Tunable band offsets in the BP/P$_4$O$_{10}$ van der Waals heterostructure: first-principles calculations

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The structural and electronic properties of the black phosphorus/phosphorus pentoxide (BP/P$_4$O$_{10}$) van der Waals (vdW) heterostructure are investigated theoretically by first-principles calculations. The BP/P$_4$O$_{10}$ vdW heterostructure is a direct bandgap semiconductor with intrinsic type-II band alignment thus facilitating separation of photoexcited charge carriers. A transition from semiconducting to metallic is predicted under a positive electric field and the transition of type-II to type-I band alignment occurs under a negative electric field. The bandgap can be modulated by adjusting the interlayer distance. The results indicate that the band offsets of the BP/P$_4$O$_{10}$ vdW heterostructure are tunable, consequently boding well for application to nanoelectronics and optoelectronics.

1. Introduction

Two-dimensional (2D) vdW heterostructures$^1$ have attracted much attention due to unique properties such as high mobility,$^2$ proximity effects,$^3$ quantum tunneling,$^4$ ultrafast charge transfer,$^5$ the spin Hall effect,$^6$ and efficient photocurrent generation.$^7$ Unlike conventional semiconductor heterostructures, there are no chemical bonds at the interface of 2D materials but instead there are weak vdW interactions thus freeing the structure from potential lattice mismatch.$^5,^9$ Many types of 2D vdW heterostructures with a wide range of band alignments, band gaps, and electron affinities$^{10}$ such as G/h-BN,$^{11}$ TMD/TMD,$^{12}$ BP/BN,$^{13,14}$ BP/G,$^{15,16}$ and BP/TMD$^{17,18}$ have been proposed. In particular, vdW heterostructures based on BP can inherit the intrinsic properties of BP such as the direct bandgap, high carrier mobility, and high responsivity and create particularly advantageous applications in electronic and optoelectronic devices.$^{13-25}$ For example, a field-effect transistor based on BP/BN allows a high field-effect mobility of $\sim 1350$ cm$^2$ V$^{-1}$ s$^{-1}$ and on-off ratios exceeding $10^5$ at room temperature,$^{14}$ the Schottky barrier height and doping of BP can be controlled by electrostatic gating in the G/BP vdW heterostructure$^{16}$ and a gate-tunable p$n$ diode comprising the BP/MoS$_2$ vdW heterostructure shows a maximum photodetection responsivity of 418 mA W$^{-1}$.$^{18}

However, BP is unstable under ambient conditions due to its high reactivity with oxygen and water and it is critical to protect the BP from contamination and damage during deposition of other 2D materials. It has been reported that native P$_4$O$_{10}$ can act as a passivation layer on BP.$^{24,27}$ It not only preserves the properties of the underlying phosphorene, but also extends the performance of the heterostructure with BP. The heterogeneous synaptic behavior of naturally oxidized BP has been observed from a BP based synaptic device$^{28}$ and furthermore, the BP/P$_4$O$_{10}$ heterostructure is a vdW heterostructure possessing some interesting properties such as enhanced photoresponse.$^{29}$ Although bandgap engineering of BP by surface oxidation has been previously investigated,$^{30,31}$ the fundamental properties of the BP/P$_4$O$_{10}$ vdW heterostructure such as interlayer coupling, charge transfer and band offsets remain indistinct. Hence, it is important to fathom the fundamental properties of the BP/P$_4$O$_{10}$ vdW heterostructure before the BP/P$_4$O$_{10}$ vdW heterostructure can be implemented in devices and it is essential to understand the underlying mechanism and give proposals for modulating the electronic properties.

In this work, the structural and electronic properties of the BP/P$_4$O$_{10}$ vdW heterostructure are investigated by first-principles calculations. The bandgap and band alignment can be modulated by interlayer coupling and an external electric field. Transitions from semiconducting to metallic and of band alignment from type-II to type-I are predicted to be a function of the external electric field. Our results show that the BP/P$_4$O$_{10}$ vdW heterostructure is promising in future nanoelectronic and optoelectronic devices.
2. Computational methods

