

Unveiling the nature of 2D boron at atomic scale

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उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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2025

CERTIFICATE

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ABSTRACT

Boron, a group 13 element, has been a fascinating subject for scientists for decades due to its electron deficiency, which gives rise to a complex array of structural variations, including several distinct allotropes and polymorphs. The discovery of boron's superconductivity under high pressure and in magnesium diboride (MgB_2) has further heightened interest in this element. The superconductivity in MgB_2 is attributed to the planarity of boron within its structure. Additionally, theoretical predictions suggest that boron clusters exhibit greater stability, particularly those corresponding to individual icosahedra. These factors collectively enhance the interest in exploring the two-dimensional (2D) counterpart of boron.

The landscape of materials science has been fundamentally transformed by the advent of 2D materials. Among the non-van der Waals 2D materials, boron stands out as one of the most complex elements predicted to form a 2D counterpart. Boron is renowned for its diverse chemistry and it possesses only three valence electrons, yet it demonstrates a fascinating capability to engage in electron-sharing through various mechanisms, resulting in the formation of two-electron, multicenter ($2e\text{-nc}$) bonds. The exploration of boron cluster stability is pivotal for evaluating the practicality of borophene, a 2D material counterpart of boron. Theoretical studies have shown that different boron clusters exhibit stability when supported on metallic substrates, and these clusters extend to form borophene and serve as foundational elements for various borophene polymorphs. Borophene was successfully synthesized on silver, marking a significant milestone that has subsequently led to various other research groups producing different phases of borophene on a range of substrates.

The exfoliation of non-van der Waals materials into 2D structures was initially considered unlikely. However, successful exfoliation of materials such as tungsten trioxide ($\alpha\text{-WO}_3$) and hematite (Fe_2O_3) has significantly strengthened confidence in the potential to isolate new 2D non-van der Waals materials. The successful synthesis of freestanding borophene using a top-down approach, specifically through liquid-phase exfoliation (LPE), paves the way for the production of substrate-free borophene.

This study investigates 2D boron at the atomic scale using scanning tunneling microscopy (STM) for both liquid-phase exfoliated (LPE) and beam-grown samples. Additionally, high-resolution transmission electron microscopy (HRTEM) was used

to explore the LPE-synthesized 2D boron.

We investigated the adsorption behavior of freestanding borophene on Au(111), including atomic-scale structural and electronic characterization of LPE borophene on the Au(111) substrate. Using experimental techniques such as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), it was complemented by density functional theory (DFT) calculations, we identified the phase as β_{12} borophene. Our study aims to elucidate the atomic structure of LPE borophene and its interaction with the gold substrate.

Subsequently, we examined a denser coverage of borophene, resulting in a complete monolayer of the β_{12} borophene phase on the Au(111) surface. Following this, a spin-coating cycle led to the self-assembly of boron clusters across the entire substrate. Wherein the borophene monolayer served as a template for the self-assembly of clusters. The interaction of boron clusters with the Au(111) substrate was investigated, and the boron clusters with the β_{12} monolayer phase were examined using STM measurements. STS measurements were employed to determine the metallicity of both the clusters and the β_{12} monolayer.

While multiple reports document polymorphisms in borophene when grown on substrates, there has been no single experimental study that has reported the evolution of various phases in liquid-phase exfoliated borophene. We provide compelling evidence from HRTEM to establish the evolution of β_{12} , χ_3 , striped phases, as well as several phases with 4-fold, 6-fold, and mixed-fold symmetries, and various borophene phases with complex geometries. Additionally, density functional theory band structure calculations of prominent borophene phases.

Following the investigation of LPE borophene and clusters, we examined electron beam-grown borophene and clusters on a silver substrate. Previous studies on borophene growth predominantly employed electron beam evaporation with a boron rod. We used boron powder in place of a boron rod to grow borophene. By employing electron beam evaporation, we achieved the formation of single-phase borophene, rather than a polymorphic phase. We employed STM, and STS to analyze the properties and phase of the synthesized borophene. Additionally, we studied the stability of the synthesized borophene, observing the evolution of clusters. The metallicity of the grown borophene and clusters was determined through STS measurements.

These investigations will be pivotal in unraveling the fundamental properties of 2D boron and clusters. The interaction between borophene and its substrates constitutes the initial step toward elucidating the behavior of Borophene when it interacts with various other materials. Such insights are critical for applications spanning sensing, catalytic activities, battery applications, and beyond, where interactions play a crucial role.

PUBLISHED CONTENT AND CONTRIBUTIONS

- [1] **Umashankar Rajput**, Md Faiz Akhtar, Giriraj Vyas, Somnath Bhowmick, Prashant Kumar, and Aparna Deshpande. “Evolution of atomistic boron clusters on borophene monolayers on Au(111)”. In: *The Journal of Physical Chemistry C* 129.15 (2025), pp. 7485–7492.
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- [4] **Umashankar Rajput**, Md Faiz Akhtar, Vaibhav Walve, Imrankhan Mulani, Giriraj Vyas, Somnath Bhowmick, Prashant Kumar, and Aparna Deshpande. “Liquid Phase Exfoliated Borophene on Au (111)”. In: *The Journal of Physical Chemistry C* 128.9 (2024), pp. 4104–4110.
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- [7] Abhijit Biswas, Arundhati Sengupta, **Umashankar Rajput**, Sachin Kumar Singh, Vivek Antad, Sk Mujaffar Hossain, Swati Parmar, Dibyata Rout, Aparna Deshpande, Sunil Nair, et al. “Growth, properties, and applications of pulsed laser deposited nanolaminate Ti_3AlC_2 thin films”. In: *Physical Review Applied* 13.4 (2020), p. 044075.

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Chapter 1

INTRODUCTION

1.1 Overview

The groundbreaking discovery of graphene by Andre Geim and Konstantin Novoselov in 2004 catalyzed the exploration of 2D materials[1]. Using a simple mechanical exfoliation technique known as the "Scotch tape method," they successfully isolated bulk graphite into a monolayer of carbon atoms. The exceptional electrical conductivity, mechanical strength, and thermal properties of graphene captured the attention of the materials science community. The unique properties of 2D materials motivated scientists to explore and discover additional 2D materials.

The fabrication of 2D materials involves various methodologies, which can be broadly classified into two main approaches: Bottom-up and Top-down techniques. Bottom-up approaches involve the construction of monolayers through advanced deposition techniques, including electron beam deposition, physical vapor deposition (PVD)[2], chemical vapor deposition (CVD)[3–5], and molecular beam epitaxy (MBE)[6]. These methods facilitate the controlled assembly of 2D materials at the atomic level, offering notable advantages such as precise regulation of layer thickness and the ability to produce materials that are not naturally layered. These sophisticated systems enable the creation of high-quality monolayers and few-layer structures, which are critical for exploring novel material properties and potential applications.

In contrast, top-down approaches such as mechanical exfoliation, ion intercalation, and liquid exfoliation are noted for their simplicity, versatility, and scalability[7–9]. These techniques have played a pivotal role in the discovery and characterization of a diverse range of 2D materials. Initially, research predominantly focused on van der Waals (vdW) materials, which are naturally layered and readily exfoliated. However, recent advancements have demonstrated the feasibility of exfoliating non-van der Waals materials. The development of top-down approach for transforming non-van der Waals (non-vdW) materials into 2D forms has progressed significantly over time, though it remains relatively limited. Various techniques such as chemical methods, liquid-phase exfoliation (LPE), and mechanical exfoliation, have successfully transformed non-vdW materials into 2D forms. For instance, the delamination

of layered MnO_2 into single sheets was reported even before the groundbreaking mechanical exfoliation of graphene in 2004[10, 11]. Similarly, the exfoliation of non-vdW layered MAX phases into MXenes has been achieved through selective etching of the A layers in the MAX phases. Examples include the transformation of Ti_3AlC_2 into Ti_3C_2 , Nb_2AlC into Nb_2C and so on[12, 13]. Additionally, other examples of exfoliating non-vdW layered materials include metal borides, such as MgB_2 and AlB_2 [14]. The LPE of non-layered, non-vdW materials has further expanded this field. The first success in this domain was achieved with monoclinic tungsten trioxide ($\alpha\text{-WO}_3$) crystals[15], followed by Tai et al.[16] who successfully produced nanosheets of olivine-type LiFePO_4 and spinel-type LiMn_2O_4 using LPE. This breakthrough in LPE for non-vdW materials has propelled further research into 2D non-van der Waals materials, including $\alpha\text{-Fe}_2\text{O}_3$ (Hematene)[17], Si[18, 19], Sn[20], B_4C [21], and β -boron[22–24]. These advancements have significantly broadened the research scope, allowing for deeper investigations into the structural evolution, physical properties, and chemical characteristics of these materials.

