable materials for researchers in nanotechnology.

Structural defect in graphene is inevitable during the growth or processing. The defect which often perceived as limiters somehow found their application in thermoelectric devices [6]. Graphene lattice can be reconstructed by forming non-hexagonal rings, which does not involve added or removed atoms. For example, hexagons are transformed into two pentagons and heptagons by rotating one of the C-C bonds by 90° forming what is known as Stone-Wales defect [7]. Foreign atoms can intentionally be introduced into graphene as impurities forming extrinsic defect that alter the type and amount of charge defect in the system. Nitrogen or boron are desirable dopants in carbon nanostructures since they have one electron more or less respectively. Single vacancy defect in graphene has been experimentally observed by transmission electron microscope [8] and Scanning tunneling microscope. The presence of single vacancy has fascinating and unanticipated implication. It leads to the emergence of a stable unit charge localized at the vacancy site and interacting with other charges of the conductor by means of an unscreened coulomb potential. It also breaks the symmetry between the two graphene sublattice hence inducing zero energy state at the Dirac point. Perfect graphene is nonmagnetic, but the existence of vacancy can cause magnetism, by breaking the symmetry of π-electron system [9].

An h-BN is the isoelectric equivalent of graphite. The boron and nitrogen atoms are alternatively arranged to form planar conjugated layers, which bundle such that the two atom types in the neighboring layers eclipse on top of one another because of polarity mismatch. Within each layer of h-BN, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces, as in graphite. Many experimental [10] and theoretical [11] studies were carried out to investigate the effect of defect on h-BN. For instance, a pristine h-BN samples containing

micrometer sized hexagonal crystalline particles were mechanically treated using a ball-milled to intentionally introduce defect on the h-BN. Common defects observed in h-BN monolayer are the missing boron or nitrogen atoms. Another type of defect found in h-BN is the substitution of either boron or nitrogen atom with carbon atom. This type of defect has its own implication. It was found that substituting single boron atom with carbon atom in an N-rich growth or a nitrogen atom in a B-rich medium, lowers the formation energy as compares to creating a vacancy defect of either boron or nitrogen. It is also observed that two deep defect level, largely localized on the carbon atom appears slightly below the conduction band.

Computational Method

We performed electronic structure calculations within the DFT framework.[12] The exchange correlation potential was handled through the generalized gradient approximation (GGA) together with the Perdew-Wang parametrization (PW91) [13]. For geometry optimizations, electronic and density of states (DOS) computations we used the Vienna Ab Initio Simulation Package (VASP, version 5.3) [14;15] employing the projected augmented wave (PAW) method [16,17].

Result

In this section we will discuss the electronic and magnetic properties of pristine h-BN and in-plane GBN hybrids systems, energetics of island implantation and defect formation energy. The total energy difference between NSP and SP is called as the magnetization energy ΔE_M

$$\Delta E_M = E_{NSP} - E_{SP} \quad (1)$$

Positive ΔE_M means that the system has a SP ground state, otherwise it refers to as NSP ground state. Each nanosheet is made of 9 x 9 unit cell with 162 atoms. Although h-BN thin film was described as an indirect band gap semi-conductor, a recent study has reported that it has a direct band gap of 5.9 eV [18]. The band gap of monolayer h-BN sheet is calculated through the LDA and G0W0 method, respectively, as 4.61 and 6.57eV. While the LDA underestimate the band gap value GGA overestimate the value, but GW method usually estimates it more accurately. We calculated the BN bond length as 1.45Å, which is consistent with the literature. [19] Calculated ΔE_M value for h-BN is 0.4meV.

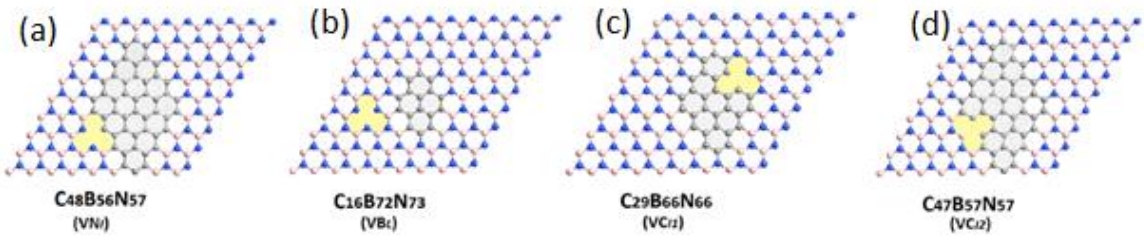

Figure 1. Optimized geometry of in-plane hybrid of graphene and h-BN GBN heterostructure. The dark blue, grey and the light orange colors show N, C and B atoms respectively. It shows a graphene layout hosting a diamond shaped h-BN island at the middle. (a) B vacancy at the interface between Cand N (b) B vacancy at the middle of N atoms (c) C vacancy at the interface between C and N (d) C vacancy at the interface between C and B

Table 8. Island formation energies for pristine GBN hybrids. The G island is in the shape of diamond (D), each having 4, 9 or 16 hexagons. Energy per atom and minimum and maximum island formation energies, $E_{if_{min}}$ and $E_{if_{max}}$ are given in eV. Minimum and maximum island formation energies per total number of atoms involved by the G island are given in eV/atom in the next two columns. The total magnetic moment μ and band gap E_g are given in units of μ_B and eV, respectively. Here, NM means that the hybrid is in a non-magnetic state or has no magnetic moment each.

