Interlayer coupling and electric field tunable electronic properties and Schottky barrier in a graphene/bilayer-GaSe van der Waals heterostructure

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In this work, using density functional theory we investigated systematically the electronic properties and Schottky barrier modulation in a multilayer graphene/bilayer-GaSe heterostructure by varying the interlayer spacing and by applying an external electric field. At the equilibrium state, the graphene is bound to bilayer-GaSe by a weak van der Waals interaction with the interlayer distance \( d \) of 3.40 Å with the binding energy per carbon atom of \(-37.71\) meV. The projected band structure of the graphene/bilayer-GaSe heterostructure appears as a combination of each band structure of graphene and bilayer-GaSe. Moreover, a tiny band gap of about 10 meV is opened at the Dirac point in the graphene/bilayer-GaSe heterostructure due to the sublattice symmetry breaking. The band gap opening in graphene makes it suitable for potential applications in nanoelectronic and optoelectronic devices. The graphene/bilayer-GaSe heterostructure forms an n-type Schottky contact with the Schottky barrier height of \( 0.72\) eV at the equilibrium interlayer spacing. Furthermore, a transformation from the n-type to p-type Schottky contact could be performed by decreasing the interlayer distance or by applying an electric field. This transformation is observed when the interlayer distance is smaller than 3.30 Å, or when the applied positive external electric field is larger than \( 0.0125\) V Å\(^{-1}\). These results are very important for designing new electronic Schottky devices based on graphene and other 2D semiconductors such as a graphene/bilayer-GaSe heterostructure.

1 Introduction

Recently, the vertically stacked van der Waals (vdW) heterostructures based on two-dimensional (2D) materials have attracted both experimentally and theoretically considerable interest due to their fascinating electronic, optical and transport properties, which may help in designing new classes of nanoelectronic and optoelectronic devices, such as field-effect transistors (FETs). From an experimental view-point, these vdW heterostructures, such as GaS/GaSe, MoS\(_2\)/h-BN, and WS\(_2\)/MoS\(_2\) can be created by stacking different 2D crystals on top of each other layer-by-layer using a direct growth method, e.g. chemical vapor deposition (CVD). These 2D vdW heterostructures showing many new interesting properties which are often absent in individual layers, are considered as a novel way to design new electronic and optoelectronic devices. Among these 2D vdW heterostructures, the graphene-based vdW heterostructures have been widely investigated both experimentally and theoretically, such as graphene/MoS\(_2\), graphene/phosphorene, graphene/g-GaN, graphene/GaSe, graphene/h-BN and so on.

It is well known that graphene, a 2D sp\(^2\)-hybridized carbon monolayer, has extraordinary electronic and quantum transport properties, such as a high carrier mobility and massless Dirac fermions, making it a promising material for designing future nanoelectronic and related devices. Unfortunately, the absence of an electronic band gap has limited graphene applications with a high on-off ratio. Recently, there have been many ways to open a tiny band gap in graphene, such as size effects, the dopant and functional group effects, or the layer effects. These results showed that a band gap of about a few tens up to a few hundreds of meV could be opened in graphene. In parallel with the efforts on a controllable way to open a band gap in graphene, new 2D materials, such as transition-metal dichalcogenides (TMDs), boron nitride, phosphorene, and others, have been recently synthesized and considered experimentally and theoretically, which can be widely used in electronic devices. Very recently, gallium monochalcogenides (GaSe and GaS crystals), a new class of 2D metal dichalcogenide materials, have been synthesized by a vapor phase deposition method, and by an epitaxy method, opening their potential applications for designing the next generation of nanoelectronic devices.
devices, such as FETs,\textsuperscript{49} and photodetectors.\textsuperscript{50} Indeed, serious theoretical investigations have also been performed to further understand the electronic, optical, mechanical and transport properties of a GaSe crystal.\textsuperscript{51–54} It has been demonstrated both theoretically and experimentally that these properties of GaSe crystals are very sensitive to external conditions such as strain, external electric field and doping. In particular, numerous nanoelectronic and optoelectronic devices based on GaSe crystals, such as an ultrathin GaSe-based photodetector\textsuperscript{55} with a fast response of 0.02 s, high responsivity of 2.8 A W\textsuperscript{-1} and high external quantum efficiency of 1367% at 254 nm, and GaSe ultrathin layer transistors\textsuperscript{49} with a good on/off ratio and electron differential mobility, have been successfully fabricated, indicating the promising potential application of GaSe crystals for nanoelectronics and optoelectronics.

