

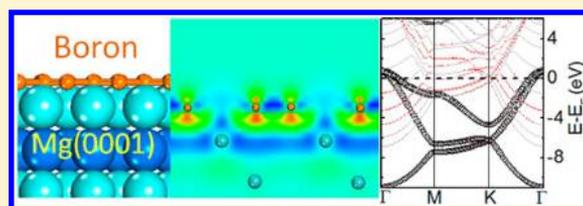
Boron Sheet Adsorbed on Metal Surfaces: Structures and Electronic Properties

L. Z. Zhang,[†] Q. B. Yan,[‡] S. X. Du,^{*,†} G. Su,[‡] and H.-J. Gao^{*,†}[†]Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China[‡]College of Physical Sciences, Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: Using first-principles calculations based on density functional theory, we studied the possible geometric configurations and electronic structures of three types of monolayer boron sheets (BSs) on different metal (Mg, Al, Ti, Au, and Ag) surfaces. We find that, when adsorbed on metal surfaces, hexagonal BS (*h*-BS) is more energy-favorable than triangular BS or mixed hexagonal-triangular BS, and the atop-site adsorption configuration is the most favored. For all *h*-BS/metal configurations, electrons are observed to transfer from

metal to BS, due to the intrinsic electron deficiency of *h*-BS. Electronic structure analyses show that the substrates could be classified into two types according to the interactions between boron and metal: (1) *h*-BS on Mg(0001), Al(111), or Ti(0001) shows a relatively larger charge transfer and stronger BS–metal interactions, and the σ (in-plane) bands have the same profile as freestanding *h*-BS, except for a Fermi level shift caused by the charge transfer. (2) *h*-BS on Au(111) or Ag(111) surfaces has in-plane bands split into several subbands. A model of coronene on *h*-BS/Mg(0001) is also investigated, which shows that it is possible to decouple the molecular electronic structure from the metal surface by a buffer of a single sheet of boron.



1. INTRODUCTION

Since the successful exfoliation of graphene from graphite,¹ two-dimensional materials have attracted intensive research interest because of their intriguing properties and potential applications.^{2,3} Experimental scientists have developed a lot of methods to prepare graphene, such as mechanical exfoliation, chemical vapor deposition, epitaxial growth, etc.⁴ In particular, epitaxy can grow graphene on a metal surface with a large area and high quality,^{5–10} implying that metal-substrate-supported graphene is easier to prepare than a freestanding sheet. In addition to graphene, a boron nitride (BN) monolayer fabricated on a metal surface has also been reported.^{11,12} As the neighbor of carbon in the periodic table, boron's nanostructures, such as boron fullerenes,^{13–15} nanotubes,^{16–18} nanowires,¹⁹ nanosheets,^{20,21} and nanoribbons,^{22–24} also draw the attention of scientific researchers. Considering that the support of a metal substrate benefits the preparation of two-dimensional materials, such as graphene and an *h*-BN monolayer, and that boron can form hexagonal layered structures in AlB_2 -type materials similar to graphene in geometry,²⁵ we anticipated that it might be possible to fabricate a single-layer boron sheet (BS) on various metal surfaces. Although a few experiments about boron and MgB_2 sheets on a Mg(0001) surface have been reported,^{26,27} few theoretical studies about BS on pure metal surfaces have been reported as far as we know.

In this paper, using first-principles calculations based on density functional theory, we investigate the binding properties and geometrical and electronic structures of several types of monolayer BS adsorbed on different metal surfaces: Mg(0001),

