

Probing the Synthesis of Two-Dimensional Boron by First-Principles Computations**

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The synthesis of novel two-dimensional (2D) materials has attracted considerable interest because of their various unique properties. While the production of 2D boron (^{2D}B) sheets remains a challenge, it is important to theoretically investigate the possible fabrication methods. Herein, we explore the formation of B sheets on metal (Cu, Ag, Au) and metal boride (MgB_2 , TiB_2) substrates using first-principles calculations. Our results suggest that B sheets can be grown on the Ag(111) or Au(111) surfaces by deposition. B atoms decomposed from a precursor, and driven by the gradient of the chemical potential, will assemble into 2D clusters and further grow into a larger sheet, while formation of three-dimensional boron (^{3D}B) structures could be impeded owing to a high nucleation barrier. In addition, saturation of a boron-terminated MgB_2 surface in a boron-rich environment can also lead to the formation of B sheets. These sheets are weakly bound to the substrates, suggesting a feasible post-synthetic separation into the free-standing forms. Our work proposes feasible approaches to synthesize ^{2D}B , and could possibly pave the way towards its application in nanoelectronics.

Boron sheets^[1] are among those 2D materials that may have interesting properties and applications, yet remain impeded by the difficulties of their synthesis.^[2] In particular, the metallic character of ^{2D}B makes it a potential complement to graphene, hexagonal boron nitride, and metal disulfides that may be ultimate building components in devices. Unlike graphene, however, the accumulated theoretical knowledge on ^{2D}B has not yet been applied experimentally. In contrast to previous theoretical studies,^[1] focused on the structures and stability of hypothetical ^{2D}B sheets, herein we attempt to assess the feasibility of their synthesis and suggest some guidelines for practical routes. Such theoretical investigation of the synthesis can quantify certain aspects and possibilities.

We propose and analyze synthesis methods based on those established for graphene. One would be the exfoliation^[3] from layered materials with weak inter-layer binding; however, no such precursor boron material exists in nature, which rules out the exfoliation approach. The possible methods include: 1) Deposition, especially chemical-vapor deposition,^[4] of B atoms on a catalytic substrate, either pure metal or metal-terminated metal boride. The observed reconstruction of B-terminated boride surfaces^[5] suggests another approach, 2) saturation by B deposition on the B-terminated surface of borides under a B-rich environment, to form a B sheet. 3) Evaporation of metal atoms^[6] from metal borides at high temperature. To probe the feasibility of these methods, we performed first-principles calculations focused on the following fundamental questions: 1) What are the atomic structures of ^{2D}B on the substrates and how they compare to the theoretically studied free-standing B sheets? 2) Is it energetically favorable to form ^{2D}B on the substrates, compared to other configurations such as B adatoms, clusters, or ^{3D}B phases? 3) If formed, would it be possible to separate the B sheets from the substrates after synthesis?

The choice of substrate is critical for the synthesis of ^{2D}B . The epitaxial growth of graphene on Cu(111) surface^[7] suggests that a good substrate should have low B atom solubility^[8] while serving as a flat template for ^{2D}B . Many metals are known to form borides, including those widely used for carbon nanotube growth (Fe, Co, Ni).^[9] Group 11 elements, Cu, Ag, and Au, do not form borides, and thus are selected here as substrates to model the deposition of B atoms. In particular, the Ag(111) surface has been used in the recent synthesis of 2D silicon^[2d] and ZnO.^[2a] ^{2D}B can also be expected to form from the borides that are composed of alternating metal and graphene-like B layers, for example, MgB_2 and TiB_2 , used herein to represent non-transition-metal borides and transition-metal borides, respectively.

A variety of ^{2D}B sheets can be described as $B_{1-x}V_x$ pseudoalloys,^[11] where V represents vacancy in a parent triangular lattice (for example, $x = 1/3$ corresponds to a hexagonal sheet). In vacuum, the energetically optimal fraction of vacancies falls in the range $0.1 < x < 0.15$, where numerous sheet structures with various vacancy patterns are found to be nearly degenerate in energy, suggesting a polymorphic state.^[11] One of the most stable sheets, the α -sheet ($x = 1/9$),^[20] and its structural relatives have been intensively studied.^[1b,c,e,h-j,n,p,q] Herein, ten types of B sheets with different vacancy concentrations $x = v/27$ ($v = 0-9$), are constructed to explore general trends in their properties as a function of x . Details of the construction procedure can be found in the Supporting Information. These sheets are among the most stable ones in vacuum for a given x .^[11] With the above

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provisions, we can formulate more specifically the scenarios for synthesizing ^{2D}B: 1) Deposition of B atoms on the (111) surfaces of face-centered cubic (fcc) Cu, Ag, Au, and the metal-terminated (0001) surfaces of MgB₂ and TiB₂; 2) saturation of B-terminated MgB₂ or TiB₂ surface in a B-rich environment; 3) evaporation of MgB₂ or TiB₂ at high temperatures. For each of these possibilities, we addressed the set of questions (1–3) posed above.

