Strain-Modulated Band Engineering in Two-Dimensional Black Phosphorus/MoS$_2$ van der Waals Heterojunction

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ABSTRACT: We investigate the band shift and band alignment of two-dimensional (2D) black phosphorus (BP)/MoS$_2$ van der Waals heterojunction (vdW HJ) via uniaxial strain in terms of first-principles calculations and atomic-bond-relaxation method. We find that the band gap of 2D BP/MoS$_2$ HJ decreases linearly with applied tensile strain and Mo—S bond breaks down at 10% tensile strain. Meanwhile, the band gap slightly increases and then monotonically decreases under compressive strain and there appears a semiconductor-to-metal transition at $-11$ and $-12\%$ strain in the y and x directions, respectively. Moreover, 2D BP/MoS$_2$ HJ maintains type-II band alignment for strain applied in the y direction whereas type-II/I band transition appears at $-5\%$ strain in the x direction. Moreover, we propose an analytical model to address the strain-modulated band engineering of 2D BP/MoS$_2$ vdW HJ at the atomic level. Our results suggest a promising way to explain the intrinsic mechanism of strain engineering and manipulate the electronic properties of 2D vdW HJs.

1. INTRODUCTION

Ultrathin two-dimensional (2D) nanomaterials, such as molybdenum disulfide (MoS$_2$) and black phosphorus (BP), have attracted intensive research interest owing to their promising potential applications in electronics and optoelectronics.1−13 These materials exhibit exotic properties due to electron confinement and interaction between atomic layers.3−6 In recent years, vertical stacking van der Waals heterojunctions (vdW HJs) have become one of the research foci to design electronic devices with desired electronic or optoelectronic performances.7−9

Very recently, several attempts have been made to explore the properties and potential applications of 2D vdW HJs owing to their novel properties beyond the corresponding single components, including graphene/hexagonal boron nitride,10 transition-metal dichalcogenides (TMDs)/TMDs,11,12 and BP/TMDs,13−15 etc. In particular, 2D p-BP/n-MoS$_2$ vdW HJ diodes exhibit high photodetection responsivity and excellent photovoltaic effect at the wavelength of 633 nm.16 Strikingly, the HJs of multilayer phosphorene-combined monolayer MoS$_2$ can be an outstanding solar cell and yield theoretical maximum efficiency of around 17.5%.17 Moreover, type-II band alignment of BP/MoS$_2$ HJ can accelerate the separation of photogenerated carriers, suggesting that it can be a great potential for an efficient photodetector.18

Importantly, the effective tunability of electronic and optical properties of 2D HJs is crucial for their various applications. Currently, a lot of considerations such as strain, doping,22,23 and applied fields24,25 have been employed to modulate the electronic and related properties. Especially, strain engineering was recognized as the best strategy to control the material properties, since strain can be easily applied by growing 2D HJs on flexible substrates, without destroying the membrane. For instance, Sharma et al.26 calculated the electronic properties of TMD/TMD HJs by using first-principles calculations and found that the biaxial strain can modulate the band gap and carrier effective mass as well as carrier mobilities. On the basis of the photoluminescence (PL) measurements, Li et al.27 reported that the neutral exciton peak and charged exciton peak of WS$_2$/MoS$_2$ HJ shows a linear redshift under uniaxial strain with rates of 53 and 62 meV/% strain, respectively. Also, He et al.28 demonstrated that both direct and indirect band gaps of MoSe$_2$/WSe$_2$ HJ decrease with applied biaxial strain.

Although several achievements have been obtained on strain engineering of monolayer MoS$_2$ and BP,19,29−31 a systematic study exploring the electronic and mechanical properties of BP/MoS$_2$ HJ under uniaxial strain is still lacking. For example, the evolutions of the band gap energy and band shift of BP/MoS$_2$ HJ under in-plane uniaxial strain are completely unknown. In particular, the limit of the strain strength and similarities and different evolutions of band structures in BP/MoS$_2$ HJ under imposed uniaxial strain in the y and x directions remain unclear. In addition, the underlying mechanism on the strain engineering of 2D BP/MoS$_2$ HJ at the atomic level is still ambiguous.

