New 2D Structural Materials: Carbon–Gallium Nitride (CC–GaN) and Boron–Gallium Nitride (BN–GaN) Heterostructures—Materials Design Through Density Functional Theory

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Supporting Information

ABSTRACT: New class of ternary nanoheterostructures have been proposed by mixing 2D gallium nitride (GaN) with graphene and 2D hexagonal boron nitride (BN) with an aim towards designing innovative 2D materials for applications in electronics and other industries. The structural stability and electronic properties of these nanoheterostructures have been analyzed using first-principles based calculations done in the framework of density functional theory. Different structure patterns have been analyzed to identify the most stable structures. It is found to be more energetically favorable that the carbon atoms occupy the positions of the nitrogen atoms in a clustered pattern in CC–GaN heterostructures, whereas boron doping is preferred in the reverse order, where isolated BN and GaN layered configurations are preferred in BN–GaN heterostructures. These 2D nanoheterostructures are energetically favored materials with direct band gap and have potential application in nanoscale semiconducting and nanoscale optoelectronic devices.

INTRODUCTION

Simulations based on quantum mechanical treatment of atoms and electrons have a great impact on computational material science research. These simulations and modeling techniques not only provide atomistic-level understanding but also give necessary information to tailor design new materials for future technologies. Density functional theory (DFT)-based techniques have found applications in academia as well as different areas of industrial research.

A great interest has been shown by semiconductor industry on gallium nitride (GaN)-based device structures.1,2 Owing to its large direct band gap3 and high peak velocity,4 GaN possesses substantial promise for optical devices and high-power electronics. Moreover, because of its larger peak electron velocity, larger saturation velocity, and higher thermal stability, GaN is an ideal material in high-power, high-temperature, and high-frequency electronic applications. Recent research shows that incorporating carbon atoms into the GaN volume strongly alters their electronic and magnetic properties.5,6 This incorporation of carbon in GaN films results in an insulating material with resistance >10⁸ Ω.7 The GaN films in their high resistive forms are finding applications as insulating buffer layers or substrates in GaN-based device technologies.

Graphene is still one of the most exciting topics of research in condensed matter physics as well as in materials science, due to its remarkable electronic, mechanical, and thermal properties,9–15 in particular as its charge carriers behave like massless Dirac particles. Additionally, through its electronic band gap tuning, graphene has found applications in nanoelectronic devices.9,16 Energy band gap can be opened in graphene through various means, including hydrogenation,17 interaction with substrate,18,19 molecules adsorption,20 and also deposition on a latticed-matched substrate, such as SiO₂ or hexagonal boron nitride (h-BN).21,22 Recently, various attempts have been made to fabricate graphene devices by engineering their band gaps through doping.23–25 Investigations on doped graphene nanoribbons23,24 indicate that upon doping by N or B, n-type or p-type semiconducting graphene can possibly be obtained, respectively. It has been experimentally established that upon N doping of graphene,23 the Dirac point in the band structure of graphene tends to move below the Fermi level (E_F) and an energy gap appears at high-symmetric K-point. Boron nitride is an insulator with strong ionic bond and can be
synthesized in hexagonal close-packed structure, similar to graphite, with lattice constants very close to those of graphite. This auxiliary closeness among graphite and hexagonal boron nitride (h-BN) drove a few examinations to make multilayers of these materials, which can have semiconducting properties with a small band gap.

A simple metal−insulator−n-type-GaN diode produces blue electroluminescence, and consequently, GaN has been studied as a suitable material in optoelectronic devices as laser and light-emitting diodes. However, the concentration of free electrons is too large (10^{18}−10^{20} cm^{−3}) for the fabrication of a p-type crystal to be successful. Nitrogen vacancies have been found as major source of free electrons rather than any unknown donor impurities. In this work, we performed first-principles electronic structure calculations based on density functional theory approximation to investigate the effects of the incorporation of CC and BN layers in 2D GaN sheet on its structural and electronic properties. We have investigated two different patterns of heterostructures: first, in the GaN 2D structure, we replaced two adjacent gallium nitride layers by two layers of carbon atoms in alternative patterns (Figure 1a,b); in the second configuration (CC-GaN2), we replaced two adjacent GaN layers by two CC layers (Figure 1b), with a carbon concentration of 50% in each case.

