Theory of Epitaxial Growth of Borophene on Layered Electride: Thermodynamic Stability and Kinetic Pathway

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ABSTRACT: Based on first-principles calculations, we propose that the layered electride can serve as an effective substrate, in place of a metal substrate, to grow borophene. We first confirm the thermodynamic stability of B@Sr2N heterostructures by energetics analysis. Then, kinetically, we identify the atomistic pathways for a preferred 2D growth mode with a mixed triangle—hexagon configuration over 3D growth on the surface of Sr2N, indicating the feasibility of epitaxial growth of borophene on layered electrides. As a weak metal, the significantly reduced density of states from the electride at the Fermi level helps to retain the most intrinsic electronic and transport properties of borophene, a significant advantage over the metal substrate. We envision that layered electrides provide an attractive family of substrates for epitaxial growth of a range of 2D materials that can otherwise only be grown on undesirable metal substrates.

INTRODUCTION

Two-dimensional (2D) materials have drawn intensive attention for both fundamental interests and potential applications.1−4 While high-quality small-size 2D materials, such as graphene5,6 and transition-metal dichalcogenides,7,8 may be prepared by mechanical exfoliation, it is highly desirable to grow 2D materials for large size and mass quantity to further our study and realize their potential applications. However, many 2D materials can only be grown on metal substrates, which is unwanted because the ample metallic states will inevitably destroy the intrinsic, especially nonmetallic properties of 2D materials. In this study, using borophene (a monolayer boron sheet) as a prototypical example, we demonstrate that layered electrides provide a new class of substrates, in place of metal, to effectively grow 2D materials with significant advantages.

Boron is one of the most versatile elements, forming various 3D bulk polymorphs.9−13 Similarly, different 2D borophene have been theoretically proposed14−20 and experimentally realized.21−25 In the well-known high-Tc superconductor MgB2, boron possesses a planar honeycomb lattice, which is primarily responsible for the superconductivity.26,27 A recent study also showed MgB2 to be a topological semimetal.28 Besides honeycomb borophene, other borophene with mixed hexagonal—triangular geometry have also been theoretically predicted to superconduct.29 Thus, the synthesis of borophene may provide new opportunities for not only 2D high-Tc superconductivity but also topological superconductivity. However, the growth of borophene on a metal substrate has some drawbacks. It is unlikely to exfoliate the thin film of B@substrate away from the thick metal substrate. The high conductivity of metal will mask the intrinsic transport properties of borophene due to the high electron density of states of metal near the Fermi level.29 Therefore, searching for an insulating or weak metal substrate to grow borophene is of great interest.

Since boron has three valence electrons, the electron deficiency makes its structure energetically unstable. Thus, neither semiconductors nor insulators can serve as good substrates to grow borophene. Instead, we have identified layered electride, a “weak metal”, to be an effective substrate to grow borophene. Electrides are crystals with cavity-trapped electrons acting as anions.30−36 The concept of anionic-alkali metal dissolved ammonia.37,38 Interestingly, a layered electride, dicalcium nitride (Ca2N), was experimentally reported in 2013 to possess delocalized “2D electron gas (2DEG)” sandwiched between the cationic layers.39 Ca2N was then studied as an effective substrate to grow borophene. Electrides are crystals with cavity-trapped electrons acting as anions.30−36 The concept of anionic electrons was first validated in alkali metal dissolved ammonia.37,38 Interestingly, a layered electride, dicalcium nitride (Ca2N), was experimentally reported in 2013 to possess delocalized “2D electron gas (2DEG)” sandwiched between the cationic layers.39 Ca2N was then studied as an effective electron donor for hydrogenation in alkenes and alkenes,40 and the stability of honeycomb borophene in a sandwich geometry.41 Several carbides, nitrides,42−46 and oxides42,43,46 have since been predicted as layered electrides. We hypothesize that the presence of 2DEG on the layered electride surface provides an effective means to...
compensate for the electron deficiency of borophene. In addition, the layered structure of electrode can facilitate the exfoliation or growth of borophene on monolayer or thin films of electrodes to minimize the substrate influence. Finally, as a weak metal, the significantly reduced density of states from the electrode at the Fermi level helps to retain the most, if not all, of the intrinsic electronic and transport properties of borophene.

