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Lattice-matched heterojunctions between blue phosphorene and MXene Y_2CX_2 (X = F, O, and Y = Zr, Hf)

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ABSTRACT

We use *ab initio* calculations to explore the geometry, bonding and electronic properties of Mxene/blue phosphorene (BLP) heterobilayers. Perfect lattice-matched and energetically stable Mxene/BLP heterobilayers are firstly predicted to be vertically stacked with less than 1% lattice mismatch. The electronic properties of the heterobilayers are consistent with the substrate Mxene and the states projected on the isolated components are preserved. The unchanged electronic properties for the components upon the formation of the heterobilayers indicate the physical vdW interaction between the BLP monolayers and Mxene sheet, instead of the chemical bonds. The most stable BLP/Y_2CX_2 (X = O, and Y = Hf, Zr) are found to be a semiconductor with a type-II band alignment where the excited electrons and holes are localized in different layers. However, for BLP/Y_2CX_2 (X = F, and Y = Hf, Zr), the most stable structure is metallic with a strong band bending which lead to the existence of a partial flat band along the Γ point to the M point that mainly originates from the BLP monolayes. The appearance of the spatial separation of electron and hole and the partial flat band in these heterostructures have potential applications in optoelectronic devices and strong electron-electron correlation field. Our analysis also suggests that Mxene is a promising substrate to grow BLP monolayer epitaxially.

1. Introduction

As the rapid development of the experimental techniques, graphene-like two-dimensional (2D) materials – silicene [1–3], hexagonal boron nitride (hBN) [4,5], transition-metal dichalcogenides (TMDCs) [6–8], MXenes [9,10], black and blue phosphorene [11,12], borophene [13,14], etc. – have been synthesized [15]. These single-layer 2D materials possess various significant electronic and optical properties which have potential applications for the next generation of nanoscale semiconductor devices, energy storage materials, solar battery materials, and chemical catalyst [16–20]. For instance, the family of 2D transition metal carbides, carbonitrides, and nitrides (collectively referred to as MXenes), which can be produced by the etching out of the layers from the MAX phases [9,10], have shown a promising performance in lithium (Li)-ion batteries and supercapacitors, exhibiting volumetric capacitances of over 300 farads per cubic centimetre that exceed those of most previously reported materials [9,17]. A previous first-principles study has shown that all of the bare MXenes are metallic. However, after functionalization, some of the MXenes, such as Ti_2CO_2, Zr_2CO_2, and Hf_2CO_2, become semiconductors with band gaps ranging from 0.24 eV to 1.80 eV, and some (Zr_2CF_2 and Hf_2CF_2) still preserves the metallic property [10].

After the successful synthesis of a single-layer black phosphorus arranged in a hexagonal puckered lattice [11], a new phase of a single-layer BLP with a buckle structure like silicene has also been realized by the molecular beam epitaxial growth on Au(1 1 1) surfaces using black phosphorus as precursor [12]. The electronic bandgap of the single layer blue phosphorus on Au(1 1 1) is determined to be 1.10 eV by scanning tunneling spectroscopy measurement [12]. The formation energy of BLP is only a few meV higher than that of black phosphorene and both types of phosphorenes can transform with each other in the process of fabrication [21].

Currently, van der Waals heterostructures stacked by the different families of 2D atomic sheets are considered as a novel way to construct the nanoelectronic and optoelectronic devices and form the interfaces where the novel states and exotic physical phenomena may emerge [15,22,23]. For example, a truly two-dimensional nanotransistor has been constructed using heterostructures of graphene, MoS_2, and hexagonal boron nitride, where graphene acts as both source or drain and gate electrodes, hCBN as the high-k dielectric, and MoS_2 as the channel

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[24,25]. In addition, the heterostructure graphene/hBN has been fabricated and observed the emergence of second-generation Dirac cones (SDCs), which has been used for the realization of Hofstadter butterfly states [26]. Although numerous 2D vdW heterostructures have been found, lattice-matched and energetically stable heterostructures are still attractive in experiment. The heterostructures formed with lattice-dismatched 2D materials lead to the electron inhomogeneous distribution and surface distortion, which decreases the carrier mobility.