To compare the stability of different B sheets (the first question), we calculate the energy of B atoms in the corresponding configurations (essentially, the chemical potential μ at zero temperature, as shown in the Supporting Information) as shown in Equation (1):

$$\mu = (E_{\text{B-sheet/substrate}} - E_{\text{substrate}} - N_{\text{B}} E_{\text{B-atom}}) / N_{\text{B}} \quad (1)$$

where $E_{\text{B-sheet/substrate}}$ is the total energy of the B sheet with the substrate, $E_{\text{substrate}}$ is the energy of the substrate without B atoms, $E_{\text{B-atom}}$ is the energy of a B atom in vacuum, and N_{B} is the total number of B atoms in the system. The calculated μ values of B sheets are shown in Figure 1.

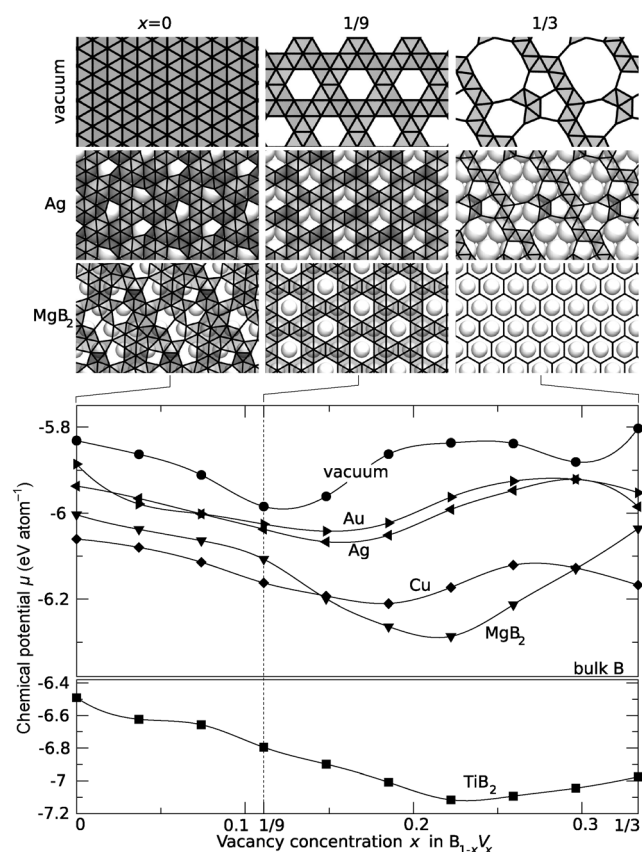


Figure 1. Atomic structure of ^{2D}B sheets ($x=0$, $1/9$, and $1/3$) in vacuum and on substrates (Ag(111) and Mg-terminated MgB₂(0001) surfaces). ^{2D}B is represented as a line network and the larger bright spheres are metal atoms (for clarity, only the topmost metal layer is shown). The plot shows the chemical potential μ [Eq. (1)] of B sheets as a function of vacancy concentration x in vacuum and on different substrates: Cu(111), Ag(111), Au(111), Mg-terminated MgB₂, and Ti-terminated TiB₂ surfaces. The vertical axis is broken at the μ of bulk α -boron.

In vacuum, we find that the free-standing hexagonal B sheet ($x=1/3$) cannot preserve its hexagonal lattice under small perturbations (in accord with the detection of unstable phonon modes). It would collapse into a disordered sheet with close-packed triangular domains and large voids, as shown in Figure 1. The nearly amorphous sheet has energy much lower than the periodic hexagonal sheet by almost 0.7 eV per atom. In this case, although “vacancy concentration” is not a well-defined term, we still use it for consistency with literature. In fact, at high vacancy concentration ($x > 5/27$), all the low-energy B sheets appear amorphous (structures are shown in the Supporting Information). The clustering of vacancies into large holes in B sheets has also been noted recently in other reports.^[1c,10] Such amorphous structures are also known to exist in the boron fullerenes.^[11] Nevertheless, at low $x < 6/27$, the hexagonal framework is sustained and the α -sheet is the most stable one in this set.

