Transition-Metal Surfaces

Hexagonal Boron Nitride–Metal Junction: Removing the Schottky Barriers by Grain Boundary

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Atomically thin hexagonal boron nitride (h-BN) layers have been used as an ultra-thin spacer layer for metal-insulator-metal (MIM) structures, which enables a wide range of applications such as nanocapacitors and field-effect tunneling transistors. Although pristine h-BN layers, produced by chemical vapor deposition (CVD) methods, are always with ubiquitous grain boundaries (GBs), the contact of such layers with transition metal (TM) has not been explored. Here, we studied h-BN monolayer with GBs on Ni(111) and Cu(111) surfaces through a comprehensively first-principles calculation. Our results show that for the free-standing h-BN monolayer with GBs, it presents a moiré pattern characteristic and its energy gap is narrowed by about 38%. When h-BN with GBs is deposited on Ni(111) and Cu(111) surfaces, the GBs containing B-B pairs are attracted to the TM surface while the GBs with N-N pairs(GBs-N) parts are repelled from the surfaces. Interestingly, the calculated Schottky barriers (SBs) for electrons between the h-BN layer and the TM surfaces almost disappear due to the existence of GB structures. Thus, our results predicted that h-BN with GBs may form ohmic contact with TM surfaces, which can be used in real electric devices.

1. Introduction

Monolayer hexagonal boron nitride (h-BN) has attracted considerable research interests because of its fascinating properties and promising characteristics. Owing to its smooth surface, chemical inertness and large energy gap, h-BN is an appealing substrate for the graphene-based devices,^[1] such as an ultra-thin spacer layer for metal–insulator–metal (MIM) structures or tunneling barrier.^[2] Although h-BN layers can be exfoliated from bulk BN

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crystal by micromechanical cleavage,^[3] chemical vapor deposition (CVD) growth of h-BN layer is the most promising way because of the commercial applications.^[4] Indeed, the successful CVD growth of h-BN monolayer on various transition metals (TM) surfaces has been reported.^[5] Importantly, such studies indicated that h-BN layers produced by low and ambient pressure CVD methods lead to the presence of grain boundaries (GBs), [^{5e,6}] composed of an array of dislocations, which will significantly change the chemical and physical properties of layers.

Yakobson et al. reported that GBs in h-BN contain square–octagon pair (4|8s) and pentagon–heptagon pairs (5|7s) dislocations, which will induce buckling and change the electronic properties of h-BN sheet.^[7] The predicted (5|7s) defects of the GBs were experimentally confirmed by Gibb et al.^[8] While Li et al. showed that both (5|7s) and (4|8s)defects can be observed in

the h-BN on Cu(111) surface.^[6] So far, in the theory aspect, although relevant researches have studied the interaction of perfect h-BN and TM surfaces,^[9] how the GBs structures affect the interaction with the TM surfaces is not clear, which is the most possible situation in real applications. Moreover, explorations of intrinsic properties of such contact may help the further applications and endow the bigger potential of h-BN monolayer.

In this work, through ab initio calculations, we comprehensively investigated the structures, electronic configuration, chemical interaction, and the Schottky barrier between the h-BN with GBs and the transition metal. Based on coincidence site lattice(CSL) theory,^[10] we constructed two types of GBs of h-BN, namely, with the misorientation angle (θ) of 21.8° (type I) and 32.2° (type II). Both types contain (5|7s) defects that are observed in experiment.^[6,8] Our results show that the energy gap of the free-standing h-BN is narrowed about 38% by GBs. And when h-BN with GBs is contacted with Ni(111) and Cu(111) surfaces, the GBs containing B-B pair (GBs-B) parts of the h-BN layer are attracted to the TM surfaces while the GBs with N-N pair(GBs-N) parts are repelled away from the surfaces. Interestingly, Schottky barriers (SBs) between the h-BN layer and the TM surface almost disappear and ohmic contact is formed due to the existence of GBs. Thus, our results provide an interesting way to tune the contact type, which can be used in future researches and real electric devices.