In this study, we have investigated six inequivalent BLP/Mxene heterostructures using the density-functional theory (DFT) method. BLP/Mxene are formed to the lattice-matched semiconductor/semiconductor and semiconductor/metal 2D vdW heterojunctions. Both systems have a perfect lattice match and the lattice mismatch is less than 1%. Although the previous works [22,23] have systematically studied the electronic structures and interface properties of heterojunctions composed of BLP and Zr-, Hf-, and Nb-based Mxenes, there are some differences and new results in our work. The BLP/Y_2CX_2 (X = O, and Y = Hf, Zr) atop-II keep a semiconductor while the BLP/Y_2CX_2 (X = F, and Y = Hf, Zr) atop-II become metals. In high-precision calculations, we found that the conduction band and the valence band for the semiconducting heterobilayers are from the Mxene and BLP sheets, respectively. The type-II band heterojunctions form when they are stacked on each other, which is in contrast with the results of the previous works [22,23]. The emergence of the flat band under the semiconductor/metal contacts result from the strong band bending of the CBM from BLP monolayer.

The paper is organized as follows: Calculation details are described in Section 2. The structural and electronic properties of single-layer BLP and Mxene structures are presented in Section 3. In Section 3, we determine the different stacking patterns and calculate the electronic properties for the energetically favorable heterobilayers. Section 4 is the summary.

2. Methods

Our calculations are performed in the frame of the density-functional theory (DFT) [27] with the generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) [28] exchange-correlation functional. The plane-wave basis projector augmented wave (PAW) method [29,30] is employed to describe the ion-electron interactions, implemented in the Vienna *ab initio*simulation package (VASP) [31,32]. Because of the absence of strong bonding, a damped van der Waals (vdW) correction (DFT-D2) [33] is adopted to consider the nonbonding forces. At the same time, the inherent underestimation of the band gap given by DFT is also corrected by using the Heyd-Scuseria-Ernzerhof (HSE) [34] screened-nonlocal-exchange functional of the generalized Kohn-Sham scheme. Analysis of the charge transfers between the heterojunctions is determined by the Bader technique [35]. The plane-wave cutoff is taken to be 520 eV and a vacuum spacing of more than 20 Å is taken to prevent interactions between adjacent images. The energy convergence threshold for electronic iteration is set to be 10^{-5} eV. All the geometries and lattice parameters are fully relaxed using the conjugate gradient algorithm until the Hellmann-Feynman forces on each atom are less than 10^{-2} eV/Å. The Brillouin zone (BZ) is sampled by a Monkhorst-Pack [36] k-point mesh of 18 × 18 × 1 for the structure relaxations, while a k-grid of 32 × 32 × 1 is generated for the static calculations and density of state (DOS) calculations, respectively. Phonon frequencies are calculated based on the density functional perturbation theory (DFPT) [37], implemented in the PHONOPY code [38] and interfaced to VASP with a supercell of 4 × 4 × 1.

3. Single-layer BLP and Mxene

Before analysis of bilayer heterostructures of BLP and Mxene, the structural and electronic properties of the monolayer constituents are studied. The top and side view of the 2 × 2 supercell for the hexagonal monolayer BLP and Mxene are shown in Fig. 1(a)-(c), respectively.