Currently, the physical properties of a graphene/GaSe heterostructure are vigorously investigated.\textsuperscript{20,55,56} More recently, Lu and co-workers demonstrated a hybrid based on a graphene/GaSe heterostructure with a high gain exceeding 10\textsuperscript{7} and fast photoreponse with the response time constants of around 10 ms.\textsuperscript{55} Kim et al. experimentally realized a graphene/GaSe dual Schottky diode device\textsuperscript{56} with a high on/off of 10\textsuperscript{3}. The electronic structure and interface characteristics of the graphene/monolayer-GaSe heterostructure have been investigated theoretically using DFT calculations.\textsuperscript{20} Also, the structural and electronic properties of the direct growth of multilayered GaSe on graphene by molecular beam epitaxy have been reported by Aziza and co-workers.\textsuperscript{57,58} These findings showed the high impact on the multilayered graphene/GaSe heterostructure in the field of nanoelectronics and optoelectronics. However, in order to design and fabricate the above-mentioned devices, it is important to understand theoretically the interface properties of the graphene/bilayer-GaSe heterostructure, as well as the effects of interlayer coupling, and electric field on these properties, which have not been investigated thoroughly.

Therefore, in this work we design a new multilayer graphene/bilayer-GaSe heterostructure and consider its electronic properties and Schottky contact by means of density functional theory from first principles calculations. The results show that the electronic properties of graphene and isolated bilayer-GaSe are well preserved in the heterostructure owing to its weak interaction. Moreover, the interlayer coupling and electric field can be used to effectively modulate the Schottky barrier height and Schottky contact type (n-type and p-type). These results may provide a useful orientation to design and fabricate future graphene-based vdW heterostructures, and understand their physical mechanism.

2 Computational methods and models

In this work, we use density functional theory (DFT) with the Quantum Espresso simulation package\textsuperscript{59} to perform all the calculations. The generalized gradient approximation (GGA)\textsuperscript{60,61} of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{62} is used to describe the exchange–correlation interactions. In order to describe the electron-ion potential, we use the projected augmented wave (PAW) potential.\textsuperscript{63} The kinetic cut-off energy is set to 500 eV for the plane wave expansion. The first Brillouin zone (BZ) sampling of a 12 × 12 × 1 Monkhorst–Pack k-point grid is used to perform geometric optimization, whereas the BZ sampling of a 9 × 9 × 1 k-point grid is used to perform all the electronic properties calculations. In order to describe the non-bonding interactions, the DFT-D2 method proposed by Grimme (DFT-D2)\textsuperscript{64} was adopted. In DFT-D2 approximation, the vdW interaction was described by adding a semi-empirical dispersion potential to the conventional DFT energy. In addition, a large vacuum region of 20 Å is used to avoid artificial interactions with spurious replica images. All geometric structures are fully relaxed until the energy and force converge to 10\textsuperscript{-6} eV and 0.001 eV Å\textsuperscript{-1}, respectively. The considered graphene/bilayer-GaSe is created by manually stacking a graphene layer on top of the bilayer-GaSe. The calculated lattice parameters of the pristine graphene and the bilayer-GaSe are 2.461 Å and 3.750 Å, respectively. Moreover, the electronic properties of the GaSe crystals are very sensitive to the strain.\textsuperscript{51} Thus, in order to design the graphene/bilayer-GaSe heterostructure, we choose to fix the lattice parameters of the graphene to match with the lattice parameters of the bilayer-GaSe. The supercell of the graphene/bilayer-GaSe heterostructure consists of (3 × 3) primitive graphene cells and (2 × 2) bilayer-GaSe primitive cells. The lattice mismatch between graphene and bilayer-GaSe in the graphene/bilayer-GaSe heterostructure is only 1.56%, which is negligibly small. In this paper, we focus on only the most stable configuration of the graphene/bilayer-GaSe heterostructure. In this configuration, Ga and Se atoms are located above the center of a hexagonal ring formed by the carbon atoms in a graphene layer, as shown in Fig. 1. The effect of stacking configurations on the electronic properties of the graphene/GaSe heterostructure has been reported in our previous study.\textsuperscript{65}