Figure 1. a) Top and b) side views of the optimized model for h-BN-GBs-I, while c) and d) for h-BN-GBs-II. Red dashed boxes denote the supercell. Dark green and light gray balls represent B and N atoms, GBs are marked by shadows. GBs1/II-B, GBs1/II-N represent the GBs containing B-B, N-N pairs, respectively. While Δh represents the global corrugation of h-BN with GBs and the numbers marked the corresponding bond lengths (Å).

2. Computational Details and Methods of Analysis

Our first-principles calculations are based on density functional theory (DFT) with generalized gradient approximation (GGA) for exchange correlation potential given by Perdew–Burke–Ernzerhof (PBE),^[11] as implemented in the Vienna Ab initio Simulation Package (VASP).^[12] A van der Waals (vdW) correction proposed by Grimme (DFT-D2)^[13] was chosen due to its good description of long-range vdW interactions. ^[14] The projected augmented wave (PAW) method with a plane-wave basis set was used.^[15] We set the energy cutoff and convergence criteria for energy and force to be 400 eV, 10⁻⁴ eV, and 0.01 eVÅ⁻¹, respectively.

The surface calculations have been performed within slab model, involving three metal layers with atoms in the bottom two layers fixed to their bulk positions and h-BN with GBs adsorbed by the top surface. Repeated slabs were separated by more than 10 Å to avoid interaction between each other. In order to eliminate the strain effect on the electronic properties of h-BN layer, during the construction process of h-BN/TM interfaces, we compressed the lattice constant of Cu(111)(2.556 Å) or stretched the lattice constant of Ni(111)(2.492 Å) to match the h-BN lattice(2.511 Å). For superstructures with GBsI and GBsII optimization, $6 \times 4 \times 1$ and $3 \times 2 \times 1$ K-points are adopted, where $12 \times 8 \times 1$ and $6 \times 4 \times 1$ K-points are used for total energy calculations, respectively.

3. Free-Standing h-BN with GBs Layer

We constructed two types of GBs of h-BN with the misorientation angle (θ) of 21.8° (type I) and 32.2° (type II), respectively, based on CSL theory.^[10] Both types contain (5|7s) defects that have been observed in experiments,^[6,8] and for convenience, we use the terms h-BN-GBs-I and h-BN-GBs-II to denote these two structures, respectively. And in each type, as shown in **Figure 1**, there exist two kinds of GBs, one containing B-B pairs and the other one containing N-N pairs, so we also use GBs-B, GBs-N to denote such two parts of each GB structures.

As is shown in Figure 1, the GBs of h-BN-GBs-I and h-BN-GBs-II consist of repeating 5–7 ring pairs with and without a single intermediate hex-ring, respectively, and these GBs not only induce the buckling (global corrugations of h-BN-GBs-I and h-BN-GBs-II are 1.255 Å and 1.327 Å, respectively) of the free-standing layers, but also change the local bond lengths (numbers marked in Figure 1, for details see Table S1, Supporting Information) in h-BN sheets.

In **Figure 2**, we display the density of states (DOS) of h-BN with or without GBs structures. Compared with the perfect h-BN monolayer, new states appear between the energy gap for both the h-BN-GBs-I and h-BN-GBs-II structures, and, as shown in Figure 2b,e, these new states below and above the Fermi level mainly come from GBs-N and GBs-B, respectively, especially the homoelemental pairs. Due to these new states, the band gap of h-BN (more than 4.5 eV) is largely decreased and both of these two structures are indirect semiconductors with band gaps of 2.92 and 2.81eV, respectively (for more details, see the band structures in Figure S2, Supporting Information). Therefore, with the emergence of the GBs, the electronic properties of h-BN layer are largely changed.

4. h-BN with GBs on Ni(111) and Cu(111) Surfaces

For the commensurate h-BN/TM systems, many studies show that the configuration in which nitride stays on top of the metal atom and boron occupy the fcc positions ($B_{fcc}N_{top}$) is energy stable.^[5a,5c,16] Thus for the h-BN with GBs on TM supercell, half of BN-pairs of h-BN layer were arranged with $B_{fcc}N_{top}$



Figure 2. a) Density of states (DOS) of h-BN, "B," "N," and "Total" stand for the DOS of boron, nitride, and the total in h-BN, respectively. b,c) The DOS of h-BN-GBs-I and h-BN-GBs-II structures, respectively, "B-GBs," "N-GBs," "B-B pair," and "N-N pair" mean the DOS of the GBs-B, GBs-N, the B-B, and N-N in GBs.