The density functional theory (DFT) scheme implemented in the Vienna ab initio simulation package (VASP) code is adopted\textsuperscript{32,33} and the generalized gradient approximation in the Perdew–Burke–Ernzerhof form (GGA-PBE) is used to describe the exchange correlation interactions.\textsuperscript{34} The projected argument wave (PAW) potential is used to describe the ion–electron potential\textsuperscript{35} and the plane-wave cutoff energy for the wave function is set to be 450 eV. The first Brillouin zone integration using the G-center scheme is sampled with a \( \mathbf{k} \) mesh of \( 1 \times 1 \times 1 \) and \( 3 \times 3 \times 1 \) for geometry optimization and static electronic structure calculation, respectively. To correctly describe the effect of the van der Waals interaction, a dispersion-corrected DFT method (optB88-vdW)\textsuperscript{36,37} which has been demonstrated to reliably describe phosphorene systems, is implemented.\textsuperscript{38,39} A vacuum region of 20 Å is added to avoid the interaction caused by the periodic image. Because the GGA-PBE method may underestimate the bandgap of semiconductors, the hybrid Heyd–Scuseria–Ernzerhof (HSE06) method is adopted to obtain the correct bandgap.\textsuperscript{40,41} All the geometry structures are fully relaxed until the energy and forces converge to 10\textsuperscript{−5} eV and −0.01 eV Å\textsuperscript{−1}, respectively.

The optimized lattice parameters of the P\(_4\)O\(_{10}\) layer and BP layer are \( a = 4.48 \) Å and \( b = 6.79 \) Å as well as \( a = 3.31 \) Å and \( b = 4.60 \) Å, respectively. These lattice constants are in good agreement with previous works.\textsuperscript{30,42} To minimize the lattice mismatch between BP and P\(_4\)O\(_{10}\), a \( 3 \times 2 \) P\(_4\)O\(_{10}\) unit cell is used to match the \( 4 \times 3 \) BP unit cell and the lattice constants of the heterostructure are \( a = 13.25 \) Å (zigzag direction) and \( b = 13.81 \) Å (armchair direction) and the resulting mismatch along the armchair and zigzag directions is less than 2%.

3. Results and discussion

3.1 Equilibrium structure of the BP/P\(_4\)O\(_{10}\) vdW heterostructure

The equilibrium geometry structure of the BP/P\(_4\)O\(_{10}\) vdW heterostructure is shown in Fig. 1a. In order to obtain the equilibrium structure, all the atomic positions are fully relaxed and the total energy is calculated by moving the P\(_4\)O\(_{10}\) layer with respect to the BP layer by consecutive finite displacements along the \( x \) (zigzag) and \( y \) (armchair) directions. Fig. 1c illustrates the evolution of the total energy difference as a function of \( \delta \) displacements, in which the total energy in Fig. 1a is set as the zero reference. The relative energy changes are isotropic with respect to atomic displacements parallel to the interface of the BP/P\(_4\)O\(_{10}\) vdW heterostructure and a similar behavior has been observed from InSe/phosphorene vdW heterostructures.\textsuperscript{43}

![Fig. 1](image-url) (a) Side view of the BP/P\(_4\)O\(_{10}\) vdW heterostructure. (b) Brillouin zone with high-symmetry points labeled. (c) Evolution of the total energy as a function of displacements \( \delta \) of the P\(_4\)O\(_{10}\) layer relative to the BP layer taking the origin at the lowest energy configuration. (d) Binding energy as a function of the interlayer distance.
In order to obtain the equilibrium vertical interlayer distance of the BP/P$_4$O$_{10}$ vdW heterostructure, the binding energy between the BP layer and P$_4$O$_{10}$ layer is calculated. The binding energy is defined as:

$$E_b = \frac{E_{BP/P_4O_{10}} - (E_{BP} + E_{P_4O_{10}})}{N}$$

(1)

where $E_{BP/P_4O_{10}}$, $E_{BP}$, and $E_{P_4O_{10}}$ are the total energies of the BP/P$_4$O$_{10}$ vdW heterostructure, isolated BP layer, and isolated P$_4$O$_{10}$ layer, respectively, and $N$ is the number of phosphorus atoms in the BP layer. Fig. 1d depicts the binding energy as a function of interlayer distance which is defined as the vertical distance between the bottom O atom in the P$_4$O$_{10}$ layer and top P atom in the BP layer. The interlayer distance between the P$_4$O$_{10}$ layer and BP layer is 2.98 Å which is larger than the covalent radius of 1.60 Å between the P and O atoms with an interlayer binding energy of $-62.16$ meV per P atom. The binding energy has the same order of magnitude as that of other vdW crystals such as graphite, the G/BP vdW heterostructure, and the BN/BP/BN vdW heterostructure.

