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Bilayer graphene on h-BN substrate: investigating the breakdown voltage and tuning the bandgap by electric field

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Abstract
By performing density functional theory calculations we show that it is possible to make the electronic bandgap in bilayer graphene supported on hexagonal boron nitride (h-BN) substrates tunable. We also show that, under applied electric fields, it is possible to insert states from h-BN into the bandgap, which generate a conduction channel through the substrate making the system metallic. In addition, we verify that the breakdown voltage strongly depends on the number of h-BN layers. We also show that both the breakdown voltage and the bandgap tuning are independent of the h-BN stacking order.

S Online supplementary data available from stacks.iop.org/JPhysCM/24/075301/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Since its inception, the 2D graphene crystal has polarized the attention of many researchers, as it exhibits intriguing properties [1–3]. Among these properties, its linear energy–momentum dispersion, low-frequency noise, high optical transparency and the high electron mobility, make it a promising material for electronic components [4–6]. To use graphene as a logic device, it is desirable to create an energy bandgap. A way to create a bandgap is to use bilayer graphene (BG) [7], where the inversion symmetry can be broken by an external electric field, leading to a bandgap that can be tuned by varying the field strength [8, 9]. However, these properties strongly depend on the environment and on the substrate on which this material is supported [10–12].

For instance, the transport properties of graphene field effect transistors on SiO_2 substrates present lower carrier mobility than devices based on suspended graphene [13–15]. This occurs due to the high roughness (corrugations), impurities, dangling bonds and charge inhomogeneities in the oxide [16, 17]. Moreover, the charge traps tend to cause the graphene to electronically break up into electron- and hole-doped regions that limit nanodevice performance and make access to the Dirac point impossible [18, 19]. For this reason, efforts have been made to find a substrate which could act as a dielectric and keep unaffected the intrinsic electronic properties of graphene when coupled with it.

Recently, such a candidate substrate has been found with the demonstration of high-quality graphene devices on hexagonal boron nitride (h-BN) [20, 21]. Hexagonal boron nitride is an insulator with boron and nitrogen atoms occupying the inequivalent A and B sublattices in the hexagonal structure. It presents a wide direct energy gap, a small lattice mismatch with graphene and can be synthesized with high purity. Hexagonal boron nitride is also relatively inert and is expected to be free of dangling bonds or surface charge traps [22]. A single layer of h-BN can be obtained through the exfoliation technique. By using a mechanical transfer process Dean *et al* [20] fabricated and characterized high-quality exfoliated mono- and bilayer graphene devices on single-crystal h-BN substrates. The bilayer graphene-based devices on h-BN substrates presented mobilities that were almost an order of magnitude higher than devices on disordered SiO_2 [20].

A few thin layers of h-BN can be obtained by chemical exfoliation. Warner *et al* [23] showed that the h-BN bulk presents an AA′ stacking[1] opposite to the AB stacking of the graphite. However, the removal of BN layers by electron beam irradiation can lead to exposure of an AB stacking, and not only the AA′ stacking, since the layers can easily slide due to weak interaction [24]. The AB stacking may not be intrinsic to the bulk and may only be possible at the top and bottom of the layered structure.

In this paper we show that by applying an external electric field it is possible make the electronic band gap tunable when the bilayer graphene is supported on h-BN thin films. We also verify that the breakdown voltage depends on both the number of h-BN layers and the direction of the applied electric field. Moreover, the behavior of the energy levels as a function of the applied electric field is h-BN stacking independent.

2. Computational details

The investigation was based on *ab initio* simulations within the density functional theory (DFT) [25, 26] framework using the SIESTA code [27, 28]. The local density approximation (LDA) [29] was used for the exchange–correlation functional ($E_{\rm xc}$). However, as we are dealing with a weakly interacting system, where dispersion (van der Waals) forces (due to long-range electron correlation effects) play a key role we also performed calculations with a semi-empirical GGA-type of functional, as proposed by Grimme [30, 31]. Since we are not interested in the asymptotic behavior of the interaction energy, unless specified, the calculations were performed using the LDA for the $E_{\rm xc}$. To describe the interaction between the valence and core electrons we used norm-conserved Troullier–Martins pseudopotentials [32]. To expand the wavefunctions of the valence electrons, a double-ζ plus polarization basis set was used [33]. For the grid integration a 250 Ryd mesh-cut-off was employed. The structures were considered optimized when the residual forces on the atoms were less than 0.02 eV Å^{-1}. We used a total of 900 k-points for Brillouin zone integration of the supercell [34].