Figure 3. a) Top and b) side views for optimized structure of 21.8-BN/Ni(111), d,e) for 32.2-BN/Ni, c) schematic of the global corrugation Δ h of h-BN and the minimum distance $d_{low, 1L}$ between h-BN and metal surface. Red dashed boxes denote the unit cell. Ni1 means Ni atoms in the first layer.

configuration, while the other BN-pairs, based on the misorientation angle θ , have different neighborhood with respect to the metal substrate. For ease of exposition, different interfaces are named as m-BN/TM, where "m" denotes the misorientation angle θ of GBs, for example, 21.8-BN/Ni means h-BN-GBs-I on Ni(111) surface.

As shown in **Figure 3**, the GBs-B parts of h-BN layer are attracted to the TM surfaces and the GBs-N parts are repelled from the substrate surfaces and the global corrugation Δh (as shown in **Table 1**) of h-BN layer that for 21.8-BN/Ni and 32.2-BN/Ni are 1.228 and 1.153 Å, respectively. Compare the $d_{low,1L}$ and Δh (also shown in Table 1) of the m-BN/Ni to that of the commensurate NiBN structure, the m-BN/Ni has smaller values, which indicates that the GBs strengthen the interaction between h-BN layer and the Ni substrate.

The morphology (shown in **Figure 4**) of m-BN/Cu shows only the GBs-B parts are attracted to the Cu(111) surface. As shown in Table 1, comparing the values of $d_{low,1L}$ and Δh in commensurate CuBN and m-BN/Cu structures, the GBs also strengthen the interaction of the interfaces. While comparing the interaction

Table 1. The $d_{min,1L}$ (defined as the minimum distance from h-BN to TM surfaces) (Å), global corrugation Δh (Å), and interaction energy (eV) of the commensurate h-BN|TM and m-BN/TM systems. Interaction energy is defined as $E_{\text{int}} = (E_{\text{tot}} - E_{\text{M}})/N_{\text{BN}}$, E_{tot} , E_{M} and E_{EN} are the energy of h-BN|metal interfaces, metallic slab, and h-BN layer, respectively, and N_{BN} is the number of the BN pairs. E_{int} and $E_{\text{int,vdW}}$ mean energies with and without vdW correction, respectively. A positive value for E indicates an unbinding system.

	$\Delta h_{B,N}[\overset{\mathrm{o}}{A}]$	d _{min,1L}	E _{int}	E _{int,vdW}
NiBN	0.124	1.945	-0.162	-0.418
21.8-BN/Ni	1.228	1.747	-0.249	-0.569
32.2-BN/Ni	1.153	1.803	-0.217	-0.521
CuBN	0.018	2.900	0.051	-0.239
21.8-BN/Cu	1.184	2.136	0.020	-0.268
32.2-BN/Cu	1.093	2.076	0.023	-0.270

energy in Ni and Cu case, the interaction between BN and Ni is stronger than the Cu case. However, in both cases, the vdW correction does greatly change the calculated energy, which means that vdW correction plays a crucial role for the interaction between BN layer and TM substrates.

In Figure 5 we display the differential charge density (CDD) of the 21.8-BN/Ni and 21.8-BN/Cu interfaces (due to the similarity, the CDD of 32.2-BN/Ni and 32.2-BN/Cu are supplied in Figure S3, Supporting Information). For m-BN/Ni, charge transfer (CR) mainly occur in the GBs-B areas and in this area every boron atom gains more than 0.1 e⁻ (calculated by the Bader's "atoms in molecules" method,^[17] for more details, see Table S2, Supporting Information), while for the Cu case, CR only takes place at the GBs-B. In both cases, as shown in Figure 5, the B p_z orbitals obtain electron density, whereas p_{x,y} orbitals loses some electrons, which makes the B atoms, especially the B-B pairs in GBs, positively charged (yellow isosurface) in the direction perpendicular to the h-BN plane. At the same time, for the metal atoms below the GBs-B area, the electron density difference indicates a transfer of electrons from the metal d_{z^2} orbitals to the $d_{xz,yz}$ orbital, thus these metal atoms are negatively charged in the z direction. Therefore, due to the coulomb interaction, the B atoms, especially B-B bonds in GBs, behave just like nails that pin the h-BN layer to the substrates.