Al(111), Ti(0001), Au(111), and Ag(111). Three types of BSs are considered: hexagonal-BS (*h*-BS),²¹ triangular-BS (*t*-BS),²¹ and mixed hexagonal-triangular-BS (*ht*-BS).²⁰ The *h*-BS is found to be more stable than *t*-BS and *ht*-BS when in contact with metal surfaces. The binding energies, band structures, and electron transfers of *h*-BS on metal surfaces are discussed. It turns out that metal substrates can be divided into two groups. One group consists of Mg(0001), Al(111), and Ti(0001), with a larger binding energy, and in-plane bands that have the same profile as freestanding *h*-BS, except that the Fermi level is shifted by the charge transfer. The other group consists of the Au(111) and Ag(111), with a smaller binding energy and σ -bonding (in-plane) bands split into several subbands. We also investigate the geometric and electronic structures of coronene located on the *h*-BS/Mg(0001) surface. We find that the interaction between the molecule and the substrate is very weak and the electron transfer is very small. This suggests that *h*-BS can be used as a decoupling layer when investigating intrinsic properties of aromatic molecules or graphene.

2. CALCULATION DETAILS

All calculations were performed within density functional theory as implemented in the Vienna Ab-initio Simulation Package (VASP)^{28,29} with the projector augmented wave (PAW) method.³⁰ Local density approximation (LDA)³¹ in the form of Perdew–Zunger³² was adopted for the exchange-

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correlation functional. For comparison, the PBE³⁴ calculations are also performed, and they result in longer bond lengths and weaker binding energies, while the electronic structures are nearly the same as those in the LDA results (see the Supporting Information, section 2, for details). The energy cutoff of the plane-wave basis sets is 400 eV. The Monkhorst–Pack scheme was used to sample the Brillouin zone,³³ and a mesh of $21 \times 21 \times 1$ k -points sampling was used for the calculations. In our calculations, we fix the lattice constants of the metals and adopt the lattice constant of a BS accordingly. The periodic slab models of the metal substrate include a four-layer substrate and a 15 Å vacuum layer. The bottom two layers of the substrate were fixed, while the other two layers of the substrate and the BS was fully relaxed in geometric optimizations until the residual forces were smaller than 0.01 eV/Å. The binding energy is defined as

$$E_{\text{ad}} = (E_{\text{B}} + E_{\text{sub}} - E_{\text{tot}}) / N_{\text{boron atom}}$$

where E_{tot} refers to the total energy for BS on the metal substrate, E_{B} represents the total energy of the BS, E_{sub} is the total energy of the substrate, and $N_{\text{boron atom}}$ is the number of the boron atoms in one unit cell.

3. RESULTS AND DISCUSSION

The different choices of substrate lead to different characteristics of the BS/metal system. Considering that the boron–boron bond length is about 1.7 Å in layered structures of AlB_2 -type materials, several metal substrates, Mg(0001), Al(111), Ti(0001), Au(111), and Ag(111), are chosen in this work to achieve lattice matching. Three types of BS are considered: h -BS, t -BS, and ht -BS (see Figure 1a). It is found that the binding

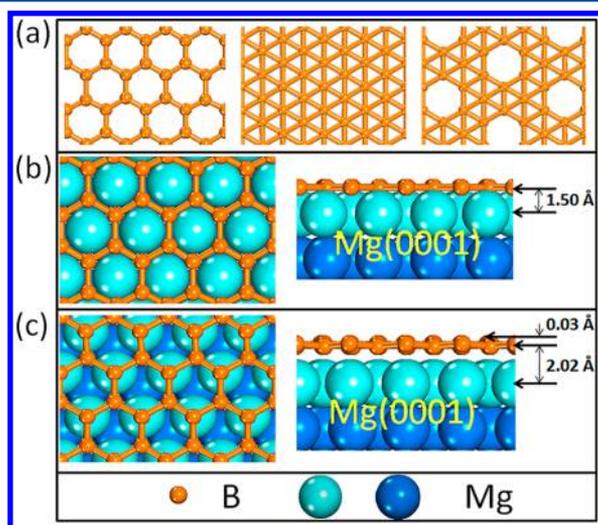


Figure 1. Schematic structures of three different BSs and h -BS on Mg(0001) surfaces: (a) h -BS, t -BS, and ht -BS from left to right, respectively. The top and side views of the atop-site configuration (b) and the hcp-site configuration (c) of h -BS/Mg(0001).

