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Introduction

Since the experimental exfoliation of graphene in 2004,¹ research on two-dimensional (2D) materials, such as transition metal dichalcogenides² (TMDCs) and phosphorene,³ has been one of the leading topics in materials science. The 2D materials possess intriguing physical and chemical properties, showing a great potential for high-performance electronic and optoelectronic applications.⁴⁻⁷ Graphene is considered as a promising candidate for many future technologies for its high carrier mobility of about 20 000 cm V⁻¹ s^{-1.8} However, its applications in electronic and optoelectronic devices are limited by the absence of an electronic band gap for controllable operations.9 The 2D transition metal dichalcogenides (TMDCs) possess desired band gaps, but their carrier mobilities (~200 cm V^{-1} s⁻¹) are relatively low, which cannot meet the future request of the high-performance electronic and optoelectronic devices.9 Phosphorene presents a moderate direct bandgap while still maintaining a high carrier mobility.^{10,11} However, the high chemical reactivity and environ-

TiS₃ sheet based van der Waals heterostructures with a tunable Schottky barrier†

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Monolayer titanium trisulfide (TiS₃), synthesized recently through exfoliation [*Adv. Mater.*, 2015, **27**, 2595], has emerged as a new 2D material with outstanding electronic and optical properties. Here, using firstprinciples calculations we show for the first time the great potential of the TiS₃ monolayer as a channel material when in contact with graphene and other 2D metallic materials to form van der Waals (vdW) heterostructures, where the intrinsic properties of both the TiS₃ monolayer and the 2D materials are preserved, different from the conventional 3D metal/TiS₃ semiconductor heterojunction [*Nanoscale*, 2017, **9**, 2068]. Moreover, the TiS₃ monolayer forms an n-type Schottky barrier (Φ_e) when in contact with graphene, exhibiting a tunneling barrier and a negative band bending at the lateral interface; the Schottky barrier character can also be changed from n-type to p-type by doping graphene with boron atoms or replacing graphene with other high-work-function 2D metals, while a Schottky-barrier-free contact can be realized by doping graphene with nitrogen atoms, thus providing a solution to the contact-resistance problem in 2D electronics.

> mental instability of phosphorene make it difficult to achieve robust device performance without protection layers.¹² Very recently, a new 2D material, titanium trisulfide (TiS_3) sheets, has been successfully isolated from its layered bulk phase.¹³ In contrast to TMDC layered materials, the TiS₃ monolayer presents a robust direct band gap of about 1.0 eV,^{14,15} which varies little with respect to layer thickness or stacking order.^{13,16} Moreover, the TiS₃ monolayer was predicted to have a high in-plane electron mobility which is much higher than that of the H-MoS₂ sheet.^{14,17} In addition, the TiS₃ monolayer possesses strong anisotropies in electrical and optical properties resulting from its quasi-one-dimensional structure, providing a new degree of freedom in the fabrication of next-generation electronic devices such as high mobility transistors.¹⁸ The modest band gap, high carrier mobility, highly anistropic electronic and optical properties, as well as high chemical stability in the open air¹⁷ make the TiS₃ monolayer a promising 2D material for electronic and optoelectronic applications.

> When using a 2D material as the semiconducting channel in an electronic or photoelectronic device, the metal/2D semiconductor junction is a critical component for injecting appropriate types of carriers into the conduction or valence band of the 2D semiconductor.^{19–21} For 2D layered TiS₃, a series of studies have been performed to investigate the interfacial properties of the 3D metal/TiS₃ junctions. In experiments, Au, Ti, and Cr have been used as electrodes in 1D TiS₃ nanoribbon and 2D TiS₃ nanosheet based transistors.^{13,22,23} The Schottky barrier height between the TiS₃ nanosheet and



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Au/Ti contacts was measured with a value of 130 meV for electrons in the fabricated TiS₃ nanosheet transistor.¹³ Theoretically, Chen et al. predicted that the interfacial properties of the TiS₃/3D metal (Au, Ag, Al and Cu) junction cannot be effectively modulated by using different metals.²⁴ In the 2D semiconductor/3D metal heterojunctions, the Fermi level pinning is strong,²⁵ which means that the Fermi level of the composed system varies little when using different 3D metals as the contact. The strong Fermi level pinning hinders the formation of low-resistance metal contacts and masks the intrinsic exceptional electronic properties of the 2D semiconductor. However, previous studies demonstrated that Fermi level pinning can be weakened by using 2D metals to form the heterojunction through van der Waals force, leading to a tunable Schottky barrier height.²⁵ In addition, the absence of dangling bonds in the 2D contact metal can prevent the strong bonding at the junction interface, hence preserving the intrinsic properties of semiconductors.^{25,26} These advantages are very desirable in TiS₃ based transistor applications.

