Band Structure Engineering of Black Phosphorus/Graphene/MoS₂ van der Waals Heterojunctions for Photovoltaic and Optoelectronic Device Application

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Abstract. In this paper, we study the band structure engineering of black phosphorus/graphene/MoS₂ (BP/graphene/MoS₂) van der Waals heterojunctions based on ab initio simulations. The density of state and charge density of BP/MoS₂, bilayer-BP/MoS₂, bilayer-BP/graphene/MoS₂ and graphene/bilayer-BP/MoS₂ heterojunctions are also investigated. It is found that the bandgaps of these four heterojunctions are smaller than the case of single layer BP or MoS₂. When graphene is inserted into or stacked upon BP and MoS₂ layers, the heterojunction can obtain a minimum bandgap and a higher density of state distribution. In the differential charge density diagram, electrons over the carbon, sulfur and phosphorus atoms are lost from those corresponding parts. These investigations based on the band structure engineering of 2D van der Waals heterojunctions can provide an effective guidance to manufacture the future nanoscale high performance photovoltaic and optoelectronic devices.

Keywords: Van der Waals heterojunction, band structure, density of state, charge density.

1. Introduction

Nanomaterials are an ideal photovoltaic cell materials. They have tunable bandgap, quantum confinement effect, good light absorption properties, multi-exciton generation ability, high carrier mobility, etc [1, 2]. By effectively capturing photon energy in a wide spectral range, and then quickly separating and transporting photogenerated carriers, nanomaterials can achieve high photoelectric
conversion efficiency [3]. It is found that two-dimensional materials represented by black phosphorus (BP), MoS$_2$ and graphene have excellent photovoltaic and optoelectronic properties. Among them, BP is a natural p-type direct energy gap semiconductor, whose energy gap (0.3-2.0eV) is adjustable with the number of layers, therefore it can effectively absorb the visible and infrared sunlight [4, 5]. It owns good application in the fields of fast, broadband photoelectric detection and solar cells. Single-layer transition metal disulfide (TMDs) compounds are n-type direct-gap semiconductors. As a typical representative of TMDs, the single-layer MoS$_2$ has a band gap of ~1.8eV. It has been found that MoS$_2$ has many excellent properties in the fields of electronics and optics [6-9]. In addition, due to high charge transport ability and good chemical stability, graphene becomes an important functional material with wide applications in the optical and electronic field.

In order to improve the performance of photovoltaic and optoelectronic devices, except for choosing high-quality opto-materials, it is necessary to design a more reasonable device structure. Recently, van der Waals heterojunction has attracted extensive research interest, which is a "new" material formed by stacking low-dimensional materials with different properties in an artificially regulated order [10-12]. Lots of studies found that van der Waals heterojunction has many advantages in photovoltaic and optoelectronic applications [13-15]. For example, Deng et al. prepared a p-type BP/n-type single-layer MoS$_2$ van der Waals p-n heterojunction, and their photocurrent imaging experiments confirmed that large photocurrent was generated in the entire overlapping p-n junction area of this device [15].

However, for achieving photovoltaic and optoelectronic application based on these suitable 2D semiconductor materials and the artificially specified stacking orders mentioned above, the study of band structure engineering is an essential prerequisite, which can continuously adjust the band gap and band edge energy by alloying different semiconductors to design almost any electronic potential energy structure [16, 17]. In this work, band structure engineering, and the related local density of state and charge density of BP/graphene/MoS$_2$ van der Waals heterojunctions will be discussed based on first-principle calculations.

2. Methods

The calculations in this work were carried out by the projector-augmented-wave (PAW) potentials with Perdew-Burke-Ernzerhof (PBE) exchange correlation function implemented in the plane-wave-basis Vienna ab initio simulation package (VASP) and Cambridge Sequential Total Energy Package (CASTEP) code [18-21]. More calculation details can refer to our previous work [22]. All bandgap data in this study are based on first-principle calculations in the spin-polarized plane wave density functional theory (DFT) framework implemented in the CASTEP program. For all structural optimization, we chose the dispersion-corrected PBE method to describe the effect of van der Waals forces due to the multi-layers of these heterojunctions.

3. Results and Discussions

The stimulated heterojunction models for BP/MoS$_2$, bilayer-BP/MoS$_2$, bilayer-BP/graphene/MoS$_2$ and graphene/bilayer-BP/MoS$_2$ studied in this work are illustrated in figure 1. One can see that in order to maintain stability, these four 2D van der Waals heterojunctions own different layer spaces calculated by our calculations.
Figure 1. 2D van der Waals heterojunctions structure for (a) BP/MoS₂, (b) bilayer-BP/MoS₂, (c) bilayer-BP/graphene/MoS₂ and (d) graphene/bilayer-BP/MoS₂, where C, P, S and Mo atoms are colored by gray, purple, yellow and blue, respectively.