3. Results and discussion

In order to simulate the BG on h-BN thin films under an external electric field, we started performing calculations for h-BN in the bulk AA′ stacking order. In figure 1 we show different views of the three possible stackings of the BG on the h-BN. In conformation I, the carbon atoms of the BG are above the B atoms or above the centers of the hexagons in adjacent layers. In II, the carbon atoms of the BG are above the N atoms or above the centers of the hexagons. Finally, in III, the carbon atoms of the BG are above both the B and N atoms. We kept the substrate in the AA′ stacking and investigated the energetics of these possible adsorption sites for the BG. In these calculations we considered a substrate of five h-BN layers. Then, by varying the distance d between the topmost h-BN layer and the lower graphene-like layer, we obtained conformation I as the most stable one with an equilibrium distance of 3.18 Å. Calculations to obtain the potential energy curves for a single graphene layer adsorbed on h-BN were also performed (see supplementary material available at stacks.iop.org/JPhysCM/24/075301/mmedia)[2].

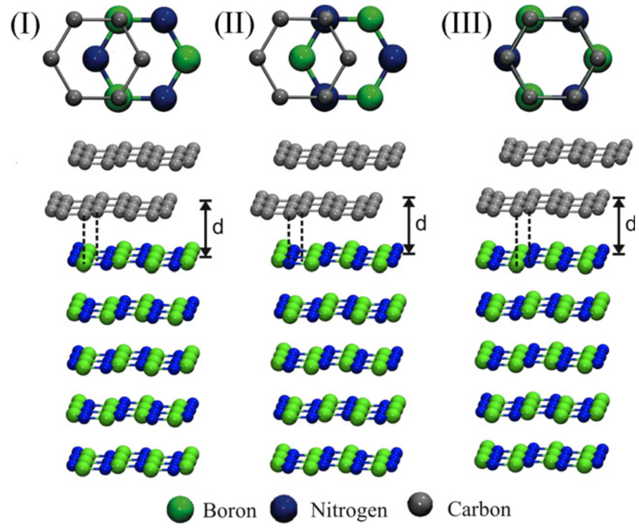


Figure 1. Ball and stick representation of top and side views of the possible stacking modes of the bilayer graphene on the h-BN substrate in the AA′ stacking. The distance d is between the topmost h-BN layer and the lower graphene-like layer.

In the energetically most stable structure for the BG on h-BN (BG + h-BN), we consider the effect of an external electric field. The evolution of the electronic band structures as a function of both the number of h-BN layers and the external electric field is presented in figure 2. The upper (lower) panels are associated with positive (negative) electric fields. The positive (+) and negative (−) signs indicate that the electric field is applied along the $+(-)\hat{z}$ direction. The first interesting point is that for the BG adsorbed on top of the h-BN substrate there is a bilayer bandgap opening up ($\Delta_{\rm g}$, which is the small gap due to a dispersion like 'Mexican hat' at low energies) of approximately 45 meV, even under zero electric field applied, due to a breaking of symmetry. When an electric field is applied to the BG + h-BN system, there is an increase of the bilayer bandgaps $\Delta_{\rm g}$ and $\Delta_{\rm K}$ (gap at the K point), when the number of h-BN layers is increased. A schematic view of the bilayer gaps $\Delta_{\rm g}$ and $\Delta_{\rm K}$ in the BG can be seen in figure 3(b), lower panel.

The variation of the intrinsic bilayer bandgaps as a function of both the electric field and the number of h-BN layers is presented in figure 3(c)[3]. To understand why this

[1] The AA′ stacking is such that the B atoms are situated just above/below the N atoms in adjacent layers. In the AB stacking a B or a N atom is situated above/below the empty centers of the hexagons in adjacent layers.

[2] See supplementary material (available at stacks.iop.org/JPhysCM/24/075301/mmedia) for potential energy curves, band structures of graphene on h-BN as function of the electric field, and band structures of the BG on h-BN in the AB/AB/AB stacking. We also present the band structures for the AB/AB/AB and AA′/AA′/AA′ stacking modes taking into account the van der Waals correction.

[3] It is worth mentioning that both the LDA and the GGA underestimate the energy bandgap. This occurs due to the lack of the integer particle number derivative discontinuity in the current exchange–correlation functionals. Therefore, the values of bandgaps presented here are lower bounds.

