

Graphene–Boron Nitride 2D heterosystems functionalized with hydrogen: structure, vibrations, optical response, electron band engineering and bonding

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Abstract. We characterise from first principles the structure and bonding in 2D heterosystems made of bilayers or trilayers of graphene and graphene-like-materials (GLMs), stacked on top of each other, and functionalized using hydrogen. The effects of electron band gap opening and tuning, as well as formation of strongly bonded multilayers have been predicted. The linear and nonlinear optical and vibrational spectra were modelled for hydrogenated alternating graphene monolayers with insulating hexagonal boron nitride (h-BN) films. Here we focus mostly on the structural aspect of the 2D heterosystems. The simulated atomic and related electron structures indicate that submonolayer hydrogenation of the outer surfaces of multilayer systems induces covalent interlayer bonds and enables electron gap engineering in otherwise gapless graphene or wide-band gap h-BN. Calculated structural, vibrational, electronic and optical properties of the systems of interest aim to enabling *in-situ* noninvasive characterization of graphene based multilayers.

Introduction

Progress of modern microelectronics relies on advanced physics concepts to enhance device performance. It is important to create materials, which allow tuning the electron band structure on demand, a process called band-structure engineering. Graphene, one atom thick 2D layer of carbon (C) atoms arranged in a honeycomb lattice with sp^2 hybridized bonds (see, *e.g.*, [1,2] and refs. therein), is a prominent example of such new materials. Each C atom has three neighbors in the xy plane. The remaining p_z orbitals are delocalized along the plane, offering unusual and exciting electronic properties of this material. In particular, graphene is a semimetal with zero electron band gap, which demonstrates record high electron conductivity due to a linear band dispersion of the delocalized p_z electrons in the vicinity of Fermi level (the so-called Dirac cone bands). However, graphene's main drawback, namely zero-band gap, excludes it from applications in p - n -junction based 2D microelectronics. The presence of the forbidden zone is required for creating p - n junctions in such devices as transistors, active region of solar cells, *etc.* As demonstrated in [3,4,5], however, a partial graphene hydrogenation opens the electron gap, which can be controlled by H coverage. This effect has also been observed experimentally [6,7,8]. Interesting both nonlinear optical response and optical spin injection effects for partially hydrogenated semiconducting graphene have been predicted theoretically [9]. On the other hand, it has also been shown that hydrogenation of outer surfaces of graphene bilayers allows opening the tunable electron gap, which can be prospective in device application [3,10,11].

Apart from purely two-dimensional (2D) graphene, other one atom thick 2D materials both with zero and nonzero gaps have been recently discovered [1]. Important examples of such materials are

graphene-like systems (GLS), for instance, insulating one atom thick monolayer of hexagonal boron nitride (h-BN) and semiconducting transition metal dichalcogenides, *etc.* (see, *e.g.*, [12-15]). While the hexagonal BN one-monolayer thick film structurally resembles semimetallic graphene, electron band-gap wise, h-BN is an insulator, which also limits h-BN films application for microelectronics.

A different avenue in band gap engineering is forming the so-called 2D heterosystems: we show here that functionalising such hetero-layers with H on the top and back of the outer surfaces of the system not only opens the electron energy gap, but also allows to tune its value by demand, similar to the case of partially hydrogenated graphene [4]. Graphene can also be combined with other 2D films or deposited on a substrate [16]. Since graphene and transition metal dichalcogenides films do not match well structurally, they cannot be considered a good combination for a heterojunction. In contrast, reasonably small 1.8% mismatch between the larger lattice constant of h-BN and smaller lattice constant of graphene makes them promising to form hetero-multilayers. It is also an interesting combination since these two materials have largely different electronic properties (semimetallic graphene *vs.* insulating h-BN with a 5.9 eV band gap). Indeed, such h-BN/graphene bilayers have been investigated experimentally and discussed theoretically (see, *e.g.*, [17] and refs. therein), where a commensurate–incommensurate transition for graphene on top of h-BN (moiré pattern) has been observed. Pure h-BN and graphene films interact through the weak van der Waals forces, and due to small lattice mismatch this spontaneously breaks the symmetry along the plane, forms the moiré pattern and leads to a very small electron gap opening. Such gap, however, is not sufficient for most of the *p-n* junction applications and cannot be efficiently tuned.