To test the above hypotheses, we investigate both the thermodynamic stability of $\text{B@Sr}_2\text{N}$ and the kinetic pathways of boron growth on the $\text{Sr}_2\text{N}$ surface using first-principles calculations. The choice of using layered electrode $\text{Sr}_2\text{N}$ as the prototypical substrate to grow borophene is because $\text{Sr}_2\text{N}$ has been experimentally synthesized and has an appropriate lattice constant matched with borophene. We identify the atomistic kinetic pathways for boron growth on the $\text{Sr}_2\text{N}$ surface with a preferred 2D growth mode over 3D mode. At large cluster size (~18 atoms), a mixed hexagonal and triangular geometry is favorable. All these findings point to the feasibility of the epitaxial growth of borophene on a layered electrode.

### COMPUTATIONAL METHODS

The first-principles calculations were performed using the Vienna ab initio simulation package (VASP) based on the projected augmented wave approach within the framework of density functional theory. The generalized gradient approximation in the Perdew, Burke, and Ernzerhof form (GGA-PBE) was used for the exchange–correlation functional. The cutoff energy of plane-wave basis was set to 500 eV. A vacuum layer with a thickness larger than 15 Å was adopted to study the 2D systems under the periodic boundary condition. The Brillouin zone integration was densely sampled according to the size of the supercell, ensuring approximately the same $k$ point density for different sized structures. All the geometry structures were fully relaxed until the atomic force was less than 0.01 eV/Å.

### RESULTS AND DISCUSSION

Bulk $\text{Sr}_2\text{N}$ has a $R\bar{3}m$ space group with a lattice constant of 3.869 Å, and Figure 1a depicts the crystal structures of $\text{Sr}_2\text{N}$, similar to that of $\text{Ca}_2\text{N}$ and $\text{Y}_2\text{N}$. The building block of $\text{Sr}_2\text{N}$ consists of three layers, where N atoms are sandwiched between two Sr layers. The calculated electron localization function (ELF) indicates the existence of interlayer free electrons in $\text{Sr}_2\text{N}$, as shown in Figure S1 in the Supporting Information (SI). Two borophene structures, $\alpha$ and $\beta$ phases, as shown in Figure 1b are adopted to investigate the thermodynamic stability of the $\text{B@Sr}_2\text{N}$ heterostructures, since $\alpha$ phase with $\eta = 1/9$ has been predicted to be a stable freestanding sheet and $\beta$ phase with $\eta = 1/6$ has been experimentally synthesized. Here, $\eta$ is the density of hexagonal holes, which is defined as the ratio of the number of hexagonal holes to the number of atomic sites in the compact triangular borophene within a unit cell. Detailed structural information of $\text{B@Sr}_2\text{N}$ is shown in Table S1 in the SI.

The substrate used to grow borophene plays a crucial role in stabilizing the structure. To better understand the stabilization mechanism, we calculate the formation energy of borophene on different substrates and perform the Bader charge analysis. The formation energy is defined as

$$E_f = \frac{E_{\text{tot}} - E_{\text{sub}} - N \times E_B}{N}$$

where $E_{\text{tot}}$ is the total energy of borophene on the substrate, $E_{\text{sub}}$ is the energy of the substrate, $E_B$ is the energy of the isolated boron atom, and $N$ is the number of boron atoms. A negative value of $E_f$ means that the growth is a favorable process with respect to the clean surface and an isolated B atom. We take the energy of isolated boron atom as $E_B$ in addition to the cohesive energy of bulk $\alpha$-$\text{B}_12$ (as used in the previous calculations) because atomic boron source prepared by e-beam evaporator under ultrahigh vacuum condition is used during growth.

The calculated formation energy and average charge transfer in $\text{B@Sr}_2\text{N}$ and $\text{B@Ag}(111)$ (see Table S1 and Figure S2 in the SI for structures) are listed in Table 1. As a comparison, we calculate the formation energy in reference to the cohesive energy of bulk $\alpha$-$\text{B}_12$ as the reference of boron atom.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Crystal structures of (a) $\text{Sr}_2\text{N}$, (b) $\alpha$-$\text{B@Sr}_2\text{N}$, and (c) $\beta$-$\text{B@Sr}_2\text{N}$. Red rhombus indicates the unit cell in the heterostructure. Yellow rhombus and rectangle indicate the unit cell in $\alpha$- and $\beta$-borophene.
honeycomb structure if sufficient electrons are transferred to boron.

