

Borophene: the next generation graphene?

Aastha Sharma

Literature Seminar

November 2, 2017

In the past decade, 2D materials have attracted extensive interest due to their remarkable potential for technological applications and fundamental research. For instance, graphene, the prototypical 2D material, exhibits high charge carrier mobilities, chemical inertness and mechanical strength.¹ Currently, majority of 2D materials are isolated from stable, bulk phases of naturally occurring layered materials (e.g. graphene, MoS₂, hexagonal boron nitride (h-BN) and black phosphorus).² Among the emerging synthetic elemental 2D materials (e.g. those based on silicon, germanium, tin, arsenic, antimony, or bismuth), borophene³, the proposed allotrope of boron made up of single-atom sheets has a rare quality: it could be a 2D metal, contrary to well-studied 2D materials with band gaps.^{4,5} Borophene's flexibility and metallic property may be suitable for flexible electrodes and contacts for nanoelectronics.

Boron, owing to its trivalent configuration, can form the expected two-center two-electron bonds up to seven-center two-electron bonds.^{6,7} Because of the extreme bonding complexity, there are around 16 bulk allotropes of boron composed of the icosahedral B₁₂ units.⁶ In 1997, using ab initio quantum mechanical techniques, Boustani predicted the ground-state structural configurations of small boron nanoclusters (B_n, where n = 2-8) to be planar.⁷ At the atomic scale,

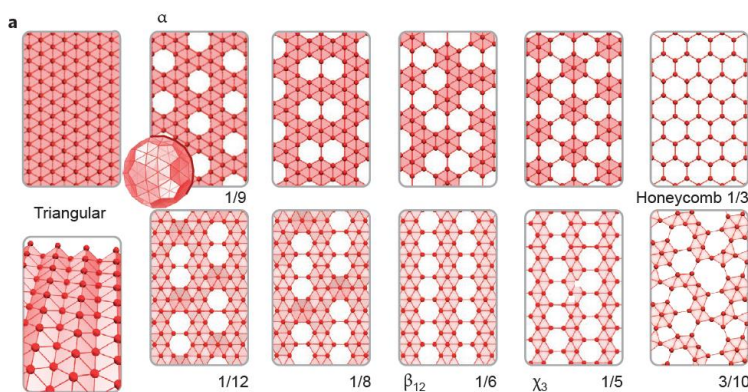


Figure 1. Theoretically predicted polymorphs for the free-standing boron monolayer, β_{12} and χ_3 were recently synthesized. The numbers below the structures denote the hole density (fraction of sites that are vacant)⁹

boron atoms form small, quasi-planar clusters with an aromatic electronic structure.^{3,6-8} Theoretical studies on pure boron molecules also showed that structures with boron in triangular arrangements could be quite stable, with the α -sheet as the most stable state due to optimal filling of its orbitals (Figure 1).^{6,9} Contrary to well-defined honeycomb lattices of graphene or h-BN, boron sheet could be polymorphic.⁸ As a result, within a narrow range near the ground state, numerous lattices with different patterns of hexagon holes in a triangular grid could exist (Figure 1).⁸ 2D boron's structure is also predicted to be dependent on the substrate, which has not been observed in any other 2D material.^{9,10} Most importantly, electronic structure calculations reveal anisotropic metallic properties of borophene. While these properties are interesting theoretically, experimental investigations of borophene are notably sparse because unlike carbon, boron in its ground state thermodynamically prefers a 3D crystalline structure.¹⁰⁻¹² To selectively suppress the 2D nucleation barrier, detailed theories suggested using a 'sticky' substrate, such as Ag or Cu, where boron atoms could continue growing in one plane.¹⁰

Experimental breakthrough in this elusive research occurred in 2015 and 2016 when two groups independently synthesized borophene using ultra high vacuum molecular beam epitaxy (UHV MBE). Mannix *et al.* and Feng *et al.* evaporated high purity solid boron-based atomic source

on pure single crystal Ag(111) substrate.^{12,13} Using *in situ* high resolution scanning tunneling spectroscopy (STM), Feng *et al.* demonstrated monoatomic layers and deduced anisotropic metallic behavior of borophene.¹³ Feng *et al.* reported the formation of S1 and S2 phase, with the S1 phase matching Zhang *et al.*'s theoretical prediction of boron on Ag(111) substrate.^{10,13} The

S1 phase, resembling the well-known β_{12} sheet structure could only be synthesized ~ 570 K, forming clusters and disordered boron with minor change in temperature.¹³ By increasing the growth temperature to 680 K or by annealing the S1 phase above 650 K, they synthesized the S2 phase which closely resembled the χ_3 sheet model in the theoretical literature.¹⁰ Both boron sheets were quite inert to oxidation and weakly interacted with the Ag (111) substrate.¹³