We present here the results of the theoretical (still in progress) investigation of the possibility of creating *covalently bonded* bi- or tri-layer graphene and boron nitride based *semiconducting* 2D heterosystems, using hydrogen adsorption. The controlled hydrogenation at the outer surfaces of the heterolayers not only form covalent bonds between the monolayers but also allows *tailoring* of the band gap and/or creating states inside the gap by demand. Such systems are formed in our computational experiment by depositing graphene on a 2D monolayer hexagonal boron nitride and adding hydrogen on top and bottom of the systems. By reacting with the outer *p_z* orbitals, H atoms passivate locally the dangling bonds on the both sides of the bilayer or trilayer outer surfaces. This causes the nonzero buckling for the initially flat both pure h-BN and graphene, that induces the covalent bonds between the layers of the heterosystems of interest. In addition to the determination of the atomic structure, thermal stability of the heterosystems, their electron bands and vibrational properties were also studied. In this paper, we mostly focus on the structure of several types of bilayer or trilayer heterosystems, their stability and optical signatures.

Technical details

Density Functional Theory (DFT) within the Local Density Approximation (LDA) plane-waves and pseudopotentials scheme as implemented in Quantum Espresso (QE) package [18] was used. The repeated slab geometry with periodic boundary conditions (PBC) and, depending on the number of layers, thicker than 16 Å vacuum region (sufficient to decouple wave functions of the neighbouring heterosystem sheets) were used to realistically describe 2D systems. 60 Ry cutoff was used for atomic structure determination, molecular dynamics and calculation of the optical properties. The Plane Wave (PW) mode of QE, which allows accurate multiple *k*-point Brillouin zone sampling, has been used for the atomic structure optimization, calculation of electron and optical properties, as well as vibrational density of states (VDOS) [19]. Ab-initio Born-Oppenheimer molecular dynamics (BOMD) [20], as implemented in the [18] package has been used. The geometry optimization is achieved through the relaxation of the structure toward its total energy minimum. Finite temperature molecular dynamics (MD) was also used to check whether the hydrogenated multilayer systems are structurally stable with respect to the thermal annealing and to extract the vibrational frequencies. The possible structural instability is indicated by appearance of the soft phonon mode in the vibrational spectra. Electron band structure, density of states (DOS),

VDOS, linear and nonlinear optical response as well as spin injection were calculated for selected bilayer configurations.

More than 40 different 2D bilayer, trilayer and more complex multilayer systems were considered in our simulations. Here we will mostly focus, as an example, on the AA stacked graphene/h-BN bilayer, passivated by hydrogen on both sides of the bilayer with maximum hydrogen coverage, equal to 50% of monolayer (complete hydrogenation). At this coverage H are adsorbed by every second host C, B or N atom in the top and bottom layers, which preserves the original hexagonal symmetry along the 2D film. For such a coverage, for example, a primitive AA stacked H-graphene/h-BN-H cell contains two C, two H, one B and one N atoms, as shown in Fig. 1 (a). Depending on the simulations mode, the structures of interest were modelled using both hexagonal and rectangular supercells with their size ranging from 1 to 16 primitive unit cells. The adsorbed H atoms induce locally sp^3 hybridization instead of sp^2 for initially flat pristine both graphene and h-BN. When performing the simulations for the pristine graphene/b-BN bilayer, van der Waals (vdW) interactions has been also included. Calculation of the optical response and the spin injection has been carried out applying the formalism similar to that one used in [9].

It should be noted that DFT LDA underestimates the band gap compared to the experimental values. This is a well-known problem and there are techniques to fix this, including accurate many-particle GW formalism (see, *e.g.*, [21]) or simple but reasonably accurate the so-called “scissors operator”, which rigidly shifts the energy of the empty surface states up by a well-defined amount. Important is that despite the underestimation of the energy gap, DFT LDA produces the correct electron wave functions for both filled and empty states. Therefore, we show here only DFT LDA results, while the many-particle effects will be considered in the next phase of the research [22].