energies of h -BS/metal are much higher, and the geometry of h -BS/metal is less distorted than that of t -BS/metal and ht -BS/metal (see the Supporting Information, section 1). Thus, we focus on the h -BS on metal surfaces in the following. For h -BS on metal surfaces, three different adsorption sites are considered: atop, fcc, and hcp. Because fcc and hcp sites are identical if only the top layer of substrate is considered, we only discuss the configurations of h -BS on atop and hcp sites of

metal substrates. Figure 1b,c shows the configurations of h -BS on atop and hcp sites of the Mg(0001) surface, respectively. For comparison, we also calculated the geometrical structures and electronic properties of h -BS on Mg-terminated $\text{MgB}_2(0001)$.

Table 1 lists the geometric parameters and binding energies of h -BS on different metal substrates. It is clear that the binding energies of all configurations are higher than those in graphene/metal systems,³⁵ suggesting a strong binding of the h -BS to these metal surfaces. For the h -BS on Mg(0001), Al(111), and Ti(0001), the binding energies are higher and the corrugations are larger than on Au(111) and Ag(111). The configurations with the h -BS on the atop site are much more stable than those with h -BS on the hcp site. Therefore, the interaction between h -BS and Mg(0001) (or Al(111) and Ti(0001)) is relatively stronger than that between h -BS and Au(111) (or Ag(111)). Besides, the binding energy of h -BS on Mg(0001) is similar to that on $\text{MgB}_2(0001)$.

As we find out in binding energies of h -BS on different substrates, the h -BS on metal surfaces can be classified into two groups. Group I has higher binding energies, such as h -BS on Mg(0001), Al(111), and Ti(0001). Group II has relative lower binding energies, such as h -BS on Au(111) and Ag(111). These two groups also have different band structures. The band structures of a freestanding h -BS and the h -BS on Mg(0001), Au(111), and Ti(0001) are indicated in Figure 2a–d, respectively. For free-standing h -BS, the in-plane bands are not fully occupied and the out-of-plane bands are partially occupied. Compared with free-standing h -BS, the in-plane bands in group I hardly change, with a downward shift due to the electron transfer from the substrate, which is similar to the $\text{MgB}_2(0001)$ surface.^{36,37} Especially for the h -BS/Ti(0001) system, the in-plane bands are fully occupied when h -BS is present on the Ti(0001) surface. Also, the out-of-plane bands split into several bands and shift down due to broken symmetry and charge transfer. The band structure of h -BS in group II is distinctly different from that of freestanding ones and those in the first group; that is, the in-plane bands split into several bands, unlike the unchanged in-plane bands of h -BS in group I. In Figure 2c, we find that the splitting is mainly around 4.0 eV below the Fermi level. As we know, the d bands of Au(111) and Ag(111) are also around this energy level. Considering the similar energy level and the diverse symmetry of d orbitals, the in-plane bands splitting of h -BS should come from the interaction between d bands of the substrate and the in-plane bands of h -BS. The splitting of out-of-plane bands is due to the broken symmetry perpendicular to the plane of h -BS, which is the same situation as that for group I.

Electron densities located between h -BS and the substrate for all configurations are calculated. Figure 3a,c shows the differential charge densities for two typical substrates of two groups, h -BS/Au(111) for weak interactions and h -BS/Ti(111) for strong interactions, respectively. For h -BS/Au(111), a few electrons transfer from the first layer of the substrate to h -BS. In the right panel of Figure 3a, a peak appears under the h -BS plane, which indicates an electron loss in this region due to the interaction between the d bands of the substrate and the in-plane bands of h -BS. This interaction also induces splitting of the in-plane bands of BS, which is shown in Figure 2c. (We provide the cross section of the electron density difference of h -BS/Au(111) 0.26 Å below the h -BS plane in the Supporting Information, section 3.) For h -BS/Ti(111), in which the interactions between h -BS and the substrate are strong,