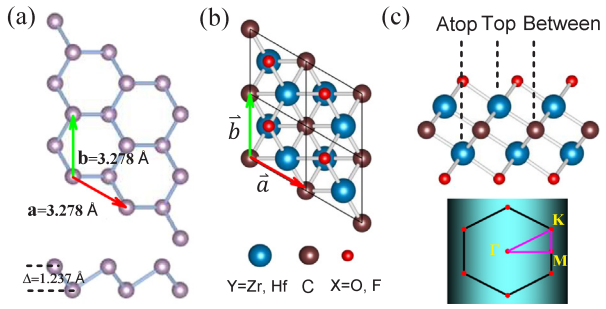

Fig. 1. (a) Top view (up) and side view (down) of 2 × 2 × 1 monolayer BLP. Top and lateral view of the Y_2CX_2 monolayer structures are shown in (b) and (c), respectively. The colors denote different elements, as seen in (b). The Brillouin zone (BZ) and high-symmetry paths corresponding to the unit cell are shown in (c).

First, BLP belongs to the space group C_{3v} with the lattice constant of 3.278 Å. Our calculated buckle height is 1.237 Å, which is consistent with the experiment value of 1.18 Å. The electronic structure calculated with the GGA and HSE06 functionals and phonon spectrum are shown in Fig. 2(a). The buckled monolayer BLP has an indirect band gap of 1.946 eV, while the HSE06 correction has a larger band gap of 2.525 eV, where the valance band maximum (VBM) and the conduction band minimum (CBM) lie along the Γ-M direction in BZ, respectively. The states at the vicinity of the Fermi level originate from the 3*p* orbitals of the P atoms. The work function for BLP is found to be 5.957 eV.

The structural, electronic properties and phonon spectrum of the AA configurations (see S1 in Ref. [39]) of Mxene Y_2CX_2 (X = F, O, and Y = Zr, Hf) used for the other building-block of heterobilayer are presented in Figs. 1(b), (c) and 2(b)-(e). The four structures belong to the $P\bar{3}m1$ space group and the lattice parameters vary from 3.306 Å to 3.266 Å, which perfectly match to the BLP. For F atoms decorated Mxene Y_2CX_2 (X = F, and Y = Zr, Hf), the systems calculated within GGA and HSE06 are metals. The states near the Fermi level are composed of the *d* orbitals of Y (Y = Zr, Hf). Similar to BLP, Mxene Y_2CX_2 (X = O, and Y = Zr, Hf) are found to be an indirect band-gap semiconductor with a band gap of 0.965 eV and 1.207 eV, respectively. The HSE06 correction band gaps are 1.083 eV and 1.123 eV for Zr_2CO_2 and Hf_2CO_2, respectively. The VBM and CBM of both systems reside at the Γ point and M point in BZ, respectively. The states in VBM are mostly contributed from 2*p* orbitals of C atoms and *d* orbitals of Y (Y = Zr, Hf) atoms. However, those in CBM are mostly from the *p* and *d* orbitals of Y atoms. The work functions for the four structures are 5.246 eV, 3.930 eV, 5.187 eV and 3.534 eV, respectively, as listed in Table 1. There is no imaginary frequency on the calculated phonon spectrums for BLP and Mxene, which indicates the structures are stable thermally.

4. Bilayer heterostructures

The calculated lattice constants and space groups of BLP and Mxene Y_2CX_2 (X = F, and Y = Zr, Hf) are very close to each other, which gives a good reason to use these monolayers as the building blocks to construct vdW heterostructures. We define the binding energy using the following formula: $E_{bind} = E_{BLP} + E_{Mxene} - E_{Hetro}$, where E_{BLP}, E_{Mxene}, and E_{Hetro} represent the total energy of BLP, Mxene and their heterostructures, respectively. By comparing the binding energies of six symmetry stacking patterns, we determine the energetically favorable structure for each configuration (see S2 in Ref. [39]). For the heterobilayers with the substrate Mxene decorated with O atoms, they favor to the atop-II pattern, while the ground states of heterobilayers with the constituent layers of Mxene Y_2CF_2(Y = Zr, Hf) are hcp-II pattern. The lattice mismatches for the four optimized ground state structures are found to be 1%, 0.85%, 0.4%, 0.4%, respectively.