In this work, we systematically study the structural and electronic properties of the vdW heterostructure formed by TiS_3 and graphene (TiS_3/G heterostructure). From the device point of view, we calculate three major parameters for carrier injection efficiency for the TiS_3/G heterostructure including the tunneling barrier, band bending, and Schottky barrier. Moreover, we show that it is possible to tune the position of the Fermi level in the band structure of the vdW heterostructure *via* doping graphene with B or N atoms or *via* replacing graphene with other high-work-function 2D metals, showing flexibilities in tuning Schottky barrier height and the prospect of device applications for the TiS_3 sheet.

Computational methods

Interface modeling

To effectively build heterostructures with a small lattice mismatch between the TiS_3 monolayer and various 2D metals with different symmetries, we use our in-house lattice-match code²⁷ to construct the supercell model. In this code, we implement the Zur–McGill's algorithm for lattice match²⁸ that can render reasonable models with a small lattice mismatch. In this method, we look for the lattice match based on the interface area, because the area of two superlattices with close lattice parameters would also be approximately the same. According to the Zur–McGill scheme,²⁸ we find all superlattices for a given area and select those that match the most given a lattice mismatch threshold and possibly the maximum number of atoms in the heterostructure.

Density functional theory calculations

The density functional theory (DFT) calculations are carried out using the Vienna *Ab initio* Simulation Package (VASP)²⁹ with the projector augmented wave (PAW) method^{30,31} and the Perdew–Burke–Ernzerhof (PBE) functional.³² In some cases (a supercell with less than 100 atoms), we also use the Heyd– Scuseria–Ernzerhof (HSE06) hybrid functional,³³ which is more accurate but computationally expensive, for the high accuracy of electronic structure calculations. The optB88-vdW functional, which gives a reasonable prediction for both the interlayer distance and binding energy,³⁴ is employed to describe the effect of the vdW interactions. The plane-wave cutoff energy for wave function is set to 500 eV for all the calculations. Monkhorst–Pack sampling with a grid density of $2\pi \times 0.02$ Å⁻¹ is used. For structure optimizations, the convergence thresholds are set to 10^{-4} eV and 10^{-3} eV Å⁻¹ for total energy and force component, respectively. The work functions are calculated by subtracting the corresponding electronic levels with respect to the vacuum level in the heterostructures.

Results and discussion

Structure design

Unlike the graphene/h-BN³⁵ or MoS₂/WS₂³⁶ heterostructure, which can be directly stacked together due to the small lattice mismatch between their unit cells, the lattice parameters of TiS₃ and graphene layers are very different from each other (see Table 1). Therefore, special care is needed in the construction of a reasonable interface model with a small lattice mismatch. Using our in-house code,²⁷ we set the mismatch of the two superlattices to be less than 2% to ensure that the lattice strain is negligible. In this method, we set the total number of atoms in the system less than 200. We found that the way to match TiS₃ and graphene layers is not unique, where there are seven possible models that meet the requirements set in the code. Table 1 lists the lattice parameters of the TiS₃ (u_1 , v_1 , and γ_1) supercells and graphene supercells $(u_2, v_2, \text{ and } \gamma_2)$ for different cases. One can see that u_1 , v_1 , and γ_1 are, respectively, very close to u_2 , v_2 , and γ_2 , therefore the two supercells can be stacked together with a minor lattice mismatch.

