2D Materials

PAPER

Band alignment of two-dimensional lateral heterostructures

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Abstract

Recent experimental synthesis of two-dimensional (2D) heterostructures opens a door to new opportunities in tailoring the electronic properties for novel 2D devices. Here, we show that a wide range of lateral 2D heterostructures could have a prominent advantage over the traditional three-dimensional (3D) heterostructures, because their band alignments are insensitive to the interfacial conditions. They should be at the Schottky–Mott limits for semiconductor–metal junctions and at the Anderson limits for semiconductor junctions, respectively. This fundamental difference from the 3D heterostructures is rooted in the fact that, in the asymptotic limit of large distance, the effect of the interfacial dipole vanishes for 2D systems. Due to the slow decay of the dipole field and the dependence on the vacuum thickness, however, studies based on first-principles calculations often failed to reach such a conclusion. Taking graphene/hexagonal-BN and MoS2/WS2 lateral heterostructures as the respective prototypes, we show that the converged junction width can be order of magnitude longer than that for 3D junctions. The present results provide vital guidance to high-quality transport devices wherever a lateral 2D heterostructure is involved.

1. Introduction

Two-dimensional (2D) materials are attractive for their unique physical properties. Graphene [1], hexagonal BN (h-BN) [2], MoS2 and WS2 [3, 4], are just some of the well-known examples. To combine the advantages of two different 2D materials, electronic or optoelectronic devices made up of stacked or in-plane heterostructures have been widely exploited [5]. A variety of vertical or lateral heterostructures formed by graphene, h-BN, phosphorene, and transition metal dichalcogenides, have been successfully fabricated [6–9].

Concerning lateral heterostructures, Gi et al [10] first synthesized large-scale monolayer h-BN sheets made of h-BN and graphene domains. Levendof et al [11] developed a ‘patterned regrowth’, which allows for a spatially controlled synthesis of graphene/h-BN (G/BN) heterostructures. Other groups [12–22] have fabricated G/BN heterostructures on Ru, Rh, Cu, Ni, Au, Ir, SiC, and SiO2 substrates. Prototypical 2D devices, such as integrated circuit [11], field-effect transistor [14, 17], and closed-loop resonator [17], have been demonstrated. New physical properties, including tunable band gap [23], robust half-metallicity [24], and unique thermal transport properties [25], have been predicted theoretically.

Another example of 2D lateral heterostructures is the MoS2/WS2 semiconductor heterostructures [26–30]. In particular, MoS2/WS2 [27] and MoSe2/WSe2 [29] heterostructures with an atomically abrupt interface along armchair (AC) or zigzag (ZZ) directions have been synthesized. Interesting physical properties for device applications, such as the rectification and photovoltaic effects, have been demonstrated experimentally [26, 27, 29].

Concerning vertical heterostructures, an entire class of them are made of by placing one atomically thin 2D material (A) on top of another atomically thin 2D material (B) [31–35], see figure 1(a) for a schematic plot. Due to the thinness of the stacked region, a classical division of the material into a vertical junction between A and B may not be meaningful. Rather, the stacked region should be treated as a new quantum
system AB as a whole. Thus, such a vertical heterostructure is not different from having two lateral junctions in series between A and AB and between AB and B. A special case of the stacked heterostructure would be A on A, which makes a lateral 2D junction between A and AA (see figure 1(b)), as recently demonstrated experimentally for MoS$_2$ [36] and MoSe$_2$ [37]. Even within a single-phase 2D material, one may effectively set up a lateral junction if one part of the material has been heavily doped, alloyed, or merely being placed near a dielectric media.