Table 1. Binding Energies, E_{ad} (in eV per Boron Atom), and Geometric Parameters (in Å) of a Boron Sheet on Different Substrates^a

substrate	Mg(0001)		Al(111)		Ti(0001)		Au(111)		Ag(111)		MgB ₂	
	atop	hcp	atop	hcp	atop	hcp	atop	hcp	atop	hcp	bulk	MgB ₂ (0001)
E_{ad}	1.03	0.58	1.10	0.72	1.87	1.21	0.58	0.61	0.63	0.55		1.07
a	1.81	1.81	1.63	1.65	1.65	1.69	1.66	1.66	1.64	1.64	1.75	1.75
d	1.50	2.03	1.46	1.82	1.51	1.77	2.00	2.17	1.97	2.14	1.73	1.69
b	0.01	0.03	0.05	0.26	0.01	0.38	0.005	0.04	0.005	0.11	0.00	0.00

^a a is the B–B bond length, d is the distance between the lowest boron atom of the boron sheet and the highest metal atom of the substrate, and b is the buckling of the boron sheet.

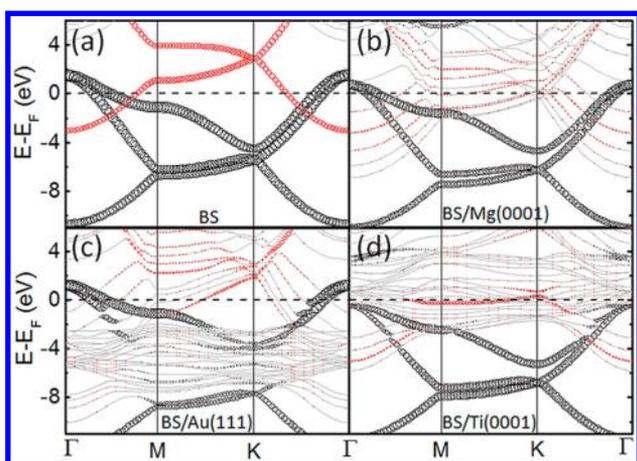


Figure 2. Band structures of freestanding h -BS (a) and h -BS on Mg(0001) (b), Au(111) (c), and Ti(0001) (d). The size of black (red) circles indicates contribution from the B in-plane p_z (out-of-plane $s + p_x + p_y$) orbitals of h -BS.

electrons transfer from the top layer of the substrate to the interface and from the in-plane bands to the out-of-plane bands of h -BS, as shown in Figure 3c. This suggests a strong binding between the h -BS layer and Ti(0001), unlike h -BS/Au(111). To clearly illustrate which orbitals contribute greatly to the interaction, the projected density of states (PDOSs) of the h -BS and the nearest Au (or Ti) atom in the substrate are, respectively, shown in Figure 3b,d. Since the interaction mainly involves the d orbitals of the substrate, only the PDOSs of d orbitals are shown. The PDOS of the Au(111) near the Fermi level is very small, and that of h -BS here is similar to that of h -BS on MgB₂ (Figure 3b).³⁸ For h -BS/Ti(0001), the d_{z^2} and d_{xy} orbitals of Ti contribute a lot to the interface interactions, and the p_z state of the h -BS layer is changed a lot compared with h -BS on a MgB₂ surface, where there is a much larger state near the Fermi level.

