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Electronic structure of graphene– and BN–supported phosphorene

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Abstract

By using first–principles calculations, the effects of graphene and boron nitride (BN) substrates on the electronic properties of phosphorene are studied. Graphene–supported phosphorene is found to be metallic, while the BN–supported phosphorene is a semiconductor with a moderate band gap of 1.02 eV. Furthermore, the effects of the van der Waals interactions between the phosphorene and graphene or BN layers by means of the interlayer distance change are investigated. It is shown that the interlayer distance change leads to significant band gap size modulations and direct-indirect band gap transitions in the phosphorene–BN heterostructure. The presented band gap engineering of phosphorene may be a powerful technique for the fabrication of high–performance phosphorene–based nanodevices.

Keywords: *ab initio* calculations, phosphorene–graphene, phosphorene–BN, heterostructure, band gap

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1. Introduction

Recently, a family of new Group-VA two-dimensional (2D) semiconducting materials [1-8] have been predicted and successfully fabricated by mechanical cleavage [9] and liquid phase exfoliation [10]. One of these materials, phosphorene, has gained an increasing interest due to its existing mechanical and optoelectronic properties [11–14]. For example, phosphorene is a direct band gap semiconductor with a high hole mobility [15] and an asymmetric electronic transport [16]. The above-mentioned advantages of phosphorene suggest it as an attractive material for applications in electronics nanodevices.

More recently, hybrid 2D materials, like graphene–boron nitride (BN), graphene–silicene and graphene–transition metal dichalcogenide, have attracted great attention because of their fabulous performance in comparison with individual 2D materials [17–23]. Moreover, many researchers have aimed to investigate various properties of these 2D materials and heterostructures subjected to different engineering modifications [24–27]. Particularly, strain engineering can effectively tune the band gap of typical 2D materials and its heterostructures [28–35]. Electric-field engineering has been found as an effective way for the band gap modifications in various systems, such as graphene, BN, and MoS₂ [36–38]. Furthermore, the band gap opening due to substrate effects for graphene and silicene has been predicted [39, 40]. Interestingly, blue phosphorene capped by graphene (BN) substrate shows the weaker adhesion energy than black phosphorene. Moreover, because of the zero band gap of graphene, the charge density of capping graphene substrates masks the host phosphorene structure, making this structure unsuitable to discriminate between different phosphorene allotropes while BN substrate permit identification of phosphorene allotropes [41].

There are also several experimental and theoretical approaches [42-48] which aim to modulate the band gap of different 2D systems, such as graphene/substrate or MoS₂/substrate, by the change of the interlayer distance.

In this work, we perform investigations on the influence of graphene and BN substrates on the electronic properties of phosphorene. The effects of the van der Waals interactions between the phosphorene and graphene or BN layers by means of the interlayer distance change are also studied.

2. Methods

The calculations were performed by Vienna *ab initio* simulation package (VASP) [49] with the Perdew–Burke–Ernzerhof (PBE) functional under the generalized gradient approximation (GGA). The van der Waals (vdW) corrected functional with Becke88 optimization (optB88) [50] was adopted to analyze the interlayer interactions. To correct the band gap value which is well-known underestimated by the normal PBE GGA calculations, the hybrid functional (HSE06) calculations [51] were performed for the pristine phosphorene. Phosphorene–graphene and phosphorene–BN systems were created by using the $3 \times 3 \times 1$ supercells of phosphorene, and $4 \times 3 \times 1$ supercells of graphene and BN (36 phosphorus, 48 carbon, 24 boron and 24 nitrogen atoms). All the structures were fully relaxed until the total energy and atomic forces were smaller than 10^{-5} eV and 0.01 eV/Å, respectively. Periodic boundary conditions were applied in the two in-plane transverse directions, together with a vacuum space with a thickness of 25 Å. For all the considered cases, the energy cutoff of 400 eV was chosen and the first Brillouin zone was sampled with $8 \times 8 \times 1$ k-mesh grid.

3. Results and Discussion

3.1. Structure and electronic properties of the monolayer and graphene– and BN–supported phosphorene. Since the van der Waals forces induced by interlayer interactions may dramatically affect the electronic structure of 2D materials [17, 52] we first study the effect of graphene and BN substrates on the monolayer phosphorene electronic properties.