While paving the way for novel electronics, the experimental successes call for a fundamental understanding of the electronic properties of these 2D in-plane metal/semiconductor (M/S) and semiconductor/semiconductor (S/S) heterostructures. The most important parameter that determines the transport across the interface is [38, 39], in the case of M/S, the Schottky barrier height (SBH), which is the mismatch between the band edges of the semiconductor and the Fermi level of the metal, or the band offset in the case of S/S, which is the mismatch between the band edges of the two semiconductors. Although the SBHs and band offsets for three-dimensional (3D) heterostructures have been studied extensively in the past, it is unclear whether the traditional wisdom in 3D systems is still applicable to 2D heterostructures. For example, the interfacial dipole is known to play a crucial role in determining the SBHs and band offsets for the 3D M/S and M/M heterostructures, respectively [39, 40]; in 2D heterostructures, on the other hand, a classical electrostatic consideration suggests that the dipole potential should vanish, instead.

In this paper, we address the fundamental difference between 2D and 3D junctions by first-principles calculations and show that the results do approach the limits set by the electrostatic dipole-line model. In other words, due to the decay of interfacial dipole potential in the asymptotic limit of large distance, band alignments for 2D lateral junctions with sufficient width are insensitive to interfacial conditions. Rather, they are determined purely by intrinsic properties of the component materials, namely, the universal Schottky–Mott limits for M/S interfaces and Anderson limits for S/S interfaces, respectively. This is in stark contrast to 3D heterostructures where such limits rarely apply. When the size of a 2D heterostructure is smaller than a characteristic width W (in the order of 10 nm), strictly speaking, the band alignment is ill-defined. In this case, the SBHs, band offsets, or even the band gap can be altered by changing the system size and interfacial conditions.

2. Results and discussion

2.1. Graphene/h-BN heterostructure

Inset in figure 2(a) shows the supercell of the G/BN heterostructure. Following our recent study [41], eight G/BN interfaces with different misorientation angles are considered. While the y direction is periodic, supercell dimensions of roughly L = 4 nm in the x (junction) direction and H = 1.5 nm in the z (vacuum) direction are initially used to compute the SBHs. Later, these dimensions will be increased to obtain more converged results. The stability of these G/BN heterostructures has been assessed by ab initio molecular dynamics simulations. As shown in figure S1 of supporting information (SI), the heterostructures with AC and ZZ (with Clar’s reconstruction [41]) interfaces are stable at room temperature.

To obtain band alignment, one needs the average electric potential energy difference across the interface
(eV\text{int}), as a result of interfacial charge transfer from one side of the junction to the other. In the supercell approach, the SBH ($\phi_p$) for p-type G/BN is given by [40]:

$$\phi_p = I_S^{\text{bulk}} - \Phi_M^{\text{bulk}} + eV\text{int},$$

(1)

where $I_S^{\text{bulk}}$ is the ionization potential of h-BN, $\Phi_M^{\text{bulk}}$ is the work function of graphene [42]. Alternatively, one may compute $\phi_p$ by locating the respective band edges of the component materials in the local density of states (LDOS) of the supercell in figure 2(a):

$$\phi_p = E_F - E_V^{\text{int}},$$

(2)

where $E_F$ is the Fermi level of the system, $E_V^{\text{int}}$ is the valence band maximum (VBM) at the center of the h-BN region. Equating equations (1) with (2), we obtain

$$eV\text{int} = (E_F - E_V^{\text{int}}) - (I_S^{\text{bulk}} - \Phi_M^{\text{bulk}}).$$

(3)

When $eV\text{int} = 0$, $\phi_p$ follows the Schottky–Mott limit [43, 44], which can be calculated independently by placing graphene and h-BN in parallel in a common supercell, as illustrated in the inset in figure 2(b). To ensure better convergence, a large vacuum space with $H = 4.5$ nm is used here. By examining the LDOS in figure 2(b), we determine the Schottky–Mott limit to be $\phi_p = 1.69$ eV.

Even at a smaller $H = 1.5$ nm, one sees a systematic trend in $\phi_p$. For example, table 1 summaries $\phi_p$ for eight p-type G/BN junctions, where the calculated SBHs fall within a narrow range, $\phi_p = 2.10 \pm 0.08$ eV. In contrast, SBH for 3D junctions depends sensitively on the details of the interfacial structure [39, 45–47].

