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Effect of electric field on the band structure of graphene/boron nitride and boron nitride/boron nitride bilayers

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Effect of electric field on the band structures of graphene/boron nitride (BN) and BN/BN bilayers is investigated within the framework of density functional theory. The calculated bandgap of the graphene/BN bilayer increases, although by small amount, with applied electric field. In the case of BN/BN bilayer, the bandgap decreases with the applied field in agreement with earlier studies. The modulation of bandgap in graphene/BN bilayers is dominated by the features of graphene and appears to be related to the modification in molecular orbitals as revealed by the calculated projected density of states. © 2012 American Institute of Physics. [doi:10.1063/1.3679174]

Periodic systems in two-dimensional arrangements have received a great deal of attention due to their electronic, electrical, and mechanical properties.¹⁻⁴ For example, graphene, a planar structure of hexagonal carbon rings shows extraordinary electrical properties in its pristine form and has been the subject of numerous recent studies.⁵ Its band structure shows zero gap at the Dirac point, which can be opened by external perturbations such as the application of strain, electric field, and chemical modification.^{6,7} The bandgaps of both bilayer (BLG) and trilayer (TLG) configurations of graphene are tunable with an applied electric field⁸ and are dependent on the symmetry. For example, in the case of TLG even though inversion symmetry is broken by applied electric field, hexagonal stacking has no bandgap, Bernal stacking has a tiny gap, and only the rhombohedral stacking has sizeable gap. Structurally similar to graphene, hexagonal boron nitride (h-BN), has also received considerable attention as a potential material for nano-scale electronics applications⁹ due to its enhanced chemical, thermal, and mechanical stabilities.

In the case of bilayer graphene, recent studies^{10,11} have shown that bandgap increases from 0 to 230 meV at 3 V/nm. Such a possibility opens the door for bilayer graphene in switchable electronic devices. Since BN is chemically more stable and already has a sizeable bandgap, it is of interest to investigate the effect of electric field on the graphene/BN and BN/BN bandgaps, both for advancing fundamental understanding of the electronic structures of these important nano-scale materials and also for their potential applications in switchable devices. In this letter, we report the results of our study of the effect of electric field on the band structures of graphene/BN and BN/BN bilayers investigated by first-principles density functional theory (DFT) approach. Our results suggest both graphene/BN and BN/BN layers to exhibit modulation of the band structure by electric field. However, significant qualitative and quantitative differences are noted. The effect on electric field on BN/BN system has

been characterized in earlier studies¹² and the band structure modulation described at the DFT level of theory, so our focus will be on graphene/BN bilayer system. Our calculations on BN/BN system agree with earlier results and will be compared against the graphene/BN system to gain further insight into the modulation of band structure with the applied electric field.

Calculations were performed using the full-potential linearized augmented plane wave (FLAPW) method within the framework of local density approximation (LDA)-(DFT). In the FLAPW method, the crystal region is split between non-overlapping muffin-tin spheres around nuclei and interstitial regions. The plane wave basis set is used to describe the interstitial region and radial functions in the muffin-tins to account for the sharply changing potential near the nuclei. The linearized augmented plane wave-based methods are known to give accurate electronic structure description of solids.¹³ The LDA-DFT has been previously used to obtain reliable results for graphitic and h-BN band structures.¹⁴⁻¹⁶

Two dimensional slab geometries were used for the systems studied; the interlayer spacing in the AB (Boron) stacking for graphene/BN and BN/BN equilibrium configurations (Fig. 1) taken from the previous work of Zhong *et al.*⁹ are 3.022 Å and 3.071 Å, respectively. The calculated equilibrium configurations associated with the graphene/BN and BN bilayers were fully relaxed, with residual forces smaller than 0.01 eV/Å. The AB stacking for graphene/BN systems was chosen as it is the energetically favored configuration

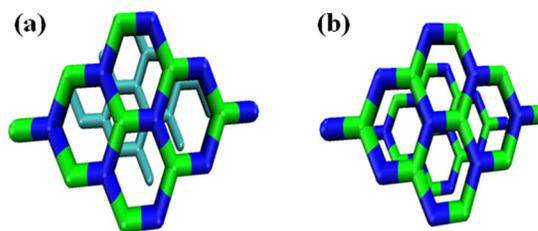


FIG. 1. (Color online) A schematic diagram of graphene/BN (a) and BN/BN (b) bilayers. The cyan, green, and blue represent carbon, boron, and nitrogen atoms, respectively.