In addition to temperature, Mannix *et al.* found that borophene morphology depended on the deposition rate.¹² At low deposition rate and high substrate temperature, they found a corrugated 'striped' phase with a rectangular lattice, closely resembling Feng *et al.*'s S1 phase.^{12,13} Contrary to the β_{12} structure with a better lattice match to Ag(111), Mannix *et al.* proposed the structure to have a close-packed triangular pattern.^{12,13} Their second phase, referred as the homogeneous phase in the paper resembled Feng *et al.*'s S2 phase. While Feng *et al.* observed S2 phase at higher

temperature, Mannix *et al.* found S2 phase at lower temperature and/or higher growth rate. Under high temperature conditions, Feng *et al.* observed the growth of 3D boron clusters.¹³ For both studies, experimental data matched the simulated scanning tunneling microscopy images. Because of these discrepancies in the literature, more studies should be done to understand the role of temperature, deposition rate and substrate on growth dynamics of structurally distinct 2D boron sheets.

Regardless of the discrepancy in borophene's atomic structure, both studies agreed on its metallic characteristics, confirming previous electronic structure calculations.^{4,12,13} In terms of mechanical properties, boron layers were composed of strong covalent bonds with high in-plane stiffness. β_{12} sheet had softer out-of-plane bending than graphene.¹² Thus, borophene's metallic

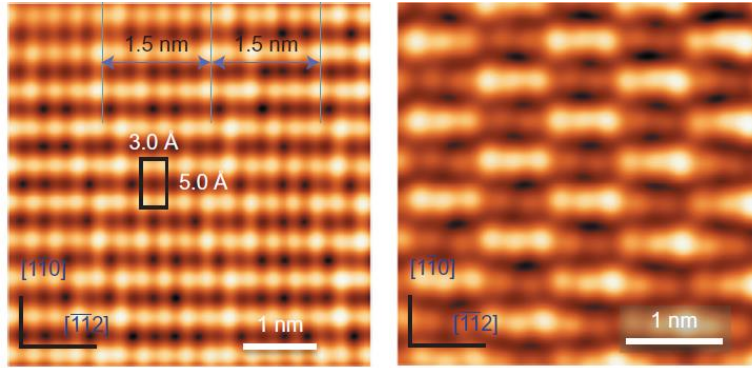


Figure 2. High-resolution STM images of 2D boron sheets on Ag(111) demonstrating S1 (left) and S2 (right) phases¹⁴

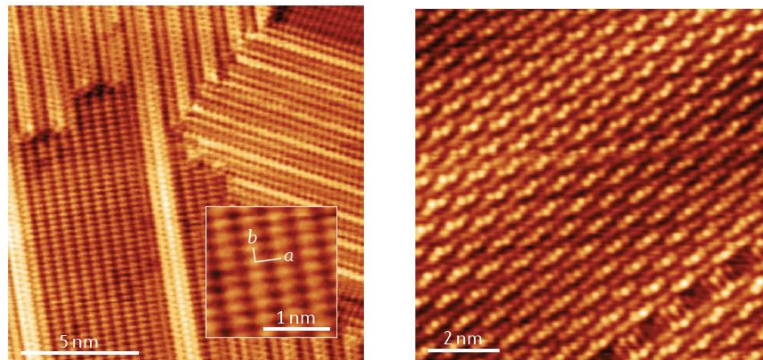


Figure 3. High-resolution STM images of 2D boron sheets on Ag(111) demonstrating striped (left) and homogeneous (right) phases¹²

and mechanical properties could be potentially combined in nanomechanical devices and flexible electronics.

For any technological application, borophene must be integrated with other materials. Because it is experimentally challenging to synthesize atomically well-defined 2D boron, lift the boron layer from the substrate and transfer it to another layer without deteriorating its properties, 2D boron has been primarily studied in isolation. Recently, Liu *et. al* demonstrated the self-assembly of lateral heterostructure between perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), an organic semiconductor and borophene.¹¹ PTCDA self-assembles on a variety of substrates, including metal, semiconductor, oxides and salt crystals.¹¹ Liu *et. al*'s report showed an electronically abrupt interface and weak interaction between borophene and PTCDA, obtaining a remarkable feat in borophene-based heterostructures.¹¹ Borophene/PTCDA interface could be used as metal/semiconductor junctions for electronic applications.

The early progress in borophene chemistry offers an interesting avenue to study metallicity in atomically thin limit. However, in terms of industrial applications, borophene needs to overcome several challenges. Borophene needs to be isolated from its growth substrate for independent characterization from multiple techniques. So far, most of the studies have relied on UHV synthesis and *in situ* characterization techniques, so high-throughput method to synthesize large-area thickness controlled borophene should be developed. While there is a great potential for borophene in the flatlands, understanding its 2D atomic structure should be the first step to explore its unique electronic and mechanical properties.

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