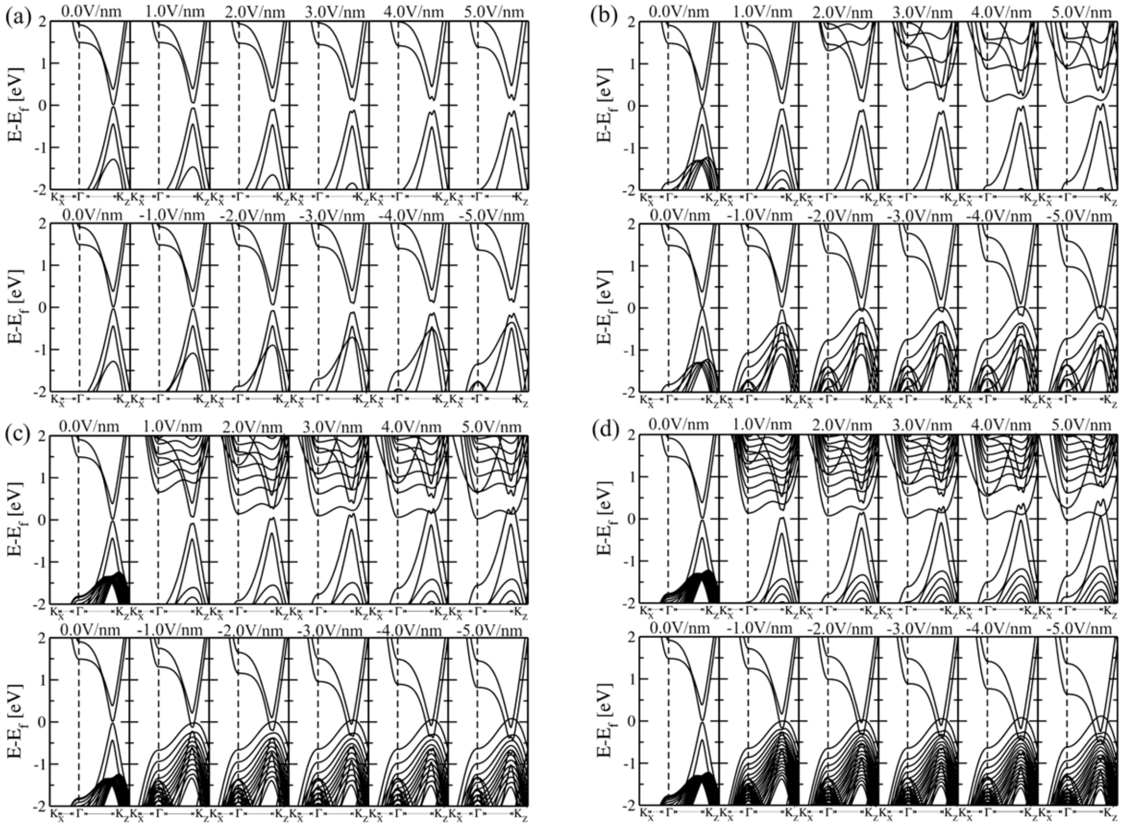


Figure 2. DFT calculated electronic band structures for bilayer graphene on h-BN, in the bulk AA′ stacking, as a function of the number of h-BN layers for (a) one h-BN layer, (b) five h-BN layers, (c) 12 h-BN layers and (d) 18 h-BN layers, under a perpendicular electric field varying from +1 to +5 V nm^{-1} (upper panels) and from −1 to −5 V nm^{-1} (lower panels). The Fermi level is set to zero.

increase occurs, we can look at the gap at the K point, for the pristine BG, that can be written as $\Delta_K = |lE_{\rm eff}e|$, where l is the inter-layer distance, e is the electron charge, and $E_{\rm eff}$ stands for the effective field on the BG [35]. Under an electric field applied to this system there is a charge transfer between the layers that can be seen as a result of the effect of charged surfaces placed above (σ_{L1}) and below the bilayer graphene (σ_{L2}) (figure 3(b) upper panel) generating a polarization field $E_{\rm BG}$, in the opposite direction to the $E_{\rm ext}$. Then, the effective field that opens the gap is given by $E_{\rm eff} = E_{\rm ext} - E_{\rm BG}$.