We choose Case 1 as the candidate, because it contains the minimum atoms so that the complex system can be easily dealt with in calculations. From Table 1, one can see that the heterojunction can be modeled by using different supercells. One may wonder how sensitive the calculated results are to the stacking orientation. Thus, we have also carried out additional calculations for Case 2 following the same procedure as Case 1. The main results are found to be consistent with each other, which confirms that our heterostructure model is reliable. Details can be found in the ESI (see Table S1 and Fig. S1[†]). Because the electronic properties of TiS₃ are very sensitive to different strain conditions,³⁷ to compensate the lattice mismatch between the TiS₃ monolayer and graphene sheet, we choose to keep the TiS₃ lattice fixed, and respectively compress and stretch the graphene lattice slightly along the x and ydirections. This strategy was also adopted in the previous study for the phosphorene/graphene heterostructure.²⁶ In addition, five different stacking patterns, denoted as S1, S2, S3, S4 and S5, of TiS_3 and graphene layers are considered (see Fig. S2[†]). As shown in Table S2,[†] the S5 structure is slightly more stable than the other configurations. Hence, in the

Table 1 Lattice parameters of the TiS₃ and graphene supercells. u_i , v_i , and γ_i represent the lattice constants (in Å) and the angle between the vectors (in degree) of the supercell, respectively. $u_{1,2}$ ($v_{1,2}$ or $\gamma_{1,2}$) and N represent the lattice mismatch between u_1 and u_2 and the total number of atoms of the heterostructure

TiS ₃ $a = 4.99 \text{ Å}, b = 3.39 \text{ Å}, \alpha = 90^{\circ}$			Graphene $a = b = 2.46$ Å, $\alpha = 120^{\circ}$						
						Mismatch (%)			
$\overline{u_1}$	ν_1	γ1	u_2	ν_2	γ_2	u_{1_2}	v_{1_2}	γ _{1_2}	Ν
4.99	16.93	90.00	4.92	17.04	90.00	1.34	0.64	0.00	72
9.97	17.65	73.59	9.84	17.74	73.90	1.33	0.49	0.42	144
8.41	22.39	80.63	8.52	22.55	79.11	1.32	0.72	1.89	160
4.99	40.64	90.00	4.92	40.50	88.26	1.34	0.36	1.93	172
10.53	19.65	78.26	10.72	19.53	77.48	1.80	0.65	1.00	174
4.99	44.03	90.00	4.92	44.76	88.43	1.34	1.65	1.75	188
8.41	26.17	86.03	8.52	25.92	85.29	1.32	0.94	0.87	188
	$ \begin{array}{r} a = 4.99 \text{ Å} \\ \overline{u_1} \\ 4.99 \\ 9.97 \\ 8.41 \\ 4.99 \\ 10.53 \\ 4.99 \\ 8.41 \\ \end{array} $	$\begin{array}{c c} a = 4.99 \text{ Å}, b = 3.39 \text{ Å}, \alpha = 1000 \text{ Å}, \alpha = 10000 \text{ Å}, \alpha = 10000 \text{ Å}, \alpha = 10000000000000000000000000000000000$	$\begin{array}{c c} a=4.99\ \text{\AA},\ b=3.39\ \text{\AA},\ \alpha=90^{\circ}\\ \hline u_1 & \nu_1 & \gamma_1\\ \hline 4.99 & 16.93 & 90.00\\ 9.97 & 17.65 & 73.59\\ 8.41 & 22.39 & 80.63\\ 4.99 & 40.64 & 90.00\\ 10.53 & 19.65 & 78.26\\ 4.99 & 44.03 & 90.00\\ 8.41 & 26.17 & 86.03\\ \hline \end{array}$	$\begin{array}{c c} a=4.99\ \text{\AA},\ b=3.39\ \text{\AA},\ \alpha=90^{\circ} & a=b=2.4\\ \hline u_1 & v_1 & \gamma_1 & u_2\\ \hline 4.99 & 16.93 & 90.00 & 4.92\\ 9.97 & 17.65 & 73.59 & 9.84\\ 8.41 & 22.39 & 80.63 & 8.52\\ 4.99 & 40.64 & 90.00 & 4.92\\ 10.53 & 19.65 & 78.26 & 10.72\\ 4.99 & 44.03 & 90.00 & 4.92\\ 8.41 & 26.17 & 86.03 & 8.52\\ \hline \end{array}$	$ \begin{array}{c c} a=4.99\ \text{\AA},\ b=3.39\ \text{\AA},\ \alpha=90^{\circ} & a=b=2.46\ \text{\AA},\ \alpha=120^{\circ} \\ \hline u_1 & \nu_1 & \gamma_1 & u_2 & \nu_2 \\ \hline 4.99 & 16.93 & 90.00 & 4.92 & 17.04 \\ 9.97 & 17.65 & 73.59 & 9.84 & 17.74 \\ 8.41 & 22.39 & 80.63 & 8.52 & 22.55 \\ 4.99 & 40.64 & 90.00 & 4.92 & 40.50 \\ 10.53 & 19.65 & 78.26 & 10.72 & 19.53 \\ 4.99 & 44.03 & 90.00 & 4.92 & 44.76 \\ 8.41 & 26.17 & 86.03 & 8.52 & 25.92 \\ \hline \end{array} $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

following we mainly consider the S5 structure. The geometric configuration of the S5 structure is displayed in Fig. 1a.