One can understand this sensitivity by examining the electrostatic models in figure 3. On the interface, the 2D dipole charge distribution of a 3D junction and the quasi-one-dimensional (1D) inhomogeneous dipole charge distribution of a 2D junction may be approximately replaced by uniform planar and linear paired charge distributions, respectively. For the 3D junction, local charge transfer at the interface leads to formation of a 2D capacitor (figure 3(a)) and the amount of the transferred charge determines $eV\text{int}$ [39, 40]. Due to the strong screening of the 3D materials, the characteristic width of the junction, $W$, is usually small, often within a couple unit cells (on the order of 1 nm) [48–51]. For the 2D case, however, the capacitor is reduced to a 1D dipole line as schematically shown in figure 3(b), where the field lines are no longer confined to a narrow region at the interface, but leaking into the vacuum that has poor screening effect.

| Misorientation angle (°) | 0 (\text{AC}) | 9.4 | 13.2 | 21.8 | 32.2 | 38.2 | 42.1 | 60 (\text{ZZ}) |
|-------------------------|-------------|-----|------|------|------|------|------|-------------|
| $L$ (nm)                |
| 3.94                    | 3.89        | 4.24 | 3.90 | 4.05 | 3.94 | 3.78 | 3.84        |
| $\phi_p$ (eV) ($H = 1.5$ nm) |
| 2.18                    | 2.07        | 2.05 | 2.05 | 2.05 | 2.02 | 2.05 | 2.18        |
This implies that $W$ for a 2D junction will be considerably longer than that for 3D, as we will demonstrate latter.

For the 2D system, one can derive analytically the asymptotic limit for $eV_{\text{int}}$ (see SI, details of the dipole line model). In particular, at a distance $\pm x$ away from the interface, the potential energy difference satisfies

$$eV_{\text{int}}(x) = 4k\lambda \ln \left(1 + \frac{4d_{\text{MS}}}{2x - d_{\text{MS}}} \right),$$

where $k = 1/(4\pi\epsilon_0)$, $\lambda$ is the line-averaged charge density, and $d_{\text{MS}}$ is an effective distance between charged lines. Since $eV_{\text{int}}(x \to \infty) \to 0$, this model suggests that the SBH should approach the Schottky–Mott limit [43, 44].

Care has to be taken, however, in the supercell calculation due to the presence of periodic image charges as schematically shown in figure 4(a). The details of the dipole line model by considering the periodic image charges due to supercell approach are described in SI, in which we show that equation (4) should be replaced by

$$eV_{\text{int}}(L, H) \approx \frac{8k\lambda \pi}{L/d_{\text{MS}}} - \Delta_{\text{HL}}(L, H),$$

where $L$ and $H$ are the supercell lengths in the $x$ and $z$ directions, respectively. Figure 4(b) shows that $eV_{\text{int}}$ in the supercell approximation depends on not only $L$ but also $H$. When they are both sufficiently large, $eV_{\text{int}}$ always vanishes, so $\phi_0$ approaches the Schottky–Mott limit (see equation (1)).

