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# First principles calculations of the geometric structures and electronic properties of van der Waals heterostructure based on graphene, hexagonal boron nitride and molybdenum diselenide

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ABSTRACT

In this work, by means of density functional theory, we systematically investigate the geometric structure and electronic properties of the vertical heterostructure by stacking graphene on top of single-layered hexagonal boron nitride and molybdenum diselenide (Gr/*h*-BN/$MoSe_2$). Our results show that the interlayer coupling in the heterostructure is mainly governed by the weak van der Waals interactions. We find that in the heterostructure, a tiny band gap of 82 meV is opened around the Dirac *K* point of graphene due to sublattice symmetry breaking, and a minigap of 39 meV is opened between the π band of graphene and the vertical orbitals of $MoSe_2$ due to their hybridization. This band gap opening in graphene makes it suitable for application in novel high-performance nanoeclectronic devices. Furthermore, the Gr/*h*-BN/$MoSe_2$ heterostructure with inserting insulated *h*-BN layer forms an *n*-type Schottky contact with a small Schottky barrier height of 0.1 eV. These findings could provide helpful information for designing novel nanoelectronic devices by stacking graphene on top of single-layered *h*-BN and $MoSe_2$.

## 1. Introduction

Graphene (Gr) [1-3], a two-dimensional (2D) material with a carbon-$sp^2$-hybridized hexagonal lattice, and graphene-like 2D materials such as silicene [4-7], phosphorene [8,9], single-layer gallium nitride [10], and others [11,12] have recently received considerable interests, owing to their extraordinary properties and wide applications in the fields of nanoelectrics and optoelectronics. However, the lack of a band gap at the Dirac *K* point near the Fermi level of graphene has limited its applications for high speed electronic devices [13]. Thus, opening a band gap in graphene becomes one of the most important topics of the research community. In recent years, many approaches have been developed to open the band gap in graphene such as cutting graphene into graphene nanoribbons due to its quantum confinement effect [14,15], doping [16,17], hydrogenation [18], strain engineering [19], and substitutional doping by 4*d* and 5*d* series transition metal [20,21]. Unfortunately, the carrier mobility of graphene with a finite band gap opened using these approaches has been shown to be very lower than that of pristine graphene.

Recently, many vertical heterostructures formed by stacking graphene on other 2D materials have been successfully synthesized experimentally and thus, are being considered as promising candidates for designing novel nanoelectronic and optoelectronic devices [22-28]. In parallel with experimental researches, the vertical graphene-based heterostructures such as Gr/GaN [29,30], Gr/$MoS_2$ [31-34], Gr/P [35,36], and Gr/*h*-BN [37,38] have been widely studied theoretically by means of first principles calculations. The results indicate that graphene-based heterostructures show many new interesting physical properties, that may not occur in distinct forms. In addition, electronic properties of these heterostructures are well kept without any degradation owing to the weak van der Waals (vdW) interactions with the lack of dangling bonds.

Currently, a multifunctional metal/insulator/semiconductor (MIS) tunneling device based on a 2D vertical heterostructure consisting of Gr, *h*-BN, and $MoSe_2$ (Gr/*h*-BN/$MoSe_2$) has been synthesized experimentally using mechanical exfoliation and a dry transfer method [39]. The results show that the multifunctional MIS based on the Gr/*h*-BN/$MoSe_2$ heterostructure has a high tunneling current on/off ratio, $5 \times 10^3$ and an ultrahigh current rectification ratio, $7 \times 10^5$, making it suitable for high-performance tunneling field-effect transistors (FETs).

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However, up to date, there still lacks a detailed theoretical investigation of the electronic properties and Schottky contact of such heterostructure. Therefore, in the present work, by means of density functional theory (DFT), we systematically investigate the geometric structure, electronic properties and the Schottky contact in the Gr/*h*-BN/$MoSe_2$ heterostructure. The effective mass and carrier mobility are also considered to verify the practical applications of such heterostructure.