The stability of boron clusters, supported by theoretical and experimental findings [25, 26], alongside the discovery of conventional superconductivity in MgB_2 and high-pressure boron, has sparked scientific interest in exploring the feasibility and properties of borophene—a quasi-two-dimensional manifestation of boron. The robust stability observed in two-dimensional boron clusters and theoretical projections regarding quasi-two-dimensional boron[27–29] collectively drive investigations into borophene and its distinct characteristics. Boron, characterized by its complexity and interesting properties, represents an exciting avenue for exploration, with its two-dimensional form promising to unveil even more exotic features while offering insights into the fundamental properties of boron.

1.2 Boron

Boron, with an atomic number of 5 and positioned in Group 13 of the periodic table, exhibits a remarkable array of chemical and physical properties that have garnered significant scientific interest[30, 31]. Renowned for its exceptional hardness, low density, high melting point, and notable stiffness, boron stands out due to its electron-deficient nature, characterized by only three valence electrons. This electron deficiency enables boron to form complex bonding structures, including two-center two-electron (2c-2e) and multi-center two-electron (nc-2e) bonds[32],

resulting in a diverse array of polymorphs[30–33]. The complexity of boron’s polymorphism is underscored by the fact that the most stable phase, β_{12} , was only confirmed in 2015 by White et al. at ambient conditions[33]. Boron’s intricate bonding capabilities and diverse crystal structures are further complemented by its potential for superconductivity, making it a focal point in materials science research. Additionally, Boron’s unique properties, including neutron capture capability, metallurgical applications, roles in electronics, etc. enhance its scientific significance and broaden its range of applications.

1.2.1 Allotropes and Polymorphism

Boron electron deficiency and the availability of only three valence electrons are crucial in the making multiple allotropes[30–33]. It demonstrates a fascinating capability to engage in electron-sharing through various mechanisms, forming two-electron, multicenter (2e-nc) bonds[32]. This unique electron-sharing ability and complex bond formation enables boron to exist in multiple allotropes, each with distinct structural characteristics. Boron forms around 16 allotropes from which only, α -rhombohedral[34], β -rhombohedral[35, 36], β -tetragonal[37, 38], and γ -orthorhombic[39] structures are determined to be thermodynamically stable at ambient conditions[31, 40, 41]. The various allotropes of boron are primarily composed of icosahedral clusters, which act as the fundamental building units of their unique crystalline structures, as depicted in Figure 1.1.

α -Rhombohedral boron allotrope is one of the simplest structures of a unit cell comprising twelve boron atoms[34, 43], arranged in β_{12} icosahedra where each atom has five nearest neighbors. These individual units are arranged at the edges of a Rhombohedral. The principles established by Higgins et al. for a boron icosahedron provide insight into the bonding within this structure[43, 44]. This treatment reveals that out of forty-eight orbitals, twelve are positioned outside the icosahedron, making them readily available to form twelve equivalent bonding orbitals with neighboring atoms. Among the internal orbitals, thirteen are classified as bonding, while seventeen are antibonding, with a substantial energy gap separating the two types. To achieve a closed electron shell within the icosahedron, which requires exactly twenty-six electrons, the highest bonding, and lowest antibonding orbitals must be highly degenerate. Each boron atom has three valence electrons. Out of these, ten electrons are designated for external bonding after accounting for internal bonding. Specifically, six electrons are utilized for conventional bonds, while the

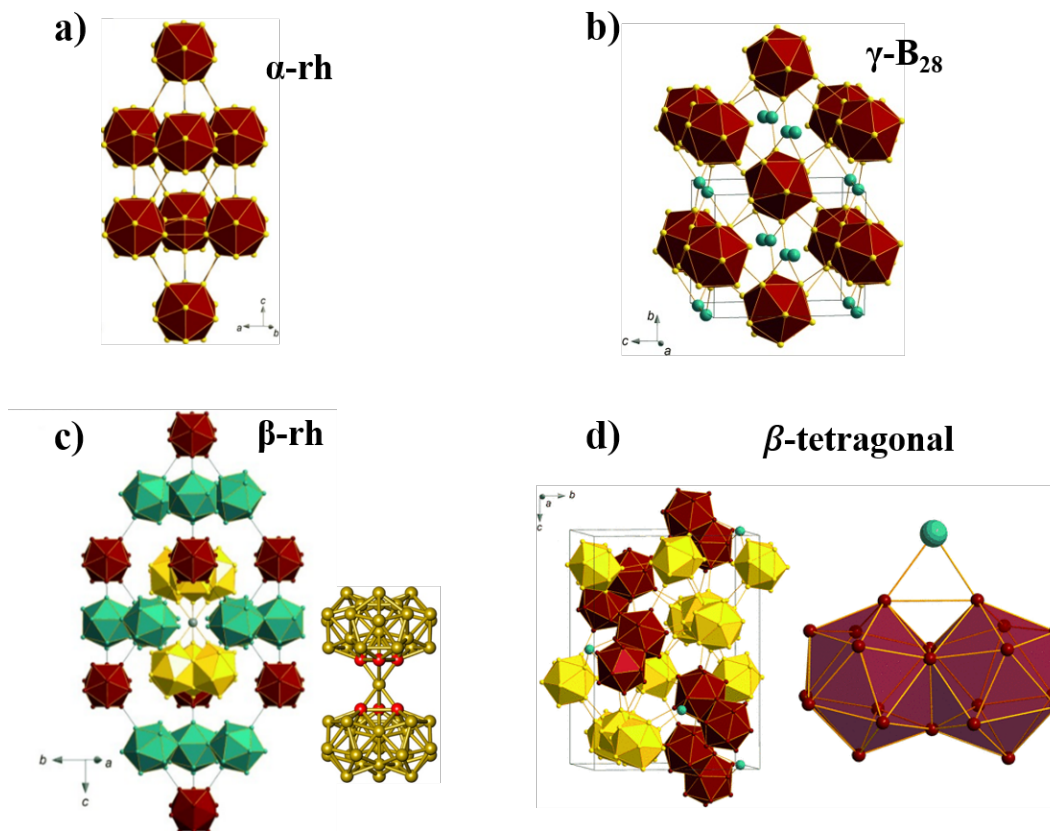


Figure 1.1: 3D structure of thermodynamically stable allotropes a) 3D illustration of α -rhombohedral boron. (b) 3D illustration β -rhombohedral boron, along with the triple fused B_{28} triply-fused icosahedron boron, a constituent part of β -rhombohedral boron (c) 3D illustration γ -orthorhombic boron. (d) 3D illustration β -tetragonal boron along with B_{21} double-fused icosahedron, which is the constituent part β -tetragonal. Images adapted with permission from Ref. [30, 42]

remaining four electrons are allocated to form delta bonds. Since each delta bond needs two electrons or two-thirds of an electron per atom, the six boron atoms in each icosahedron involved in delta bonding collectively provide four electrons, ensuring a complete electron balance.