Average buckling and dimerization of the host carbon, boron and nitrogen atoms for partially hydrogenated systems have been also calculated. Different arrangements of graphene and h-BN films (AA, AB stacking and their mixture) have been considered. Similar to [10], we have found that for the heterosystem with the maximum H coverage AB and AA stackings are practically degenerate in the total energy, although AB stacking is slightly more energetically favorable in the case of 50% hydrogen coverage of top and bottom of the system, the maximum possible amount.

Hydrogenated bilayer and trilayer of graphene/h-BN

When the pristine graphene/h-BN bilayer is formed (Fig. 1 (c)), the weak van der Waals forces do not practically modify the atomic geometry of the each film. This is the reason for a commensurate–incommensurate transition in the pristine graphene/h-BN bilayer [17]. The situation is changing drastically when the hydrogen bonds to the top and the bottom of the bilayer.

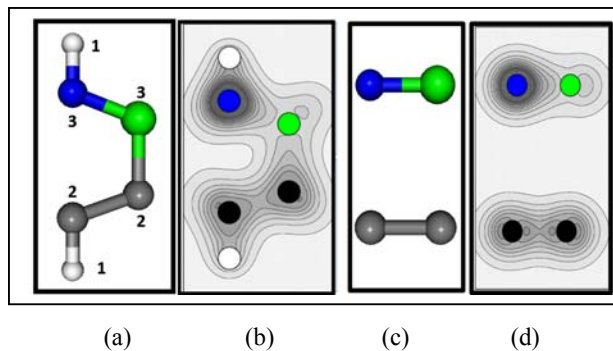


Fig. 1. (Color online) Ball and stick model of 50% H covered h-BN/graphene bilayer (a) and corresponding charge density distribution (b). Panels (c) and (d) the bilayer h-BN/graphene without H and the charge density. Only primitive unit cells are shown, side views. Atoms and numbers are: (1) H – white, (2) C – grey, (3) B – green, (4) N – blue.

The above shown “H on N structure” (Fig. 1(a)) has 0.4 eV lower energy than “H on B structure” (with hydrogen atoms bonded to N atoms, not shown here). Bonding to H atoms and resulting change to sp^3 hybridization causes a substantial buckling of the host films and the corresponding charge density redistribution compared to the non-hydrogenated bilayer. As it is

clear from the charge density plot in Fig. 1 (b), the covalent bonds are formed between the layers. Formation of the covalent bonds makes the bilayer commensurated by compressing h-BN and stretching the graphene layer, the energy gain due to the bond formation is substantially higher than the elastic energy that makes the bilayer commensurated.

In contrast to the case (b), where the interlayer bonding is clearly visible, there is no electron charge, localized between the layers in the case (c), indicating that there is no strong interlayer bonding. Only weak van der Waals forces instead are responsible for formation of the pristine graphene/h-BN bilayer without hydrogen. The ball and stick model of the periodically translated 50% hydrogenated supercells with AB and AA stacking are shown in Fig. 2 and Fig. 3 respectively. The calculated total energy (TE) difference between AA and AB stacked bilayers is 0.01 eV per the primitive unit cell with six atoms, which slightly favors AB system.

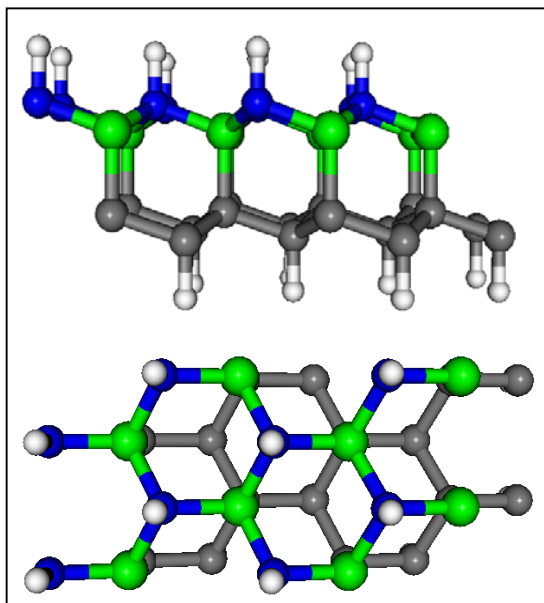


Fig. 2. Most energetically stable graphene/h-BN 2D heterosystem, 50% hydrogenated at both sides with AB stacking: side view (upper panel) and top view (at the bottom)

