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Electronic properties of heterostructures of Graphene with Boron, Nitrogen and Boron Nitride – A first principles study

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Abstract : New graphene like 2D materials such as BN, MoS_2 and WS_2 have exotic electronic properties. Forming heterostructures of these 2D materials with graphene influence and alter the electronic character of graphene. But how the added 2D materials influence the electronic properties of graphene is not fully understood. We in this first principles study try to understand this problem and help the experimentalists to identify useful heterostructures. We have computationally designed the heterostructures of graphene by combining it with Boron, Nitrogen and Boron Nitride. Out of all the heteronanostructures designed, the Gra-BN heterostructure turns out to be interesting and has more applications than the other heterostuctures. This heterostructure behaves like a graphene and has improved electronic properties. Also this design paves way for the design of 3D graphene.

Intruduction

Graphene is a 2D allotrope of carbon, single layer of sp^2-bonded carbon atoms densely packed into a honeycomb structure. An intense research effort has been devoted to its fundamental physics and possible applications in nanodevices. However, the zero-energy-gap character of graphene has prevented its development in modern electronics. To make graphene into a practical electronic device, such as a transistor, semiconducting graphene is highly desired. Many methods have been suggested to open an energy gap in graphene, such as molecular adsorption[1], defects [2], hydrogenation [3] and graphene−substrate hybrid structures[4]. Among these methods, graphene−substrate hybrid structures are easier to fabricate. In a recent study [4,5,6], it has been shown that forming heterostructure of some of the 2D materials with graphene improve the electronic character of graphene and this has led to new applications of graphene. To understand fully the mechanism which is operative in these heterostructures and to identify useful heterostructures, we have computationally designed the heterostructures of graphene by combining it with single layer of Boron Nitride, Boron and Nitrogen. We have investigated their electronic property by obtaining their band structures.

Computational Details

The calculations are carried out using density functional theory (DFT) implemented plane wave code, Vienna ab-initio simulation package (VASP) [7]. The generalized gradient approximation with PW91 [8] functional and projector augmented wave (PAW) [9] potentials are used in the calculation. To simulate graphene, we have taken a slab of 96 carbon (C) atoms in the super cell of suitable a , and $\alpha = \beta = \gamma = 90^{o}$. Similarly we have designed suitable super cell for other heterostrucures. A vacuum space of 11 Å is introduced between the periodic images of graphene sheets along the z-axis such that the interaction between them is negligible. The gamma centered 10×10×1 k-point grid is used in structural relaxations. The k-point grid is made denser with 50×50×1 k-points for accurate DOS analysis with the smearing width of 0.1 eV and band structure calculations. The structures are relaxed until the force on each atom becomes 1×10^{-3} eV/Å.

Results and Discussion

As a first step, before designing the Gra-BN heterostructure, we designed the heterostructures of Graphene with Boron (G96B96) and Nitrogen (G96N96) checked their stability.

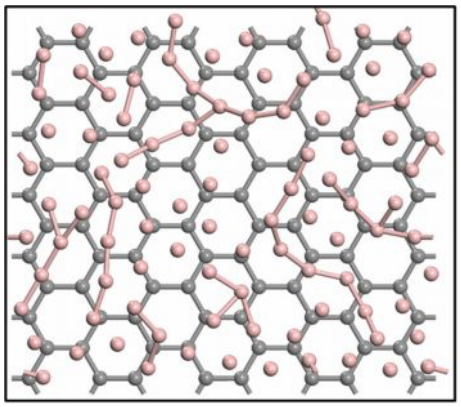

Figure 1: The optimized structure for G96B96. Gray and Pink colour spheres represent the Carbon and Boron atoms.

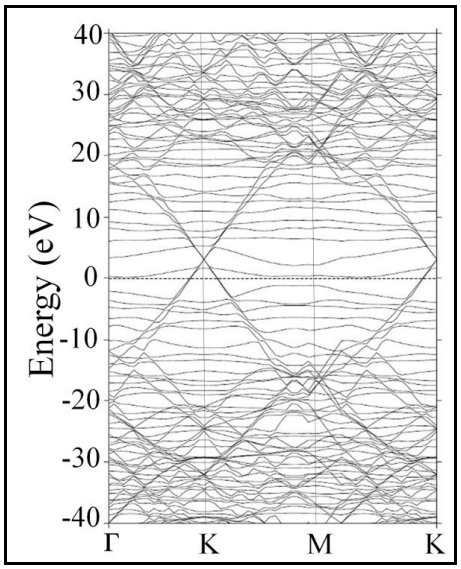

Figure 2: Band structure for G96B96.