3 Results and discussion

The atomic geometric structure of the graphene/bilayer-GaSe heterostructure after geometric optimization is displayed in Fig. 1. The obtained equilibrium interlayer distance between the graphene layer and the topmost bilayer-GaSe layer d is 3.40 Å. This distance is consistent with the equilibrium interlayer distances of the previous graphene-based van der Waals heterostructures, such as graphene/MoS\textsubscript{2}\textsuperscript{13,66} graphene/phosphorene,\textsuperscript{15,17,67} and graphene/SnS.\textsuperscript{68} For example, by using the DFT method Padilha and co-workers have demonstrated that graphene is bound to the phosphorene substrate in the graphene/phosphorene heterostructure by weak vdW interaction with the interlayer distance of 3.45 Å.\textsuperscript{13} Similarly, Xiong et al. have shown that the equilibrium interlayer distance between graphene and a SnS monolayer is 3.32 Å, which specifies a weak vdW interaction in the graphene/SnS heterostructure.\textsuperscript{68} These results indicated that our calculated interlayer distance of 3.40 Å in the graphene/bilayer-GaSe heterostructure is specified by a weak vdW interaction. In addition, the interlayer distance d\textsubscript{Se–Ga} of the bilayer GaSe decreases to 4.345 Å as compared to that in the bulk GaSe.\textsuperscript{4} Moreover, in order to determine the stability of the graphene and bilayer-GaSe, we
calculate the binding energy per carbon atom of the graphene/bilayer-GaSe heterostructure, which can be calculated as follows: 

$$E_b = \frac{E_H - E_G - E_{b-GaSe}}{N},$$

where $E_H$, $E_G$, and $E_{b-GaSe}$ are the total energy of the graphene/bilayer-GaSe heterostructure, freestanding graphene, and isolated bilayer-GaSe, respectively. $N$ is the number of carbon atoms in the calculated supercell. Our calculated binding energy per carbon atom in the graphene/bilayer-GaSe heterostructure at the equilibrium interlayer spacing is $37.71$ meV. This binding energy per carbon atom is the same as that in other graphene-based vdW heterostructures, such as graphene/MoS$_2$, graphene/phosphorene, and graphene/ZnO. Moreover, compared with the graphene/monolayer-GaSe heterostructure reported by Si et al., such binding energy per carbon atom is much lower, which indicates that the graphene/bilayer-GaSe heterostructure is reliable in experiments.

Before investigating the electronic properties of the graphene/bilayer-GaSe heterostructure, it should be noted that the band gap of materials plays an important role as an essential part of the electronic devices, such as field effect transistors. Therefore, in order to understand the electronic structures of the graphene/bilayer-GaSe heterostructure, we show the band structures of freestanding graphene, isolated bilayer-GaSe, and graphene/bilayer-GaSe heterostructures, as illustrated in Fig. 2. First, one can observe from Fig. 2(a) that freestanding graphene has a cone-like band structure with linear dispersion which crosses the Fermi level, causing a gapless electronic band structure. Fig. 2(b) shows the band structure of the isolated bilayer-GaSe, which presents an indirect band gap opening between the lowest unoccupied energy state of the conduction bands located at the $\Gamma$ point and the highest occupied energy state of the valence bands lying in the $\Gamma$–$M$ direction. Our calculated band gap of the isolated bilayer-GaSe is $1.46$ eV, which is smaller than the optical band gap of $2.1$ eV of bulk GaSe measured by using photoluminescence. It can also be seen from Fig. 2(b) that the isolated bilayer-GaSe is a p-type semiconductor.

