



Influence of interface geometry on phase stability and bandgap engineering in boron nitride substituted graphene: A combined first-principles and Monte Carlo study



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ARTICLE INFO

Article history:

Received 15 November 2016

Received in revised form

23 February 2017

Accepted 2 March 2017

Available online 6 March 2017

Keywords:

Graphene

Boron nitride

First-principles electronic structure

Monte Carlo simulations

Alloy theory

ABSTRACT

Using combination of Density Functional Theory and Monte Carlo simulation, we study the phase stability and electronic properties of two dimensional hexagonal composites of boron nitride and graphene, with a goal to uncover the role of the interface geometry formed between the two. Our study highlights that preferential creation of extended armchair interfaces may facilitate formation of solid solution of boron nitride and graphene within a certain temperature range. We further find that for band-gap engineering, armchair interfaces or patchy interfaces with mixed geometry are most suitable. Extending the study to nanoribbon geometry shows that reduction of dimensionality makes the tendency to phase segregation of the two phases even stronger. Our thorough study should form a useful database in designing boron nitride-graphene composites with desired properties.

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1. Introduction

Graphene [1,2] and its structural analog, a single sheet of hexagonal boron nitride (h-BN) comprising of alternating boron and nitrogen atoms [3,4] in hexagonal ring, provide prototype models for the study of two-dimensional (2D) systems. Besides being interesting from fundamental physics point of view, they offer technological importance for possible applications in the field of nanoelectronics [5–8]. In spite of sharing the same structural motif with only about 2% difference in their lattice constants, h-BN is an insulator with a large band-gap of more than 5 eV, while graphene is a zero-gap semi-metal with Dirac cone band structure. It was thus thought that band gap engineering may be achieved by mixing graphene with h-BN (termed as h-CBN hereafter). Films of h-CBN were initially synthesized by Panchakarla et al. [5] and by Ci et al. [6] using Chemical Vapor Deposition (CVD) technique, in which concentrations of C and BN could be carefully controlled. Liu et al. [9] showed that planar graphene/h-BN hybrid can be seamlessly

stitched together by growing graphene in lithographically patterned h-BN atomic layers. However, the formation of solid solution of graphene and h-BN is found to be thermodynamically limited, as graphene and h-BN have been reported to phase segregate both experimentally and theoretically [6,10–13]. The h-CBN system thus consists of segregated graphene or BN nanophases embedded in the matrix of the other. In presence of metal support laterally joined structure of h-BN and graphene has been achieved [12].

The interface formed between graphene and h-BN can be of zig-zag type or arm-chair type in case of laterally joined strip structures, or can be of mixed type as would be the case for isolated patches. With the advancement of synthesis technique, specially on metal support, it may be possible to synthesis samples with preferential control of one geometry of interface over another. Though there exists certain theoretical studies in this respect [14–22], a systematic study of the influence of the interface geometry on the phase stability of h-CBN will be highly desirable. In the present study, we address this issue by considering periodic array of h-BN and graphene strips, with zig-zag and armchair interfaces, formed by replacing graphene rows with boron-nitride rows within a given supercell. We study the phase stability of the constructed structures within the first-principles density functional theory (DFT) approach together with regular solid solution model.

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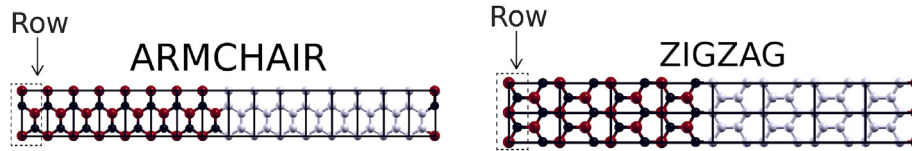


Fig. 1. The arm-chair (left panel) and zig-zag interface created between h-BN and graphene within the supercell. The 16×1 armchair and 8×2 zigzag supercells generated by the orthorhombic unit cells are shown by the solid black lines. The row used for replacing C atoms by BN atoms in two cases have been marked by the black dotted boxes. The carbon, B and N atoms are shown as white (light gray), red (dark gray) and black colored balls. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We further investigate the microstructures formed by considering Monte Carlo (MC) simulations based on an underlying bond Hamiltonian with DFT derived bond energies. MC simulations also enable us to compute the spinodal line for the MC generated interfaces with patchy structures. We additionally explore the effect of dimensionality reduction on phase stability of h-CBN. The miniaturization required for device applications use the so-called nanoribbon geometry with finite width in one direction and infinite in other direction. Both graphene nanoribbons (GNR) and boron nitride nanoribbons (BNNR) have been synthesized. Just as surface effects become predominant in 3D physics, edge effect would play a crucial role in GNR and BNNR. For example BNNR has been predicted to have narrow band gap and improved conductivity tuned by a transverse electric field or edge structure [23,24]. Within the framework of MC simulation with DFT derived model Hamiltonian, we thus also study the phase stability properties of h-CBN in nanoribbon geometry.

Finally we study the influence of interface geometry, which can be of arm-chair type or zig-zag type formed by connection of h-BN and graphene strips, or mixed type formed by patches of h-BN domain in the matrix of graphene or visa-versa, on the electronic structure and band gap of h-CBN system. Our extensive study should provide useful information on the influence of interface geometry on the phase stability and band gap engineering.