The relaxed structure of G96B96 heterostructure is shown in Figure 1. While the G96 structure is stable and the B96 structure is completely distorted. However the bandstructure of this G96B96 (Figure 2) heterostructure is having the necessary but interesting features. The Dirac cones are retained inspite of the presence of large number of the boron bands near the Fermi level. The Dirac cones are shifted up (~ 3.0 eV) with reference to the Fermi level. This heterostructure turns out to be very good conductor with contributions from graphene's massless Dirac fermions and the electrons from boron . This causes considerable increase in the mobility of carriers.

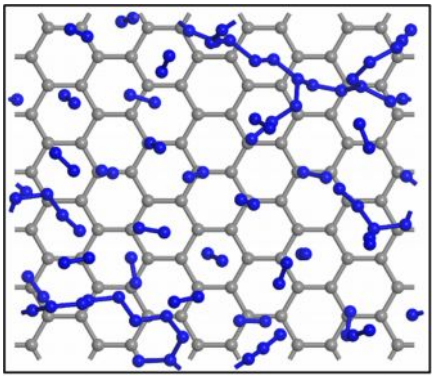

Figure 3: The optimized structure for G96N96. Gray and Blue colour spheres represent the Carbon and Nitrogen atoms.

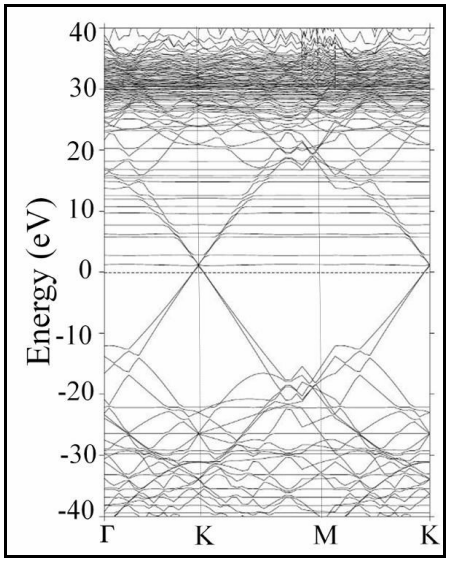

Figure 4: Band structure for G96N96.

Then we designed the heterostructure G96N96. The relaxed structure of G96N96 heterostructure is shown in Figure 3. While the G96 structure is stable and the N96 structure is completely collapsed. The N96 sheet has disintegrated into nitrogen molecules N2. Starting from 3.3Å the N2 molecules spread above the G96 structure up to a distance of 7.5Å. The bandstructure of this G96N96 (Figure 4) heterostructure is having some interesting features like the G96B96 heterostructure. The Dirac cones are retained. Flat bands of N96 are appearing above the Fermi level. The Dirac cones are shifted up slightly (~ 1.0eV) with reference to the Fermi level. There are no flat nitrogen bands near the lower part of the Dirac cones , below the Fermi level. As a result the graphene's lower part of Dirac cones are fully retained without any distortion.

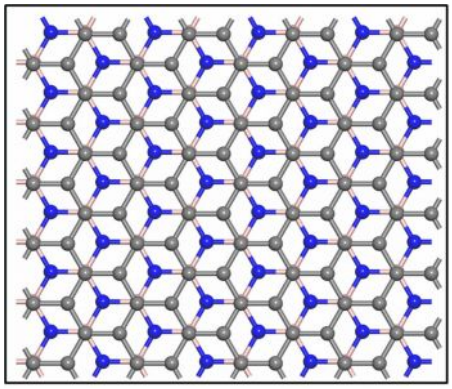

Figure 5: The optimized structure for G96BN-96. Gray, Blue and Pink colour spheres represent the Carbon, Nitrogen and Boron atoms.