Given the equilibrium position of the TiS_3 sheet with respect to the graphene layer, we calculate the binding energy of the TiS_3/G heterojunction as a function of the interlayer distance (see Fig. 1b), which is defined as:

$$E_{\rm b} = [E_{\rm TiS_3/G} - (E_{\rm TiS_3} + E_{\rm G})]/N, \tag{1}$$

where $E_{\text{TiS}_3/\text{G}}$ is the total energy of the TiS₃/G heterostructure, E_{TiS_3} is the total energy of the isolated TiS₃ layer, E_{G} is the total energy of the isolated graphene layer, and *N* is the number of carbon atoms in the unit cell of the heterostructure. The calculated binding energy is 58 meV with an equilibrium distance of 3.39 Å. The binding energy is very close to the values of some typical van der Waals crystal, such as graphite ($E_{\text{b}} =$ 61 meV)²⁶ and bulk hexagonal boron nitride ($E_{\text{b}} =$ 65 meV).³⁴

Electronic structure

The band structures of the TiS₃/G heterostructure projected on TiS₃ and graphene (at the GGA-PBE level) are displayed in Fig. 2a and b, respectively (see Fig. S3[†] for the band structures aligned with respect to the vacuum level). The high-symmetry q-point path in the first Brillouin for the band structure calculation is displayed in Fig. S4.† For comparison, the band structures of the isolated TiS₃ and graphene sheets are plotted in Fig. S5.[†] We find that the electronic structures of both TiS₃ and graphene are well preserved in the heterostructure. However, a band gap of 4.6 meV is opened for graphene in the TiS₃/G heterostructure. The existence of a small band gap of graphene results from the breaking of the structural symmetry and the asymmetric potential normal to the layers.³⁸ Compared with the band gap (0.25 eV at the GGA-PBE level) of the isolated TiS_3 layer, the band gap (0.24 eV at the GGA-PBE level) of the TiS_3 layer in the TiS_3/G heterostructure is nearly unchanged. As we can see in Fig. 2b, the conduction band minimum (CBM) of the TiS₃ layer is located below the Fermi



Fig. 1 (a) Top view of the TiS₃/G heterostructure. (b) Binding energy as a function of the interlayer distance between the TiS₃ layer and the graphene sheet. The inset image is the graphic illustration of the interlayer distance. The cyan, yellow, and brown spheres represent Ti, S, and C atoms, respectively.



Fig. 2 Electronic band structure of the TiS_3 /graphene heterostructure projected on (a) the TiS_3 layer, and (b) the graphene sheet. (c) Charge density distributions for the VBM and CBM of the TiS_3 layer, and all of the electronic states between the VBM and CBM. The results are calculated by using the GGA–PBE functional.

level, showing a Schottky-barrier-free contact for electrons, indicating a spontaneous electron transfer from TiS_3 to graphene.³⁹ However, due to the underestimation of the band gap by using the GGA-PBE functional, one may wonder if the results predicted "a fake Schottky-barrier-free contact". Thus, we further examine the Schottky barrier of the TiS_3/G heterostructure by using the HSE06 functional in the Contact Evaluations part of this work.

To investigate the origin of the electronic states of the valence band maximum (VBM) and the conduction band minimum (CBM) energy interval, we calculate the charge density distributions of the VBM, CBM, and the states between the VBM and CBM in the heterostructure. As shown in Fig. 2c, we find that the metal-induced gap states, i.e. the states contributed by the TiS₃ layer between the VBM and CBM are negligible. This feature is in contrast to the metal-semiconductor junction (MSJ) constructed by the conventional 3D metal and TiS₃ layer, where the metal-induced gap states are significant.²⁴ The suppression of metal-induced gap states in the TiS₃/G heterostructure is attributed to the vdW interaction between the 2D metal and the 2D semiconductor, which is much weaker than the chemical bonding in the conventional 3D metal contact.²⁵ These results imply that graphene can be a promising candidate as a sandwiched layer between the TiS₃ layer and metal electrode to enhance the contact performance while still maintaining the electronic properties of the TiS₃

layer.³⁸ Also, graphene can serve as a capping or supporting layer³⁸ for encapsulating the TiS_3 layer.