Next, we establish the preferred growth mode and identify the atomic pathways for boron growth on the Sr$_2$N substrate by investigating the initial stage of growth up to 18 atoms. Although the growth of borophene on metal substrates$^{60-64}$ has been studied previously, fundamental mechanisms of borophene growth on layered electride are unknown. We adopted a 5×5 monolayer Sr$_2$N as the substrate, which is confirmed to be sufficiently large to avoid the intercluster interaction for up to 36-atom clusters, as shown in Figure 3. For the 36-atom boron cluster on the Sr$_2$N surface (Figure 3a), we calculated the corresponding ELF, as shown in Figure 3b. The contour plots of cuts 1 and 2 in ELF shown in Figure 3c,d explicitly indicate that the 5×5 supercell of Sr$_2$N is large enough to avoid the interaction from the neighboring boron clusters for the size of $N \leq 36$.

We first determine the preferred adsorption site for boron adatom. Figure 4 shows the nudged elastic band (NEB) calculation for boron atom diffusion on the Sr$_2$N surface. The insets present the adsorption structures at the local minima and saddle points, indicated by red dots.

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Figure 2. Distribution of onsite charge transfer from Bader charge analysis for (a) α-B@Sr$_2$N, (b) β-B@Sr$_2$N, (c) α-B@Ag(111), and (d) β-B@Ag(111). Positive (negative) value represents electron accumulation (depletion). Red rhombus indicates the unit cell. To more clearly show the charge distribution, only the boron lattice is presented without the Sr$_2$N substrate.

Figure 3. (a) Top and side views of a boron cluster ($N = 36$) on 5×5 Sr$_2$N surface. (b) Top and side views of ELF for (a). (c, d) Contour plots of ELF for a 2×2 supercell along the cuts 1 and 2 as indicated in (b).

Figure 4. NEB calculation for boron atom diffusion on the Sr$_2$N surface. The insets present the adsorption structures at the local minima and saddle points, indicated by red dots.

Figure 5a–i, respectively. As illustrated in Figure 5a, the most stable positions for a boron dimer are sites 1 and 3, which is expected from the adatom adsorption energy. For a larger
cluster, such as a trimer, a triangular structure occupying sites 1 and 3 is most stable, as shown in Figure 5b. Adding another adatom to the triangle trimer, it prefers to diffuse to the periphery to form a 2D rhomboid-shaped tetramer (Figure 5c), with two atoms located in site 1 and one located in site 3. By continuously adding adatom, the pentamer (Figure 5d), hexamer (Figure 5e), and heptamer (Figure 5f) are formed in sequence, and they all have the 2D structures as the most stable configurations. The hexamer with a hexagonal 6-ring geometry will transform into a rhomboid, which is the same as that in Figure 5e. For octamer and decamer, the compact-triangular structures (Figure 5g,i) are most stable, and for nonamer, the network with one pentagon is the most stable configuration (Figure 5h). In particular, all the preferred 2D configurations have the adatoms mostly occupying exclusively sites 1 and 3, and buckled 3D clusters are less stable than the corresponding 2D ones (see Figure S3 in the SI for details). In addition, we also performed the NEB calculations of boron atom diffusing from the periphery to the top of the 2D cluster, and there is a diffusion barrier of $\sim0.55$ eV/atom to form a 3D cluster (see Figure S4 in the SI).

Due to the numerous possible geometries for large boron clusters, we cannot exhaust all of them through calculations. Therefore, we use six boron clusters with $N=18$ as a typical example to illustrate the relative stability of boron clusters between mixed triangle–hexagon and compact-triangular configurations. As shown in Figure 6, clusters with hexagonal hole (Figure 6a–c) are more stable than the compact structures (Figure 6d–f). The most stable boron cluster in Figure 6a has a triangular geometry with a hexagonal hole in the center, which is the signature structural motif in $\alpha$-borophene. Another two clusters, the triangle-belt structure in Figure 6b with a hexagonal hole in the middle and the triangle-based geometry with a hexagonal hole on the periphery in Figure 6c, are metastable with the formation energy of 0.094 and 0.097 eV/atom higher than that of the stable one.