The charge transfer between the P$_4$O$_{10}$ and BP layers is further analyzed to confirm the weak interlayer coupling. Fig. 2a shows the plane-averaged difference charge density $\Delta \rho(z)$ along the direction normal to the surface calculated as follows:

$$\Delta \rho(z) = \rho_s(x, y, z)dx.dy - \rho_{BP}(x, y, z)dx.dy - \rho_{P_4O_{10}}(x, y, z)dx.dy,$$

(2)

where $\rho_s(x, y, z)$, $\rho_{BP}(x, y, z)$, and $\rho_{P_4O_{10}}(x, y, z)$ are the charge densities at the $(x, y, z)$ points in the BP/P$_4$O$_{10}$ super cell and BP and P$_4$O$_{10}$ monolayer super cells, respectively. As shown in the corresponding 3D difference charge density in Fig. 2b, the charges are redistributed mainly around the interfacial region of the two monolayers and the BP layer donates electrons to the P$_4$O$_{10}$ layer. Bader charge analysis is performed to quantitatively determine the degree of charge transfer between the BP layer and P$_4$O$_{10}$ layer, and about 0.22 electrons are transferred from the BP layer to the P$_4$O$_{10}$ layer. The degree of charge transfer between the BP and P$_4$O$_{10}$ layers is thus quite small further confirming that the interface is weakly coupled via vdW interactions. The plane-averaged electrostatic potential along the stacking direction is shown in Fig. 2c and the potential drop is 7.04 eV indicating a strong electrostatic field across the interface.

3.2 Electronic structure of the BP/P$_4$O$_{10}$ vdW heterostructure

To understand the electronic properties of the BP/P$_4$O$_{10}$ vdW heterostructure, the band structures of each monolayer as well as the projected band structure of the BP/P$_4$O$_{10}$ vdW heterostructure are determined and shown in Fig. 3a. The bandgap of the BP and P$_4$O$_{10}$ layers is 1.62 eV and 7.25 eV, respectively, in good agreement with those reported previously. With regard to the CBM and VBM at the $\Gamma$ point, the BP/P$_4$O$_{10}$ vdW heterostructure has a direct bandgap of 1.32 eV which is smaller than those of each monolayer, indicating that the bandgap is reduced due to interlayer coupling. The direct bandgap semiconductor facilitates optical absorption since it involves only a two-particle process of photons and electrons as a result of momentum conservation.

The projected band structure of the BP/P$_4$O$_{10}$ vdW heterostructure is exhibited in Fig. 3a and the bands dominated by BP
and P₄O₁₀ are shown as blue and red circles, respectively. The size of the bubbles implies the electron proportion for the contribution from the corresponding layer. According to the projected band structure, the VBM of the heterostructure is contributed solely by the BP layer whereas the CBM mainly originates from the P₄O₁₀ layer. The corresponding band decomposed charge densities of the VBM and CBM in Fig. 3b also indicate that the CBM and VBM states are localized on the P₄O₁₀ and BP layers, respectively. The total and partial densities of states in Fig. 3c show that the VBM is mainly contributed by the BP layer but the CBM is mainly contributed by the P₄O₁₀ layer. Moreover, according to the band alignment of the BP/P₄O₁₀ vdW heterostructure using the vacuum level as the reference as shown in Fig. 3d, the VBM and CBM of the P₄O₁₀ layer are less than that of the BP layer in terms of energy, thus revealing that BP and P₄O₁₀ form a type-II heterostructure which benefits separation of electron–hole pairs. The results are in good agreement with previous work and the reason of the higher photocurrent value at the interface of BP/P₄O₁₀ can be explained. When the BP absorbs the energy of photons, the electron–hole pairs will be excited and then be separated due to the type-II band alignment between the P₄O₁₀ and the BP layer, which will yield larger photocurrent. Thus, the maximum photocurrent can be observed at the interface of the BP/P₄O₁₀ vdW heterostructure.