The projected band structure of the graphene/bilayer-GaSe heterostructure is illustrated in Fig. 2(c). We found that the band structure of the graphene/bilayer-GaSe heterostructure seems to be a combination of the band structure of freestanding graphene and bilayer-GaSe. The electronic band structures of freestanding graphene and bilayer-GaSe are well preserved in the graphene/bilayer-GaSe heterostructure due to weak interaction. Interestingly, a tiny band gap of $10.4$ meV for graphene in the graphene/bilayer-GaSe heterostructure is opened at the Dirac point due to sublattice symmetry breaking. The opened band gap in the graphene/bilayer-GaSe heterostructure may lead to the possible application of graphene in nanoelectronics. To explain in detail the physical mechanism of the band gap opening in the
graphene/bilayer-GaSe heterostructure, we use the tight-binding (TB) model analysis. According to the p-electron TB approximation of graphene, the dispersion relation near the Fermi level can be approximated as follows: $E(k) = \pm \sqrt{D^2 + (\hbar v_F k)^2}$, where $k$ is the wave vector related to the Dirac point, $v_F$ is the Fermi velocity, and $\Delta$ is the on-site energy difference between the two sub-lattices of graphene. The $\pm$ signs correspond to the conduction band and the valence band, respectively. For a freestanding graphene monolayer, the on-site energies of two sub-lattices are identical ($\Delta = 0$), resulting in the zero band gap and the linear dispersion relation near the Dirac point. For the graphene/bilayer-GaSe heterostructure, the charge redistribution breaks the equivalence of two graphene sub-lattices. Thus the opened band gap of graphene in the graphene/bilayer-GaSe heterostructure is non-zero as $E_g = 2\Delta$. In addition, it can be seen from Fig. 2(c) that the band gap of bilayer-GaSe in the graphene/bilayer-GaSe heterostructure increases to 1.50 eV upon contact with graphene. An increase in the band gap of the bilayer-GaSe can be understood as follows: first, the band gap of bilayer-GaSe is very sensitive to its lattice symmetry. Secondly, upon contact with graphene the Fermi level moves upward from the valence bands to the conduction bands, making an n-type semiconductor of the bilayer-GaSe. This indicates that in the graphene/bilayer-GaSe heterostructure electrons transfer from graphene to the isolated bilayer-GaSe semiconductor at the equilibrium state of the interlayer spacing. In order to better understand the band structure of the graphene/bilayer-GaSe heterostructure, in Fig. 2(c) we also provide its partial density of states (PDOS). We find that the PDOS of the C-2p$_z$ orbitals in the heterostructure is nearly unchanged in comparison with that of the freestanding graphene because of the weak vdW interaction in the heterostructure. However, compared to the PDOS of Se-p and Ga-d of the isolated bilayer GaSe, one can observe that both the valence and conduction bands of Se-p and Ga-d near the Fermi level shift downwards to the lower energy region, forming an n-type Schottky contact in the heterostructure. Furthermore, we find that a minigap is opened at $-0.78$ eV below the Fermi level along the $\Gamma$–$M$ path, owing to the weak hybridization between the C-2p$_z$ of graphene.
and Ga-d and Se-p orbitals of the bilayer GaSe, as shown in the three right panels of Fig. 2(c). The opening minigap at \(-0.78\) eV below the Fermi level is only 86 meV. This observation has also been confirmed experimentally for other graphene-based heterostructures.\(^{71,72}\) For instance, Batzill and co-workers\(^{72}\) have observed a small gap in the graphene \(\pi\) band below the Fermi level of the graphene/MoS\(_2\) vdW heterostructure, due to hybridization between the graphene \(\pi\) band and the orbitals of a MoS\(_2\) substrate. Ouerghi and co-workers\(^{71}\) have demonstrated the formation of miniband gaps in the \(\pi\) band of the epitaxy graphene in the graphene/MoS\(_2\) heterojunction. They have shown that these miniband gaps are associated with the overlay of MoS\(_2\) and the graphene layer lattice.

Fig. 2(d) shows the electrostatic potential of the graphene/bilayer-GaSe heterostructures at the equilibrium state of \(d = 3.40\) Å along the \(z\)-direction. We find that graphene has a deeper potential than that of bilayer-GaSe. In addition, there is a strong electrostatic field across the heterostructure owing to a large potential drop (the electrostatic potential difference between the graphene and bilayer-GaSe). This may considerably impact the carrier dynamics and charge injection when the graphene layer is used as an electrode. It should be noted that in order to design novel high-performance nanoelectronic devices based on the graphene/bilayer-GaSe heterostructure, it is required that the graphene/bilayer-GeSe heterostructure should be able to maintain graphene’s high carrier mobility. It is well known that the effective mass for electrons \((m_e^\ast)\) and holes \((m_h^\ast)\) of graphene is closely related to its carrier mobility as \(\mu = e\Delta m^\ast.\) Therefore, in order to estimate the carrier mobility of the heterostructure, we further calculate its effective mass. The effective mass of electron/hole is calculated by fitting parabolic functions to the VBM and CBM of the bilayer-GaSe heterostructure for the wave vector as follows:\(^{73}\) \(m^\ast = h^\ast(\hbar^2/E(k)/\hbar^2)^\frac{1}{3}.\) Here, \(k\) is the wave vector and \(h\) is Planck’s constant. At the equivalent interlayer distance \(d = 3.40\) Å, the effective mass for electrons and holes at the \(\Gamma\) Dirac point is very small, \(1.07 \times 10^{-2}\) \(m_0\) and \(1.08 \times 10^{-2}\) \(m_0\), respectively. These small effective masses for electrons and holes indicate that the graphene/bilayer-GaSe heterostructure can maintain a high carrier mobility, which makes the graphene/bilayer-GaSe heterostructure a suitable material for application in high speed nanoelectronic and optoelectronic devices.