In contrast, β -rhombohedral is Boron's most complex known structure. The structure was, initially proposed by Hughes et al. in 1963[35], was subsequently validated by Hoard et al., Geist et al., and Callmer[36, 46–48]. The structure of the unit cell is believed to encompass 105 atoms, with its principal component being a B_{84} polyhedron. This polyhedron features a central B_{12} icosahedron encircled by twelve B_6 pentagonal pyramids. To better understand the atomic arrangement and

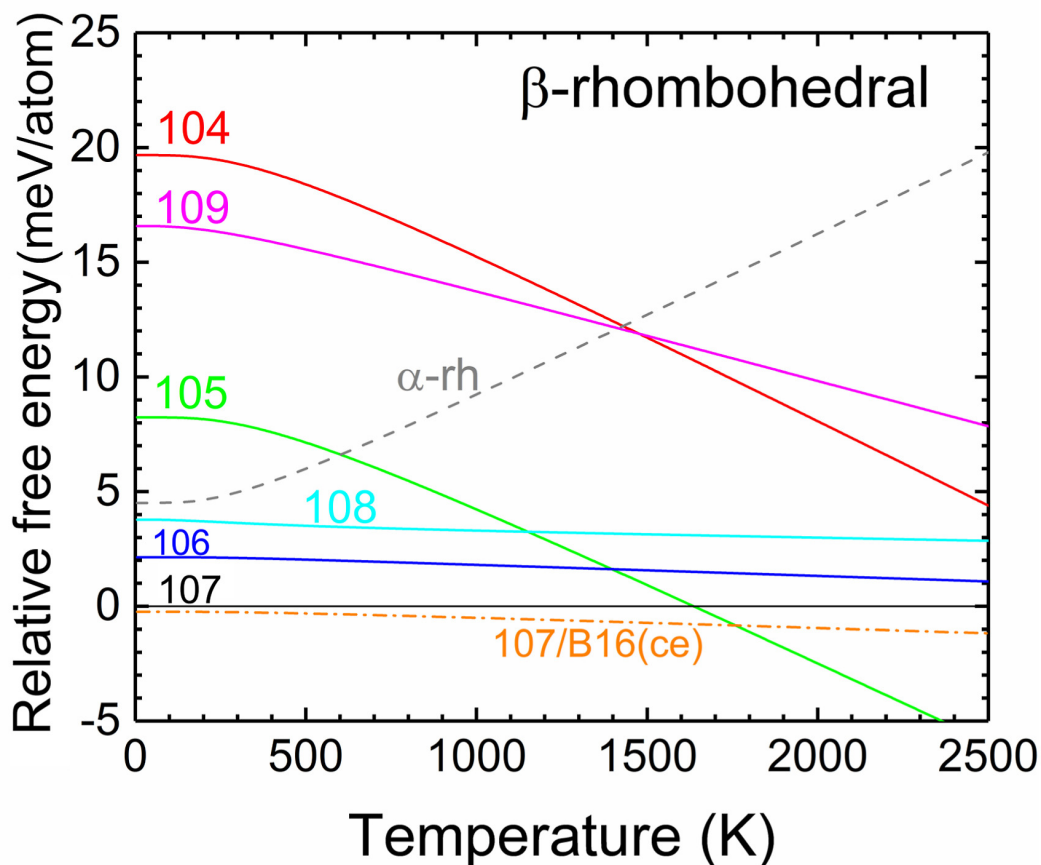


Figure 1.2: Temperature dependency of phase transition with varying interstitial atoms. Reproduced with permission from Ref. [45]

the relationship between electronic structures, one can consider the crystal structure from an alternative viewpoint: it involves the assembly of B_{12} icosahedra, which combines with triply fused icosahedra (B_{28}) composed of 28 atoms. In the idealized β -boron structure, the rhombohedral unit cell, which includes 105 boron atoms, features an outer layer composed of 20 icosahedra. Of these, 8 are located at the corners of the cell, while 12 are situated along the edges. At the center of the unit cell, two icosahedra triply fused are present, joined by an interstitial boron atom. These icosahedral clusters are likely interconnected via conventional two-center two-electron (2c2e) bonds.

The stability of the β -rhombohedral and α phases of boron has been a subject of debate, with both phases predicted to be the most stable form of boron by various studies [49–51]. However, White et al. conclusively demonstrated that the β phase is indeed the most stable [33], thereby resolving the longstanding ambiguity regarding

the comparative stability of the α and β phases of boron. Widom et al. predicted that the β phase's most probable arrangement of interstitial atoms consists of a unit cell with 107 atoms[50]. The number of atoms in β -rhombohedral boron is influenced by the occupancy of interstitial sites, which is contingent upon various factors such as temperature and cooling rate.

Hayami et al. investigated the thermodynamic robustness of various boron allotropes, each with different numbers of interstitial sites[45]. The β -rhombohedral boron structure with 107 atoms was identified as the most stable arrangement. However, at elevated temperatures, specifically around 1700 K, the free energy of the 105-atom cell decreases substantially and becomes less than the free energy of the 107-atom arrangement. When liquid boron cools down, it first solidifies into a 105-atom structure upon reaching its melting point. As cooling continues, it then transitions into either a 107-atom or 106-atom structure, depending on the rate at which the temperature decreases. Rapid cooling results in the formation of the 106-atom phase, while slow cooling leads to the 107-atom phase. Consequently, the β -rhombohedral boron structure exhibits a variable number of atoms. The temperature-dependent evolution of the stability of the β -rhombohedral phase with different numbers of atoms is illustrated in the accompanying Figure 1.2.

A new structure closely related to the β was reported by An et. al. known as τ [52]. Initially, An et al. predicted that this phase is more stable than the β phase but finally, they also concluded that β_{106} is the most stable elemental-boron phase.

The γ -phase of boron is achievable by compressing α -Rhombohedral boron phases by applying pressure of 19 GPa[39, 53], while β -rhombohedral starts evolving to the γ - B_{28} around 1000 K at a pressure of 9 GPa[53, 54]. The phase reversibility was also tested for γ - B_{28} , it got reversed back to the β -rhombohedral when heated by the laser below 7 GPa[54]. It is stable up to the pressure of 89 GPa, while another report by Zhong et al. has shown if the pressure increased slowly it could be stable up to 126 GPa at room temperature afterward it gets converted to α -Ga-type[53]. The γ -phase comprises 28 atoms in a unit, also known as the γ - B_{28} [30, 39]. In the γ - B_{28} structure, the centers of the B_{12} icosahedra are arranged in a slightly distorted cubic close packing, akin to the arrangement seen in α - B_{12} . However, a key distinction lies in the occupation of all octahedral voids by B_2 pairs in the γ - B_{28} structure, which results in an increased density compared to α - B_{12} . Oganov et al. showed the ionic nature of γ -phase and the structural configuration of γ - B_{28} resembles a

NaCl-type structure, where the B_{12} icosahedra and B_2 pairs function analogously to anions and cations, respectively, in this phase, which can also be referred to as boron boride ($B_2^{\delta+}B_{12}^{\delta-}$) due to the charge transfer between these two components [39]. However, Haussermann et al. reported that there is no ionic contribution during bonding in γ - B_{28} [55]. Subsequently, Mondal et al. confirmed the results of Oganov et al. regarding charge transfer in γ - B_{28} through Bader analysis of the experimental charge density[56, 57].

Despite the structural similarities, the electronic properties of ionic γ - B_{28} and covalent α - B_{12} exhibit notable differences. Ionic γ - B_{28} demonstrates a distinct electronic structure characterized by minimal variation in its bandgap under pressure. Even at extreme pressures of up to 200 GPa, γ - B_{28} remains an insulator with a relatively wide bandgap of 1.25 eV. In contrast, the bandgap of α - B_{12} undergoes a rapid decrease upon compression, closing completely at approximately 160 GPa. These contrasting behaviors can be attributed to the presence of charge transfer in γ - B_{28} , which is absent in α - B_{12} . This charge transfer significantly influences the electronic properties, leading to the observed disparity in bandgap behavior under varying pressures. In a study by Shirai et al., it was shown that α -boron, a semiconductor, can close its electronic band gap without a phase transition occurring[58]. This transition is due to the gradual strengthening of the three-center bonds, which drives the shift from a semiconducting phase to a metallic phase. This results in a higher coordination number of icosahedra, indicating a continuous transition. This study identifies a critical turning point at approximately 50 GPa, where the metallization process becomes significant. Shimizu et al. demonstrated that at 160 GPa, α -boron exhibits a superconducting transition without any associated phase change[43, 59]. The transition temperature for superconductivity in α -boron is observed at 6 K, which is marginally higher than that of β -boron under similar pressure conditions.