The band offsets are crucial to optoelectronic devices and can affect quantum confinement of the electrons and holes in the heterostructure. The valence (conduction) band offset is defined as $\Delta E_V = E_{V-BP} - E_{V-P_{4}O_{10}}$, $\Delta E_C = E_{C-BP} - E_{C-P_{4}O_{10}}$ and

![Fig. 3](image-url)
$E_{V\text{-BP(P}_4\text{O}_{10})}$ and $E_{C\text{-BP(C-P}_4\text{O}_{10})}$ are the VBM and CBM of the BP (P$_4$O$_{10}$) layer in the BP/P$_4$O$_{10}$ vdW heterostructure. $\Delta E_{V}$ and $\Delta E_{C}$ are calculated to be about 0.47 eV and 5.67 eV, respectively, in the BP/P$_4$O$_{10}$ vdW heterostructure. When the BP/P$_4$O$_{10}$ vdW heterostructure absorbs the energy of a photon, the electron in the valence band of the BP and P$_4$O$_{10}$ will be excited to the conduction band of the BP and P$_4$O$_{10}$, respectively. The electrons in the conduction band of the BP layer will then transfer to the conduction band of the P$_4$O$_{10}$ layer, while the transfer of holes is opposite to that of electrons due to the type-II band alignment leading to efficient electron–hole separation. The separation of electron–hole pairs to different layers can prolong the lifetime bonding well for photovoltaics and photodetection.

3.3 Modulation of electronic properties in the BP/P$_4$O$_{10}$ vdW heterostructure

Usually, interlayer coupling and application of an electric field are effective methods to improve the performance of electronic devices and so the effects of interlayer coupling and an external electric field on the BP/P$_4$O$_{10}$ vdW heterostructure are studied.

3.3.1 Effects of interlayer coupling. Interlayer coupling is an effective way to tune the electronic properties of the 2D vdW heterostructure by changing the interlayer distance. Here, the interlayer distance is selected to be between 2.5 Å and 4.0 Å. The bandgap as a function of interlayer distance is shown in Fig. 4a and as the interlayer distance decreases, the bandgap decreases. As the interlayer distance decreases from 4.0 Å to 2.5 Å, the bandgap is reduced from 1.41 eV to 1.21 eV. The reason is that as the interlayer distance decreases, the increased interaction between the BP and P$_4$O$_{10}$ layers enhances charge transfer as shown in Fig. 4b. More charge transfer leads to a larger built-in electric field which increases the band offsets and reduces the bandgap of the heterostructure.$^{49}$ It is noted that the BP/P$_4$O$_{10}$ vdW heterostructure retains the type-II band alignment as the interlayer distance is changed as shown in Fig. 4c, indicating that interlayer coupling is effective in modifying the bandgap of the BP/P$_4$O$_{10}$ vdW heterostructure.

3.3.2 Effects of an external electric field. It is found that an applied electric field is another effective method to tune the electronic properties of the BP/P$_4$O$_{10}$ vdW heterostructure. In this work, the direction of the electric field is perpendicular to the layers and from BP to P$_4$O$_{10}$ is taken to be the positive direction. Here, the electric field is applied ranging from $-0.6$ to $0.6$ V Å$^{-1}$ with steps of $0.1$ V Å$^{-1}$. The effects of an external electric field on the electronic structure of the BP/P$_4$O$_{10}$ vdW heterostructure are illustrated in Fig. 5. Fig. 5a exhibits the evolution of the bandgap as a function of the electric field. It is shown that the bandgap is sensitive to the electric field strength and specifically, under a positive electric field, the bandgap decreases linearly with increasing field strength and a metal state is obtained when the positive electric field...
exceeds 0.5 V Å\(^{-1}\). Compared to the bandgap variations in the presence of a positive electric field, a negative electric field gives rise to the opposite variation. The bandgap exhibits a linear increase with increasing negative electric field. The BP/P\(_4\)O\(_{10}\) vdW heterostructure shows a maximum bandgap of 1.57 eV which changes slightly in the electric field range of \(-0.5\) V Å\(^{-1}\) \(< E < -0.6\) V Å\(^{-1}\).