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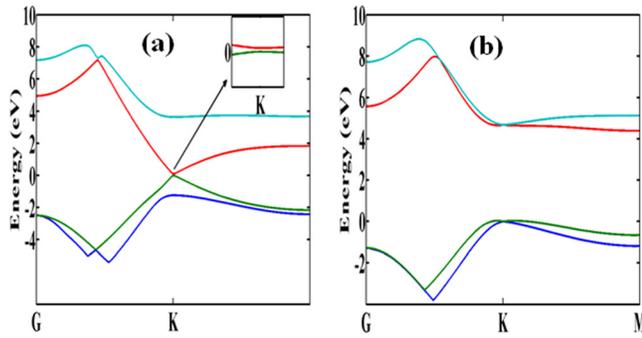


FIG. 2. (Color online) Band structure of (a) graphene/BN and (b) BN/BN bilayers at zero bias. Zero of the energy is set to the valence band maximum. The inset in (2a) shows the bandgap near the K point of graphene/BN bilayer.

over AA stacking at the LDA-DFT (Ref. 9) level of theory. The electric field was applied in the direction perpendicular to the planes of the bilayer by setting up two plates of opposite charges on either side of the bilayer systems as implemented in FLEUR (Ref. 17) electronic structure code.

Fig. 2 shows the band structures of graphene/BN and BN/BN bilayer systems. As expected, the graphene/BN and BN/BN bilayer band structures exhibit sharp distinctions from each other. The zero-field band structure for the graphene/BN bilayer is dominated by the bands associated with the carbon atoms near the Fermi level, with a very small gap of ~ 104 meV at the Dirac point. The bands near the Fermi level exhibit linear dispersion characteristic of graphene with their slopes less steep than bilayer graphene due to the presence of BN layer. The presence of non-zero gap implies lifting of degeneracy of the bands at the K point. In contrast, the BN/BN bilayer exhibits a nearly two-orders of higher direct gap of ~ 4.6 eV at the Dirac point. This is in accordance with earlier calculations⁹ on BN/BN bilayer system.

The change in the bandgaps of graphene/BN and BN/BN bilayers due to externally applied electric field is depicted in Table I. It is clear from this figure that both bilayer systems exhibit modulation of their bandgaps by the external field. While the graphene/BN bilayer bandgap shows an increase with increasing external field, opposite is the case with the BN/BN bilayer. Further, the relative change in the graphene/BN bandgap appears to be larger than that in the BN/BN bilayer, although the magnitude of the change in the latter is much higher than the former. The decrease in the gap with increase in the electric field in the BN/BN bilayer is consistent with the previously reported results on BN bilayers.¹²

An examination of the band structure reveals that the conduction bands are affected more strongly than the valence bands (Table I) by the external electric field, E , for both the graphene/BN and BN/BN bilayers. For the graphene/BN system, the valence and conduction bands are pushed higher with increasing field with a net increase in the gap. In contrast, the conduction band of BN/BN bilayer is pushed towards the Fermi level with increasing field. While the valence band is pushed higher with increasing field until $E = 2.0$ V/nm, it decreases until $E = 2.5$ V/nm and then again increases monotonically from $E = 2.5$ V/nm onwards. This results in an overall decrease in the bandgap. The effect of applied field on bands closer to Fermi level can be sum-

TABLE I. Energies of bands at Dirac point of the graphene/BN and BN/BN bilayers.

SYSTEM	E (V/nm)	VB (eV)	CB (eV)	Bandgap (eV)
Graphene/BN	0.0	2.157	2.262	0.104
Graphene/BN	1.7	2.219	2.329	0.109
Graphene/BN	2.1	2.227	2.339	0.111
Graphene/BN	2.5	2.235	2.349	0.112
Graphene/BN	3.0	2.241	2.357	0.115
Graphene/BN	3.4	2.245	2.362	0.116
Graphene/BN	4.1	2.251	2.370	0.118
BN/BN	0.0	0.580	5.174	4.594
BN/BN	0.4	0.581	5.172	4.591
BN/BN	0.8	0.585	5.169	4.584
BN/BN	1.2	0.592	5.162	4.570
BN/BN	1.6	0.602	5.159	4.557
BN/BN	2.0	0.805	5.141	4.537
BN/BN	2.5	0.624	5.125	4.501
BN/BN	2.9	0.636	5.102	4.466
BN/BN	3.3	0.648	5.074	4.427
BN/BN	4.0	0.666	5.028	4.362

marized as follows: (1) For graphene/BN bilayer, both the conduction and valence bands move in the same direction toward higher energies, (2) for the BN/BN bilayer, the valence and the conduction bands move in opposite direction toward the Fermi level. The net result is an increase, although very small in the bandgap of graphene/BN bilayer but a decrease in BN/BN bilayer case.