The α -Ga phase of boron was initially predicted through theoretical calculations[60]. The α -Ga structure of elemental boron can be interpreted in two distinct ways. Firstly, it can be perceived as a layered configuration composed of sheared honeycomb networks, characterized by thicker connections at the shorter B-B distances. Secondly, it can be described as comprising layers of buckled trigonal networks interconnected by the short B-B contacts noted in the first interpretation. It is important to note that the boron atoms, represented in light green and dark green, do not reside within the same plane. Subsequently, Ma et al. in 2004[61],

demonstrated that the α -Ga phase is stable both at normal and high pressures, with no phonon softening observed. The strong electron-phonon coupling is primarily due to the in-plane σ -bonding states from the py and pz orbitals interacting with y - z vibrations. This two-dimensional structure results in significant anisotropy and indicates that α -Ga B is a promising superconductor. Following the theoretical predictions, Chuvashova et al. synthesized a boron phase resembling the α -Ga-type structure, which they designated as the ζ -B phase[62]. They demonstrated that this boron allotrope can be achieved by laser heating single crystals of β -B to temperatures exceeding 2100 K under pressures greater than 115 GPa. This newly identified phase, ζ -B, exhibits an orthorhombic structure analogous to α -Ga, as confirmed by single-crystal X-ray diffraction. Examining interatomic distances and linear compressibilities along the principal crystallographic axes reveals that the structure is not layered, contrary to previous claims. Within the examined pressure range (115 to 132 GPa), ζ -B exhibits lower compressibility than any other known boron allotrope. Experimental observation does not show any relation between the metallic characteristics of the high-pressure phase of boron and ζ -B as predicted earlier[61, 63, 64].

β -tetragonal boron features form a three-dimensional complex framework primarily composed of B_{12} icosahedra, and B_{21} double-fused icosahedra, along with boron interstitials[37, 38, 40]. These structural units, B_{12} and B_{21} , are interconnected through direct B-B bonds aligned along the quasi-fivefold axis of the icosahedra or through a few B-B bonds shared with isolated boron atoms. Consequently, the β -tetragonal boron unit cell encompasses eight simple B_{12} icosahedra, four double B_{21} icosahedra, and ten isolated boron atoms. Each B_{12} icosahedron is connected to six adjacent B_{12} icosahedra, five B_{21} double icosahedra, and one isolated boron atom. Similarly, each B_{21} double icosahedron is linked to ten neighboring B_{12} icosahedra and four other B_{21} double icosahedra, with its remaining four bonds shared with isolated boron atoms. Hayami's predictions suggest that the lowest-energy structure for β -t boron is achieved by incorporating eight interstitial atoms, corresponding to 192 atoms ($N=192$)[40]. This configuration results in a more stable structure for β -t boron.

In a recent report by Hayami et al., a similar phase transition observed in β -rhombohedral boron is hypothesized to occur in β -tetragonal boron[45]. Figure 1.3 illustrates the enthalpy variations of different phases as a function of pressure, providing a comprehensive view of how these phases behave under varying condi-

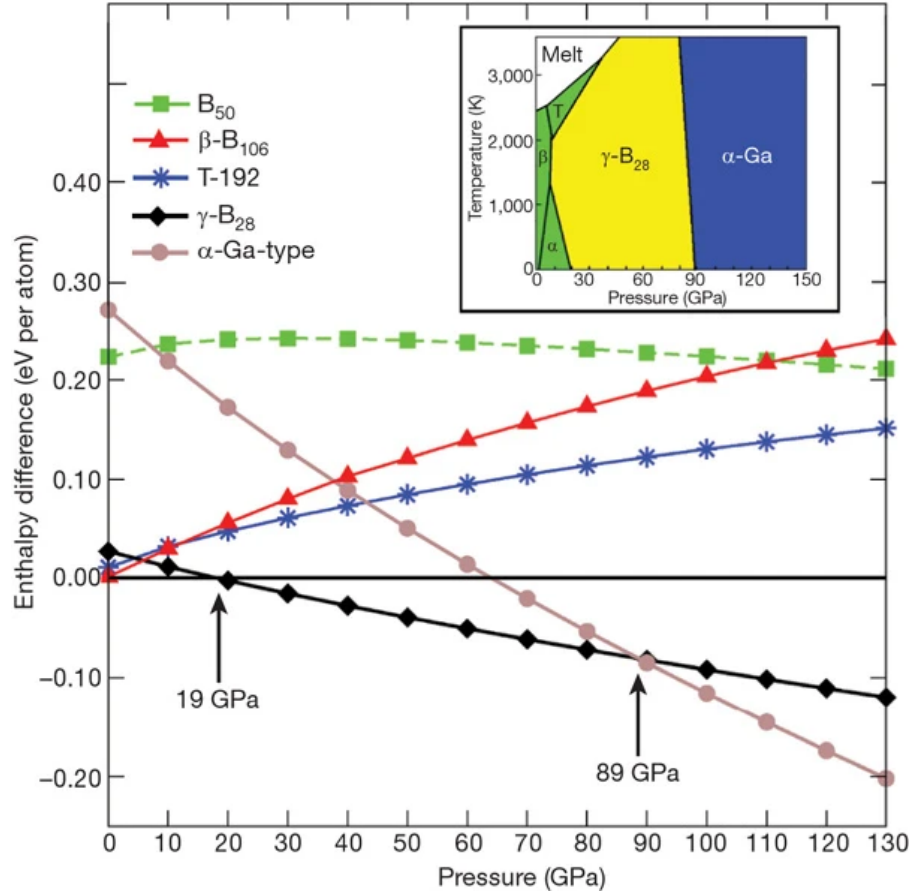


Figure 1.3: Figure showing the enthalpies of different phases upon pressure. inset showing the phase evolution on varying temperature and pressure. Reproduced with permission from Ref. [39]

tions. Additionally, the inset of Figure 1.3 offers a depiction of the transformation of the thermodynamically stable phase into other phases, highlighting the specific conditions under which these phase transitions occur. Their computational analyses indicate that the free energy of the 190-atom cell becomes lower than that of the 192-atom cell at approximately 2000 K. Consequently, cooling from high temperatures is predicted to induce a phase transition from the 190-atom cell to the 192-atom cell. Nevertheless, rapid cooling, similar to what is observed in β -rhombohedral boron, may impede the diffusion of interstitial atoms, preventing the unit cells from reaching the full 192-atom configuration. This theoretical framework could explain why a sample produced via chemical vapor deposition (CVD) retained the 190-atom structure[38]. Pure β -t boron is most likely to be unstable and may require stabilization through the incorporation of impurities[45]. An experimental investigation conducted under high temperature and high-pressure conditions reported

the successful synthesis of β -t boron[65]. However, other studies performed under similar conditions failed to observe this phase[45, 66–69]. Consequently, further experimental validation is necessary to confirm the existence of pure β -t boron conclusively.

Amorphous boron can be synthesized using various techniques such as physical vapor deposition (PVD) [70], chemical vapor deposition (CVD) [71–73], pyrolysis [74], and rapid cooling of melt [75]. Each method consistently identifies β_{12} as the primary constituent of amorphous boron. However, there have been numerous claims regarding the structural arrangement of amorphous boron.

Kobayashi, et al. proposed that amorphous boron is characterized by randomly bonded β_{12} icosahedra, lacking long-range order [76]. Conversely, Badzian suggested an icosahedral arrangement of boron and posited that the structure of amorphous boron represents a frozen stage in the transition from α -rhombohedral to β -rhombohedral boron [72]. Additionally, another report by Kobayashi indicated that the short-range order structure of amorphous boron is closer to that of β -rhombohedral boron[77]. In contrast, a study by Maita et al. in 2020 reported that chemically vapor-deposited amorphous boron is more closely related to α -rhombohedral boron [73].

The exploration of two-dimensional boron compounds, including borophene and other 2D boron polymorphs, highlights boron’s remarkable ability to form diverse crystallographic structures. These structures range from periodic porous arrangements to intricate three-dimensional protrusions. In borophene, polymorphism is notably pronounced, with each polymorph displaying unique structural and electronic characteristics. The various polymorphs of borophene are distinguished by different configurations of boron atoms, which lead to a wide array of electronic band structures and mechanical properties, underscoring the material’s versatility and potential for various applications.