When placed on Cu, Ag, or Au, the B sheets with $x > 6/27$ are also amorphous. Figure 1 shows the atomic structures of B sheets on Ag. At low B coverage (high x), the sheet is composed of stripes and voids, while it gradually restores the hexagonal framework at high B coverage (low x). In contrast, on MgB₂ and TiB₂, the B sheets with high x retain the hexagonal lattice, as a natural continuation of the bulk structure. One common feature shared by the B sheets is that they become more buckled with the decrease of x (increase of B atom coverage). In vacuum, the amorphous sheet is flat, while the α -sheet buckles by 0.4 Å,^[1e] and the triangular sheet has a height variation of 0.9 Å. On Ag, the buckling increases from 0.4 Å for $x=1/3$, to 0.8 Å for $x=1/9$, then to 1.8 Å for $x=0$. Similarly, on MgB₂, it varies from flat, to 0.4 Å, and then to 1.6 Å. Figure 1 also shows that on these substrates the α -sheet is no longer the most stable one. Interestingly, the optimal vacancy concentration of ^{2D}B sheets shifts to a higher x value, that is lower density, compared to that in vacuum.

Which type of B sheet could be synthesized depends on the formation route; with deposition, B adatoms from the decomposed precursor could assemble into a sheet with the lowest μ in Figure 1. For illustration, Figure 2 shows the atomic structures on MgB₂ and Ag. On the Mg-terminated surface of MgB₂, the B sheet has a hexagonal framework located on top of threefold hollow sites at approximately 1.8 Å from the surface, which is slightly larger than the distance between the B layer and Mg layer in bulk MgB₂, approximately 1.7 Å. A third of the hexagon centers ($x=2/9$) are filled with B atoms, which sit on top of metal atoms with approximately 0.4 Å separation from the hexagonal plane. On Ag, the B sheet (β -type^[1e]) is flatter ($x=4/27$) but more distant from the substrate, approximately 2.5 Å, implying a weaker interaction.

Unlike the deposition method, where the lowest- μ sheet is expected to grow,^[12] methods (2) and (3) lead to different forms of ^{2D}B. For surface saturation (2), B atoms from the environment fill in the centers of B hexagons on the boron-terminated surface.^[5] The vacancy concentration is fully determined by μ of B atoms in the environment. By tuning μ , one can in principle obtain various B sheets, from hexagonal to triangular,^[13] in contrast to the mono-type sheet produced by method (1). Figure 2c shows the sheet with

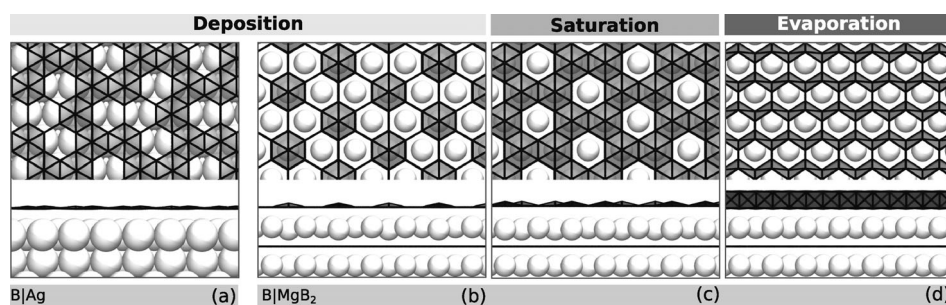


Figure 2. Atomic structure of B sheets, representing different synthetic methods: deposition on metals (a) and metal-terminated surface of borides (b), saturation of B-terminated surface of borides (c), and evaporation of borides (d). Ag and MgB_2 are shown as representatives for metals and metal borides, respectively. Both top and side views are shown.

the weakest adhesion to the MgB_2 substrate ($x = 1/9$; that is, the α -sheet, at approximately 2.2 \AA from the surface). At the surface of metal borides, two hexagonal B layers are intercalated with one metal layer. According to the phase diagram of MgB_2 ,^[14] at approximately 1100 K and 1 atm pressure, the Mg atoms sublime, leaving behind two hexagonal B layers interconnected and forming a hexagonal bilayer on the surface, Figure 2d. Our calculations show that the interlayer distance of the bilayer is only 1.5 \AA . A similar mechanism operates in the formation of graphene from SiC evaporation,^[15] where, in contrast, the two carbon hexagonal layers bind with each other very weakly,^[16] resulting in an easy separation of the top graphene sheet from the underlying material.

In the saturation (2) and evaporation (3) methods, hexagonal B layers pre-exist on the substrate. However, in the deposition method (1), it is not obvious whether the B adatoms on the substrate would aggregate, or would tend to form disconnected populations. We find that on all the substrates, $\mu_{\text{adatoms}} > \mu_{\text{2D-cluster}} > \mu_{\text{sheet}}$, providing a driving force for growth. Figure S3 in the Supporting Information shows the decrease of μ as B atoms assemble on Ag as an example, which asymptotically approaches the μ of a B sheet. However, as shown in Figure 1, aside from TiB_2 , the other substrates cannot decrease μ of $^{2\text{D}}\text{B}$ below the value for bulk $^{3\text{D}}\text{B}$.^[17] At first glance, the bulk $^{3\text{D}}\text{B}$ instead of the 2D sheet could be the growth product on these substrates. However, as shown in the Supporting Information, the high nucleation energy of $^{3\text{D}}\text{B}$ could impede its formation, and thus the small B nuclei always have planar structures.^[18] In addition, the low solubility of B into the substrates and fast diffusion on surfaces could help the B adatoms transport in a 2D channel,^[8] and grow the nucleus into a monolayer structure. A detailed analysis can be found in the Supporting Information.