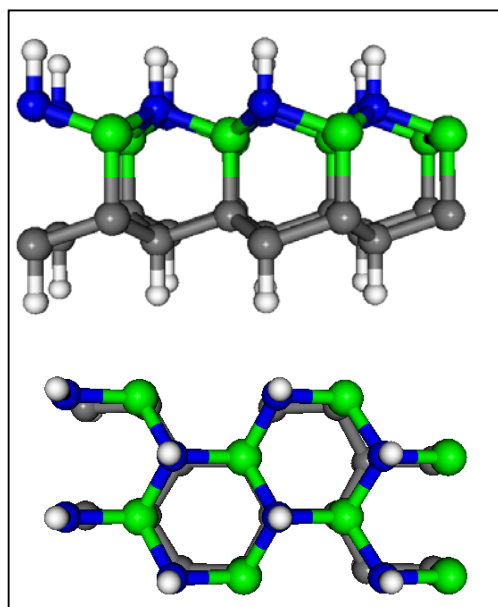


Fig. 3. 50% hydrogenated at both sides AA stacked graphene/h-BN 2D heterosystem with marginally less TE than for AB: side view (upper panel) and top view (at the bottom)

The covalent bond formation should also be responsible for the modification of the electron band structure in the hydrogenated heterosystem vs. pristine bilayers. In agreement with the well-known results, our calculations show that the pristine graphene is gapless, while the calculated DFT LDA gap of h-BN is 4.1 eV. However, 50% hydrogenated AA stacked 2D heterostructure (Fig. 1 (a) and its extended version, shown in Fig. 3) demonstrates DFT-LDA energy gap of 0.9 eV. On the other hand, marginally more stable AB stacked heterosystem 1.0 eV energy gap is opened. Considering DFT-LDA underestimation of the energy gap, formation of the 50% hydrogenated 2D bilayer in experiment should cause the electron energy gap to open to about 1.5 eV, close to the optimal gap value for the microelectronics applications.

When reducing the hydrogen dose at both sides of the bilayer, for instance, to 25% (twice less than the maximum possible coverage of 50%) a more complex structure is formed, its side view is shown in Fig. 4, upper panel. Important is that reducing of the hydrogen coverage causes a decrease in the energy gap for this structure: its DFT-LDA value is 0.2 eV. This clearly demonstrates that the partial hydrogenation enables 2D electron band energy gap engineering. Experimentally, the

hydrogen adsorption below the maximum coverage is a random process, which forms non-periodic 2D hydrogenation pattern. Even though we did not carry out more complex and CPU demanding modeling of such random system, we should expect the monotonous increase of the gap with higher H coverage. Indeed, the experimental finding of the possibility of the gap tailoring in partially hydrogenated graphene [6] has been theoretically proven independently in [3,4].

The lower panel in Fig. 4 shows the side view of 50% hydrogenated at *one side* graphene/h-BN bilayer, with no hydrogen adsorbed at the graphene film. Although the buckling of the carbon atoms is clearly visible, this is not semiconducting system anymore: the band structure contains intermediate electron states inside the gap, prospective for applications in photovoltaics.

Examples of more complex and interesting heterosystems, such as 50% hydrogenated graphene/b-BN /graphene trilayer (Fig. 5 upper panel) and 50% hydrogenated graphene layer *covalently* bonded to cubic BN substrate are shown in the lower panel of Fig. 5. Hydrogenated trilayer heterosystem demonstrates 0.1 eV DFT LDA gap, smaller than the ones for Figs. 3 and 4.