Figures 1a–c show the optimized atomic configurations of the monolayer phosphorene and graphene– and BN–supported phosphorene, respectively. The optimized interlayer distance (d)

between graphene and phosphorene (BN and phosphorene) surfaces is 3.44 Å (3.40 Å). Considering the lattice mismatch of the monolayer phosphorene (optimized $a_{\text{phosphorene}} = 3.335$ Å, $b_{\text{phosphorene}} = 4.571$ Å) with the monolayer graphene (optimized $a_{\text{graphene}} = 2.456$ Å, $b_{\text{graphene}} = 4.254$ Å) and BN (optimized $a_{\text{BN}} = 2.498$ Å, $b_{\text{BN}} = 4.327$ Å), a co-periodic lattice is used to simulate the considered systems as it is discussed in Methods. Due to the fixed boundaries along in-plane directions during relaxation, the strain in the phosphorene lattice after relaxation was $\epsilon_{\text{phosphorene}} = 0\%$ while the graphene and BN lattices are subjected to the compressive strain along the armchair direction which is equal to the mismatch strain after relaxation. For graphene and BN, the mismatch strain is calculated as $\epsilon_{\text{mismatch}} = (3 \cdot a_{\text{phosphorene}} - 4 \cdot a_{\text{graphene}}) / (3 \cdot a_{\text{phosphorene}}) \approx 1.8\%$ and $\epsilon_{\text{mismatch}} = (3 \cdot a_{\text{phosphorene}} - 4 \cdot a_{\text{BN}}) / (3 \cdot a_{\text{phosphorene}}) \approx 1.3\%$, respectively. Since the graphene and BN lattices are well-matched with the phosphorene lattice along the zig-zag direction, the mismatched strain after the structure relaxation along this direction is negligible.

Figure 1. Atomic configurations (side view: upper panel and top view: lower panel) of a) monolayer phosphorene, b) graphene- and c) BN-supported phosphorene. Spheres coloured in purple, grey, pink and blue show phosphorus, carbon, boron and nitrogen atoms, respectively.

Figure 2a shows that the monolayer phosphorene is a direct band gap semiconductor with the band gap of 0.91 eV (black lines, GGA method) and 1.53 eV (red lines, HSE method), which is well-consistent with previous studies [53–56]. The band structures for the monolayer phosphorene calculated by using the PBE and HSE06 functionals are qualitatively comparable and the both methods predict similar atomic structures and lattice parameters. Based on that and due to a high computational demand of HSE calculations, the GGA method is used for all the systems considered in our work.

Figure 2. Band structure of a) monolayer phosphorene. Black and red lines show the band structure calculated by GGA and HSE methods, respectively; b) graphene-supported phosphorene. Bands coloured in black and red represent phosphorene and graphene, respectively; c) BN-supported phosphorene. Bands coloured in black and orange represent phosphorene and BN, respectively. Blue horizontal line indicates the Fermi level.

Figures 2b and c present band structures for the monolayer, graphene- and BN-supported phosphorene, respectively. Graphene-supported phosphorene shows a metallic nature, which is due to the presence of the Dirac cone formed by graphene bands (Figure 2b). More interestingly, BN-supported phosphorene possesses a semiconducting behaviour and has a moderate band gap of 1.02 eV (Figure 2c). The wider band gap of BN-supported phosphorene in comparison with the band gap of the monolayer phosphorene suggests a significant impact of the BN substrate on the band structure of phosphorene. Particularly, from Figure 2c, it is seen

that the conduction band minimum (CBM) and the valence band maximum (VBM) of original phosphorene are upwardly and downwardly shifted, respectively.