1.2.2 Superconductivity

Boron itself is not a superconductor at ambient pressure; however, magnesium diboride MgB_2 is particularly notable, with the highest critical temperature (T_c) of 39 K for conventional superconductors[63]. The superconductivity in MgB_2 is primarily attributed to strong electron-phonon coupling (EPC) within the boron

planes[78]. Various experimental[79, 80] and theoretical models[81–85] have attempted to clarify the two-band model of MgB_2 . The boron atoms in MgB_2 form hexagonal, honeycomb-like layers, with magnesium atoms positioned above the centers of these hexagons between the boron planes. The electronic states at the Fermi level mainly derive from σ - or π -bonding boron orbitals. The σ -bonding states, unique in their partial occupancy, are confined within the boron planes and exhibit strong coupling to the in-plane vibrations of the boron atoms, leading to significant electron-pair formation with a large energy gap of 6-7 meV. This strong pairing is the primary contributor to MgB_2 's superconductivity. Conversely, the π -bonding states form weaker pairs with an average energy gap of 1-2 meV, their pairing enhanced by interaction with the σ -bonding states. Furthermore, the findings were confirmed by Angle-Resolved Photoemission Spectroscopy (ARPES), demonstrating that the σ band plays a significant role in the superconductivity due to its stronger coupling with phonons. In contrast, the π band has a minor influence on superconductivity, exhibiting a substantially weaker phonon coupling.

Elemental β -boron has been found to exhibit superconductivity under high-pressure conditions, as demonstrated by Eremets et al.[63]. Utilizing diamond anvil cell electrical conductivity techniques, they investigated boron's superconducting properties and observed a phase transition from a nonmetallic to a superconducting state at approximately 160 gigapascals (GPa). The study revealed that the critical transition temperature (T_c) increased from 6 kelvin (K) at 175 GPa to 11.2 K at 250 GPa, indicating a positive pressure coefficient of 0.05 K/GPa. Although the exact phase was not determined, it is theorized to align with the α -Ga phase. However, the experimentally synthesized boron phase resembling α -Ga, referred to as ζ -B[62], as shown in Figure 1.4, has not displayed the anticipated metallic transition[61, 63, 64]. Therefore, further experimental evidence is required to ascertain the precise phase corresponding to the observed superconducting state under pressure.

Shimizu et al. demonstrated superconductivity in alpha-boron (α -boron) under high-pressure conditions[59]. Specifically, they measured the temperature dependence of the electrical resistivity of α -boron at pressures of 100, 136, and 159 GPa to identify superconducting behavior. The negative slopes of the curves at these three pressures indicate semiconductive characteristics. However, a sharp drop in resistance was observed around 6 K at 159 GPa, indicating the onset of a superconducting transition in α -boron. The superconducting transition temperature of α -boron, recorded at 6 K, is marginally higher than that of β -boron when subjected

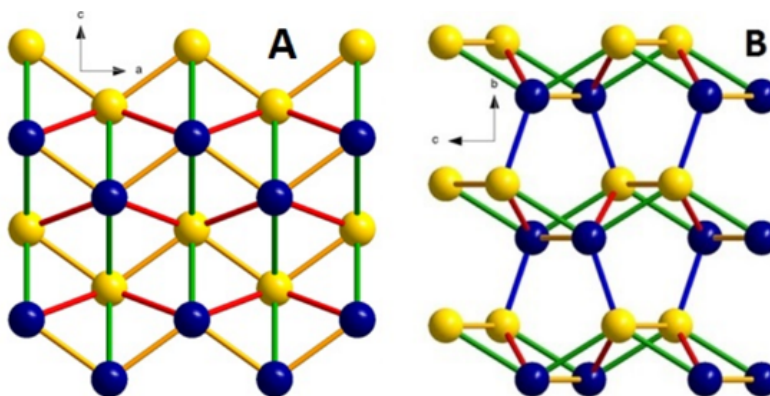


Figure 1.4: The experimentally observed layered nonicosahedral boron allotrope ζ -B is shown, Reproduced with permission from Ref. [62]

to equivalent pressure conditions.

1.3 Borophene

The synthesis of borophene, a monolayer of boron atoms, marks a substantial advancement in materials science. This achievement is underpinned by boron's distinct electron-deficient characteristics and its tendency to form unique two-dimensional cluster structures. The advancement in both theoretical modeling and experimental methodologies and understanding of boron clusters underpins the successful realization of borophene synthesis.

1.3.1 Boron clusters: Foundation of borophene

The role of boron clusters in the synthesis of borophene underscores the journey from theoretical speculation to practical realization. Early computational studies and theoretical calculations indicated that boron clusters, even those with significant size, tend to adopt stable 2D configurations, unlike the three-dimensional polyhedral forms found in bulk boron.

A comprehensive understanding of boron clusters is crucial and highly interesting. The study of boron clusters began with the recognition of the instability of the isolated B_{12} icosahedron, the fundamental unit of many boron allotropes[86]. In 1995, Boustani predicted the existence of multiple stable quasi-planar boron clusters[87], attributing their exceptional stability to the strong interaction between outward-pointing π -hybrids[88]. These clusters possess electron clouds on both sides of the plane due to the perfect overlap of π orbitals. Zhai et al. later provided experimental evidence supporting the stability of planar boron clusters and also iden-

tified that planar was the most stable structure for a cluster of 12 boron atoms. This planar structure was found to be energetically more favorable by 3 eV compared to the B_{12} icosahedron[26]. The enhanced stability of these 2D structures is attributed to boron's electron deficiency and its propensity to form multi-centered bonds[89, 90]. Recent research has explored relatively large boron clusters, which are predominantly planar or quasi-planar[90]. Lau et al. (2007) used density functional theory to demonstrate the stability of various boron structures, including buckled 1212, restructured 1221, hexagonal graphene-like, 2D sheets of icosahedrons, low symmetry amorphous-like, and hybrid 2D sheets. Among these, the buckled triangular boron sheet structure was identified as the most stable[91].

Tang et al. predicted that α and β borophene sheets exhibit greater stability compared to buckled triangular structures[92], introducing the concept of "hexagon hole density" (η), defined as the ratio of hexagonal holes to the total number of atoms in the original sheets. Independent studies by Tang et al.[92] and Yang et al.[27] identified the α phase as the most stable form of borophene. Furthermore, Lau et al. suggested that borophene sheets with a hybrid structure combining both triangular and hexagonal configurations would be thermodynamically stable. Galeev et al. further analyzed the bonding characteristics of the α -sheet, noting that hexagonal holes act as absorbers for excess electrons from neighboring filled hexagons.

Liu et al. investigated the growth of boron clusters on Cu (111) and the formation of borophene on a Cu(111) surface via first-principles calculations. Theoretical studies have demonstrated the stability of different boron clusters when supported on a metallic substrate, and these clusters extend to form borophene[28]. This theoretical prediction was the first to demonstrate the evolution of clusters into mono-layer boron.

In Figure 1.5, we have illustrated the progressive development of the theoretical framework surrounding borophene, tracing its evolution over time. This figure highlights how the theoretical predictions, which were refined and enhanced through ongoing research, ultimately played a crucial role in guiding and supporting the experimental realization of borophene.

The experimental synthesis of borophene faced challenges due to boron's complex bonding and polymorphism. However, breakthroughs in 2015 using physical vapor deposition on a silver single-crystal surface under ultra-high vacuum conditions successfully produced various borophene polymorphs. These polymorphs exhibited exceptional mechanical properties, thermal conductivity, and metallic