5. The Schottky Barriers of the Interfaces

Schottky barrier's (SBs) height (Φ) is defined as the energy difference between the Fermi level and the band edge of the h-BN layer in the interface^[18]

$$\Phi_e = E_{CBM} - E_F, \Phi_h = E_F - E_{VBM}$$

where Φ_e and Φ_h are the SBs heights for electrons and holes, respectively; E_{CBM} and E_{VBM} denote the conduction band minimum (CBM) and the valence band maximum (VBM) of the h-BN with or without GBs layer in the interfaces, respectively; and E_F denotes the Fermi level of the interface.



Figure 4. a) Top and b) side views of the optimized model for 21.8-BN/Cu(111), c,d) for 32.2-BN/Cu. Cu1 means the first layer Cu atoms.



Figure 5. Differential charge density with an isosurface value of 0.0065 $e^{A^{-3}}$ for a) top and b) side views of 21.8-BN/Ni and 0.002 $e^{A^{-3}}$ for c) top and d) side views of 21.8-BN/Cu, respectively. The yellow and cyan regions indicate an increase and decrease in electron density, respectively.

The SBs for the electrons Φ_e and holes Φ_h of the h-BN/MT interfaces are listed in (**Table 2**), which originated from **Figure 6**. For the commensurate structures, as shown in Figure 6, Φ_e and Φ_h for NiBN are 1.5 and 4.1 eV and for CuBN are about 1.8 and 2.7 eV, respectively, which agree with the Bokdam et al.'s results.^[19] However, for the m-BN/TM structures, Φ_e of all the interfaces, as shown in Figure 6, very interestingly, disappear and the VBM is marked by red dished circle in Figure 6, which

 Table 2. The Schottky barrier heights of the h-BN/MT interfaces.

	NiBN	21.8-BN/Ni	32.2-BN/Ni	CuBN	21.8-BN/Cu	32.2-BN/Cu
$\Phi_{e}[eV]$	1.6	0	0	1.8	0	0
$\Phi_{h}[\text{eV}]$	4.1	0.9	1.2	2.7	0	0

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Figure 6. a-c) denote the perfect NiBN, 21.8-BN/Ni, and 32.2-BN/Ni band structures, respectively; d-f) for the perfect CuBN, 21.8-BN/Cu, and 32.2-BN/Cu, respectively. The green and blue color measure the projection of the wave function on the orbitals of B and N atoms, respectively. The Fermi level is set at zero energy.

indicate Φ_h are about 0.9 eV for 21.8-BN/Ni and 1.2 eV for 32.2-BN/Ni, respectively. While for the m-BN/Cu interfaces, the states of B atoms appear in the vicinity of Fermi level, this phenomenon is more obvious for 32.2-BN/Cu, therefore Φ_h for m-BN/Cu interfaces are zero.

Thus, we can see that, due to the appearance of GBs in h-BN layer, the SBs height for the electrons Φ_e totally disappear in the h-BN/TM interfaces and the Φ_h also vanishes in the Cu case and dramatically reduces in the Ni case.

6. Summary

In this work we have presented a DFT study of the h-BN with GBs layer and its contact with Ni(111) and Cu(111) surfaces. The main conclusion we obtained is that the calculated SBs for electrons almost disappear due to the existence of GBs. Thus, our results suggest that h-BN with GBs may form ohmic contact with TM surfaces. Furthermore, this effective and convenient method can be used in the other 2D materials|TM interfaces to modify the contact barrier for the electric devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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