More interestingly, we find that a Schottky contact is formed between the metallic graphene and the semiconductor bilayer-GaSe. Based on the Schottky–Mott model\(^{74}\) at the metal-semiconductor interface,\(^{75,76}\) the n-type Schottky barrier \((\phi_{\text{n}})\) is defined as the energy difference between the Fermi level \((E_F)\) and the conduction band minimum \((E_{\text{CBM}})\), namely \(\phi_{\text{n}} = E_{\text{CBM}} - E_F.\) Similarly, the p-type Schottky barrier \((\phi_{\text{p}})\) is defined as the energy difference between the Fermi level \((E_F)\) and the valence band maximum \((E_{\text{VBM}}))\) that is \(\phi_{\text{p}} = E_V - E_{\text{VBM}}.\) Note that the sum of the n-type and the p-type Schottky barriers is approximately equal to the band gap of the semiconductor, i.e., \(\phi_{\text{n}} + \phi_{\text{p}} \approx E_G.\) We find that the graphene/bilayer-GaSe heterostructure is formed by the n-type Schottky contact with the Schottky barrier height of 0.72 eV at the equilibrium state with the interlayer distance of 3.40 Å. Whereas, the p-type Schottky contact is 0.78 eV. The small difference implies a transition from the n-type to p-type Schottky contact under some external conditions, such as strain or electric field. The transition from the n-type to p-type Schottky contact is very important to design new electronic Schottky devices based on graphene and other 2D semiconductors.

Although the interaction between the graphene layer and the bilayer-GaSe in the heterostructure is a weak vdW interaction, the charge density can be redistributed in the graphene/bilayer-GaSe heterostructure, forming an interface dipole. An interface dipole formed by the charge redistribution can push the electronic levels from their original positions, leading to a deviation from the Schottky–Mott limit.\(^{77-79}\) Thus, it is necessary to understand the mechanism of the charge distribution and charge transfer between the graphene and bilayer-GaSe in the graphene/bilayer-GaSe heterostructure, which can be visualized by the charge density difference (CDD), as shown in Fig. 3. The CDD is calculated as follows:

\[
\Delta \rho = \rho_{\text{G/b-GaSe}} - \rho_{\text{G}} - \rho_{\text{p-GaSe}},
\]

where \(\rho_{\text{G/b-GaSe}}, \rho_{\text{G}},\) and \(\rho_{\text{p-GaSe}}\) are the charge densities of the graphene/bilayer-GaSe heterostructure, the graphene layer, and bilayer-GaSe, respectively. It can be observed from Fig. 3 that the charge is transferred from the graphene to bilayer-GaSe at the equilibrium state. Moreover, one can observe that the charge density is redistributed in the graphene/bilayer-GaSe heterostructure, resulting in the formation of electron-rich and hole-rich regions. The charge is depleted in the graphene layer and accumulated in the topmost bilayer-GaSe layer, indicating that the charges are transferred from the graphene layer to the bilayer-GaSe.