Now, looking at the BG + h-BN system, there is a charge transfer within the BG and between the BG and the h-BN layers due to the applied electric field. The charge redistribution on the entire system (BG + h-BN) reduces the polarization field $E_{\rm BG}$ and increases the $E_{\rm eff}$, leading to an increase of the intrinsic gaps, as shown in figure 3(c). Thus, the energy gap depends on the electric field applied and the number of h-BN layers. Figure 3(a) shows the difference between the charge densities ($\Delta\rho$) with (+2 V nm^{-1}) and without external electric field. We can clearly note that, depending on the number of h-BN layers, there is an increase in $\Delta\rho$ inside the BG generated by an increased $E_{\rm eff}$ leading to an enlarged bandgap. Moreover, depending on the strength of the field, the h-BN layers do not screen the applied electric field which allows the shift of the energy levels.

Under applied electric field, besides the increase of the intrinsic BG bandgap, the energy levels that come from the h-BN substrate can be shifted to the Fermi level, making the system metallic. Therefore, the breakdown voltage of the insulator, that is the minimum voltage that causes a portion of the insulator to become electrically conductive, can be estimated, here, as a function of the number of h-BN layers. It has been reported that the breakdown voltage of thin BN films is 0.3–0.7 V nm^{-1} [36]. Starting with the case of a single layer of h-BN (figure 2(a)), we note that by applying an external electric field, varying from −5 to +5 V nm^{-1}, the electronic chemical potential is in the middle of the bandgap and there is no insertion of energy levels keeping the system semiconducting. Increasing the number of h-BN layers, without a electric field applied, more boron nitride states are introduced near the valence band maximum, around −1.2 eV, below the Fermi energy, as can be seen in figures 2(b)–(d) upper panels. When negative external electric fields are applied (figure 2, lower panels), the occupied states of the boron nitride (initially at −1.2 eV) can gradually be upshifted to the Fermi energy. The electric field needed to place these energy levels at the Fermi energy was lower, depending on the number of h-BN layers. For five h-BN layers, the electric field needed to place a level at the Fermi energy was −1.5 V nm^{-1}, whereas for 12 and 18 h-BN layers it was approximately −0.6 V nm^{-1}, in agreement with the measured value of 0.3–0.7 V nm^{-1} [36]. If a positive electric field is applied, the same behavior is verified but, now, for the unoccupied states, as can be seen in figure 2, upper

