Supporting Information of

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

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The Supporting Information (SI) contains supporting figures and discussion.



Fig. S1. (a) ELF of bulk Sr_2N . (b) Contour plot of ELF for (100) plane of bulk Sr_2N .

Heterostructure	a _{borophene} (Å)	a _{sub} (Å)	Lattice mismatch (%)
α -B@Sr ₂ N	10.122 ^a	10.236 ^b	-1.11
β -B@Sr ₂ N	10.147 ^c	10.236 ^b	-0.87
α-B@Ag(111)	5.061 ^d	5.023 ^e	0.76
β-B@Ag(111)	10.147 ^c	10.045 ^f	1.02

Table S1. Detailed structural information for B@Sr₂N and B@Ag(111).

^a 2×2 supercell of α -borophene. ^b $\sqrt{7}$ × $\sqrt{7}$ supercell of Sr₂N.

^c supercell of β -borophene with $\begin{bmatrix} \overline{A_1} \\ \overline{A_2} \end{bmatrix} = \begin{bmatrix} 3 & -1 \\ 3 & 1 \end{bmatrix} \begin{bmatrix} \overline{a_1} \\ \overline{a_2} \end{bmatrix}$, where $\overline{a_1} = (2.93, 0)$ and $\overline{a_2} = (0, 5.07)$ define

the unit cell of β -borophene.

^d unit cell of α -borophene.

^e $\sqrt{3} \times \sqrt{3}$ supercell of Ag(111). ^f $2\sqrt{3} \times 2\sqrt{3}$ supercell of Ag(111).



Fig. S2. Heterostructures: (a) α -B@Ag(111); (b) β -B@Ag(111). Red rhombus indicates the unit cell in the heterostructure.



Fig. S3. Top and side views of metastable configurations of boron clusters on Sr_2N surface. The number below indicates the formation energy in unit of eV/atom.

Fig. S3 shows some of the metastable configurations of boron clusters on Sr_2N surface. For boron clusters with N=3, 4, 5, 6, metastable chain [Fig. S3(a) to (c), and (e)] configurations can be formed on the surface, which are less stable than the compact configurations owing to the unsaturated atoms along the chain. Hence, chain boron clusters are not considered with N > 7. The hexamer can assume another less stable 2D structure [see Fig. S3(d)]. Fig. S3(g), (i) to (l) show the metastable clusters for heptamer, octamers, and nonamers. One can add a boron adatom on the top of the 2D clusters, such as tetramer in Fig. 5(d) and hexamers in Fig. S3(d). Slightly buckled hexamers [Fig. S3(f)] and heptamer [Fig. S3(h) were formed. However, these buckled 3D clusters are less stable than the corresponding 2D configurations, which explicitly indicates that 3D islands are not favored on Sr₂N surface.



Fig. S4. The NEB calculation for boron atom diffusion between 2D and 3D clusters on Sr_2N surface. The insets present the corresponding structures, and the diffused boron atom is indicated by red color. The electride substrate is not shown.

We performed the NEB calculations of boron atom diffusing from the periphery to the top of 2D cluster, as shown in Fig. S4. In addition to the fact that 3D cluster is less stable than 2D one, there is a diffusion barrier of ~0.55 eV/atom to form 3D cluster. Thus, the results of the the NEB calculation further support our conclusion about the growth of borophene on layered electride with preferred 2D configuration.



Fig. S5. (a) Energy of B@Sr₂N as a function of density of hexagonal holes. (b) to (f): Top and side views of B@Sr₂N with $\eta = 0$, 1/36, 1/18, 1/12, and 1/3, respectively.

Figure S5 shows the energy as a function of density of hexagonal holes. The lowest energy of B@Sr₂N appears at $\eta = 1/6$ (β phase), which is the same as most of the metal substrates, such as, Ag, Cu, and Ni.¹ The second stable configuration is α phase with $\eta = 1/9$. The compact phase with $\eta = 0$ as an electron donor and honeycomb structure with maximum $\eta = 1/3$ as an electron acceptor are not stable on the electride substrate, respectively.



Fig. S6. (a) Cleavage energy as a function of separation distance for fractures of α -B@Sr₂N (red) and α -B@Ag(111) (blue). (b) and (c) Illustrations of separating α -B@monolayer-Sr₂N and α -B@three-layer-Ag(111) from the remaining substrate.

The exfoliation process should overcome the cleavage energy E_c , as shown in Fig. S6(a), which can be calculated by introducing a fracture in the substrate, as illustrated in Fig. S6(b) and S6(c). The calculated cleavage energy for α -B@Ag(111) is 1.47 J/m², which is more than twice of 0.70 J/m² for α -B@Sr₂N. Therefore, exfoliation of borophene with thinner substrate from electride is much easier than that from metal.



Fig. S7. The energy for boron atom on Sr_2N surface, inside Sr_2N layer, and on Sr_2N subsurface sites. The insets present the corresponding sites.

We have studied the stability of boron monomer in the subsurface sites of Sr_2N , which is more stable than that of surface site. We also calculated the energy of one possible transition state from surface site to subsurface, as shown in Fig. S7. There is a large energy barrier of ~1.35 eV/atom to overcome, which makes the boron atom difficult to diffuse from surface site to subsurface even though subsurface site is more stable. On the other hand, one expects in epitaxial growth process, the borophene overlayer can be grown by temperature control to minimize the subsurface diffusion.

References

(1) Zhang, Z.; Yang, Y.; Gao, G.; Yakobson, B. I. Two-Dimensional Boron Monolayers Mediated by Metal Substrates. *Angew. Chemie - Int. Ed.* **2015**, *54* (44), 13022–13026.