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Therefore, in this contribution, we investigate the effect of uniaxial strain on the electronic properties of BP/MoS2 HJ by first-principles calculations and atomic-bond-relaxation (ABR) consideration. It is demonstrated that the band gap and band edge of BP/MoS2 HJ can be effectively modulated by uniaxial strain. For the case of BP/MoS2 HJ, the atomic bonds break down and a semiconductor-to-metal transition occurs at the critical strain. In addition, the BP/MoS2 HJ maintains type-II band alignment for strain applied in the y direction, whereas type-II band alignment changes to type-I at −5% compressive strain in the x direction. Moreover, we establish an analytic model to address the strain-dependent band gap and band shift of BP/MoS2 HJ in terms of ABR consideration. Our results reveal the underlying mechanism of uniaxial strain modulation on electronic properties of BP/MoS2 HJ, which provides new insights toward the comprehension of strain engineering, suggesting an effective route for the applications of BP/MoS2 vdW HJ in flexible electronics and optoelectronics.

2. COMPUTATIONAL DETAILS

In this study, first-principles calculations are performed by using the Virtual Nanolab Atomistix ToolKit (ATK) package with the density functional theory (DFT). The generalized gradient approximation (GGA) within Perdew–Burke–Ernzerhof is adopted for electron exchange-correlation function. The electron wave function is expanded using a double zeta polarized basis set. The electron temperature is set to 300 K, and mesh cutoff energy is set at 310 Ry. The supercell of BP/MoS2 HJ was chosen with a periodic boundary condition. The Brillouin zone of the simulation supercell was sampled with a 20 × 5 × 1 Monkhorst–Pack k-grid mesh in our calculations. A vacuum spacing larger than 15 Å was used to minimize the interaction between adjacent monolayers. All atomic positions and lattice constants were optimized by using the limited-memory Broyden–Fletcher–Goldfarb–Shanno algorithm. All atoms are optimized until the force on each atom is less than 0.01 eV/Å, and the maximum stress tolerance of each atom is less than 0.0005 eV/Å³. The vdW interaction between the monolayers was considered in our calculations by adding a semiempirical DFT-D2 method of Grimme. We have further calculated the band gap of BP/MoS2 HJ under uniaxial strain using local density approximation (LDA) as the exchange-correlation functional to verify the reliability of the GGA calculation method, and we obtained very similar trends in the two calculation methods.

3. THEORETICAL MODEL

Generally, the abrupt termination of bonding network at the surface and interface will leave a lot of dangling bonds and coordination deficiencies, which will generate completely new effects, resulting in distinctive features compared to those of their corresponding bulk. Thus, the system will remain in a self-equilibrium state based on the atomic-bond-relaxation (ABR) mechanism. The lattice periodicity and the Hamiltonian of the system will change, which will tailor the electronic and related properties.

In fact, for bilayer HJs, the epitaxial layer will relax to a self-equilibrium state due to surface relaxation and interfacial mismatch; thus, the mass, charge, and energy will redistribute. The lattice constants will undergo converse variation in the in-plane direction due to lattice mismatch, and the out-of-plane bond angles will also change due to Poisson’s effect. Notably,
the schematic illustration of a bilayer HJ consisting of BP and MoS$_2$ is shown in Figure 1. In general, the bilayer is constrained by bending but can be freely stretched or contracted in the in-plane direction. Ignore the effect of dislocation formation; the matched strain can be calculated as: 

$$
\varepsilon_{\text{M0}} = (a - a_0)/a_0
$$

where $\varepsilon_{\text{M0}}$ is the mean elastic extensional strain in the MoS$_2$ and BP, respectively. Noticeably, the internal plane perpendicular to the interface must satisfy the mechanical balance under the condition of self-equilibrium state, thereby obeying

$$
Y_{\text{M}}a_{\text{M0}}^2 + Y_{\text{B}}a_{\text{B0}}^2 = 0
$$

where $Y_{\text{M}}$ and $Y_{\text{B}}$ denote Young's modulus of MoS$_2$ and BP and $a_{\text{M0}}$ and $a_{\text{B0}}$ are the thickness of MoS$_2$ and BP, respectively. For bilayer BP/MoS$_2$ HJ, under uniaxial strain, the total strain in MoS$_2$ and BP is

$$
\varepsilon_{ij}(i = \text{M}, \text{B}; j = x, y) = (1 + \varepsilon_0)(1 + \varepsilon_j) - 1
$$

where $\varepsilon_{ij} = \varepsilon_{xy}$ is the uniaxial tensile strain, whereas $L_0$ and $a_0$ are the strained length of the superunit and that of the corresponding equilibrium length, respectively.