One may test equation (5) by performing a set of DFT calculations at different $L$ and $H$. For example, figure 5(a) shows $eV_{\text{int}}(H) = eV_{\text{int}}(L_0, H)$ at fixed $L_0 = 9.84$ nm for AC interface and $8.52$ nm for ZZ interface, respectively. Figures 5(b) and (c), show, on the other hand, $eV_{\text{int}}(L) = eV_{\text{int}}(L, H_0)$ for fixed $H_0 = 4.5$ nm. In all cases, a monotonic decrease is observed. In these plots, the results from the dipole line model in equation (5) are also given for comparison. It is clear that the dipole line model reproduces the DFT results reasonably well except for small $L$, at which the model no longer holds due possibly to length-dependent interference of the wave function of graphene [53] and to the deviation of the realistic
charge transfer from the simplified uniform dipole line. Similar length-dependent decay behavior was found in 1D heterojunction formed by a semiconducting carbon nanotube and metal contact [54]. A slow decay of $eV_{int}$ can be misorientation-angle dependent. For example, $eV_{int}(L)$ decays more rapidly for the AC case than for the ZZ case. This might be attributed to a larger interfacial charge transfer in the former than the latter (1.314 electrons nm$^{-1}$ for AC and 1.205 electrons nm$^{-1}$ for ZZ on the G/BN interface, respectively, from Bader analysis of the DFT results). In principle, a misorientated interface can be seen as a collection of small segments of the AC and ZZ interfaces with their relative portions determined by the misorientation angle. As such, the interfacial charge transfer on a misorientated interface may be approximated by a linear combination of the amounts of charge transfers at the AC and ZZ interfaces. Known the interfacial charge transfer, one can use equation (4) to estimate $W$, which is distance to the interface in the $x$ direction when $eV_{int}(L)$ falls within a predetermined small value $\varepsilon$. Figure 6(a) gives the results for $\varepsilon = 0.05$ eV, showing a ratio between $W$ for ZZ and $W$ for AC to be $11/14 = 0.786$ and an anisotropic dependence of $W$ on the misorientation angle.

Figure 5. Interfacial energy change $eV_{int}$ versus supercell sizes for (a)–(c) G/BN and (d)–(f) MoS$_2$/WS$_2$. In (a) $L = 8.52$ nm for ZZ and 9.84 nm for AC; in (d) $L = 11.54$ nm for ZZ and 6.38 nm for AC; and in (b), (c), (e) and (f), $H = 4.5$ nm. Dashed lines in (b) and (c) are the dipole model results for G/BN with $\lambda = 0.19$ electrons nm$^{-1}$ for AC and 0.11 electrons nm$^{-1}$ for ZZ, and $d_{MS} = 0.05$ nm, whereas those in (e) and (f) are the corresponding results for MoS$_2$/WS$_2$ with $\sigma = 0.18$ electrons nm$^{-2}$, $d_{MS} = 0.1$ nm, and $h = 0.7$ nm. The details of model and definition of the parameters can be found in SI.

Figure 6. Junction width $W$ (for $\varepsilon = 0.05$ eV) calculated using equation (1), as a function of misorientation angle $\theta$ for (a) G/BN and (b) MoS$_2$/WS$_2$, respectively. The parameters $\lambda$ and $d_{MS}$ come from fitting of the DFT supercell calculations in figure 5.
a question: what happens if sample dimension $D$ is smaller than $W$? In such case, strictly speaking, band alignment is no longer a uniquely defined quantity, thus SBHs and band offsets should show great sensitivity to sample size and interfacial structure, as well as to interfacial chemistry.

### 2.2. MoS$_2$/WS$_2$ heterostructures

Note that the existence of an interfacial dipole potential is not a property of the metal–semiconductor interfaces alone, but a general behavior of all lateral heterojunctions. Hence, equation (5) should also apply to 2D lateral S/S heterostructures where the band offsets are the key parameters for carrier transport. As a demonstration, we consider lateral MoS$_2$/WS$_2$ heterostructures with AC and ZZ interfaces. By analogy, one can expect that the band offsets for a S/S junction follow the Anderson limit [55] also, which is 0.25 eV for MoS$_2$/WS$_2$ according to our PBE calculation.