Similarly, we modeled the BN:GaN nanoheterostructures and considered two different configurations of alternate BN−GaN layers (BN-GaN3)(Figure 2a) and two alternate BN−BN and GaN−GaN layers (BN-GaN3)(Figure 2b), with a BN layer concentration of 50% in each case.

We evaluated the stability of the CC:GaN nanoheterostructures by calculating the formation energy of each substitution to find the energetically most favorable configurations, as

### RESULTS AND DISCUSSION

#### Structure and Stability

In this section, we discuss the structures and different configurations of heteronanostructures investigated in the present work. First, we investigated CC:GaN heterostructures by replacing gallium nitride (GaN) layers with carbon (CC) layers in a 2D GaN sheet of 32 atoms. We tried two different configurations: (a) in the first configuration (CC-GaN1), we replaced single gallium nitride layers by single layers of carbon atoms in alternative patterns, and in the second configuration, single gallium nitride layers are replaced by single carbon−carbon layers in alternate patterns. Similar configurations are investigated by replacing GaN layers by BN layers, keeping boron concentration of 25% in both cases. The paper is organized as follows: Under Results and Discussion section (Structure and Stability sub-section), we first define the heterostructures and their different configurations and discuss their stability on the basis of formation energies and structural changes. Next, we describe the electronic properties, including band structure and density-of-states (DOS) plots, and explain the band gap changes due to incorporation of CC and BN layers in 2D GaN sheet. We conclude the work in the Conclusions section, whereas computational and other technical details of the calculations are given at the end in Computational Methodology section.

Figure 1. Simulated structures of CC:GaN: (a) CC:GaN heterostructure in configuration 1 (CC:GaN1), (b) CC:GaN heterostructure in configuration 2 (CC:GaN2). A 2 × 2 unit cell is shown for the better representation of chemical bonding and structures, where a 32-atom GaN supercell is doped with C atoms with carbon concentrations of 50% used in the calculations.

Figure 2. Simulated structures of BN:GaN: (a) BN:GaN heterostructure in configuration 1 (BN:GaN1), (b) BN:GaN heterostructure in configuration 2 (BN:GaN2). A 2 × 2 unit cell is shown for the better representation of chemical bonding and structures, where a 32-atom GaN supercell is doped with B atoms with boron concentrations of 25% used in the calculations.
\[ \Delta E = E_{\text{CC:GaN}} - N_C E_C - N_G E_G - N_N E_N \]  

where \( E_{\text{CC:GaN}} \) is the total ground-state energy of the CC–GaN nanoheterostructure; \( E_C, E_G, \) and \( E_N \) are the ground-state energies of carbon, gallium, and nitrogen atoms, respectively; \( N_C, N_G, \) and \( N_N \) are the number of carbon, gallium, and nitrogen atoms in the heterostructure, respectively. 

Similarly, we calculated the formation energy of BN:GaN nanoheterostructures as

\[ \Delta E = E_{\text{BN:GaN}} - N_B E_B - N_G E_G - N_N E_N \]

with \( E_{\text{BN:GaN}} \) as the ground-state energy of the BN:GaN nanoheterostructure; \( E_B, E_G, \) and \( E_N \) as the ground-state energies of isolated boron, gallium, and nitrogen atoms, respectively; and \( N_B, N_G, \) and \( N_N \) are the number of boron, gallium, and nitrogen atoms in the heterostructure, respectively. 