Notably, the interaction potential of monolayer MoS$_2$ is determined by the bond parameters, which can be expressed by

$$
E_B = \sum E_{\text{bond}} + \sum E_{\text{angle}} + \sum E_{\text{C}}
$$

Here, $E_{\text{bond}} = D \times \left[ 1 - e^{-a(k_i - k_j)^2} \right]^2$, $E_{\text{angle}} = \frac{1}{2}k_\psi(h\Delta \theta)^2 + \frac{1}{2}k_\psi(h\Delta \omega)^2$, and $E_{\text{C}} = C_q q_i q_j / \hbar^2$ denote the bond-stretching energy, the bond angle variation energy, and the Coulomb electrostatic energy, where $D$, $a$, $k_\psi$, and $k_\omega$ are the potential parameters, $q_i$ and $q_j$ are the local electrostatic charges of the atoms $i$ and $j$, $\Delta \theta$ and $\Delta \omega$ are the changes in-plane and out-of-plane S–Mo–S bond angles, $\hbar$ is the distance between atoms $i$ and $j$, and $C$ is the Coulomb electrostatic potential parameter, respectively.

Notably, the Stillinger–Weber (SW) potential has been proved suitable for the description of the potential of BP with the bond-stretching interaction and bond angle bending interaction. Thus, the total potential energy is

$$
E_B = \sum_{i<j} V_2(i, j) + \sum_{i<j<k} V_3(i, j, k)
$$

with

$$
V_2(i, j) = A_{ij} (B_{ij} r_{ij}^{-4} - 1) e^{\beta_1 (\varepsilon_0 - \varepsilon_{ij})^2}
$$

and

$$
V_3(i, j, k) = K_{ijk} e^{\beta_2 (\varepsilon_0 - \varepsilon_{ij})^2 + \beta_3 (\varepsilon_0 - \varepsilon_{ik})^2} \cos (\theta_{ijk} - \cos \theta_{ijk})^2
$$

where $V_2(i, j)$ and $V_3(i, j, k)$ are the two-body and three-body terms, respectively; $A_{ij}$, $B_{ij}$, and $K_{ijk}$ are the fitting coefficients, $r_{ij}$ is the distance between atom $i$ and atom $j$, $\theta_{ijk}$ is the angle between bond $ij$ and $jk$, $r_{cij}$ is the corresponding cutoff distance, and $\theta_{ijk}$ is the equilibrium angle between two bonds.

Furthermore, in 2D layered structures, different layers are weakly bonded to each other by vdW force, which is much weaker than that of the covalent intralayer interaction. In general, the interlayer vdW interaction is described by the well-known Lennard-Jones form,

$$
E_{\text{LJ}} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
$$

where $r$ is the distance between two interacting atoms. $\xi$ and $\sigma$ are the potential parameters that can be extracted by the standard geometric combination rules for HJs constructed using different layered materials, i.e., $\xi = \sqrt{\xi_M \xi_B}$ and $\sigma = (\sigma_M + \sigma_B)/2$ where $\xi_M(\sigma_M)$ and $\xi_B(\sigma_B)$ are potential parameters of MoS$_2$ and BP, respectively.

Considering the joint effect of lattice mismatch and uniaxial strain, the cohesive energy of a unit cell is

$$
E_C(e)(i = \text{M, B}) = N z_1 (E_{\text{Di}} + \Delta E_{g}(e) + \Delta E_{g}(e))
$$

where $z_i = 4$ is the CN of monolayer MoS$_2$ or BP and $N$ refers to the number of atoms. In addition, the bond order loss of the surface atoms will cause the system to contract spontaneously, resulting in the relaxation of interaction potential between atoms. The single-bond energy of the system will relax from the $E_{\text{Di}}$ of the bulk to the $E_{\text{Di}} = E_{\text{Di}}(\text{bulk})$, where $m$ is the bond nature factor and $\xi_1 = 2(1 + \exp((12 - z_i)/8z_i))$ is the bond contraction coefficient. Furthermore, the band gap energy ($E_g$) of the system is mainly determined by the first Fourier series of the lattice period.$^{4,5}$ In addition, the band gap of the system is proportional to the single-bond energy $E_g \propto (E_{\text{Di}} - E_{\text{Di}})/N_{\text{Z}}$.