## 2. Computational methodology

In this work, all calculations are carried out by DFT method, which is implemented in the Quantum Espresso (PWscf) simulation package [40]. To describe the core–valence and the electron exchange–correlation interactions, the frozen-core projector augmented wave (PAW) [41] and the generalized gradient approximation (GGA) [42] of Perdew, Burke, and Ernzerhof (PBE) functional [43] is adopted. Notice that the traditional DFT methods are unable to describe correctly vdW interactions in 2D vdW heterojunctions. Thus, to describe correctly the weak vdW interactions in the vdW heterostructures, we use the semi-empirical DFT-D2 method with London dispersion corrections [44]. The cut-off energy for the plane-wave expansion and the convergence of energy are set to be 500 eV and $10^{-5}$ eV, respectively. For relaxation process, we use $6 \times 6 \times 1$ $k$ point grid, whereas for electronic calculations a $9 \times 9 \times 1$ one is used. The atomic structures are relaxed until the forces are less than 0.001 eV/Å. To break the interaction between the periodic images of layers in the $z$ direction, we use a large vacuum space of 25 Å. Dipole corrections are also applied perpendicularly to the $x$-$y$ plane of the Gr/*h*-BN/$MoSe_2$ heterostructure. Our results show that dipole corrections result only in tiny energy variations of less than 0.05 meV per atom in the considered heterostructure.

## 3. Results and discussion

First, we check the geometric structures and electronic properties of single-layered graphene (Gr), hexagonal boron nitride (*h*-BN) and molybdenum diselenide ($MoSe_2$), as shown in Fig. 1. After geometric optimization, the obtained lattice constants of single-layered Gr, *h*-BN, and $MoSe_2$ are 2.461 Å, 2.520 Å, and 3.280 Å, respectively. These results are in good agreement with the previous reports [45]. In order to check the stability of each single-layered crystal, we calculate its corresponding phonon dispersion curves. One can observe clearly that the single-layered form of these crystals is stable at the equilibrium state.

Before studying electronic properties of the vertically stacked Gr/*h*-BN/$MoSe_2$ heterostructure, we also investigate band structures of the freestanding Gr, *h*-BN, and $MoSe_2$, as shown in Fig. 2. At the equilibrium state, the Gr is a semi-metal with a zero band gap around the Dirac $K$ point, as shown in Fig. 2(a). In contrast to graphene, both the *h*-BN and $MoSe_2$ are semiconductors with the band gaps of 4.6 eV, and 1.50 eV, respectively. These results are well consistent with the previous theoretical calculations [46,47], but smaller than that of experimental measurements [48,49]. It is well known that the traditional DFT methods underestimate the band gap of materials. This issue can be solved by using hybrid functionals [50-52] or many-body GW methods [52,53]. However, this trend is not generalized, and more often depends on the materials. In addition, our present DFT results show that the band characteristics of the materials considered here are qualitatively reasonable and reliable. Thus, we believe that our DFT method is suitable for describing the main characteristics of the Gr/*h*-BN/$MoSe_2$ heterostructure (Fig. 3).

We now consider the geometric structure and electronic properties of a vertical vdW heterostructure based on single-layered Gr, *h*-BN, and $MoSe_2$. To design the vertically stacked Gr/*h*-BN/$MoSe_2$ heterostructure, we use (4 × 4) primitive cells of graphene to match with (4 × 4) primitive cells of *h*-BN and (3 × 3) cells of $MoSe_2$. The lattice constant of the heterostructure is set to be 10 Å. Thus, the overall lattice mismatch is 1.6 %, which is reasonably small. Thus, this small lattice mismatch has little influence on our main results. Here we consider only the most stable stacking configuration of the Gr/*h*-BN/$MoSe_2$ heterostructure. After geometric optimization, the obtained interlayer distance between the Gr and *h*-BN layers, $d_1$, is 3.28 Å, between *h*-BN layer and the topmost layer of $MoSe_2$, $d_2$ is 3.29 Å. Notice that these interlayer distances $d_1$ and $d_2$ have the same range of magnitude as those in our previous vdW heterostructures [31,33,54,55]. It also suggests that the Gr/*h*-BN and *h*-BN/$MoSe_2$ interactions are dominated by the weak vdW interactions. In order to check the stability of the heterostructure, we further calculate its binding energy as: $E_b = [E_{HS} - E_{Gr} - E_{hBN} - E_{MoSe_2}]/N$. Here, $E_{HS}$, $E_{Gr}$, $E_{hBN}$, and $E_{MoSe_2}$, respectively, are the total energies of the considered heterostructure, single-layered Gr, *h*-BN, and $MoSe_2$. $N$ is the number of carbon atoms in the heterostructure. Our calculated binding energy per carbon atom in the heterostructure is −8 meV. The negligible binding energy per carbon atom and the large interlayer distances $d_1$ and $d_2$ show that weak vdW interactions dominate in the heterostructure considered here.