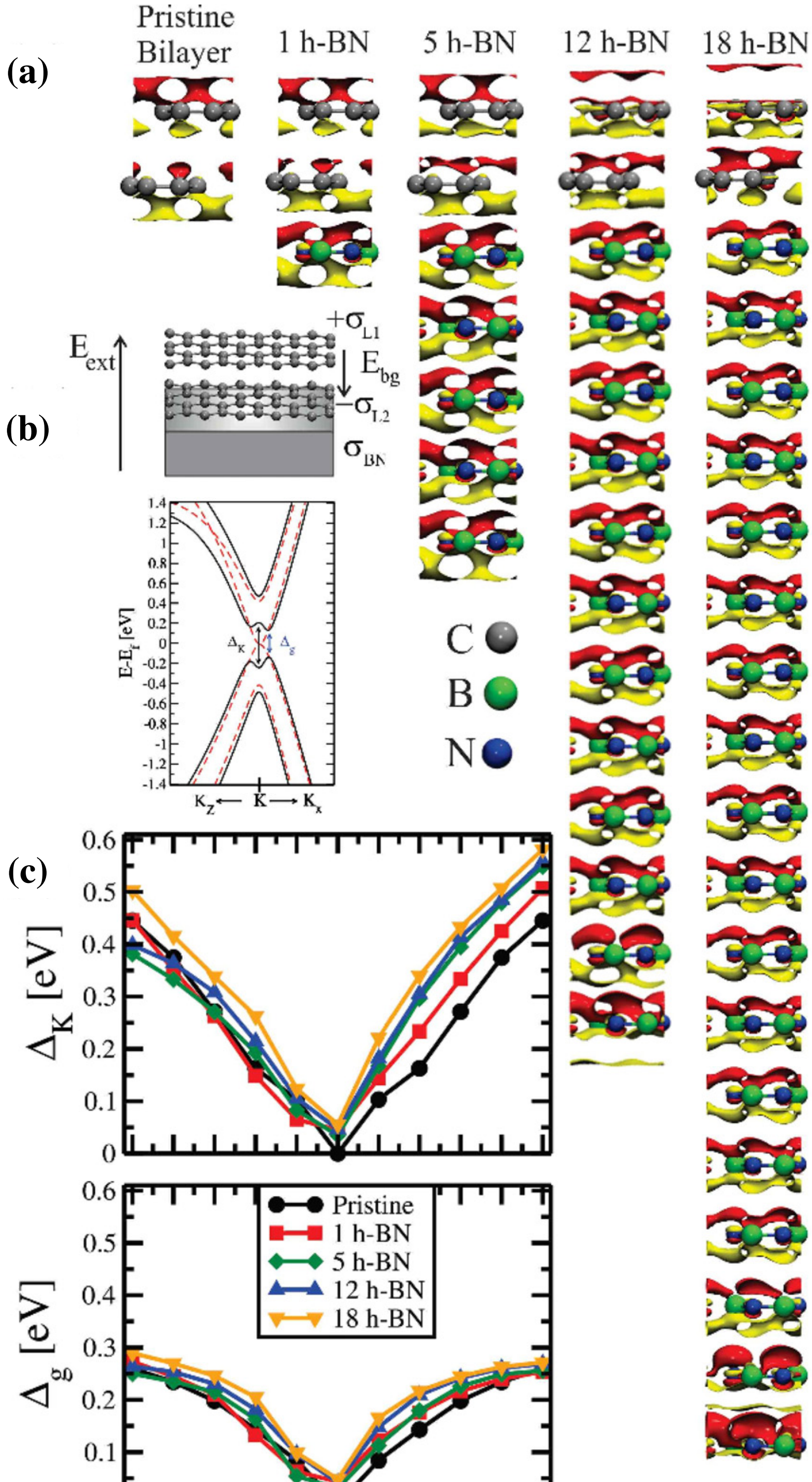


Figure 3. (a) Difference between the charge densities with ($+2$ V nm^{-1}) and without applied electric field, $\Delta\rho = \rho_{\mathrm{E}} - \rho_0$. Red indicates positive $\Delta\rho$, whereas yellow indicates negative $\Delta\rho$. The isovalue used was 1×10^{-4} e/bohr^3. (b) Schematic view of the bilayer energy gaps Δ_{K} and Δ_{g}. (c) The intrinsic bilayer energy gaps as functions of both the number of h-BN layers and the applied electric field.

panels. In this case, the unoccupied states of the boron nitride (initially at $+3.5$ eV) can gradually be downshifted to the Fermi energy. For five h-BN layers, the electric field needed to place a level at the Fermi energy was $+4$ V nm^{-1}, whereas for 18 h-BN layers it was approximately $+1$ V nm^{-1}. Thus, the breakdown voltage not only depends on the number of h-BN layers but also on the direction of the applied electric field.