Thus, the band gap of a monolayer MoS$_2$ (BP) under uniaxial tensile strain can be expressed as

$$
E_g(e)(i = \text{M, B}) = E_g(1 + \Delta_e)
$$

where $\Delta_e = (e_{1m} - 1 + \Delta(e_{1m} + e_{1m}))/E_{\text{Di}}$ the former denotes the perturbation caused by the size, and the latter is the perturbation induced by the uniaxial strain and interlayer vdW interaction, respectively; $E_{\text{Di}}$ is the band gap of the bulk.

Moreover, the shifts of conduction band minimum (CBM) and valence band maximum (VBM) are tightly related to the effective mass of electron and hole, i.e., $\Delta E_{\text{CBM}} \propto 1/m_e$ and $\Delta E_{\text{VBM}} \propto 1/m_h$, respectively, where $m_e$ and $m_h$ are the effective mass of electron and hole.$^{34,54}$ Therefore, the offsets of CBM and VBM can be derived as

$$
\begin{align*}
\Delta E_{\text{CBM}}(e)(i = \text{M, B}) &= \Delta E_{\text{g}}(e)(m_e/m_h) \frac{m_i}{m_h} \\
\Delta E_{\text{VBM}}(e)(i = \text{M, B}) &= \Delta E_{\text{g}}(e)(m_i/m_h) \frac{m_i}{m_h}
\end{align*}
$$

4. RESULTS AND DISCUSSION

4.1. Band Structure of BP/MoS$_2$ HJ. The simulated structures of BP/MoS$_2$ HJ are depicted in Figure 1. Notably, the top and side view structures of BP/MoS$_2$ HJ are shown in Figure 1a,b. The optimized lattice parameters of monolayer BP are $a_0 = 3.31$ Å and $b_0 = 4.54$ Å, and the lattice parameters of monolayer MoS$_2$ are $a_{\text{M}} = 3.19$ Å and $b_{\text{M}} = 5.52$ Å. The supercell of BP/MoS$_2$ HJ is constructed from a $5 \times 1$ (armchair $\times$ zigzag) unit cell of BP and a $4 \times 1$ (armchair $\times$ zigzag) unit cell of MoS$_2$, and the optimized lattice constants for the supercell are $a = 3.25$ Å and $b = 22.08$ Å.
To determine the equilibrium state of BP/MoS$_2$ HJs, we consider the total energy with varying interlayer distances and lateral displacements, as shown in Figure 1c,d. Clearly, the total energy shows an obvious dependence on the interlayer distance and the equilibrium distance is 3.24 Å. Furthermore, the total energy increases with the displacements of BP both along the $x$ and $y$ directions (see Figure 1a), indicating that the initial bilayer stacking is the most stable configuration.

Next, we calculate the band gaps of monolayer BP and MoS$_2$. In our calculation, the selected supercell of monolayer BP (MoS$_2$) is consistent with that before the formation of HJ. Also, the band gaps of monolayer BP and MoS$_2$ are 0.94 and 1.68 eV, respectively, which is consistent with the previous calculations. The projected band structure and the Brillouin zone with high-symmetry $k$ points are presented in Figure 2a. In the figure, the blue (red) dots represent the contribution of BP (MoS$_2$) to the band structure and the size of dots indicates the contributions of each layer. Clearly, the CBM of the HJ located at the middle of $\Gamma$ and $X$ ($\Gamma$−$X$) high-symmetry points is mainly from the MoS$_2$, whereas the VBM, also located at $\Gamma$−$X$ points, is from BP. Significantly, BP is an indirect band gap with a value of 0.90 eV and MoS$_2$ is an indirect band gap of 1.35 eV, and the HJ possesses an indirect band gap of 0.48 eV. Evidently, our calculations are in good agreement with the previous results, indicating that the method is feasible. The band gaps of BP and MoS$_2$ in the HJ are slightly smaller than those in the monolayer. This can be attributed to the interlayer vdW interaction and the interface lattice mismatch. More importantly, the essential electronic properties of the corresponding monolayers have been largely preserved, which can serve as the ideal substrates for each other without undue disturbance of their intrinsic electronic structures.