Figures 5(d) and (f) show the asymptotic behaviors of $eV_{\text{int}}(L, H)$. In contrast to G/BN, however, here the convergence is noticeably slower especially for $H$. This can be attributed to the fact that both MoS$_2$ and WS$_2$ have three atomic layers, rather than a single layer as G/BN. To take this finite thickness into account, equation (5) is modified to include a ribbon of thickness $h$ (see the schematic in figure 4(c)). Detailed derivation is given in SI. The model results are given in figures 5(e) and (f), showing good agreement with the DFT results. Note that at $L = 13$ nm, $eV_{\text{int}}(L) > 0.05$ eV. To reach $\varepsilon = 0.05$ eV, the dipole model predicts $L = 21$ nm, which would be too large for current DFT calculations. On the other hand, this choice for $\varepsilon$ is arbitrary and as such it should not alter the qualitative picture that the Anderson limit is the correct limit for lateral MoS$_2$/WS$_2$ heterostructures. Also, lateral MoS$_2$/WS$_2$ junction can be noticeably different for lateral G/BN junction in that the orientation anisotropy in W is much smaller (see figure 6(b)).

Therefore, in the design of 2D devices using lateral M/S or S/S heterostructures, one can directly use the intrinsic electronic band parameters of each component material without conducting a supercell calculation of the junction [56], as long as the sample size is large enough. At present, experimentally realized samples for h-BN, graphene, MoS$_2$, and WS$_2$ typically have a domain size of hundreds to thousands nanometers [14, 17, 19, 26–28], much larger than the characteristic junction width $W$. In such cases, as supported by DFT calculations and guaranteed by classical electrostatic theory, any local changes at the interface will not affect the long-range electrostatic potential alignment of an in-plane 2D heterostructure. In spite of the insensitivity of the band alignment, on the other hand, the transmission function of the 2D heterostructure may still be affected by the interfacial details [57–62].

### 3. Conclusion

To summarize, our combined study of first-principles calculations and analytic model lays the ground for understanding the intrinsic band alignments in broadly defined 2D lateral heterostructures, which is expected to dictate future experiment and design of 2D electronic/optoelectronic devices. We show the fundamental differences between 2D and 3D junctions, not just by a simple electrostatic argument but by rigorous and extensive first-principles calculations. In particular, when the dimension of a device is considerably larger than the characteristic junction width $W$ (which can be one order of magnitude longer than that in 3D), band alignments in the 2D lateral heterostructures should follow the Schottky–Mott (M/S) and Anderson (S/S) limits, respectively, and are insensitive to interfacial details. When such a condition is not satisfied, the band alignment is ill defined, and thus the SBHs or band offsets can be tailored by the component domain size and interfacial conditions.

### 4. Computational methods

Our calculation employs the density functional theory (DFT) and the projector-augmented wave method (PAW) [63], as implemented in the Vienna $ab$ initio simulation package (VASP) [64, 65]. The Perdew–Burke–Ernzerhof (PBE) [66] functional is used to describe the exchange–correlation interactions. The cutoff energy for the plane-wave expansion is 550 eV. The 2D Brillouin zones are sampled by a series of $k$ point grids with a constant separations of 0.015 Å$^{-1}$ along the interface direction to ensure the convergence. Supercell of lateral G/BN or MoS$_2$/WS$_2$ junction was constructed by merging two nanoribbons in one plane. The details can be found in our recent paper on in-plane G/BN heterostructures [41].