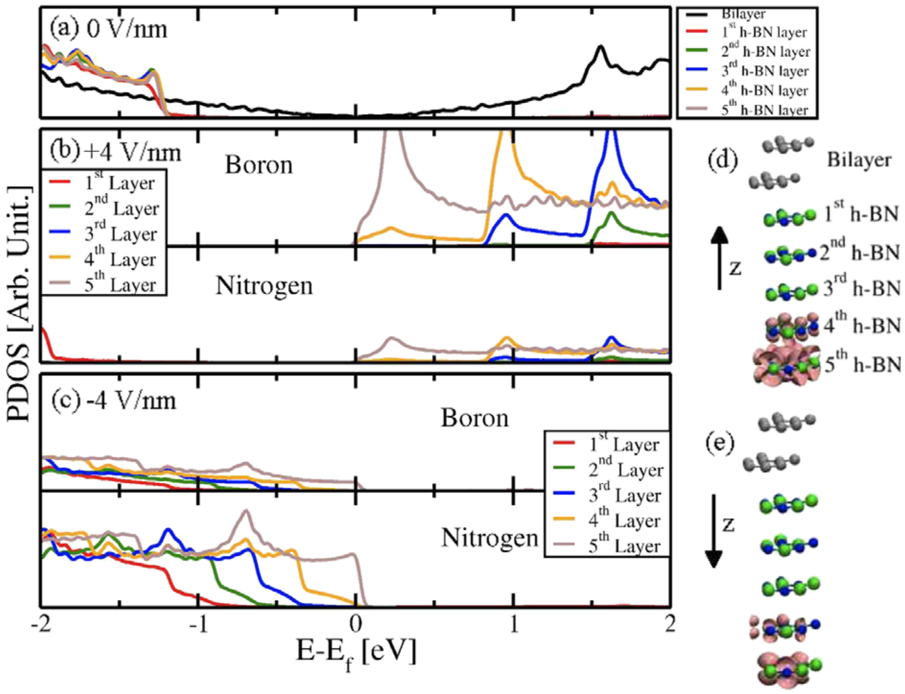
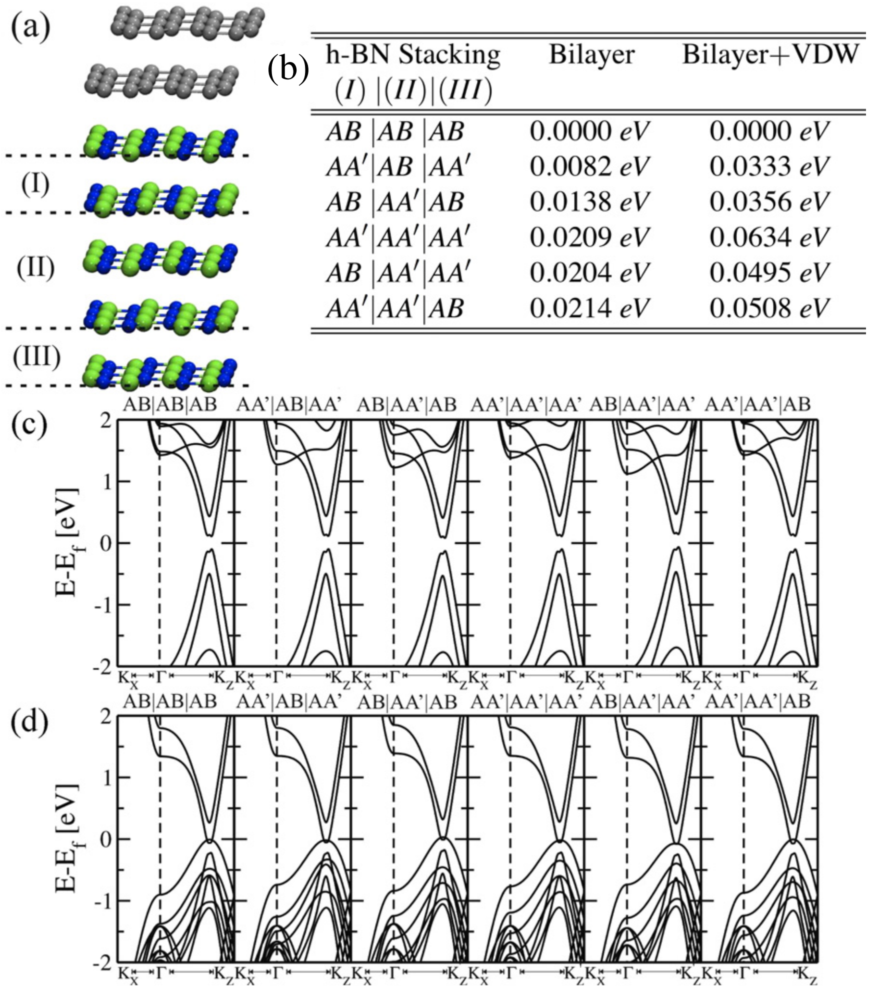


Figure 4. Projected density of states for bilayer graphene on h-BN (five layers) without (a) and with an external positive (b) and negative (c) electric field. The dashed lines identify a region near the Fermi level where we have plotted the LDOS ((d), (e)). The Fermi level is set to zero.

In order to illustrate the behavior of the energy levels, we analyzed the projected density of states (PDOS) for the system with five h-BN layers. In figure 4(a) we present the PDOS, for each layer, for the system without electric field. The levels associated with the occupied states of the BN layers appear around -1.2 eV below the Fermi level (set as zero energy) and the levels associated with the unoccupied BN states appear around $+3.5$ eV (outside the scale of the figure). In figures 4(b) and (c) we present the PDOS, for each layer, decomposed on boron and nitrogen atoms, under an applied electric field. Considering a positive electric field applied ($+4$ V nm^{-1}) (figure 4(b)), we verify an upshift of the boron and nitrogen p-character energy levels. The energy levels associated with the deepest h-BN layer (in this case the fifth layer) are shifted the most. In particular, these states are shifted to around the Fermi level and inside the gap opened in the BG. The local density of states (LDOS) for the region around the Fermi level, marked by the dashed line in figure 4(b), illustrates this characteristic (figure 4(d)). The same behavior is verified for a negative electric field applied (figure 4(c)). However, the occupied levels of the BN are closer to the valence band maximum as compared to the unoccupied levels with respect to the conduction band minimum. By applying an electric field of -4 V nm^{-1}, the boron and nitrogen p-character energy levels of the h-BN fourth layer were upshifted to the bandgap. The local density of states (LDOS) for the region around the Fermi level illustrates these orbitals (figure 4(e)). The energy levels of the h-BN fifth layer were upshifted to the conduction band. These h-BN conduction channels are well separated from the graphene bilayer, which implies that they interact little with the bilayer such that they can be considered as isolated.