Table 1. The lattice parameters, partial bond angles and formation energies of these four van der Waals heterojunctions as shown in figure 1.

| Layer Structure                  | Lengths (Å) | Angles (°) | E_{form} (eV) |
|----------------------------------|-------------|------------|---------------|
|                                  | a  | b          | c  | α  | β  | γ  |               |
| BP/MoS₂                          | 27.71 | 6.144      | 32.07 | 90.91 | 86.12 | 37.86 | -3.24        |
| bilayer-BP/MoS₂                   | 27.61 | 6.023      | 32.09 | 90.98 | 86.38 | 38.84 | -7.98        |
| bilayer-BP/graphene/MoS₂          | 28.26 | 6.353      | 30.71 | 88.63 | 89.41 | 37.06 | -7.64        |
| graphene/bilayer-BP/MoS₂          | 28.25 | 6.351      | 30.99 | 90.66 | 85.91 | 37.07 | -7.99        |

As shown in table 1, the lattice parameters, partial bond angles and formation energies of these four heterojunction structures (see figure 1) are listed. It is found that the modification of single or double layer of BP stacked upon the MoS₂ would not lead to the large lattice parameter change. However, when the layer number of 2D materials in these heterojunctions is more than 2, the formation energy $E_{\text{form}}$ is almost doubled compared with the bilayer case of BP/MoS₂. $E_{\text{form}}$ was calculated by the following formula [22]:

$$E_{\text{form}} = E_{\text{total}} - E_{\text{MoS}_2} - E_{\text{graphene}} - E_{\text{total}}^{(\text{bilayer-BP})}$$

The above results indicated that the modified BP layer stacked on the MoS₂ surface has a decent lattice matching, and the increment of BP thickness would enhance the integral stability. Furthermore, the latter two model heterostructures with the graphene layer intercalated in the different positions (bilayer-BP/graphene/MoS₂ and graphene/bilayer-BP/MoS₂) as shown in figure 1c and d, the corresponding lattice parameters in table 1 have been transformed due to the imperfect lattice matching.
As shown in Figure 2, the bandgaps of the 2D heterojunction structures of BP/MoS$_2$, bilayer-BP/MoS$_2$, bilayer-BP/graphene/MoS$_2$ and graphene/bilayer-BP/MoS$_2$ are 0.64eV, 0.44eV, 0.21eV, 0.25eV, respectively. It is obvious that the bandgaps of these heterojunctions are smaller than that of their corresponding single layer component, which suggests that the bandgaps of new semiconductors proposed by us can be regulated artificially by changing the stacked orders and the types of the 2D materials. Among these four 2D-heterostructures mentioned above, the bandgaps of the latter two types with graphene as intercalation/surface layer decrease notably compared with models without graphene layer. The reason is that graphene has no gap between its valence and conduction bands. This phenomenon means that the usage of graphene in these 2D heterojunctions will help increase the absorption of long-wave photons and thus expand optical response range of the devices, such as solar cells and photodetectors.

Figure 3. Local density of state for the 2D heterojunctions: (a) BP/MoS$_2$, (b) bilayer-BP/MoS$_2$, (c) bilayer-BP/graphene/MoS$_2$ and (d) graphene/bilayer-BP/MoS$_2$. 
In figure 3, the local density of state (LDOS) was calculated for each element in 2D heterojunctions to explore bonding characteristics and electronic interactions. There is more overlap between P and S elements with a strong orbital hybridization. The bottom of conduction bands of the 2D heterojunction is formed predominantly by the Mo element and the negative energy \( E_F \) state below the fermi energy \( E_F \) is primarily occupied by P element. Besides, the C element in graphene contributes a small increase in the DOS near the top of valence band. These findings suggest that electronic interaction from the van der Waals heterojunction multilayers models mainly exists between BP and MoS\(_2\). As shown in figure 3a and b, the phosphorus as an electron-rich element would consolidate the distribution of electronic DOS in valence band with the increment of its layer thickness. Graphene, as a two-dimensional carbon nanomaterial consisting of carbon atoms in a hexagonal honeycomb lattice with sp\(^2\) hybridization orbitals, can significantly enhance the LDOS comprehensively. Also, when it was inserted into BP and MoS\(_2\) layers, the heterojunction model obtained a minimum band gap and a higher DOS distribution. As shown in figure 3, the LDOS results for the multilayer model do not show an overlap at the fermi energy, indicating no chemical interaction. These results provide an effective guidance for us to manufacture the opto-electronic device based on 2D van der Waals heterojunctions.

![Figure 4](image_url)

**Figure 4.** The deformation charge density of the 2D heterojunction structures: (a) BP/MoS\(_2\), (b) bilayer-BP/MoS\(_2\), (c) bilayer-BP/graphene/MoS\(_2\) and (d) graphene/bilayer-BP/MoS\(_2\).

In the differential charge density diagram as shown in figure 4, the charge transfer is marked by different colors, which demonstrates the charge distribution of non-bonding in the system, namely, the interlayer charge transfer. The red areas in the figure represent a large number of electrons; while the blue areas indicate the reduced number of electrons. The electrons gathering region with a positive differential charge density is mainly around the Mo atom. Oppositely, over the carbon, sulfur and phosphorus atoms, the differential charge density diagram is mostly shown in blue, meaning that electrons are lost from those parts. In addition, the differential charge density distribution of graphene is surrounded with darker blue color, obviously.
4. Conclusions

In this paper, the band structure engineering, local density of state and charge density of BP/MoS$_2$, bilayer-BP/MoS$_2$, bilayer-BP/graphene/MoS$_2$ and graphene/bilayer-BP/MoS$_2$ van der Waals heterojunctions based on ab initio simulations have been studied. We found that by stacked with different 2D materials, the bandgap of these heterojunctions is smaller than the case of single layer BP or MoS$_2$ case. When graphene is inserted into or stacked upon BP and MoS$_2$ layers, the bilayer-BP/graphene/MoS$_2$ and graphene/bilayer-BP/MoS$_2$ heterojunction models can obtain a minimum band gap and a higher DOS distribution. Differential charge density diagram showed that electrons over the carbon, sulfur and phosphorus atoms were lost from those corresponding parts. In the photovoltaic and optoelectronic fields, our findings will expand the application range of 2D materials.

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