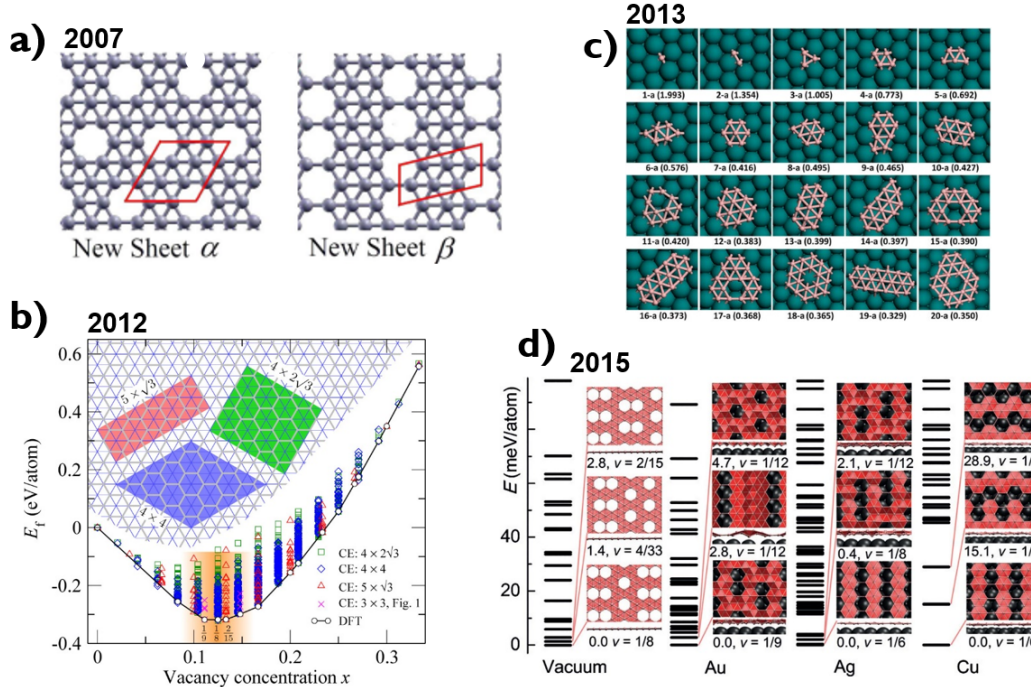


Figure 1.5: Progressive development of the theoretical framework of borophene over the years. a) presents the structural configurations of α and β boron sheets, which were predicted based on the concept of "hexagon hole density." This structural prediction forms the foundation for understanding the stability and variations of boron-based two-dimensional materials. b) illustrates the polymorphic nature of borophene based on formation energy. c) The growth process of Boron clusters, which eventually expand into continuous borophene sheets. d) displays the most stable phases of borophene when grown on different substrates. Images adapted with permission Ref. [28, 29, 92, 93]

electronic characteristics, surpassing graphene in some configurations.

1.4 Borophene Synthesis

The theoretical prediction of borophene has catalyzed extensive research into its synthesis. Initial studies on boron clusters paved the way for exploring 2D boron sheets. In 2012, Penev et al. identified the polymorphic nature of borophene through theoretical modeling, highlighting its diverse structural possibilities[93]. The successful deposition of these two-dimensional boron sheets necessitates a metal substrate with appropriate binding strength to boron atoms. This is crucial to counterbalance the thermodynamic disadvantage posed by the non-layered structure of bulk boron, which renders borophene metastable due to its higher energy than three-dimensional boron. In 2013, Liu proposed synthesizing borophene on metal

or metal boride surfaces using first-principles calculations[94]. This study revealed that a high nucleation barrier impedes the formation of three-dimensional boron during boron atom deposition on Au or Ag(111) surfaces, leading to the formation of two-dimensional boron. The weak binding between borophene sheets and these substrates suggests a relatively simple post-growth separation process.

1.4.1 Bottom-Up Approach

The bottom-up approach refers to the fabrication of nanostructures by precisely assembling single atoms or molecules[95, 96]. The growth of 2D materials starts with nucleation. When feedstocks enter the system, they undergo adsorption and desorption on the substrate, decompose into active species, and cluster at specific sites, forming initial nuclei. These nuclei expand into single-crystal domains as adatoms attach and bond along one-dimensional edges until coalescence occurs. Thus, precise control over nucleation is crucial for epitaxial growth. Nucleation typically occurs at high-energy sites such as atomic steps, grain boundaries, defects, and impurities. However, random distribution of nuclei often results in polycrystals with grain boundaries. Minimizing active sites on the substrate has emerged as a key strategy for achieving large-scale single-crystal films.

The first experimental confirmation of monolayer boron, or borophene, was achieved with the discovery of the planar hexagonal B36 cluster[41, 97]. In comparison, the B35 cluster, characterized by two neighboring hexagonal vacancies, offers greater versatility. These paired vacancies induce an asymmetric arrangement in B35, which facilitates the creation of borophenes with varying hole densities and orientations. Earlier reviews of boron clusters, including a 2006 study and a 2014 brief on structural fluxionality and chemical bonding, highlight the evolution of boron cluster research. The geometric structures and chemical bonding of size-selected boron clusters have become foundational for discovering new boron-based nanostructures, requiring extensive experimental and theoretical efforts.

Zhang et al. investigated various substrates including Au, Ag, Cu, and Ni to determine the optimal structures of borophene on each substrate[29]. Their findings suggest that a planar $\nu_{1/6}$ -sheet configuration is generally preferred on most metals studied and should be a focus in experimental borophene growth on metal substrates. They demonstrated that the interaction between boron and the specific metal substrate can influence the formation of two-dimensional boron structures. This provides a pathway for guided synthesis through tailored boron-metal interactions.

Borophene growth via Physical Vapor Deposition (PVD)

In 2015, Mannix et al. synthesized atomically thin borophene for the first time using an electron beam evaporator[98]. Under ultrahigh-vacuum conditions, crystalline sheets of 2D boron were grown on silver surfaces. STM provided atomic-scale characterization, identifying two distinct phases: a homogeneous phase characterized by atomic chains exhibiting periodic vertical buckling with a periodicity of 0.30 nm, and a striped phase exhibiting a rectangular lattice structure with dimensions of 0.51 nm (± 0.02 nm) and 0.29 nm (± 0.02 nm), as validated by theoretical simulations.

Experimental findings, supported by theoretical calculations, confirm that the striped phase corresponds closely to the lowest-energy mono-layer structure of borophene, showcasing metallic characteristics, unlike bulk boron allotropes. This behavior aligns with predictions of a highly an-isotropic 2D metal. The relative prevalence of each phase depends on deposition conditions: lower rates favor the striped phase, promoting the formation of nanoribbons with striped-phase characteristics, whereas higher rates encourage the growth of the homogeneous phase. Furthermore, elevated growth temperatures favor the stabilization of the striped phase over the homogeneous phase, indicating that the homogeneous phase is likely metastable by comparison.

Feng et al. conducted an experimental synthesis of borophene, achieving the growth of two-dimensional boron sheets on Ag(111) substrates using epitaxial techniques[99]. Their study characterized two specific configurations: β_{12} and χ_3 sheets, characterized by triangular lattices with different arrangements of periodic apertures, as visualized through scanning tunneling microscopy. Density functional theory simulations corroborated experimental findings, confirming the planarity of both sheet types without significant vertical undulations. Notably, boron sheets exhibited high resistance to oxidation and displayed weak interaction with the Ag(111) substrate. Their combined experimental and computational results unequivocally establish the formation of these two structural variants of 2D boron on Ag(111), suggesting potential applications in microelectronic devices. Furthermore, alternative substrates such as Au(111), Cu(111), and metal borides may offer promising platforms for synthesizing monolayer boron sheets, each influencing the resulting structure due to varying interactions with boron atoms. Density functional theory (DFT) simulations and experimental validation consistently demonstrate the planarity of boron sheets without significant vertical undulations. These sheets exhibit high oxidation resistance and weak interaction with substrates such as Ag(111).

their combined experimental and computational efforts have verified the existence of two distinct 2D boron structures on Ag(111).

Based on comparative STM experiments conducted by Mannix et al. and Feng et al., similarities and distinctions in borophene phases are evident. Mannix et al. identified a homogeneous phase which is exactly the χ_3 phase observed by Feng et al. They characterized a second phase as a high-temperature striped phase with a buckled triangular close-packed structure (Pmmn). In contrast, Feng et al. identified a β_{12} phase instead of a striped phase. The hexagon hole density (η) for β_{12} is 1/6 while for χ_3 is 1/5.

Following the initial growth of borophene on the silver substrate, researchers explored several other metallic substrates using Physical Vapor Deposition (PVD). Successful growth of borophene was achieved on Au(111), Al(111), and Cu(111) surfaces. Among these, Cu(111) was identified as particularly favorable, supporting the growth of larger borophene domains.

Li et al. demonstrated the synthesis of hexagonal borophene through molecular beam epitaxy (MBE), achieving the fabrication of a two-dimensional boron sheet with a honeycomb lattice on an Al(111) substrate[100]. Aluminum, with its three free electrons, compensates for borophene's electron deficiency. STM images confirmed the presence of a perfect monolayer borophene film exhibiting a honeycomb structure. Theoretical calculations indicate that honeycomb borophene on Al(111) is thermodynamically stable. Notably, each boron atom receives nearly one electron from the Al(111) substrate, whereas the charge transfer is minimal in the case of B/Ag(111). This study reveals that one can effectively manipulate the borophene lattice by regulating the charge transfer between the substrate and the borophene film. The height of hexagonal borophene, as determined from the STM image, was measured to be 320 pm.