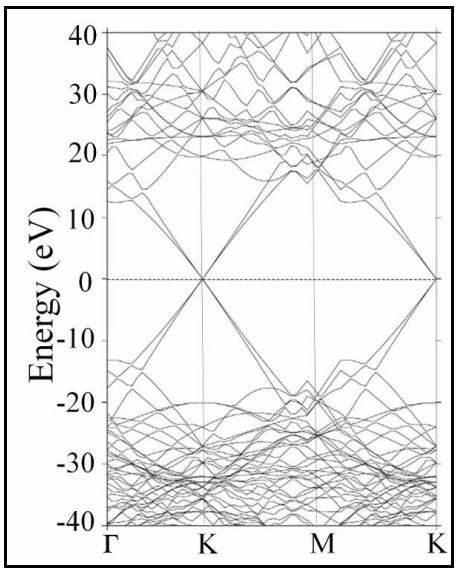

Figure 6: Band structure for G96BN-96.

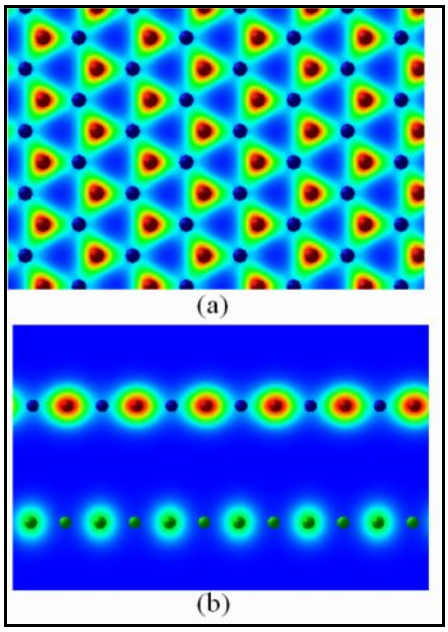

Figure 7: The charge density distribution for G96BN-96 (a) top (b) side view.

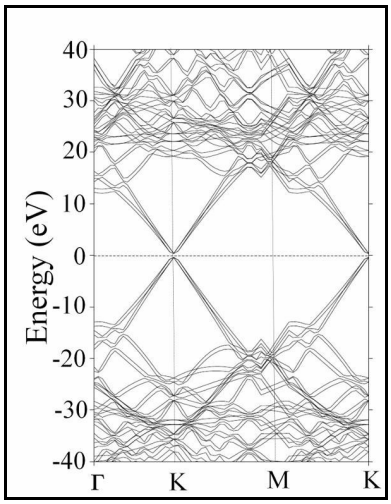

Figure 8: Band structure for Bilayer of Graphene.

Finally we designed the Gra-BN heterostructure G96BN-96 and relaxed it. The relaxed structure of Gra-BN heteronanostructure is shown in Figure 5. It is clear from the figure that there is no lattice mismatch between Gra and BN and the interlayer separation is 0.435 nm. One can note that there is a lateral displacement between the two honeycomb lattices of both the structures and there is no eclipsing one structure by the other . The coupling between Graphene and h-BN is moderate and as a result there is no rotational orientation between their lattices, and there are no moire patterns as observed earlier[10]. The bandstructure and charge density distribution plot of Gra-BN heterosructure is shown in the Figure. 6 & 7. Surprisingly the bandstructure of G96BN96 heterostructure exactly looks like the bandstructure of graphene. The bands arising from the BN sheet are well below or well above the Fermi level, as a result the graphene's Dirac cones are fully retained with nil distortion. It has become a good conductor contributions coming only from massless Dirac Fermions. As a result it is endowed with enormous mobility may be better than graphene. In Figure 8 we have given the bandstructure of bilayer graphene for comparison.

In conclusion one can say that the heterostructures of graphene with B,N and BN can be formed in principle. The heterostructures G96B96 and G96N96 behave like a surface doped system may be useful in device fabrication. But the Gra-BN heterostructure G96BN-96 is quite interesting may have more important applications in device electronics compared to the two heterostructures. It is now definite that by introducing suitable lattice mismatch between Gra and BN one can design different types of Gra-BN heterostructure with required mobility. Finally our design of Gra-BN heterostructures turns out to be a new route for the design of 3D graphene[11].

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