Next, we proceed to explore the electronic properties of the Gr/*h*-BN/$MoSe_2$ heterostructure. In Fig. 4(a), we present the projected band structure of the heterostructure. One can observe that the projected band structure of the Gr/*h*-BN/$MoSe_2$ heterostructure shows many interesting characteristics. First, the projected band structure of the heterostructure seems to be a combination of all components. This is due to the weak vdW interactions occurring in the heterostructure as we have mentioned above. Secondly, the Gr/*h*-BN/$MoSe_2$ heterostructure show a tiny band gap, opening between π-bonding and $\pi^*$-antibonding states at high symmetry Dirac $K$ point of the Gr. The band gap opening in the Gr/*h*-BN/$MoSe_2$ heterostructure at $K$ point is small of 82 meV, as marked by the red circle in Fig. 4(a). This band gap is quite larger than that in Gr/$MoSe_2$ without inserting single-layered *h*-BN, 2 meV [56], and in Gr/*h*-BN without inserting single-layered $MoSe_2$, 53 meV [57]. This band gap opening is significantly larger than $k_BT$ at room temperature, 26 meV, and may promise the fabrication of logic devices operating with a high on/off current ratio. The cause of the band gap opening in the heterostructure is the sublattice symmetry breaking phenomena[54,57]. Thirdly, we find that the Gr/*h*-BN/$MoSe_2$ heterostructure has a linear dispersion around the Dirac $K$ point. It indicates that a high carrier mobility can be achieved for both electrons and holes in the considered heterostructure. The effective mass of electrons and holes in the heterostructure will be focused in next part of the present work. Finally, we find that a minigap of 39 meV opened along the $K - \Gamma$ path due to the hybridization between the graphene π band and the vertical orbitals of single-layered $MoSe_2$, as marked by the blue circle in Fig. 4(a). This finding was also observed in other vdW heterostructures, such as Gr/$MoS_2$ [58,59] and Gr/GaSe [60,61] heterostructures. It should be noted that such minigap opening imposes a superperiodic potential of graphene and lead to a band gap opening at a lower energy relative to its Fermi energy level. It also suggests that $MoSe_2$ monolayer is an appropriate substrate for tuning band gap in the π-band of graphene, and thus proposes an approach for tuning its optical transitions. The electrostatic potential of the Gr/*h*-BN/$MoSe_2$ heterostructure at the equilibrium state along the $z$-direction is illustrated in Fig. 4(b). One can observe that in the heterostructure considered here, the Gr layer has a deeper potential than that of the *h*-BN and $MoSe_2$ layers, showing a strong electrostatic field across the heterostructure. It may considerably impact the carrier dynamics and charge injection when the graphene layer is used as an electrode.

An important key that should be focused in the metal/semiconductor heterostructure, such as Gr/$MoSe_2$ heterostructure, is the understanding of the Schottky contact. Notice that based on the Schottky-Mott rule [62], an $n$-type Schottky barrier height is defined by the difference in energy between the conduction band minimum of semiconducting $MoSe_2$ and the Fermi level of metallic graphene,

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