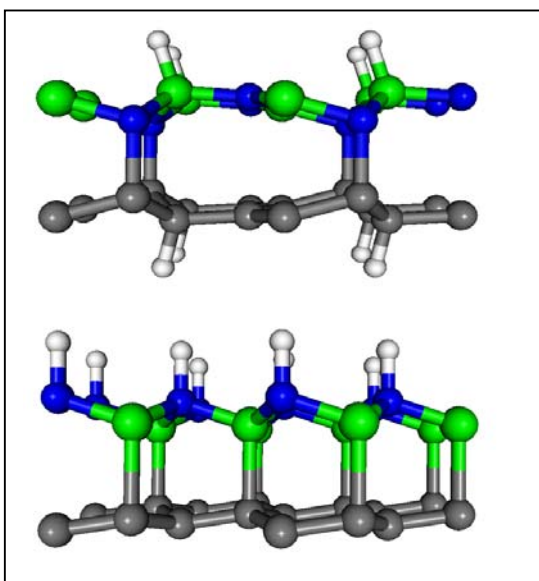


Fig. 4. 25% hydrogenated at both sides semiconducting stable graphene/h-BN 2D heterosystem, side view (upper panel). Lower panel shows hydrogenated at one side graphene/h-BN bilayer. This system contains intermediate electron states inside the gap.

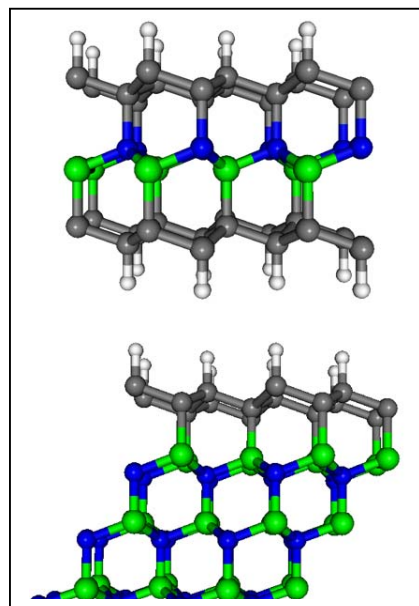


Fig. 5. 50% hydrogenated at both sides AA stacked graphene/h-BN/graphene trilayer, side view (upper panel). 50% at one side hydrogenated graphene layer covalently bonded to cubic BN substrate, side view is at the bottom.

The above discussed atomic structure determination through the system total energy (TE) minimisation gives the microscopic geometry at the absolute zero temperature and does not indicate whether the structures are stable. To investigate the hydrogenated heterosystems' thermal stability we carried out the finite temperature MD simulations. As an example, the time dependent instantaneous MD temperature of the 50% hydrogenated AB stacked graphene/b-BN bilayer (shown in Fig. 2) is plotted in Fig. 6 (a). It shows that the average MD temperature is close to 700K and does not exhibit sudden and strong temperature change, thus indicating on the heterosystem thermal stability and strong interlayer covalent bonds.

In contrast, when the MD run, starting at 400K, was carried out for the hydrogenated at one side graphene/h-BN bilayer (shown in Fig. 4, lower panel), after 6000 MD steps the temperature has suddenly jumped above one thousand degrees and continued to grow (this temperature graph is not

shown here). Structural visualization of the instantaneous atomic geometry indicates that the graphene layer becomes detached from the BN layer.

The vibrational density of states (VDOS) for the thermally stable structure (from Fig. 2) is shown in Fig. 6 at the right. Two peaks close to 3000 cm^{-1} are from hydrogen stretching vibrations, the bilayer vibrations are below 500 cm^{-1} .

In contrast, the VDOS spectrum of the thermally unstable system (Fig. 4, lower panel) clearly demonstrates the so called soft mode, appearing in low frequency region (not shown here).