The calculated formation energies per atom for different heterostructures is tabulated in Table 1, and it can be seen that for all concentrations, the formation energy is lower when a carbon atom or a boron atom occupies the position of a gallium atom; therefore, it is energetically more favorable that carbon or boron atoms occupy the positions of gallium atoms in the GaN 2D structure. Additionally, all of the new 2D nanoheterostructures have negative formation energies, which shows that these graphene–GaN and BN:GaN structures are thermodynamically stable. Further, we calculated the formation energy per atom for GaN sheet and found the value to be \(-5.720\) eV, which is greater than the formation energy per atom (Table 1) for all of the new CC:GaN and BN:GaN structures designed, indicating new heterostructures to be more stable.

Our calculations indicate that in CC:GaN heterostructures, clustering of CC chains and GaN chains is favored over scattering of CC and GaN chains within the ternary structure, with clustered configurations (CC:GaN\(^x\)) being more stable compared to isolated chains configuration (CC:GaN\(^2\)). In contrast to CC:GaN, clustering of chains is not favored in BN:GaN configurations and GaN and BN single isolated layered structure is more stable (BN:GaN\(^3\)), as depicted in Table 1, reporting the formation energies. From Table 2, we observe that as a result of incorporating CC and BN layers in GaN structures, the supercell shrinks and the volume of the simulated 32-atom GaN supercell decreases from 981.09 to 825.70 Å\(^3\) and to 776.86 Å\(^3\) for most stable CC:GaN and BN:GaN structures, respectively.

In two CC:GaN configurations investigated, we observe that C–C bonds and Ga–N bonds are of slightly smaller length in the second configuration (1.505 Å in CC:GaN\(^2\)) compared to that in the first configuration (1.515 Å in CC:GaN\(^1\)), indicating more stronger bonding in the second configuration and preferring bigger clusters of Ga–N and C–C chains over isolated CC and GaN chains in graphene and gallium nitride heterostructures (Table 3). However, in BN:GaN, shorter bond lengths and hence stronger bonds are found to be indicative of more stability of segregated layered structures of BN–GaN. Moreover, Ga–N bonds are found to be more stiffer in CC:GaN and BN:GaN structures than in pristine GaN 2D structure, resulting in their stability and rigidity due to a strong covalent bonding character.

### Table 1. Formation Energy Per Atom Calculated Using Eq 1 for Ternary C\(_n\)Ga\(_{1-x}\)N and B\(_n\)Ga\(_{1-x}\)N (\(x = 0.25, 0.50\))

| Compounds     | nanoheterostructure | % doping of C/B atoms | formation energy (eV) |
|---------------|----------------------|------------------------|-----------------------|
| GaN          | CC:GaN\(^1\)         | 0.50                   | -6.8989               |
|              | CC:GaN\(^2\)         | 0.50                   | -6.9634               |
|              | BN:GaN\(^1\)         | 0.25                   | -6.9671               |
|              | BN:GaN\(^2\)         | 0.25                   | -6.9527               |
| GaN          | C–C                  |                        |                       |
|              | CC                   | 1.426                  |                       |
|              | BN                   | 1.451                  |                       |
|              | CC:GaN\(^1\)         | C–C                   | 1.893                 |
|              | CC:GaN\(^2\)         | B–N                   | 1.906                 |
|              | BN:GaN\(^1\)         | B–N                   | 1.790                 |
|              | BN:GaN\(^2\)         | Ga–N                  | 1.845                 |

### Table 2. Optimized Lattice Parameters, Cell Volume, and Energy Band Gap of Different Heterostructures

| nanoheterostructure | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(V\) (Å\(^3\)) | \(E_g\) (eV) |
|---------------------|-----------|-----------|-----------|----------------|-------------|
| GaN                 | 12.852    | 12.856    | 6.889     | 981.09         | 2.285       |
| CC:GaN\(^1\)       | 10.851    | 11.586    | 7.418     | 824.09         | 1.92        |
| CC:GaN\(^2\)       | 10.840    | 11.544    | 7.461     | 825.70         | 1.70        |
| BN:GaN\(^1\)       | 11.168    | 11.567    | 6.866     | 776.86         | 2.44        |
| BN:GaN\(^2\)       | 11.178    | 11.579    | 6.580     | 745.74         | 2.14        |