2. Results and discussions

2.1. First-principles study of zig-zag and arm-chair interfaces between strips of h-BN and graphene

Ab-initio DFT calculations were carried out on a 16×1 and 8×2 orthorhombic supercell (indicated by the black solid lines in Fig. 1) for the arm-chair and zigzag case respectively using the plane wave based Quantum Espresso code [25].¹ In these calculations, strips of h-BN and graphene connected either by zig-zag interface or arm-chair interface was created by replacing rows (indicated by the black dotted box in Fig. 1) of C hexagons by BN hexagons of varying width within the unit cell, as shown in Fig. 1. Ultrasoft pseudopotential [27] was used to describe the core electrons and the generalized gradient approximation (GGA) for the exchange-correlation kernel [28]. A 550 eV kinetic energy cutoff for the plane-wave basis set and 2200 eV for the charge density was used, obtaining an accuracy of 10^{-10} eV in the self-consistent calculation of the total energy, using a converged Monkhorst-Pack k-point grids [29] of $6 \times 6 \times 1$. The convergence of the computed ground state properties in terms of kinetic energy cut-off for the basis set and charge density has been checked. The positions of the atoms in

the unit cell were relaxed toward equilibrium until the Hellmann Feynman forces became less than 0.001 eV/Å.

In order to study the phase stability of h-CBN, we first computed the cohesive energy (ΔE) of $(C_2)_x(BN)_{1-x}$, which is also termed as mixing energy since it is related to the energies of the alloy related to the energies of pristine graphene and boron nitride. The negative value of ΔE indicates tendency to form homogeneous solid solution while positive value of ΔE indicates the tendency to phase separate. For each concentration x , we calculated the mixing energy per formula unit (f.u.) of the system using DFT, which is given by the following formula,

$$\Delta E_B = E\{(C_2)_x(BN)_{1-x}, a(x)\} - [xE(C, a_C) + (1-x)E(hBN, a_{hBN})], \quad (1)$$

where $E\{(C_2)_x(BN)_{1-x}, a(x)\}$ is the total energy per formula unit of $(C_2)_x(BN)_{1-x}$ at the equilibrium in-plane lattice constant $a(x)$; $E(C, a_C)$ and $E(hBN, a_{hBN})$ are the total energies per formula unit of pristine graphene and h-BN at the equilibrium in-plane lattice constants a_C and a_{hBN} , respectively. ΔE_B for different values of concentration, x is shown in left panel of Fig. 2, for the arm-chair and zig-zag interface. First of all, we find that mixing energy is positive in all cases, suggesting phase segregation between h-BN and graphene, in conformity with the literature [10,11,30]. Very interestingly we find that the mixing energy is substantially reduced in case of arm-chair interface compared to zig-zag interface. This reduction is most effective at $x = 0.5$, for which the reduction is about 30%. The difference in the mixing energy between the armchair and zigzag interfaces arise because of unequal number of CN and CB bonds per unit length along the interface. We have estimated the number of such bonds to be $\frac{1}{a_0}$ for the zigzag interface while for armchair interface is $\frac{2}{\sqrt{3}} \cdot \frac{1}{a_0}$, where a_0 is the relaxed lattice constant of $(C_2)_x(BN)_{1-x}$.

From the knowledge of mixing energy, the phase stability of $(C_2)_x(BN)_{1-x}$ can be computed from a mean field approach, using the so-called regular solution model. The configuration entropy of mixing is defined as $S = -k_B \sum x \ln x$, where the sum runs over all configurations. Hence for $(C_2)_x(BN)_{1-x}$ alloys, the entropy of mixing is given by $S = -2k_B[x \ln x + (1-x) \ln(1-x)]$ [11], where k_B is the Boltzmann constant and x is the concentration of carbon. The factor 2 arises because of the mixed occupancy of the two sublattices. The free energy is then given by $F(T, x) = \Delta E(x) - TS$, where $\Delta E(x)$ is the mixing energy, as plotted in left panel of Fig. 2. The critical temperature within the regular solution model can be obtained from the condition $\frac{d^2 F}{dx^2} = 0$ at x when $\frac{dF}{dx} = 0$. Fitting the mixing energy to the analytical form, $\Delta E = \frac{1}{b} \text{Sech}\left[a\left(x - \frac{1}{2}\right)\right]$, it can be shown that

the critical temperature will be given by $T_c = \frac{a^2}{8bk_B}$. Fitting parameters for $x = 0.5$, for arm-chair and zig-zag interfaces were found to be $a = 1.208$, $b = 1.511$ and $a = 1.720$, $b = 1.087$ respectively, resulting in a critical temperature of 1400 K and 3948 K. Our computed value of critical temperature for zig-zag interface is in

¹ We have checked the validity of the code by comparing the calculations of structural optimization, total energies, density of states and bandstructures of pristine graphene and BN sheets with VASP [26] and find both codes show extremely good agreement with each other, as expected, since they provide similar computational platforms for planewave pseudopotential calculations.

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