In nature, the band alignment of vdW HJs plays an important role for the application and design of electronic nanodevices. Figure 2a shows the band alignment of BP/MoS$_2$ HJ. Obviously, it exhibits the character of type-II band alignment. The CBM is 0.24 eV for MoS$_2$ and 0.66 eV for BP, whereas the VBM is −1.10 eV for MoS$_2$ and −0.24 eV for BP in the HJ. The CBM of MoS$_2$ sheet is lower than that of BP, whereas the conduction band offset $\Delta E_C = E_{B(M)} - E_{M(C)}$ ($E_{B(M)}$ and $E_{M(C)}$ are the CBM and VBM of BP (MoS$_2$) in the HJ) is 0.42 eV. Also, the VBM of BP is higher than that of MoS$_2$ and the valence band offset $\Delta E_V = E_{B(V)} - E_{M(V)}$ is 0.86 eV. It is indicated that the p-type BP and n-type MoS$_2$ layers form a type-II HJ, which favors the separation of carrier electrons and holes, making the BP/MoS$_2$ HJ a kind of a good candidate for applications in nanoelectronic devices and solar cells.

To understand the different electronic properties for constructing a HJ and assembling each monolayer, we further analyze the partial density of states (PDOS) of the monolayer MoS$_2$ (BP) and BP/MoS$_2$ HJ. In Figure 2b, it is revealed that the electronic properties of the BP layer are mainly determined by the local state density of the 3p orbital of P atom and those of the MoS$_2$ layer are mainly determined by the 4d orbital of Mo atom and the 3p of S atom. The CBM of the HJ is mainly contributed by the Mo d$_{z^2}$, d$_{xy}$, d$_{z^2-y^2}$ and S p$_x$, p$_y$ states; these atomic orbital contributions are the same as those of the monolayer MoS$_2$, whereas the VBM of HJ is mainly contributed by the P p$_x$, p$_y$ and s states. However, the atomic orbital superimposition is different from that of the monolayer.
BP (the VBM of the monolayer BP is mainly contributed by the P p\_z and s states) due to interlayer vdW interaction.

4.2. Band Shift of BP/MoS\_2 HJ under Uniaxial Strain in the y Direction. To investigate the effect of applied strain on the electronic properties of BP/MoS\_2 HJ, we explore the evolutions of band structure in BP/MoS\_2 HJ under uniaxial strain along the y and x directions, respectively. The uniaxial strain is defined as \( \varepsilon_y = (b - b_0)/b_0 \) and \( \varepsilon_x = (a - a_0)/a_0 \), where \( b \) (\( a \)) and \( b_0 \) (\( a_0 \)) are the strained and unstrained supercell parameters, respectively.

Figure 3a−e shows the band structures of BP/MoS\_2 HJ under −5, −2, 0, 2, and 5% strain applied in the y direction. In the figures, we can see that the CBM of MoS\_2 in the HJ continuously decreases with strain and the VBM of BP moves toward the Fermi level as the strain increases. Although the CBM and VBM of BP/MoS\_2 HJ show an opposite trend, the HJ has an indirect band gap. In the case of compressive strain, the CBM of MoS\_2 increases with the increase of compressive strain and the VBM of BP decreases with increasing strain, resulting in the enhancement of band gap of HJs from 0.48 to 0.51 eV. When the compressive strain is greater than −2%, however, the CBM of MoS\_2 and VBM of BP move toward the Fermi level as the compressive strain increases so the band gap of the HJ continuously decreases with increasing strain. Strikingly, when the compressive strain reaches −11%, the band gap of the HJ decreases to 0 eV and the BP/MoS\_2 HJ experiences a semiconductor-to-metal transition. Interestingly, these trends are consistent with the previous calculations.26,58

Figure 4 depicts the evolutions of band gap (GGA and LDA), band offset (a), and band edge (b) of BP/MoS\_2 HJ versus the uniaxial strain in the y direction. Comparisons between first-principles calculations and theoretical predictions for the band gap of BP (MoS\_2) counterparts (c) and the band edge of BP/MoS\_2 HJ versus the uniaxial strain in the y direction (d). \( E_{B(M)-C} \) and \( E_{B(M)-V} \) are the CBM and VBM of BP (MoS\_2) in HJ.
increases. The CBM of BP under compressive strain decreases with the increase of compressive strain, whereas the VBM of MoS2 keeps decreasing with increase of compressive strain far away from the Fermi level.