In 2018, Wu et al. demonstrated the large-area single-crystal growth of borophene on a Cu (111) substrate using electron beam deposition[101]. The real-time growth and nucleation dynamics of borophene were observed using low-energy electron diffraction (LEED). they started borophene growth on Ag(111) as substrate. This study identified both the β_{12} and χ_3 phases of borophene. The β_{12} phase was predominant at lower growth temperatures, specifically between 550 K and 600 K. In this range, weak diffraction peaks corresponding to the χ_3 phase indicated the coexistence of both phases. At elevated growth temperatures, between 650 K and 720 K, only the χ_3 phase was detected. Increasing the substrate tem-

perature further induces the formation of additional orientations for χ_3 domains, specifically those rotated by 30° (χ_3 -R30). Additionally, there is a reappearance of the β_{12} phase with domains similarly rotated by 30° (β_{12} -R30). In situ, post-growth temperature ramps within the 550–850 K and 750–910 K ranges reveal that the χ_3 phase demonstrates greater stability compared to the β_{12} phase. Based on their investigation, they examined substrates less inert than silver to facilitate the growth of larger borophene domains while avoiding the formation of metal-boride compounds. Their findings indicated that copper (Cu) substrates proved effective. On Cu(111) substrates maintained at 770 K with a deposition rate of 0.05 monolayers per minute, borophene demonstrated an anisotropic growth pattern on lower terraces and isotropic growth on upper terraces. Ambient AFM data confirm the formation of monolayer borophene islands and the step height of borophene was found to be 3 Å. Borophene sheets, observed using LEED and dark-field LEEM, exhibit extensive single-crystal domains up to 10 μm along terrace directions, with widths ranging from 1 to 3 μm perpendicular to terraces due to surface miscut angles. Domain boundaries often span multiple step edges rather than aligning with copper terraces. The research utilizes Low-Energy Electron Microscopy (LEEM) to investigate key issues such as the formation of borides, the solubility of boron in copper, and the impacts of boron evaporation and dissolution of boron atoms in subsurface. Through thermal cycling of a Cu(111) substrate covered with a full monolayer (ML) of borophene, the researchers successfully induced the dissolution of boron atoms into the subsurface and the reappearance of crystalline borophene sheets.

The growth of borophene on Cu and Ag substrates exhibits a self-limiting behavior, which can be beneficial for fabricating heterostructures composed of atomically thin layers. Once coverage exceeds one monolayer (ML), the growth rate on both substrates drops markedly, despite a higher flux of boron. Substrate choice significantly influences growth dynamics, structure, film adhesion, and rippling, crucial for device fabrication and large-domain heterostructure engineering. The findings highlight the critical role of interactions between borophene and substrate materials, as well as the selection of substrate types. The effectiveness of concurrent real- and k-space mapping is showcased in its ability to control the development and analysis of novel 2D phases. Additionally, using several elemental sources simultaneously with this mapping technique enables visualization of heterostructure growth.

In a follow-up study, Wu et al. successfully grew standard Cu(111) crystal films on sapphire substrates, paving the way for large-area borophene synthesis under ultra-high vacuum (UHV) conditions[102]. Utilizing iterative high-temperature annealing cycles at approximately 900 K, followed by re-growth at 760 K, researchers achieved the synthesis of well-oriented micrometer-sized triangular borophene islands. This method involves depositing boron atoms onto a surface where they nucleate as borophene at step edges, promoting the growth and merging of these islands into a full monolayer. This achievement establishes a critical foundation for future endeavors in borophene transfer and device manufacturing.

In 2019, Kiraly et al. investigated the growth of borophene on Au(111) substrates[103]. They discovered that at elevated temperatures, boron diffuses into gold, subsequently segregating to the surface upon cooling to form borophene islands. X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS), complemented by ab initio modeling, confirmed significant boron diffusion into the gold subsurface. The synthesis of borophene altered the Au(111) herringbone reconstruction, resulting in a trigonal network that facilitated the initial growth as discrete nanoclusters. As the boron concentration increased, these nanoclusters coalesced into larger borophene islands. Spectroscopic analysis revealed that borophene on Au(111) is metallic.

Further, there was another report of borophene growth via the PVD method, Vinogradov et al. reported the growth of the χ_6 phase of borophene on Ir(111) using electron beam evaporation[104].

Borophene growth via Chemical Vapor Deposition (CVD)

Parallel to investigations utilizing Physical Vapor Deposition (PVD), research has also concentrated on the epitaxial growth of borophene via Chemical Vapor Deposition (CVD) techniques. In 2015, Tai et al. successfully fabricated a γ - B_{28} monolayer on copper foil through CVD[106]. Their method involved reducing boron oxide and boron at 1100°C to generate B_2O_2 vapor, which was then further reduced to atomic boron in the presence of hydrogen gas and deposited on copper foil at 1000°C. This process yielded borophene with semiconducting properties, a direct band gap of 2.25 eV, and an orthorhombic crystal structure. The borophene film was subsequently transferred onto a SiO_2/Si substrate, resulting in a continuous boron film with a thickness of 0.8 nm. Characterization through techniques such as Atomic Force Microscopy (AFM), Raman spectroscopy, and X-ray Photoelectron