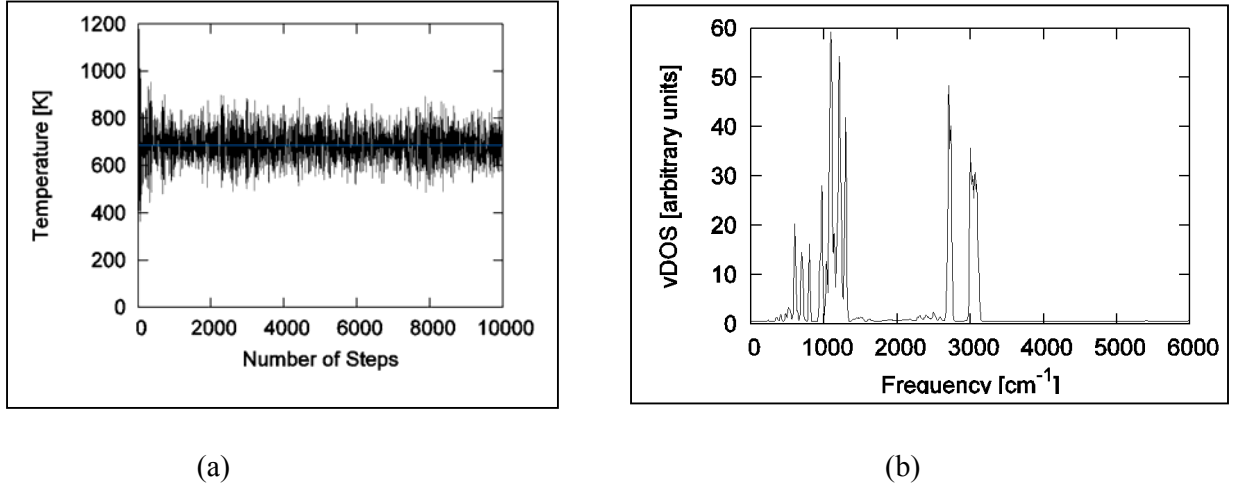


Fig. 6. Time dependent instantaneous temperature of the thermally stable 50% hydrogenated at both sides bilayer from Fig. 2, left panel (a). At the right, panel (b) shows vibrational frequencies density of states for the same structure.

Finally, the hydrogenation of 2D layered heterosystems substantially modifies the linear and nonlinear optical response compared to that of the pristine graphene/h-BN bilayer. We demonstrate the energy dependent spin injections for 50% hydrogenated AA stacked graphene/h-BN bilayer in Fig. 7 (see also [9] for the formalism), leaving more detailed discussion of the linear and nonlinear optical response, its dependence on H dose and the structure specific optical signatures for the forthcoming paper [22].

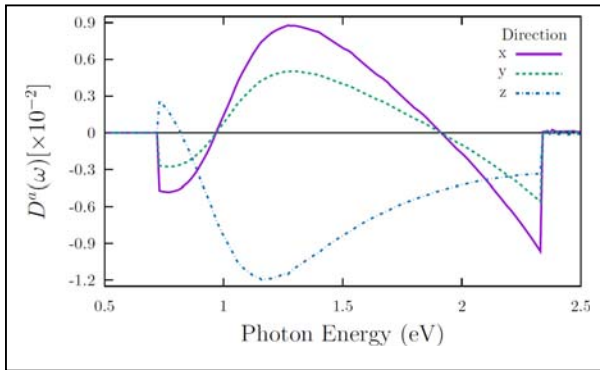


Fig. 7. Spectra of the degree of spin polarization $D^{\alpha}(\omega)$ ($\alpha = x, y, z$) for 50% hydrogenated AA stacked graphene/h-BN heterosystem.

Summary

It was proven theoretically that a partial hydrogenation of bilayer and trilayer of graphene/hexagonal boron nitride (h-BN) can produce semiconducting heterosystem with a possibility of the electron gap engineering: the variable electron band gap between that of practically gapless pristine graphene and insulating h-BN bilayer can be achieved through the variable dose hydrogenation. Out of the various structures considered, the example of the thermally stable 50% hydrogenated at each side heterosystem would be appropriate for 2D microelectronics application, based on its band gap.

In addition, other structures with a gap within 0.2 – 2.0 eV were produced computationally and investigated. The main physical mechanisms of the gap opening is that hydrogen coverage causes both buckling and dimerization of carbon, B and N host atoms, leading to electron localization.

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