Hybrid	Name	Energy (eV/atom)	$\mathcal{E}_{if_{min}}$ (eV)	$\mathcal{E}_{if_{max}}$ (eV)	$\mathcal{E}_{if_{min}}$ (eV/atom)	$\mathcal{E}_{if_{max}}$ (eV/atom)	μ μ_B	E_g (eV)
$B_{81}N_{81}$	h-BN	-8.837						4.59
$C_{16}B_{73}N_{73}$	4G(D)@h-BN	-8.843	-102.229	120.518	-6.389	7.532	NM	2.13
$C_{30}B_{66}N_{66}$	9G(D)@h-BN	-8.861	-193.582	224.068	-6.453	7.469	NM	1.12
$C_{48}B_{57}N_{57}$	16G(D)@h-BN	-8.887	-311.652	356.588	-6.493	7.429	NM	0.65

As is seen in Table 1, each hybrid system has a wide range of formation energies. The energetics prove that the reactions can both be endothermic (positive $\mathcal{E}_{if_{max}}$ values) or exothermic (negative $\mathcal{E}_{if_{min}}$ values) ion implantation processes. Energetics of hexagonal and triangular shaped island implantation for the pristine hybrids have been discussed through the solid-state reactions in our previous work.

References

[1] Allen, Matthew J., Vincent C. Tung, and Richard B. Kaner. "Honeycomb carbon: a review of graphene." Chemical reviews 110.1 (2009): 132-145.
[2] Gao, Gao, Yabo, et al. "Toward single-layer uniform hexagonal boron nitride graphene patchworks with zigzag linking edges." Nano letters 13.7 (2013): 3439-3443.
[3] Westervelt, R. M. "Graphene nanoelectronics." Science 320.5874 (2008): 324-325.
[4] Long, Donghui, et al. "Preparation of nitrogen-doped graphene sheets by a combinedchemical and hydrothermal reduction of graphene oxide." Langmuir 26.20 (2010): 16096-16102.
[5] Reddy, Arava Leela Mohana, et al. "Synthesis of nitrogen-doped graphene lms for lithium battery application." ACS nano 4.11 (2010): 6337-6342.
[6] Quandt, Alexander, et al. "Functionalizing graphene by embedded boron clusters."Nanotechnology 19.33 (2008): 335707.
[7] Meyer JC, Kisielowski C, Erni R, Rossell MD, Crommie MF, Zettl A. Direct imaging of lattice atoms and topological defects in graphene membranes. Nano letters. 2008 Jun 19;8(11):3582-6.
[8] Zhou, Wu, et al. "Direct determination of the chemical bonding of individual impurities in graphene." Physical review letters 109.20 (2012): 206803.
[9] Gonzalez-Herrero, H., et al. "Atomic-scale control of graphene magnetism by using hydrogen atoms." Science 352.6284 (2016): 437-441.
[10] Museur, Luc, Eduard Feldbach, and Andrei Kanaev. "Defect-related photoluminescence of hexagonal boron nitride." Physical Review B 78.15 (2008): 155204.
[11] Hussain, Habibu Aminu, Nurten Akman, and Cem Özdoğan. "Investigation of the mono vacancy effects on the structural, electronic and magnetic properties of graphene hexagonal-boron nitride in-plane hybrid embracing diamond shaped graphene island." Solid State Sciences (2020): 106395.
[12] Kohn, Walter, and Lu Jeu Sham. "Self-consistent equations including exchange and correlation effects." Physical review 140.4A (1965): A1133.
[13] Perdew, John P., and Yue Wang. "Accurate and simple analytic representation of the electron-gas correlation energy." Physical Review B 45.23 (1992): 13244.
[14] Perdew, John P., et al. "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation." Physical review B 46.11 (1992): 6671.
[15] Kresse, Georg, and Jrgen Furthmller. "Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set." Physical review B 54.16 (1996): 11169.
[16] Blöchl, Peter E., Ove Jepsen, and Ole Krogh Andersen. "Improved tetrahedron method for Brillouin-zone integrations." Physical Review B 49.23 (1994): 16223.

[17] Kresse, Georg, and Daniel Joubert. "From ultrasoft pseudopotentials to the projectoraugmented-wave method." Physical review b 59.3 (1999): 1758.
[18] Watanabe, Kenji, Takashi Taniguchi, and Hisao Kanda. "Direct-bandgap propertiesand evidence for ultraviolet lasing of hexagonal boron nitride single crystal." Nature materials 3.6 (2004): 404.
[19] Zhi, Chunyi, et al. "Large scale fabrication of boron nitride nanosheets and their utilization in polymeric composites with improved thermal and mechanical properties."Advanced Materials 21.28 (2009): 2889-2893.