Contact evaluations

We then evaluate the carrier injection efficiency of the TiS₃/G heterostructure by analyzing the three major criteria in the composed system, including the tunneling barrier, band bending, and Schottky barrier. The tunneling barrier is characterized by its width (w_B) and height (ΔV), and is formed when electrons cross the vdW gap at the interface, and measured by the electrostatic potential.¹⁹ As shown in Fig. 3, there is an obvious tunneling barrier at the TiS₃/graphene interface with a barrier height of 2.34 eV. Here, we use a square potential barrier to replace the real potential barrier and evaluate the tunneling probability T_B by using the WKB formula^{19,40}

$$T_{\rm B} = \exp \left(-2 rac{\sqrt{2m\Delta V}}{\hbar} imes W_{\rm B}
ight)$$

where *m* and \hbar are the free electron mass and Planck's constant, respectively. The calculated tunneling probability $T_{\rm B}$ of the TiS₃/G heterostructure is 15.7%. We note that the ΔV of TiS₃/G (2.34 eV) is larger than that of the TiS₃/3D metal heterostructures,²⁴ such as TiS₃/Au (2.15 eV), TiS₃/Ag (1.67 eV), and TiS₃/Al (1.55 eV). Generally, a small physical separation at the



Fig. 3 Average electrostatic potential in the plane normal to the interface of the TiS_3/G heterostructure. The green rectangular box indicates the tunneling barrier.

interface may lead to a small ΔV .⁴¹ The interlayer distance of TiS₃/G (3.39 Å) is larger than that of TiS₃/3D metal heterostructures (1.75–2.78 Å). In addition, the metallization of the TiS₃ sheet stemming from the strong bonding with 3D metal surfaces can also decrease the ΔV , which is absent in the TiS₃/G heterostructure. From these two factors, it is easy to understand why the value of ΔV is larger in the TiS₃/G heterostructure, as compared to that in the $TiS_3/3D$ metal junctions.²⁴ The existence of the tunneling barrier in the TiS_3/G heterostructure makes it a type-1 contact, similar to the cases of Au- and In-TMD contacts.⁴¹

Next we discuss the Schottky barrier in the TiS_3/G heterostructure, which is one of the most important factors that determines the contact resistance of the MSJ.⁴² The Schottky barrier height is defined by the energy difference between the Fermi level and the band edge of the semiconductor in MSJ:

$$\Phi_{\rm e} = E_{\rm CBM} - E_{\rm F}, \quad \Phi_{\rm h} = E_{\rm F} - E_{\rm VBM},$$

where $\Phi_{\rm e}$ and $\Phi_{\rm h}$ are the Schottky barrier heights for electrons and holes, respectively; $E_{\rm F}$ is the Fermi energy of the stacked system; $E_{\rm CBM}$ and $E_{\rm VBM}$ denote the CBM and the VBM of the semiconductor, respectively. To obtain the Schottky barrier heights of the TiS₃/G heterostructure, we calculate its projected band structure by using both GGA-PBE and HSE06 functionals, respectively. As shown in Fig. 4a, we obtain a negative $\Phi_{\rm e}$ (-0.01 eV) at the GGA-PBE method. However, the $\Phi_{\rm e}$ increases to 0.22 eV by using the HSE06 functional. This difference comes from the well-known underestimated band gap by using the GGA-PBE functional. Because the Fermi level is close to the CBM of TiS₃, the TiS₃/G heterostructure possesses an n-type Schottky barrier. Thus, the conduction will be through electrons in the TiS₃/G heterostructure.