We next investigate the effect of the interlayer coupling on the electronic properties of the graphene/bilayer-GaSe heterostructure. It should be noted that in view of device application, the interlayer coupling is an effective way to improve the electronic device performance. Thus, it is necessary to study the effect of the interlayer coupling on the electronic properties of the graphene/bilayer-GaSe heterostructure. In this work, the interlayer coupling is applied by changing the interlayer distance between graphene and the topmost Se layer, and it can be defined as follows: \(\varepsilon = (d_0 - d)/d,\) where \(d_0\) and \(d\) are the strained and equilibrium interlayer distances, respectively.
The variation of the binding energy per carbon atom in the graphene/bilayer-GaSe heterostructure as a function of the interlayer spacing is displayed in Fig. 4(a). It is the lowest when the interlayer distance is 3.40 Å, showing the most stable distance. In Fig. 4(b) we present the electrostatic potential of the graphene/bilayer-GaSe heterostructure at the different interlayer distances. We find that in the graphene/bilayer-GaSe heterostructure the graphene layer has a deeper electrostatic potential than that of bilayer-GaSe. The difference between them across the graphene/bilayer-GaSe heterostructure is large, indicating a strong electrostatic field across the heterostructure. It may considerably impact the carrier dynamics and charge injection when the graphene layer is used as an electrode.

In Fig. 5 we present the electronic band structure of the graphene/bilayer-GaSe heterostructure with different interlayer distances. As mentioned above, at the equilibrium state with the interlayer distance of 3.40 Å, the graphene/bilayer-GaSe heterostructure is large, indicating a strong electrostatic field across the heterostructure. It may considerably impact the carrier dynamics and charge injection when the graphene layer is used as an electrode.

Notice that the Schottky barrier height plays a key role in the metal/semiconductor heterostructure because the current flow crossing the system strongly depends on the magnitude of the Schottky barrier height. The graphene/bilayer-GaSe heterostructure becomes a unified electronic system upon contact. Even without any charge transfer between the graphene and the bilayer-GaSe layers, there is an interface dipole, that is accompanied by an interface potential step \( D \) formed in the heterostructure. The interface potential step can be defined as:

\[
D = \frac{W_{\text{hetero}}}{C_0} - \frac{W_{\text{gra}}}{C_0}
\]

where \( W_{\text{hetero}} \) and \( W_{\text{gra}} \) are the work functions of the graphene/bilayer-GaSe heterostructure and graphene, respectively. Moreover, for the semiconducting bilayer-GaSe, the ionization potential, \( I_{\text{b-GaSe}} \), and the electron affinity, \( \omega_{\text{b-GaSe}} \), are different. The ionization potential is the difference between the vacuum level and the VBM of the semiconducting bilayer-GaSe, that is \( I_{\text{b-GaSe}} = E_{\text{b-GaSe}}^{\text{vac}} - E_{\text{VBM}} \). Whereas the electron affinity is the energy difference between the vacuum layer and the CBM of the semiconducting bilayer-GaSe, that is...
The n-type Schottky barrier height in this case is $\Phi_{B,n} = (W_{\text{gra}} + \Delta V) - E_{\text{CBM}}$, while the p-type Schottky barrier height is $\Phi_{B,p} = I_{\text{b-GaSe}} - (W_{\text{gra}} + \Delta V)$. Our calculated work function for the graphene/bilayer-GaSe heterostructure and freestanding graphene are 4.50 eV and 4.25 eV, respectively. Thus, an interface potential step is small of 0.25 eV. Also, our calculated electron affinity, $w_{\text{b-GaSe}}$, and ionization potential, $I_{\text{b-GaSe}}$, for the isolated bilayer GaSe, respectively, is 3.78 eV, and 5.28 eV. One can observe that with increasing the interlayer distance $d$ less electrons are transferred from the graphene layer to the bilayer-GaSe, resulting in a decrease in the interface potential.

Another approach that can be used effectively to tune the electronic properties of materials is the application of an electric field. In this work, an electric field is applied perpendicular to the heterostructure along the z direction. The direction of the electric field from the bilayer-GaSe to the graphene layer is defined as the positive direction. Fig. 6(b) shows the dependence of the Schottky barrier height as a function of the applied electric field. It can be seen that by applying a positive electric field, the n-type Schottky barrier height increases, whereas the corresponding p-type one decreases. When the positive electric field is larger than 0.025 V Å$^{-1}$ the n-type Schottky barrier height becomes larger than the p-type one, resulting in a transition from an n-type to p-type Schottky contact. By increasing the positive electric field from 0 V Å$^{-1}$ to 0.1 V Å$^{-1}$ and then to 0.2 V Å$^{-1}$, the n-type Schottky barrier height increases from 0.72 eV to 0.93 eV and then to 1.11 eV, whereas the p-type Schottky barrier height decreases from 0.78 eV to 0.57 eV and then to 0.37 eV, respectively. By applying a negative electric field, it can be seen from Fig. 6(b) that the n-type Schottky barrier height decreases, while the p-type Schottky barrier height increases. Thus, a transition from n-type to p-type Schottky contact is not observed when a negative electric field is applied perpendicularly to the heterostructure surface.