Figure 5. Top and side views of the preferred 2D configurations of boron clusters on the Sr$_2$N surface: (a) dimer, (b) trimer, (c) tetramer, (d) pentamer, (e) hexamer, (f) heptamer, (g) octamer, (h) nonamer, and (i) decamer. The numbers indicate the formation energy in the unit of eV/atom.
respectively. Therefore, the triangle and hexagon mixed boron clusters are more stable than compact-triangular ones on the surface of Sr₂N. We further confirmed this at the infinite 2D limit of a periodic structure. We constructed the configurations of borophene with different densities of hexagonal holes \( \eta = 0, 1/36, 1/18, 1/12, \text{ and } 1/3 \) (Figure S5 in the SI) and calculated their formation energies, which are less stable than \( \alpha \)- and \( \beta \)-B@Sr₂N owing to the excessive electrons in compact-triangular borophene (\( \eta = 0 \)) and the deficient electrons in honeycomb structure (\( \eta = 1/3 \)), respectively. The above results imply that the electrode substrate facilitates not only the 2D growth mode of the planar island but also a transition to the ultimate triangle and hexagon mixed borophene sheet with the increasing coverage of boron atoms during growth.

Finally, after establishing the 2D growth of borophene on the Sr₂N substrate, we further briefly illustrate the advantage of the layered electride substrates over the conventional metal substrates. The calculated cleavage energy for \( \alpha \)-B@Ag(111) is 1.47 J/m², which is more than twice of 0.70 J/m² for \( \alpha \)-B@Sr₂N (see Figure S6 in the SI). Therefore, the exfoliation of borophene with a thinner substrate from electride is much easier than that from metal. Specifically, two substrates made

Figure 6. 2D configurations of boron clusters (\( N = 18 \)) on the Sr₂N surface. The numbers indicate the formation energy in the unit of eV/atom.

Figure 7. Band structures of (a) \( \alpha \)-B@Sr₂N, (b) \( \alpha \)-B@Ag(111), (c) \( \beta \)-B@Sr₂N, and (d) \( \beta \)-B@Ag(111). The orange, green, and blue indicate the contribution from B, Sr₂N, and Ag, respectively.
of a monolayer Sr$_2$N versus a four-layer Ag(111) for growing borophene are compared. The band structures of α-B@Sr$_2$N, α-B@Ag(111), β-B@Sr$_2$N, and β-B@Ag(111) are shown in Figure 7a–d, respectively. The orange, green, and blue indicate the contribution from B, Sr$_2$N, and Ag, respectively. One clearly sees that the electronic states of boron sheet in α-B@Sr$_2$N and β-B@Sr$_2$N are much less perturbed than those in α-B@Ag(111) and β-B@Ag(111) by the substrate because there are much less metallic states coming from the substrate. Bands of boron sheet in B@Sr$_2$N are well distinguished from those of Sr$_2$N, and, in contrast, boron bands in B@Ag(111) are completely suppressed by those of Ag. In fact, the number of metallic states is severely underestimated using only four layers of Ag for α-B@Ag(111) and β-B@Ag(111). This signifies a distinctive advantage of layered electride substrate over the metal substrate for growing borophene.

CONCLUSIONS
We propose for the first time that a layered electrode can serve as an effective substrate to grow borophene. Both thermodynamic stability of B@Sr$_2$N and kinetic pathways of boron growth have been investigated using first-principles calculations. The free electrons in the Sr$_2$N surface will compensate for the electron deficiency in borophene to stabilize the structure and facilitate the 2D growth mode. Our findings open a new avenue for epitaxial growth of borophene using layered electrode substrates with notable advantages over metal substrates, which will stimulate immediate theoretical and experimental interests. Broadly speaking, the layered electrides may be used as effective substrates for epitaxial growth of various 2D materials that can otherwise only be grown on undesirable metal substrates.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10438.

ELF of bulk Sr$_2$N; NEB calculation for boron atom diffusion between 2D and 3D clusters; energy of B@Sr$_2$N as a function of density of hexagonal holes (PDF)

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