Even without any charge transfer between the TiS_3 layer and graphene sheet, if we consider a current-in-plane device, there will be a small band bending as charge carriers move



Fig. 4 Schematic depictions of the Schottky barrier heights and band edges of the TiS_3/G heterostructure calculated at the (a)–(b) GGA–PBE level and the (c)–(d) HSE06 level, respectively.

from the stacked region to the pristine TiS_3 . If we ignore the coupling between the stacked system and the non-contacted TiS_3 ,⁴³ the band bending can be estimated by the energy difference between the Fermi levels of the TiS_3/G heterostructure and the free-standing TiS_3 layer:

$$\Delta E_{\rm F} = W_{\rm H} - W_{\rm TiS_3}$$

where $W_{\rm H}$ is the workfunction of the heterostructure and $W_{\rm TiS_3}$ is the workfunction of the pristine TiS₃ layer. As shown in Fig. 4b and d, we estimate that the band bending is -0.38 eV and -0.54 eV at the GGA-PBE and HSE06 level, respectively. As $\Delta E_{\rm F} < 0$, electrons move from the contacted region to the pristine TiS₃ layer, making the channel n-type. From the device point of view, the smaller the band bending, the better the contact. The band bending in the TiS₃/G heterostructure is comparable to that of some metal/phosphorene (TMDs) contacts, ^{41,44} which shows the potential of the TiS₃/G heterostructure for nanoscale electronic devices.

Schottky barrier height modulation

For device applications, it is better to get a small Schottky barrier height (Φ_e or Φ_h) to reduce the contact resistance. A Schottky-barrier-free contact can be achieved when the Schottky barrier height becomes zero or negative, making a spontaneous carrier injection from the stacked system to the TiS₃ channel. For a defect-free MSJ, neglecting the interaction between the semiconductor and the metal, the Schottky barrier height follows the Schottky–Mott model:

$$\Phi_{\mathrm{e}} = E_{\mathrm{CBM}}^0 + W, \quad \Phi_{\mathrm{h}} = -W - E_{\mathrm{VBM}}^0,$$

where E_{CBM}^0 and E_{VBM}^0 are the CBM and VBM energies of the semiconductor in the vacuum. *W* is the work function of the metal electrode. These two equations provide a general guidance for tuning the Schottky barrier height by using a contact metal with different work functions. It has been reported that the Schottky barrier heights of the van der Waals heterostructures can be tuned by applying a perpendicular external electric field.^{26,45,46} Here, we propose two different approaches to tune the Schottky barrier heights of the TiS₃ based van der Waals heterostructure *via* doping or changing the 2D contact metal.

We first show that the Schottky barrier heights of the TiS_3/G heterostructure can be tuned *via* doping boron or nitrogen atoms into graphene. If we ignore the band structure rearrangements, the Fermi level of graphene can be modified by changing the total number of electrons in the system. Thus, by increasing or decreasing electrons in graphene, the work function of graphene can be changed accordingly. Because boron has one less electron than carbon, B doping can increase the work function of graphene. On the contrary, nitrogen is right next to carbon, thus N doping can provide additional electrons, leading to a smaller work function of graphene.

In this study, we examine B (N) doped graphene at the doping concentrations of 1/32 and 1/16 by substituting carbon atoms with 1 and 2 boron (nitrogen) atoms (structures

can be seen in Fig. S6[†]). The Schottky barrier heights of the heterostructure formed by TiS₃ and B (N) doped graphene are evaluated by using the HSE06 functional (see Fig. 5). The results calculated by the PBE-GGA functional are also displayed in the ESI for comparison (see Fig. S7[†]). According to the results calculated at the HSE06 level, the Schottky barrier is changed from n-type to p-type with the increase of the doping concentration for B doping (see Fig. 5b and c). At the B doping concentration of 1/32, the Schottky barrier remains to be n-type with the Φ_e of 0.46 eV. The Schottky barrier becomes p-type at the B doping concentration of 1/16 with the $\Phi_{\rm h}$ of 0.23 eV. Interestingly, $\Phi_{\rm e}$ is negative for N doping at both doping concentrations of 1/32 and 1/16 (see Fig. 5d and e) with a value of -0.09 and -0.14 eV, respectively, indicating that electrons can spontaneously inject into the TiS₃ layer. From Table S3,[†] we can see that although the Schottky barrier heights calculated by using the GGA-PBE and HSE06 functionals are different, the two functionals predict the same variation tendency of the Schottky barrier height for the B (N) doped systems, implying that the PBE-GGA functional is acceptable to investigate the variation tendency of the Schottky barrier height.