The question (3) posed in the beginning can be addressed by calculating the adhesion energy, the work required to separate $^{2\text{D}}\text{B}$ from the substrate. Figure 3 shows the adhesion energies for different growth methods. As discussed above, growth by surface saturation of borides can result in various 2D forms depending on the μ of B atoms in the environment, but only weakly bound ones can be separated from the substrate. Therefore the sheet with the lowest adhesion energy is chosen for comparison. The adhesion energies of

graphite^[19] and graphene on a $\text{Cu}(111)$ surface^[20] are taken from the literature. The TiB_2 surface has strong adhesion with the B sheet, more than 0.2 eV \AA^{-2} , in agreement with the high cohesive energy of bulk TiB_2 .^[9b] Only the $^{2\text{D}}\text{B}$ grown by deposition on Ag or Au or saturation of the B-terminated MgB_2 surface has an adhesion energy of the same order of magnitude as graphene on Cu, less than 0.10 eV \AA^{-2} , thereby narrowing the synthesis options

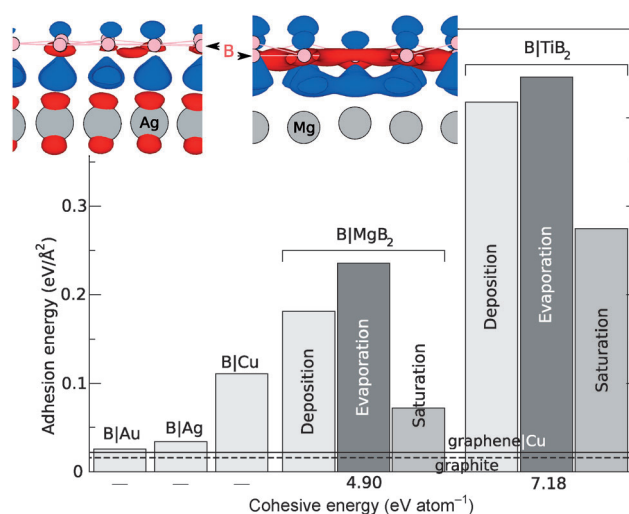


Figure 3. Adhesion energies of B sheets to substrates, representing different synthetic methods: deposition (light gray) on Cu, Ag, Au, MgB_2 , and TiB_2 ; evaporation of borides (black), and saturation (dark gray) of B-terminated surfaces of borides- MgB_2 and TiB_2 . The adhesion energies of graphite^[19] and graphene on Cu ^[20] are indicated. The cohesive energy values are those of bulk MgB_2 and TiB_2 . Inset: the isosurfaces of the difference in charge density for a B sheet on Ag and MgB_2 . Electron accumulation = blue; electron depletion = red; B layers = pink ball-and-stick figures; topmost metal layers = gray circles.

to deposition on Ag, Au, and saturation of a B-terminated MgB_2 surface. The weak adhesion of the B sheet to Ag and Au surfaces has already been hinted at above by the large distance from the substrates, approximately 2.5 \AA . Plots of the difference in charge density, shown in the inset of Figure 3, illustrate how the electrons are redistributed upon the sheet–substrate contact formation. The electrons are transferred from Ag to B, while the Mg atoms under the B sheet retain their original ionic states. Both substrates cause the depletion of in-plane σ states and accumulation of out-of-plane π electrons. However, it should be noted that the computational method employed here (density-functional theory, PBE exchange-correlation functional) generally underestimates the adhesion energy between substrates and adsorbates,^[20] and an efficient computational scheme to obtain very accurate values is still lacking. Nevertheless, the current

method is helpful, at least, to screen out the strongly-adhesive substrates.

In conclusion, our analysis of growth scenarios based on first-principles calculations suggests the possibility of synthesizing ^{2D}B on metals or metal boride surfaces. 1) Deposition of B atoms on a Au or Ag(111) surface can result in growth of ^{2D}B , whereas a high nucleation barrier could impede the formation of 3D-structures; 2) saturation of B-terminated MgB_2 surface under B-rich conditions can also lead to the formation of ^{2D}B . In both cases, the B sheets bind weakly to the substrates, suggesting a relatively easy post-growth separation. The present analysis may be potentially beneficial not only for boron but could also provide a basis for the theoretical investigation of growth of 2D materials in general, and possibly help with their experimental realization.

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