In order to understand the calculated effect of the applied electric field on band structure in terms of the corresponding effect on the contributing atomic states, the total density of states (DOS) and projected density of states (PDOS) are plotted in Figs. 3 and 4, respectively. The bands closer to Fermi level have dominant contributions from $2p_z$ orbitals of each atom (data not shown) and so we focused on them for the PDOS plots. Fig. 3 represents DOS and PDOS when no electric field is applied to the graphene/BN bilayer. As can be seen the contribution of $2p_z$ orbital from N atom dominates DOS below Fermi level and contributions from B atom dominate unoccupied states, while C and N levels contribute nearly the same in lower valence band region. Without the contributions from the carbon atoms there would be a gap of about 4 eV, reflecting the characteristics of BN

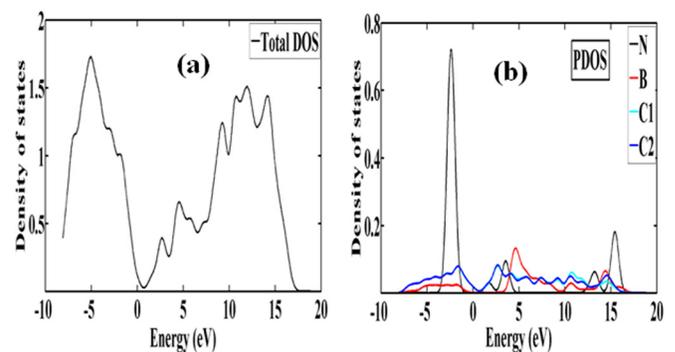


FIG. 3. (Color online) (a) Total DOS and (b) PDOS of $2p_z$ orbitals for graphene/BN bilayer at an applied electric field, $E = 0$. The energies are subtracted from the Fermi level E_F (-5.525 eV) and a factor of 0.015 used for broadening the DOS.

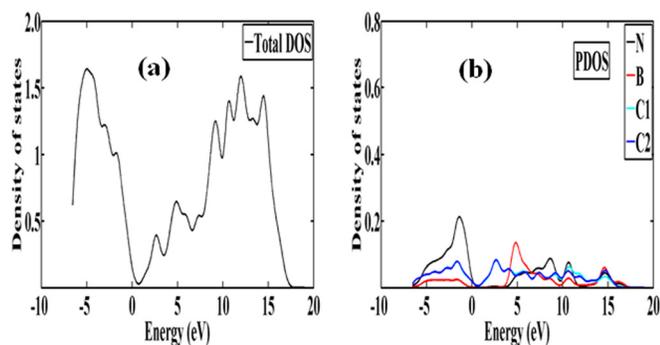


FIG. 4. (Color online) (a) Total DOS and (b) PDOS of $2p_z$ orbitals for graphene/BN bilayer at an applied electric field, $E \neq 0$. The energies are subtracted from the Fermi level E_F (-7.052 eV) and a factor of 0.015 used for broadening the DOS.

system. The presence of graphene layer carbon atoms introduces DOS around the Fermi level, narrowing the gap from 4 eV to around 100 meV. This is not apparent from the figure due to the use of a Gaussian smear (broadening) factor of 0.015 in order to make the plots continuous. The gap is clear in a scattered plot¹⁸ without the broadening factor. It is also interesting to note that in the absence of the field (Fig. 3), the N states are localized in a narrow energy range, both below and above Fermi levels, while the C and B states appear to be more broadened.

Upon application of the electric field, E (Fig. 4), the N states, both below and above the Fermi level, experience a reduction in the density and shift to higher magnitude in the energy, while little change is noticed in C and B states. Also, the N states exhibit considerably broadening (Fig. 4(b)). The overall effect on the modulation of the N levels in the conduction and the valence bands is to introduce a finite, though small, net increase in the bandgap of the graphene/BN bilayer.

We have investigated the effect of the electric field on the graphene/BN and BN/BN bilayer systems. The calculated results show the bandgap in graphene/BN bilayer is dominated by graphene features and is electric field tunable.

The inverse relation of bandgap with the applied field in BN/BN bilayer is consistent with earlier results. The calculated electric field tunability of graphene/BN bilayer bandgap suggests new applications for this system in semiconductor devices.

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¹⁸See supplementary material at <http://dx.doi.org/10.1063/1.3679174> for calculated total density of states (DOS) for graphene/BN bilayer with and without external electric field, E , and a gaussian broadening (smearing) factor = 0.