Generally speaking, there are two types of contributions to the band alignment: (1) the band edges with respect to the electrostatic potential within each component material of the heterostructure; (2) the alignment of the electrostatic potentials across the interface. The first part is sensitive to the functional form used in the calculation and PBE is often insufficient. However, our present conclusion concerns mainly with the second part, namely, the long-range electrostatic potential which depends only on the charge distribution. Since DFT is known to yield rather reasonable charge distribution, the difference between PBE and the hybrid functional like HSE06 and G$_0$W$_2$ calculation should be zero as the latter uses the DFT charge distribution. More importantly, the electrostatic potential alignment is accurately determined by classical electrostatic theory. Therefore, our current conclusion is expected to be valid regardless computational methods.
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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[2] Kubota Y, Watanabe K, Tsuda O and Taniguchi T 2007 Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure Science 317 932–4
[3] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805
[4] Ramakrishna Matte H S, Gomathi A, Manna A K, Late D J, Datta R, Pati S K and Rao C N R 2016 Epitaxial growth of in-plane and vertically stacked graphene–boron nitride heterostructures Nat. Commun. 7 125401
[5] Novoselov K S, Fal’ko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 A roadmap for graphene Nature 490 192–200
[6] Pant A, Mutuţu Z, Wickramaratne D, Cai H, Lake R K, Ozkan C and Tongay S 2016 Fundamentals of lateral and vertical heterojunctions of atomically thin materials Nanoscale 8 3870–87
[7] Lim H, Yoon S J, Kim G, Jang A R and Shin H S 2014 STACKING of two-dimensional materials in lateral and vertical directions Chem. Mater. 26 4891–903
[8] Wang H, Liu F, Fu W, Fang Z, Zhou W and Liu Z 2014 Two-dimensional heterostructures: fabrication, characterization, and application Nanoscale 6 12250–72
[9] Geim A K and Grigorieva I V 2013 Van der Waals heterostructures Nature 499 41–7
[10] G.L. et al 2010 Atomic layers of hybridized boron nitride and graphene domains Nat. Mater. 9 430–5
[11] Levendovitch M P, Kim C-J, Brown L, Huang P-Y, Havenner R W, Muller D A and Park J 2012 Graphene and boron nitride lateral heterostructures for atomically thin circuitry Nat. Comm. 4 627–32
[12] Sutter P, Cortes R, Lahiri J and Sutter E 2012 Interface formation in monolayer graphene–boron nitride heterostructures Nano Lett. 12 4869–74
[13] Gao Y et al 2013 Toward single-layer uniform hexagonal boron nitride–graphene patches with zigzag linking edges Nano Lett. 13 5439–43
[14] Han G H, Rodriguez-Manzo J A, Lee C-W, Kybert N J, Lerner M B, Qi J, Dattoli E N, Rappe A M, Dmochowski M and Johnson A T C 2013 Continuous growth of hexagonal graphene and boron nitride in-plane heterostructures by atmospheric pressure chemical vapor deposition ACS Nano 7 1029–38
[15] Havenner R W, Kim C-J, Brown L, Kevek J W, Slepy J D, McEuen P L and Park J 2013 Hyperspectral imaging of structure and composition in atomically thin heterostructures Nano Lett. 13 3942–6
[16] Kim S M, Hou A, Araujo P T, Lee Y-H, Palacios T, Dresselhaus M, Idrobo J-C, Kim K K and Kong J 2013 Synthesis of patched or stacked graphene and hBN flakes: a route to hybrid structure discovery Nano Lett. 13 933–41
[17] Liu Z et al 2013 In-plane heterostructures of graphene and hexagonal boron nitride with controlled domain sizes Nat. Nanotechnol. 8 119–24