Furthermore, the theoretical predictions in terms of ABR consideration are also shown in Figure 4c,d. Evidently, the band gap energy of MoS2 increases with compression strain and decreases with tensile strain in the range of −5−5% strain whereas BP possesses an opposite tendency. Actually, for the consideration are also shown in Figure 4c,d. Evidently, the band gap energy of MoS2 increases with compression strain, whereas the VBM of MoS2 keeps decreasing with increase of compressive strain far away from the Fermi level.

To analyze the strain engineering on electronic properties of BP/MoS2 HJ substantially, we plot the variations of PDOS of the condition of applied uniaxial strain. In the case of BP/MoS2 HJ, the lattice constant will be extension and where BP possesses an opposite tendency. Actually, for the condition of applied uniaxial strain.

In addition, the BP/MoS2 HJ will change from type-II to type-I under certain critical strains. Under tensile strain, the CBM of HJ is from Mo dxy and P px, py states whereas the VBM is from P px, py states. In the case of −5%, the states at CBM and VBM are from Mo dxy, dxz−dyz and S px, py and P px, py orbits, respectively. Under uniaxial compressive strain, the electronic component of MoS2 is not contributed by the same electronic components but mainly contributed by the p orbital of P atom and from px to py. Therefore, we believe that the electronic component of VBM is changed under the compressive strain, leading to a band gap reduction for the BP/MoS2 HJs. At a strain of 5%, the states at CBM and VBM are from Mo dxy, dxz−dyz, S px, py and P px, py, respectively. Therefore, it can be found that the electronic component of CBM and VBM is not changed under tensile strain yet the Mo 4d and P 3d orbits move closer to the Fermi level with increasing strain, thereby lowering the band gap.

4.3. Band Shift of BP/MoS2 HJ under Uniaxial Strain in the x Direction. Figure 6a−e shows the band structures of BP/MoS2 HJ under the condition of −5, −2, 0, 2, and 5% strain applied in the x direction. Evidently, the band structure of HJ varies greatly when the strain is applied in the y direction. In addition, the BP/MoS2 HJ will change from type-II to type-I under certain critical strains. Under tensile strain, the CBM of HJ gradually decreases and CBM of MoS2 increases, leading to the CBM of HJ changing from Mo dxy and P px, py to Mo dxy, dxz−dyz and S px, py, respectively. Therefore, it can be found that the electronic component of CBM and VBM is not changed under tensile strain yet the Mo 4d and P 3d orbits move closer to the Fermi level with increasing strain, thereby lowering the band gap.

Figure 5. PDOS of BP/MoS2 HJ under (a) −5% and (b) 5% uniaxial strain in the y direction.

Figure 6. (a−e) Projected band structures of BP/MoS2 HJ under −5, −2, 0, 2, and 5% uniaxial strain in the x direction, respectively.
−4−0%. When the compressive strain is larger than −4%, the CBM and VBM of HJ (CBM and VBM of BP) are close to the Fermi level as the strain increases and the band gap of the HJ decreases as the strain increases. Strikingly, when the strain is −12%, the band gap of the HJ decreases to 0 eV, which means that the HJ undergoes a semiconductor-to-metal transition. Obviously, the ΔEC and ΔEV of HJ are different from the case when the strain is applied in the y direction, as shown in Figure 7a. The ΔEC increases linearly with the increase of strain in the range of 0−5% tensile strain and decreases linearly with strain that is greater than 5%. The change trend of ΔEV tends to a stable average of 0.82 eV throughout the strain process. In Figure 7b, the CBM of BP increases during the tensile strain in the range of 0−5%, then decreases when the strain is greater than 5%. Also, the VBM of MoS2 continuously moves to the Fermi level during the tensile strain, whereas the CBM of BP gradually decreases with increasing strain and the VBM of BP is away from the Fermi level at 0−5% and moves to the Fermi level when the compressive strain is greater than 5%. Moreover, the CBM and VBM of MoS2 under compressive strain are away from the Fermi level at 0−8 and 0−6% and approach to the Fermi level when the strain becomes larger.