To further understand the electric field effect on the electronic properties of the graphene/bilayer-GaSe heterostructure, we plot its electronic band structures under different positive and negative electric fields, as shown in Fig. 7. One can observe that the transition from the n-type to p-type Schottky contact due to applied positive electric field is caused by the charge transfer between graphene and bilayer-GaSe, which affects the Fermi level. Indeed, as already pointed out, at the equilibrium state (without applied electric field), the graphene/bilayer-GaSe heterostructure forms an n-type Schottky contact with the lowest energy state of the conduction bands closer to the Dirac point. When a positive electric field is applied, the Fermi energy level moves downward from the conduction bands to the valence bands of the semiconducting bilayer-GaSe, resulting in an (a) increase (decrease) in the n-type (p-type) Schottky barrier height, as shown in Fig. 7(c–e). Our results show that a transformation from n-type to p-type Schottky contact occurs when the applied positive electric field is larger than 0.0125 V Å$^{-1}$. In contrast, by applying a negative electric field the position of the Fermi level moves from the valence bands to the conduction band of the semiconducting bilayer-GaSe, leading to a (an) decrease (increase) in the n-type (p-type) Schottky barrier height. It also indicates that under a negative electric field, the heterostructure still keeps an n-type Schottky contact. Therefore, an external electric field is also an efficient approach to control the Schottky barrier height and dynamically switching the Schottky contact between n-type and p-type for the graphene-based vdW heterostructures, such as the graphene/bilayer-GaSe heterostructure with the dynamic switching between n-type and p-type Schottky contact. Finally, we would like to discuss some important advantages in this work. First, it should be noted that graphene-based heterostructures by stacking graphene on few-layered GaSe materials, have recently been fabricated experimentally by molecular beam epitaxy. Secondly, compared to other graphene-based Schottky heterostructures, the graphene/bilayer-GaSe heterostructure has many advantages, such as high...
on/off ratio and high carrier mobility of graphene in the heterostructure, making it suitable for application in high speed nanoelectronic and optoelectronic devices. Thirdly, it should be noted that the interlayer distance $d$ in 2D vdW heterostructures can be easily changed in experiments by applying hydrostatic pressure with a scanning tunnelling microscopy tip,\textsuperscript{80} by vacuum thermal annealing,\textsuperscript{81} or by inserting hexagonal BN dielectric layers.\textsuperscript{82} Furthermore, a strong electric field of about 0.3 V Å\textsuperscript{-1} can be applied perpendicularly to the heterostructure by using an electrolyte top gate,\textsuperscript{83} or by the pulsed ac field technology.\textsuperscript{84}

4 Conclusions

In conclusion, by using the DFT-D2 method, we studied the electronic properties and Schottky barrier height modulation of a graphene/bilayer-GaSe heterostructure by changing the interlayer distance and applying an electric field perpendicular to the heterostructure. These results showed that due to the weak vdW interaction the electronic band structure of a graphene/bilayer-GaSe heterostructure is well preserved upon contact. Moreover, we have found that a tiny band gap of about 10 meV can be opened due to the sublattice symmetry breaking. At the equilibrium state with the interlayer distance of 3.40 Å, the heterostructure has an n-type Schottky contact with the Schottky barrier height of 0.72 eV. Furthermore, the electronic properties and Schottky barrier of the heterostructure could be controlled by changing the interlayer spacing and applying an electric field. Our results show that a transformation from n-type to p-type Schottky contact is observed when the interlayer distance is smaller than 3.30 Å, or when the applied positive electric field is larger than 0.0125 V Å\textsuperscript{-1}. This controllability of the types of Schottky contact is very important for designing and fabricating novel electronic Schottky devices based on graphene vdW heterostructures, such as graphene/bilayer-GaSe heterostructures.

Conflicts of interest

There are no conflicts to declare.

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