[18] Liu L, Park J, Siegel D A, McCarty K F, Clark K W, Deng W, Basile L, Idrobo J C, Li A-P and Gu G 2014 Heteroepitaxial growth of two-dimensional hexagonal boron nitride templated by graphene edges Science 343 163–7
[19] Zhang C, Zhao S, Jin C, Koh A L, Zhou Y, Xu W, Li Q, Xiong Q, Peng H and Liu Z 2015 Direct growth of large-area graphene and boron nitride heterostructures by a co-segregation method Nat. Commun. 6 7519
[20] Liu M et al 2014 Quasi-free-standing monolayer heterostructure of graphene and hexagonal boron nitride on Ir(111) with a zigzag boundary Nano Lett. 14 6342–7
[21] Shin H-C et al 2015 Epitaxial growth of a single-crystal hybridized boron nitride and graphene layer on a wide-band gap semiconductor J. Am. Chem. Soc. 137 6897–905
[22] Gao T, Song X, Du H, Nie Y, Chen Y, Ji Q, Sun J, Yang Y, Zhang Y and Liu Z 2015 Temperature-triggered chemical switching growth of in-plane and vertically stacked graphene–boron nitride heterostructures Nat. Commun. 6 6835
[23] Shinde P P and Kumar V 2011 Direct band gap opening in graphene by BN doping: ab initio calculations Phys. Rev. B 84 125401
[24] Pruneda JM 2010 Origin of half-semimetallicity induced at interfaces of C–BN heterostructures Phys. Rev. B 81 161409
[25] Kincai A, Haskins J B, Sevik C and Çagın T 2012 Thermal conductivity of BN–C nanostructures Phys. Rev. B 86 155410
[26] Duan X et al 2014 Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions Nat. Nanotechnol. 9 1024–30
[27] Gong Y et al 2014 Vertical and in-plane heterostructures from WS2/MoS2 monolayers Nat. Mater. 13 1135–42
[28] Huang C, Wu S, Sanchez A M, Peters J J P, Bealantid R, Ross J S, Rivera P, Yao W, Cobden D H and Xu X 2014 Lateral heterojunctions within monolayer MoSe2–WSe2 semiconductors Nat. Mater. 13 1096–101
[29] Li M-Y et al 2015 Epitaxial growth of a monolayer WSe2–MoS2 lateral p–n junction with an atomically sharp interface Science 349 524–8
[30] Zhang X-Q, Lin C-H, Tseng Y-W, Huang K-H and Lee Y-H 2015 Synthesis of lateral heterostructures of semiconducting atomic layers Nano Lett. 15 410–5
[31] Deng Y, Luo Z, Conrad N J, Liu H, Gong Y, Najmaei S, Ayajan P M, Lou J, Xu X and Ye P D 2014 Black phosphorus–monolayer MoS2 van der Waals heterojunction p–n Diode ACS Nano 8 6897–91
[32] Cheng R, Li D, Zhou H, Wang C, Yin A, Jiang S, Liu Y, Chen Y, Huang Y and Duan X 2014 Electroluminescence and photocurrent generation from atomically sharp WSe2/MoS2 heterojunction p–n Diodes Nano Lett. 14 5590–7
[33] Fuchi M M, Pospischil A, Libisch F, Burgdorfer J and Mueller T 2014 Photovoltaic effect in an electrically tunable van der Waals heterojunction Nano Lett. 14 4785–91
[34] Chiu M-H, Zhang C, Shiu H-W, Chou C-P, Chen C-H, Chang C-Y S, Chen C-H, Chou M-Y, Shih C-K and Li L-J 2015 Determination of band alignment in the single-layer MoS2/WSe2 heterojunction Nat. Commun. 6 7666
[35] Lee C-H et al 2014 Atomically thin p–n junctions with van der Waals heterointerfaces Nat. Nanotechnol. 9 676–81
[36] Howell S L, Jarviswa D, Wu C-C, Chen K-S, Sangwan V K, Kang I, Marks T J, Hersam M C and Lauhon L J 2015 Investigation of band offsets at monolayer–multilayer MoS2 junctions by scanning photocurrent microscopy Nano Lett. 15 2278–84
[37] Zhang C, Chen Y, Huang J-K, Wu X, Li L-J, Yao W, Tersoff J and Shih C-K 2016 Visualizing band offsets and edge states in bilayer–monolayer transition metal dichalcogenides lateral heterojunction Nat. Commun. 7 10349
[38] Monch W 1990 On the physics of metal–semiconductor interfaces Rep. Prog. Phys. 53 221
[39] Tung R T 2014 The physics and chemistry of the Schottky barrier height Appl. Phys. Rev. 1 011304
[40] Tung R T 2000 Chemical bonding and fermi level pinning at metal–semiconductor interfaces Phys. Rev. Lett. 84 6078–81