Figure 7c,d shows the theoretical predictions of band shift of HJ under uniaxial strain applied in the x direction. Evidently, the band gap of MoS2 increases with compression strain and decreases with tensile strain in the range of −5−5% strain, whereas BP possesses an opposite tendency, which is consistent with the uniaxial strain applied in the y direction. Actually, the mechanical properties of BP show obviously anisotropy whereas MoS2 shows isotropy. Also, the band gap is determined by the atomic distance and interaction potential. Thus, our method provides an approach to connect the band offset and band alignment with uniaxial strain through bond identities, demonstrating that strain engineering has great potential for tunable electronic devices.

Meanwhile, we also analyzed the PDOS of BP/MoS2 HJ under the imposed strain in the x direction. In detail, the PDOS of HJ with a strain of −5 and 5% is presented in Figure 8a,b. In the case of −5%, the states at CBM and VBM are from P pₓ, pᵧ, pₓ, and s and P pₓ, s, and pᵧ orbits, respectively. Under

\[
\begin{align*}
\Delta E_C & = E_{C}^{\text{BP}} - E_{C}^{\text{MoS2}} \\
\Delta E_V & = E_{V}^{\text{BP}} - E_{V}^{\text{MoS2}}
\end{align*}
\]

Figure 7. Band gap (GGA and LDA), band offset (a), and band edge (b) of BP/MoS2 HJ versus the uniaxial strain in the x direction. Comparisons between first-principles calculations and theoretical predictions for the band gap of BP (MoS2) counterparts (c) and band edge of BP/MoS2 HJ versus the uniaxial strain in the x direction (d). E_{B(M)-C} and E_{B(M)-V} are the CBM and VBM of BP (MoS2) in HJ.

Figure 8. PDOS of BP/MoS2 HJ under (a) −5% and (b) 5% uniaxial strain in the x direction.
compressive strain, the states of Mo 4d and S 3p shift away from the Fermi level and the state of P 3p has an opposite trend, leading to the HJ changes from type-II to type-I at ~5% strain. Moreover, the states at CBM and VBM are from Mo d_z^2, d_yz, d_xy, S p_x, p_y, and P p_x, p_y, s orbits at 5% strain. These states are close to the Fermi level as the tensile strain increases, resulting in a decrease of band gap. Therefore, the electronic properties of HJs can be effectively modulated by the strain engineering.6,59

In fact, the change of electronic properties of BP/MoS2 HJ under uniaxial strain applied in y and x directions is different. From the first-principles calculations, the band gap displays a linear trend against the uniaxial tensile strain and increases first and drops at the end under the uniaxial compressive strain applied in both y and x directions. However, the band gap of the BP/MoS2 HJ reaches a maximum and the semiconductor-to-metal transition occurs in two directions with different compressive strains. In addition, the changes of CBM and VBM in BP/MoS2 HJ show an opposite trend in the y and x directions, as well as a transformation from type-II to type-I can be found when the uniaxial compressive strain is applied in the x direction. According to the ABR consideration, the band gaps of BP and MoS2 in HJ show the same trend when the uniaxial strain is applied but the changes of band edges are different. In fact, the discrepancy of band edge shift in both directions can be attributed to the different intrinsic strains at two directions and the anisotropicity of BP layer.

5. CONCLUSIONS

In summary, the band engineering of BP/MoS2 vdW HJs via uniaxial strain is investigated by first-principles calculations and ABR mechanism. Our results show that the band gap and band edge of BP/MoS2 HJ can be effectively modulated by uniaxial strain. Under uniaxial tensile strain (x or y directions), the band gap of HJs monotonically decreases with strain, until the Mo=S bonds break down at 10% strain. However, under uniaxial compressive strain, the band gap increases slightly at first and then monotonically decreases, as well as the BP/MoS2 HJ has a semiconductor-to-metal transition at ~11% uniaxial compressive strain in the y direction and at ~12% uniaxial compressive strain in the x direction. In particular, the BP/MoS2 HJ has the type-II band alignment with p-type BP and n-type MoS2, under the uniaxial strain in the y direction, which is beneficial in applications of solar cells and logical devices. In addition, the BP/MoS2 HJ will change from type-II to type-I at ~5% compressive strain in the x direction. Furthermore, we propose an analytical model to clarify the physical mechanism on the uniaxial strain tunable band gap and band edges of BP/MoS2 HJ on the basis of ABR mechanism. Importantly, our results agree well with the available evidence, which provides physical insights into band engineering of BP/MoS2 HJ and indicates the potential applications in flexible electronics and photovoltaic cells.

Notes

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