To elucidate the bandgap dependence on the external electric field, the variation of the band edge, band offsets, and plane-averaged difference charge density of the BP/P\(_4\)O\(_{10}\) vdW heterostructure as a function of the electric field is shown in Fig. 5b, c and d, respectively. The plane-averaged difference charge densities under different electric fields are determined as:

\[
\Delta \rho_E(Z) = \int \rho_E(x,y,z)dx\,dy - \int \rho_s(x,y,z)dx\,dy,
\]

where \(\rho_E(x,y,z)\) and \(\rho_s(x,y,z)\) are the charge densities at the \((x, y, z)\) point of the BP/P\(_4\)O\(_{10}\) vdW heterostructure with and without the external electric field, respectively. When the BP and P\(_4\)O\(_{10}\) layers are stacked together, owing to the difference in the work functions of BP and P\(_4\)O\(_{10}\), charge transfer occurs between BP and P\(_4\)O\(_{10}\). Electrons in BP are transferred to P\(_4\)O\(_{10}\) and the holes in P\(_4\)O\(_{10}\) move to BP and hence, the bands of BP drop together with the Fermi level and the bands of P\(_4\)O\(_{10}\) rise together with the Fermi level. Eventually, an equilibrium state in which both layers possess the same Fermi level forms and the BP/P\(_4\)O\(_{10}\) vdW heterostructure has type-II band alignment. When a positive electric field is applied, the direction of the positive electric field is consistent with the built-in electric field, which can facilitate electron transfer from the P\(_4\)O\(_{10}\) layer to the BP layer to reinforce the built-in electric field. Thus, the band offsets increase and the CBM (VBM) of P\(_4\)O\(_{10}\) (BP) shifts downward (upward) to approach the quasi-Fermi level. As a result, the downward CBM and upward VBM close the bandgap.

When a negative electric field is applied, the direction of the negative electric field is opposite to the built-in electric field. The amount of transferring charge also increases with the strength of the negative electric field; electrons tend to transfer from BP to P\(_4\)O\(_{10}\) and holes transfer from P\(_4\)O\(_{10}\) to BP. As a result, the built-in electric field is weakened and the band offsets decrease. In this case, the CBM and VBM tend to shift away from the quasi-Fermi level resulting a larger bandgap.

The external electric field modulates not only the bandgap, but also the band alignment of the BP/P\(_4\)O\(_{10}\) vdW heterostructure. As shown in Fig. 5c, both the VBM and CBM of BP change slightly under the electric field, while the VBM and CBM of P\(_4\)O\(_{10}\) decrease linearly. When the electric field exceeds \(-0.2\) V Å\(^{-1}\), the BP/P\(_4\)O\(_{10}\) vdW heterostructure experiences the transition from type-II to type-I band alignment and the type-I band alignment facilitates recombination of electrons and holes beneficial to light-emitting diodes (LEDs).

To gain more insight into the physical mechanism of band alignment, the projected band structures and corresponding band decomposed charge densities of the VBM and CBM under a negative electric field are calculated and presented in Fig. 6a and b. The BP/P\(_4\)O\(_{10}\) vdW heterostructure initially shows a
type-II band alignment. The CBM is primarily of P4O10 and VBM is primarily of BP. Under a negative electric field and as the negative electric field increases, the contribution from P4O10 to the CBM disappears gradually and at the same time, the contribution of BP to the CBM increases gradually as shown in Fig. 6a. When the negative electric field exceeds $-0.2 \text{ V Å}^{-1}$, the heterostructure shows a type-I band alignment. The results are corroborated by the band decomposed charge densities of the VBM and CBM in Fig. 6b, indicating that electronic modulation can be achieved with an external electric field.

4. Conclusion

Our theoretical assessment demonstrates that the BP/P4O10 vdW heterostructure has a type-II band alignment with a direct bandgap of 1.32 eV. A transition from semiconducting to metallic is observed under a positive electric field of $0.6 \text{ V Å}^{-1}$ and a transition from type-II to type-I occurs under a negative field of $-0.2 \text{ V Å}^{-1}$. The bandgap can be tuned by changing the interlayer distance but the band alignment remains the same. Our results show that the BP/P4O10 vdW heterostructure has large potential for application in nanoelectronics and optoelectronics.

Conflicts of interest

There are no conflicts to declare.

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