Thus, an applied external electric field not only makes a widely tunable electronic bandgap [35], but can also insert BN states into the bandgap, generating a conduction channel through the substrate. As a function of the number of h-BN layers, there is an increase of the density of states near the Dirac point. These states are split depending on whether an electric field is applied. The split depends on the strength of the electric field and the amount of h-BN layers. Then, the voltage breakdown is smaller if the bilayer graphene is supported on several layers of h-BN.

As mentioned above, the AA′ stacking is the h-BN bulk stacking. However, during the chemical exfoliation several types of stacking of h-BN can be obtained. Therefore, it is important to verify whether the doping of bilayer graphene occurs for the different types of stacking modes. We investigate the energetics as well as the effect of an external electric field applied in several possible stacking modes (figure 5). Six possible stacking modes for the h-BN substrate were investigated (figure 5(a)). From the energetics point of view, even considering a correction for the dispersion interaction (van der Waals correction) following the Grimme scheme [31], we obtained that the most stable h-BN stacking is AB/AB/AB. The total energy difference between the conformations is small, as shown in figure 5(b), confirming that non-AA′ stacking can occur in h-BN layers. For instance, the total energy difference between the AB/AB/AB stacking mode and the AA′/AA′/AA′ conformation was 0.02 eV. When applying the van der Waals correction the total energy difference was approximately 0.06 eV. Figure 5(c) also presents the band structures for the six stacking modes investigated, for a given applied electric field of ± 2 V nm^{-1}.



(b)

h-BN Stacking (*I*) |(*II*)|(*III*)	Bilayer	Bilayer+VDW
$AB\ |AB\ |AB$	0.0000 *eV*	0.0000 *eV*
$AA'|AB\ |AA'$	0.0082 *eV*	0.0333 *eV*
$AB\ |AA'|AB$	0.0138 *eV*	0.0356 *eV*
$AA'|AA'|AA'$	0.0209 *eV*	0.0634 *eV*
$AB\ |AA'|AA'$	0.0204 *eV*	0.0495 *eV*
$AA'|AA'|AB$	0.0214 *eV*	0.0508 *eV*

Figure 5. Types (a) and energies (b) for six possible stacking modes of the h-BN surface. The reference energy is the lowest total energy for the AB/AB/AB stacking. Band structures of six possible types of stacking of the bilayer graphene on h-BN under an applied external electric field of $+2$ V nm^{-1} (c) and -2 V nm^{-1} (d).

The important point and remarkable feature is that, for any stacking of the substrate, the general shape of the band structures does not change. The band structures as a function of the number of h-BN layers, in the AB/AB/AB stacking, are presented in the supplementary material (available at stacks.iop.org/JPhysCM/24/075301/mmedia) (see footnote 2). We also calculated the band structures as a function of the electric field applied, for the AA′/AA′/AA′ and AB/AB/AB stacking modes, considering the van der Waals correction (see supplementary material available at stacks.iop.org/JPhysCM/24/075301/mmedia) (see footnote 2). The behavior of the band structures was not modified and the main conclusions obtained using the LDA for E_{xc} are valid, named the tunability of the bandgap and the dependence of the breakdown voltage as a function of the h-BN layers.

4. Conclusions

In conclusion, the *ab initio* electronic structure calculations based on DFT showed that it is possible make the electronic bandgap tunable. We show that under an applied electric field, besides the increase of the intrinsic BG bandgap, the energy levels that come from the h-BN substrate can be shifted to the Fermi level, making the system metallic. Moreover, the breakdown voltage strongly depends on the number of h-BN layers. Finally, a remarkable feature is that the breakdown voltage and the bandgap tuning are independent of the h-BN stacking.

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