3.2. The effects of the interlayer distance between the phosphorene and graphene and BN surfaces on the electronic structure of phosphorene–graphene and phosphorene–BN heterostructures. Figures 3a–c show the optimized atomic configurations of the phosphorene–graphene heterostructure where the interlayer distance (d) between phosphorene and graphene surfaces are 2.57, 3.51 and 3.78 Å, respectively. Figure 4a (red line) shows that for the phosphorene–graphene heterostructure, the equilibrium distance d is 3.29 Å for which the total energy of the system (E_{tot}) is the lowest. We also found that for $d < \sim 2.50$ Å the structural distortion can destroy the symmetry and damage the heterostructure while for $d > \sim 4$ Å the van der Waals interactions become almost insignificant.

Figure 3. Atomic configurations (top view: upper panel and side view: lower panel) of the phosphorene–graphene heterostructure for a) $d = 2.57$ Å, b) $d = 3.51$ Å and c) $d = 3.78$ Å. Spheres coloured in purple and grey show phosphorus and carbon atoms.

Figure 4. a) The total energy of the system as a function of the interlayer distance d for phosphorene–graphene (red line) and phosphorene–BN (black line) heterostructures. b) Modulation of the band gap of the phosphorene–BN heterostructures as a function of the interlayer distance d .

Figures 5a–c present the band structures for the structures shown in Figures 3a–c, respectively. Despite the original VBM and CBM of phosphorene are significantly upwardly shifted with the increase of d , the phosphorene–graphene bulk system remain metallic for all d because of Dirac–like bands which originate from graphene.

Figure 5. Band structure of the phosphorene–graphene heterostructure for a) $d = 2.57$ Å, b) $d = 3.51$ Å and c) $d = 3.78$ Å. Bands coloured in black and red represent phosphorene and graphene. Blue horizontal line indicates the Fermi level.

Figures 6a–d show the optimized atomic configurations of the phosphorene–BN heterostructure where the distances d between phosphorene and BN surfaces are 2.37, 3.84, 3.08 and 4.01 Å, respectively. Figure 4a (black line) shows that for the phosphorene–BN heterostructure the equilibrium distance d is 3.33 Å for which E_{tot} is the lowest. From Figure 6a, it is clearly seen that for $d < \sim 2.4$ Å the BN surface symmetry is broken which further leads to structure destruction while for $d > \sim 4$ Å the van der Waals interactions become almost insignificant.

Figure 6. Atomic configurations (top view: upper panel and side view: lower panel) of the phosphorene–BN heterostructure for a) $d = 2.37$ Å, b) $d = 2.84$ Å, c) $d = 3.08$ Å and d) $d = 4.01$ Å. Spheres coloured in purple, pink and blue show phosphorus, boron and nitrogen atoms, respectively.

Figures 7a–d present the band structures for the structures shown in Figures 6a–d, respectively. Here, on the band structure plot for phosphorene–BN heterostructure (when $d = 2.37$ Å) one can see a moderate band gap of 0.91 eV. With increasing d to 2.84 Å, the VBM and CBM respectively shift upwardly and downwardly (Figure 7b), which leads to the band gap increase up to 1.23 eV. However, according to Figure 4b, further increase of d causes the upward shift of the VBM which leads to the band gap decrease to 0.95 eV. More importantly, for d in a range from 2.37 to 3.08 Å, the CBM shifts from a point between the Y and Γ points to the Γ point (Figures 7a–d), indicating a direct-to-indirect band gap transition.

Figure 7. Band structure of the phosphorene–BN heterostructure for a) $d = 2.37$ Å, b) $d = 2.84$ Å, c) $d = 3.08$ Å and d) $d = 4.01$ Å. Bands coloured in black and orange represent phosphorene and BN. Blue horizontal line indicates the Fermi level.

4. Conclusions

By using first–principles calculations, the effect of graphene and boron nitride substrates on the electronic properties of phosphorene is shown. Particularly, a metallic nature of the graphene–substarated phosphorene is predicted while the BN–substarated phosphorene is found to be a semiconductor with a band gap of 1.02 eV which is larger than that for a monolayer phosphorene.

In addition, the effect of the van der Waals interactions between the phosphorene and graphene (BN) surfaces by means of the interlayer distance change is investigated. The found possibility of phosphorene–BN heterostructure band gap modulation and direct-indirect band gap transition by the change of the interlayer distance may render new ways in the fabrication of high–performance phosphorene–based nanodevices.

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