[41] Zhang J, Xie W, Xu X, Zhang S and Zhao J 2016 Structural and electronic properties of interfaces in graphene and hexagonal boron nitride lateral heterostructures Chem. Mater. 28 5022–8
[42] Van de Walle C G and Martin R M 1987 Theoretical study of band offsets at semiconductor interfaces Phys. Rev. B 35 8154–65
[43] Mott N F 1939 The theory of crystal rectifiers Proc. R. Soc. A 171 27–38
[44] Schottky W 1939 Zur halbleitertheorie der sperrschicht- und spitzengleichrichter Z. Phys. 113 367–414
[45] Lu J, Gomes L C, Nunes R W, Castro Neto A H and Loh K P 2014 Lattice relaxation at the interface of two-dimensional crystals: graphene and hexagonal boron–nitride Nano Lett. 14 5133–9
[46] Martins T B, Miwa R H, da Silva A J R and Fazzio A 2007 Electronic and transport properties of boron-doped graphene nanoribbons Phys. Rev. Lett. 98 196803
[47] Heslinga D R, Wetering H H, van der Werf D P, Klapwijk T M and Hibma T 1990 Atomic-structure-dependent Schottky barrier at epitaxial Pb/Si(111) interfaces Phys. Rev. Lett. 64 1589–92
[48] Zhang S B, Cohen M L, Louie S G, Tománek D and Hybertsen M S 1990 Quasiparticle band offset at the (001) interface and band gaps in ultrathin superlattices of GaAs–AlAs heterojunctions Phys. Rev. B 41 10058–67
[49] Zhang S B, Cohen M L and Louie S G 1986 Structural and electronic properties of the Al–GaAs(110) interface Phys. Rev. B 34 768
[50] Christensen N E 1988 Dipole effects and band offsets at semiconductor interfaces Phys. Rev. B 37 4528–38
[51] van Schilfgaarde M and Newman N 1990 Electronic structure of ideal metal/GaAs contacts Phys. Rev. Lett. 65 2728–31
[52] Wang D, Han D, Li X B, Xie S Y, Chen N K, Tian W Q, West D, Sun H B and Zhang S B 2015 Determination of formation and ionization energies of charged defects in two-dimensional materials Phys. Rev. Lett. 114 196801
[53] Venema L C, Wildoer J W G, Janssen J W, Tans S J, Tünstru H J T, Kouwenhoven L P and Dekker C 1999 Imaging electron wave functions of quantized energy levels in carbon nanotubes Science 283 52–5
[54] Léonard F and Tersoff J 2000 Role of fermi-level pinning in nanotube Schottky diodes Phys. Rev. Lett. 84 4693–6
[55] Anderson R L 1960 Germanium–gallium arsenide heterojunctions IBM J. Res. Dev. 4 283–7
[56] Ongun Özçelik V, Azadani J G, Yang C, Koester S J and Low T 2016 Band alignment of two-dimensional semiconductors for designing heterojunctions with momentum space matching Phys. Rev. B 94 035125
[57] Zhang J, Gao J, Liu L and Zhao J 2012 Electronic and transport gaps of graphene opened by grain boundaries J. Appl. Phys. 112 053713
[58] Fediai A, Ryndyk D A and Cuniberti G 2015 Electron transport in extended carbon-nanotube/metal contacts: ab initio-based Green function method Phys. Rev. B 91 165404
[59] Casterman D, De Souza M M, Tahraoui A, Durkan C and Milne W I 2009 Role of hybridization on the Schottky barrier height of carbon nanotube field effect transistors Phys. Rev. B 79 125307
[60] Palacios J J, Tarakeshwar P and Kim D M 2008 Metal contacts in carbon nanotube field-effect transistors: beyond the Schottky barrier paradigm Phys. Rev. B 77 113403
[61] Gao F, Qu J and Yao M 2012 Electrical resistance at carbon nanotube/copper interfaces: capped versus open-end carbon nanotubes Mater. Lett. 82 184–7
[62] Kim Y H and Kim H S 2012 Anomalous length scaling of carbon nanotube-metal contact resistance: an ab initio study Appl. Phys. Lett. 100 213113
[63] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75
[64] Kresse G and Furthmüller J 1996 Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set Comput. Mater. Sci. 6 15–50
[65] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86
[66] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8