Electronic Properties. The electronic band structures at high-symmetry \(k\)-points for both CC:GaN and BN:GaN heterostructures are shown in Figures 3 and 4. The band gap of GaN 2D sheet is found to be 2.285 eV (Figure S4). The calculated band gaps of CC:GaN heterostructures (Figure 3a, b) are 1.92 and 1.70 eV for CC:GaN\(^1\) and CC:GaN\(^2\), respectively, while for two BN:GaN heterostructures (25% B concentration, Figure 4a, b), the band gaps are found to be 2.44 and 2.14 eV, respectively, for BN:GaN\(^1\) and BN:GaN\(^2\) heterostructures. Hence, incorporation of graphene CC layers in GaN 2D structure lowers the electronic band gap, whereas incorporation of BN layers increases the band gap of GaN 2D structure. The gaps occur due to mixed hybridization of valence states of Ga and N with that of C atoms and due to mixed hybridization of valence states of Ga and N with that of B atoms in their respective compounds. The calculated values of band gap are presented in Table 2.
such hybridization is very crucial such that upon doping of GaN by different coverage or configurations of C or B, the energy gap occurs at the $E_F$. For the ternary structures, the calculated band gaps are given in Table 2. From the electronic band structure plots analysis, we observe that these structures are direct band gap materials with band gap values of 1.92, 1.70, 2.44, and 2.14 eV, with the valance band and conduction band to be located at the $\gamma$ k-point. A comparison with the band structures of graphene and GaN with the new 2D structures shows that new bands are formed due to hybridization of states in the new 2D ternary compounds.

**CONCLUSIONS**

In this article, we describe a successful example of the application of DFT to design new structural materials. We used DFT calculations to investigate the ground-state structural and electronic properties of new 2D heterostructures of 2D gallium nitride, graphene, and h-boron nitride. We discussed the stability through calculation of formation energies of different heterostructures, investigating two different doping patterns for both the CC:GaN and BN:GaN heterostructures. Similar to borocarbonitrides, these new 2D materials have tunable band gap and may find applications in various fields. These results may provide guidance in practical engineering applications, especially to tune the band gap in 2D materials. Finally, our
results are useful to provide an explanation of the formation of hybridized 2D nanomaterials. This new form of hybridized 2D material facilitates the development of band gap engineering and applications, in particular, in nanoelectronics and nanooptics. To generalize, we would like to emphasize that DFT calculations should not only be considered useful for studying some selected cases, i.e., compounds with a given composition as in the present case, but they are very useful to produce a database for searching a large space of possible structural configurations. Our case study could provide some guidelines for the industrialists and academic scientists in the development of new materials.

■ COMPUTATIONAL METHODS

The first-principles calculations performed in the present work use generalized gradient approximation (GGA) of density functional theory (DFT) through Quantum ESPRESSO package. The calculations are based on ultrasoft pseudopo-
tentials for modeling the ion—electron interactions employing the Perdew—Burke—Ernzerhof (PBE) exchange—correlation functional. We have used the Methfessel—Paxton smearing technique with a Gaussian broadening of 0.003 Ry. A full variable-cell relaxation of the structure has been performed with the Broyden—Fletcher—Goldfarb—Shanno scheme to get minimum total energy using the Hellmann—Feynman forces calculations on atoms, with a tolerance on forces on each atom of 0.001 Ry/Bohr. To model monolayer of 2D sheets, interactions between the periodic images of the sheets have been made negligible through a 10 Å z-direction. A 30 Ry cutoff has been used for representing wave functions in plane wave basis, while a 180 Ry cutoff for the density has been implemented in the calculations. We have included dispersion interaction corrections using semiempirical Grimme’s DFT-D2 approach.

After getting the relaxed structures, we performed self-consistent calculations, and Brillouin zone integrations were performed with the Broyden—Fletcher—Goldfarb—Shanno—Paxton approach.

ASSOCIATED CONTENT

Supporting Information

Structures and electronic density of states (DOS) of 2D gallium nitride, graphene, and boron nitrides are given in Supporting Information file.

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