For freestanding graphene and h -BN nanomesh, the valence band is a π band that is fully filled. The band structure of h -BS shows that both π and σ bands contribute to the valence band, and they are partially filled due to the intrinsic electron deficiency of BS.¹⁷ The electronic properties will be different when the same materials reside on a metal surface. The

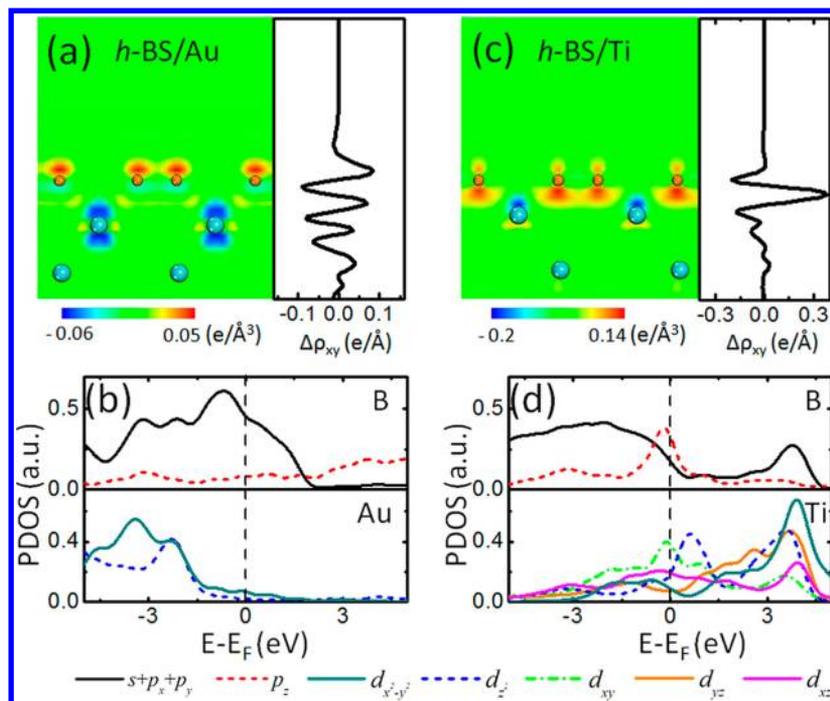


Figure 3. Cross sections of electron density difference along the c direction (left) and the integrated electron density differences (right) of h -BS on Au(111) (a) and Ti(0001) (c) with atop-site configurations. Panels (b) and (d) show the PDOS of B and of the first layer of metal for these two systems.

graphene/metal systems can be divided into two classes according to the interaction between graphene and metals. First, graphene on Co, Ni, and Pd substrates shows highly perturbed graphene bands because of the strong interaction between graphene and the metal substrate (~ 0.1 eV per carbon atom). Second, graphene on Al, Cu, Ag, Au, and Pt substrates shows slight *p*-doping or *n*-doping, and the π bands can still be clearly identified.³⁵ For *h*-BN on Ni(111), the σ and π bands retain their structures only with a Fermi level shift.^{39,40} According to our calculations, the *h*-BS is strongly *n*-doped on metal surfaces, showing that *h*-BS is an electron-deficient material, and all the out-of-plane bands (π bands) split into several bands because of the strong interaction between *h*-BS and the metal substrate.

It is reported that the single layer of graphene grown on Ru(0001) can be used as a buffer layer to decouple the molecules electronically from the metallic substrate, and the intrinsic electronic structures of aromatic molecules are easily obtained.⁴¹ Therefore, we also investigate the decoupling ability of *h*-BS on the metal substrate using coronene on *h*-BS/Mg(0001) as an example (see Figure 4a). Coronene is chosen