Next, we show another approach to tune the Schottky barrier heights of the TiS3 based van der Waals heterostructures by using different 2D metals as the electrode. We consider the triangular (T) phase of MoX_2 and WX_2 (X = S or Se). The motivation is that these 2D materials have larger work function than graphene,²⁵ hence electrode replacement may change the Schottky barrier character of the TiS₃ based heterostructure from *n*-type to p-type. Because of the limitation of the computation resources and the large number of atoms in the heterostructures, e.g. 162 atoms for the TiS₃/T-MoSe₂ heterostructure, we here just carry out calculations using the PBE-GGA functional. The lattice parameters, geometry configurations, and the electronic band structure projected on the TiS₃ layer are displayed in the ESI (see Table S4 and Fig. S8-S11[†]). Fig. 5f and g show the variation of the Schottky barrier heights of the 2D TiS₃ layer on top of various 2D contact metals. As expected, we find that the Fermi level of the heterostructure shifts down gradually with increasing work function of the contact metal, thus leading to a change of the Schottky barrier character from n-type to p-type. Interestingly, it is worth noting that the Fermi level of the heterostructure is above the CBM (a negative $\Phi_{\rm e}$) and below the VBM (a negative $\Phi_{\rm h}$) of TiS₃ when using T-WSe₂ and T-MoS₂, respectively, showing the possibility to achieve Schottky-barrier-free contact by using 2D metals with low/high work function. Note that the $\Phi_{\rm e}$ may be underestimated by using the GGA-PBE functional for its known deficiency to underestimate the band gap as mentioned before. Compared to the ideal conditions of the Schottky-Mott model where $\Phi_{\rm e}$ (or $\Phi_{\rm h}$) is linearly dependent on the work function of the contact metals with a slope of 1,⁴⁷ the TiS₃ based vdW MSJs possess a smaller slope of 0.6, indicating a Fermi level pinning attributed to the interface dipole induced by the charge density redistribution.⁴⁸ This charge density redistribution can also be found in the TiS₃/G heterostructure as dis-



Fig. 5 Schematic depictions of the Schottky barrier heights calculated by the HSE06 functional of the van der Waals heterostructure constructed by the TiS₃ layer making contact with (a) pristine, (b) 1/32 B-doped, (c) 1/16 B-doped, (d) 1/32 N-doped, and (e) 1/16 N-doped graphene. Schottky barrier heights calculated by the PBE functional for (f) electrons and (g) holes for the heterostructures formed by the TiS₃ layer and various 2D contact metals (T-WSe₂, T-MoSe₂, T-WS₂, and T-MoS₂).

played in Fig. S12.[†] However, the Fermi level pinning of the TiS_3 based van der Waals heterostructures is much weaker than the conventional 3D metal/ TiS_3 heterostructures²⁴ due to the chemical bonding between the TiS_3 layer and the contact 3D metals, making it possible to tune the Schottky barrier heights of the TiS_3 based van der Waals heterostructure in a much wider range by using different 2D metals.

Conclusions

In summary, on the basis of first-principles calculations, we have studied the interfacial properties of the MSJs composed of the TiS₃ monolayer and graphene or other 2D metals including T-MoS₂, T-MoSe₂, T-WS₂, and T-WSe₂. We show that both the properties of TiS₃ and graphene layers are preserved in the TiS₃/G heterostructure due to the vdW interactions

between the metal and semiconductor, which is weaker than the chemical bonding in the conventional 3D metal/semiconductor junction. In addition, a negative value of band bending appears at the lateral interface of the current-in-plane system for the TiS₃/G heterostructure, implying that electrons move from the stacked system to the TiS₃ monolayer channel. Moreover, compared to the conventional 3D metal/TiS₃ junctions,²⁴ the contact properties of the TiS₃ based vdW heterostructure can be effectively tuned by using different 2D metals. We find that an n-type Schottky barrier height (Φ_e) is formed between the TiS₃ monolayer and graphene, and the Schottky barrier character can be changed from n-type to p-type by doping graphene with boron atoms or replacing graphene with other high-work-function 2D metals, while a Schottky-barrierfree contact can be achieved by doping graphene with nitrogen atoms. This work not only provides insight into the fundamental properties of the TiS₃ based vdW heterostructure, but also

uncovers the great potential of 2D layered $\mathrm{Ti}\mathrm{S}_3$ for device applications.

Conflicts of interest

There are no conflicts of interest to declare.

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