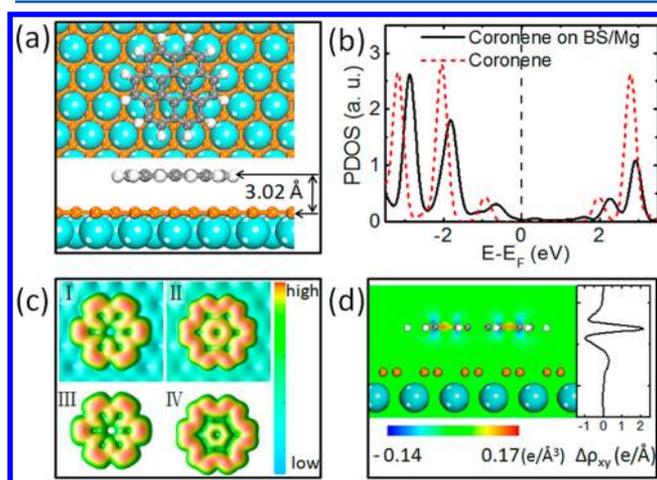


Figure 4. (a) Schematic structures of top and side views of coronene on *h*-BS/Mg(0001). (b) PDOS of the inner six carbon atoms of the single coronene molecule and of coronene on *h*-BS/Mg(0001). (c) HOMO (I) and LUMO (II) of coronene on *h*-BS/Mg(0001) and those of an isolated coronene molecule (III and IV). (d) Differential charge densities of coronene/*h*-BS/Mg(0001).

because its configuration is similar to a segment of graphene, and the environment of the central benzene ring is the same as that in a graphene layer. If the electronic structure of the central benzene ring in coronene remains unchanged when it is put on *h*-BS/metal, the *h*-BS can be used to investigate intrinsic electronic structures of either aromatic molecules or graphene. According to our calculation, the most stable adsorption site is the central benzene ring of coronene on one of the B atoms. The distance between the molecule and the substrate is about 3.02 Å, a typical distance of van der Waals interaction, suggesting a weak interaction between coronene and the substrate. The binding energy is about 1.28 eV, which is a little larger than that of the coronene on graphene (about 0.91 eV). Comparing the PDOS of the central benzene ring of a single coronene (red dashed line in Figure 4b) with that of the *h*-BS/Mg(0001) (black line in Figure 4b), we find that they look almost the same, except for a slight energy shift. The similar shape and slight energy shift suggest that, in coronene, the

electronic structures of the central benzene ring are almost unchanged, with only a tiny charge transfer. Figure 4c shows the HOMO (I) and LUMO (II) of coronene/B/Mg(0001), which are similar to those of a single molecule (III and IV in Figure 4c). The electron transfers between the molecule and the substrate are also shown in Figure 4d. From this figure, we find that few electrons transfer from coronene to the *h*-BS/Mg(0001) substrate (less than 0.017 electrons per carbon atom). The electron redistribution (less than 0.05 electrons per carbon atom) occurs between the in-plane and the out-of-plane orbitals inside the molecule. These results imply that the *h*-BS can be used as a buffer layer to decouple the molecules electronically from the metal substrate.

4. CONCLUSIONS

We have done DFT calculations on single-layer BSs adsorbed on various metal substrates. The interactions between BSs and the metal substrate are found to be much stronger than that in graphene/metal systems, and *h*-BS is more favorable in energy than *t*-BS or *ht*-BS when in contact with metals. The band structure, density of states, and the charge transfer in *h*-BS/metal systems are also investigated. We find that *h*-BS on Al(111), Mg(0001), and Ti(0001) substrates has in-plane band structures similar to those of freestanding *h*-BS, but with an energy shift. Also, for *h*-BS on Au(111) and Ag(111) surfaces, the in-plane bands split into several subbands due to the interactions of the d orbitals of the metal and the *h*-BS. Our calculations are helpful to understanding the effects of different metal substrates on the electronic structures of the BS layer. Using coronene on *h*-BS/Mg(0001) as an example, we find that *h*-BS can be used as a buffer layer to investigate the intrinsic properties of aromatic molecules or graphene.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information includes the structures and binding energies of *t*-BS and *ht*-BS on Mg(0001), Au(111), and Ti(0001) surfaces; the PBE results of *h*-BS on metal substrates; and the electron density difference of *h*-BS/Au(111). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sxdx@iphy.ac.cn (S.X.D.), hjgao@iphy.ac.cn (H.-J.G.).

Notes

The authors declare no competing financial interest.

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