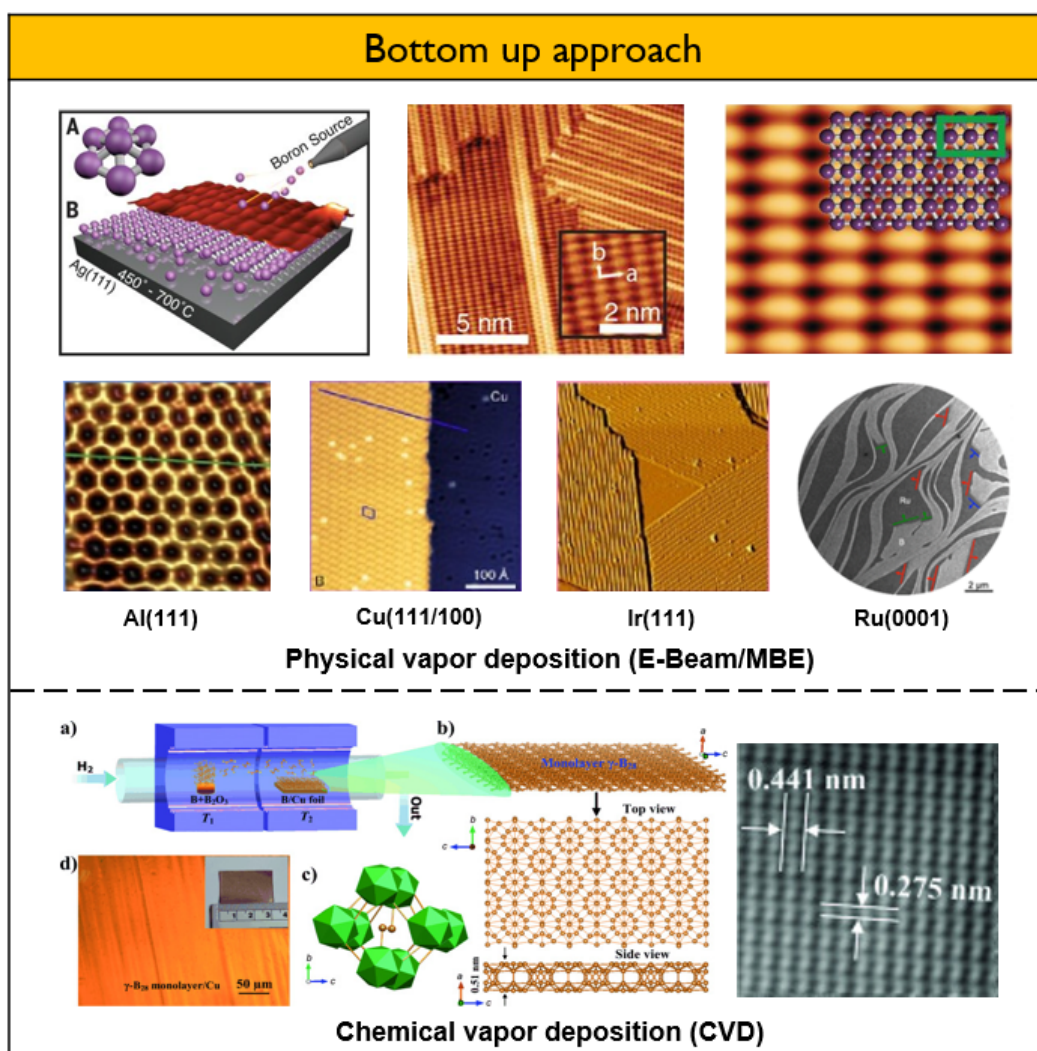


Figure 1.6: The figure illustrates the experimental synthesis of borophene on various substrates, beginning with image (a), which depicts the first successful growth of borophene on an Ag(111) surface using electron-beam deposition. This image is complemented by a schematic representation of the process and includes an atomic resolution image of the striped phase, with the atomic structure overlaid. Additionally, the figure presents borophene growth achieved through physical vapor deposition on different substrates, such as (b) Al(111), (c) Cu(111), (d) Ir(111), and (e) Au(111). The final image, (f), showcases borophene synthesized on copper foil using chemical vapor deposition (CVD). Images adapted with permission Ref. [98, 100, 101, 104–106]

Spectroscopy (XPS) confirmed the successful synthesis of γ - B_{28} -borophene.

Additionally, Mazaheri et al. synthesized borophene through the thermal decomposition of diborane on an aluminum substrate[107]. The borophene layers obtained via chemical vapor deposition (CVD) exhibit an average thickness of 4.2 Å, a χ_3 crystalline structure, and metallic conductivity. Additionally, experimental evidence indicates the formation of stacked bilayer and trilayer borophene sheets.

Omambac et al. demonstrated that borophene can be synthesized in large single-phase domains through segregation-enhanced epitaxy by thermally decomposing borazine with CVD [108]. X-ray photoelectron spectroscopy (XPS) showed that dosing borazine at 1100 °C onto an Ir(111) surface creates a boron-rich layer. Low-energy electron microscopy (LEEM) revealed that borophene forms only after the borazine supply ceases and the temperature drops to approximately 950 °C. During the high-temperature dosing, borazine decomposes, with nitrogen and hydrogen desorbing from the surface, leaving boron to diffuse into the iridium substrate. Upon cooling, this subsurface boron segregates to the surface and forms borophene. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) confirms that the boron migrates back to the surface during cooldown. Electron diffraction identifies a reconstructed borophene χ_6 -polymorph while STS indicates Dirac-like electronic behavior.

Several other studies have explored borophene growth using Chemical Vapor Deposition (CVD) techniques. For example, Sutter et al. demonstrated the growth of large-area borophene on Ru(0001)[105] and while borophene nanosheets were synthesized on carbon cloth substrates via CVD, resulting in a crystal structure aligned with α' -2H-borophene[109]. These nanosheets display exceptional electrocatalytic performance, high hydrogen evolution activity, robust cyclic stability, corrosion resistance, and metallic properties. Another study demonstrated the synthesis of borophene on n-type gallium arsenide (GaAs) substrates, resulting in α' -4H-borophene with a thickness of 6.1 nm, using $NaBH_4$ as the boron source in the CVD process. Additionally, mica has been employed as a substrate for borophene growth via CVD, with hydrogen and $NaBH_4$ serving as the carrier gas and boron source, respectively[110]. The resulting borophene's lattice structure aligns with the predicted α' -2H-borophene. Quartz substrates have also been used under similar temperature conditions, yielding borophene closely matching the α' -2H-borophene structure, which has been further utilized to create borophene hydroelectric generator[111]. Another notable study on the synthesis of borophene

on graphene/Cu substrates, resulting in the formation of vertical heterostructures of borophene (α' -boron) sheet and graphene[112]. This process involves the deposition of borophene via chemical vapor deposition (CVD) on epitaxially grown multilayer graphene, which is initially fabricated on copper. Hydrogen is utilized as the carrier gas, while $NaBH_4$ serves as the boron precursor. It is used as a photodetector showing excellent photo response.

1.4.2 Top-Down approach

The mechanical exfoliation of monolayer graphene marked the pioneering demonstration of the top-down approach for monolayer exfoliation, revolutionizing the field of materials science. This breakthrough initiated one of the most interesting areas of research in 2D materials. Techniques developed from this approach have been crucial in discovering and characterizing a wide variety of 2D materials. The top-down approach encompasses several exfoliation methods, including mechanical exfoliation, liquid phase exfoliation, ion intercalation, and chelation-assisted exfoliation among others.

Liquid-phase exfoliation (LPE) is one of the most prominent top-down techniques for separating Nano-sheets from a parent crystal. This process involves applying energy through various methods, including ultra-sonication, shear mixing, chemical reactions, or their combinations[113].

Ultrasonication: High-frequency sound waves generate cavitation bubbles, creating shock waves that break Bonds and induce exfoliation.

Shear Mixing: High-shear forces from rotors or blenders apply tangential stress, peeling off layers with minimal defects.

Chemical Exfoliation: Chemical interactions such as oxidation or intercalation weaken interlayer bonds, enabling exfoliation through agitation or sonication.

Initially, this technique was believed to be limited to van der Waals materials, which are characterized by their weak interlayer forces. However, the successful exfoliation of MnO_2 , Ti_3AlC_2 , Nb_2AlC , metal borides such as MgB_2 and AlB_2 , followed by exfoliation of non-layered, non-vdW materials monoclinic tungsten trioxide (α - WO_3) and other non-van der Waal material exfoliation challenged this notion and demonstrated the potential for exfoliating non-van der Waals materials. These milestones indicated that the principles of top-down exfoliation could be applied more broadly than previously thought. In 2017, James et al. demon-

strated the synthesis of 2D boron using chelation-assisted exfoliation of MgB_2 and AlB_2 [14]. Guan et al. achieved the exfoliation of a non-van der Waals material using an electrostatic-driven method with monoclinic tungsten trioxide ($\alpha\text{-WO}_3$) crystals[15]. Subsequent studies have successfully applied liquid-phase exfoliation (LPE) to a range of materials, including $\alpha\text{-Fe}_2\text{O}_3$ (Hematene)[17], Si[18, 19], Sn[20], B_4C [21] and β -boron[22–24] and numerous such reports have highlighted the feasibility and advancements in exfoliating various non-van der Waals materials. Thereby expanding the horizon for research and development, demonstrating the versatility and potential of processing non-van der Waals materials.

James et al. demonstrated that chelation effectively exfoliates ionic solids with layered structures, such as MgB_2 and AlB_2 , resulting in the formation of boron nanosheets with a thickness of just a few layers[14]. Their research provides compelling evidence for the efficacy of exfoliating layered ionic compounds through selective extraction through chelation. Their research shows that employing a disodium EDTA solution effectively removes a significant amount of Mg atoms situated between the boron layers in MgB_2 crystals, resulting in the production of boron nanosheets with few layers and a deficiency in Mg. This approach was effectively applied to AlB_2 , leading to the creation of boron nanosheets with a significantly lower aluminum content compared to those exfoliated from MgB_2 . In both instances, the selective removal of interlayer metal atoms through this methods enabled the exfoliation of boride crystals, eliminating the need for traditional techniques like sonication or shearing. The use of a chelating agent to target and remove interlayer metal atoms facilitates the separation of boride crystals in a single step, thereby eliminating the need for further delamination procedures. This method enhances the variety of selective separation techniques currently being thoroughly explored for the production of 2D materials, providing a simple yet effective approach for the targeted removal of interlayer atoms, which facilitates exfoliation.

Li et al. introduced borophene synthesis through the liquid-phase exfoliation (LPE) method, representing a significant breakthrough in producing few-layer boron sheets in substantial quantities[22]. Utilizing dimethylformamide (DMF) and isopropanol (IPA) as exfoliating solvents, they successfully produced few-layer boron sheets with controllable dimensions, achieving average thicknesses of 1.8 nm in DMF and 4.7 nm in IPA. Following this, Ji et al. and Ranjan et al.[23, 24] also demonstrated the synthesis of borophene via the LPE method. Ji et al. combined liquid exfoliation with thermal oxidation etching to fabricate borophene, achieving

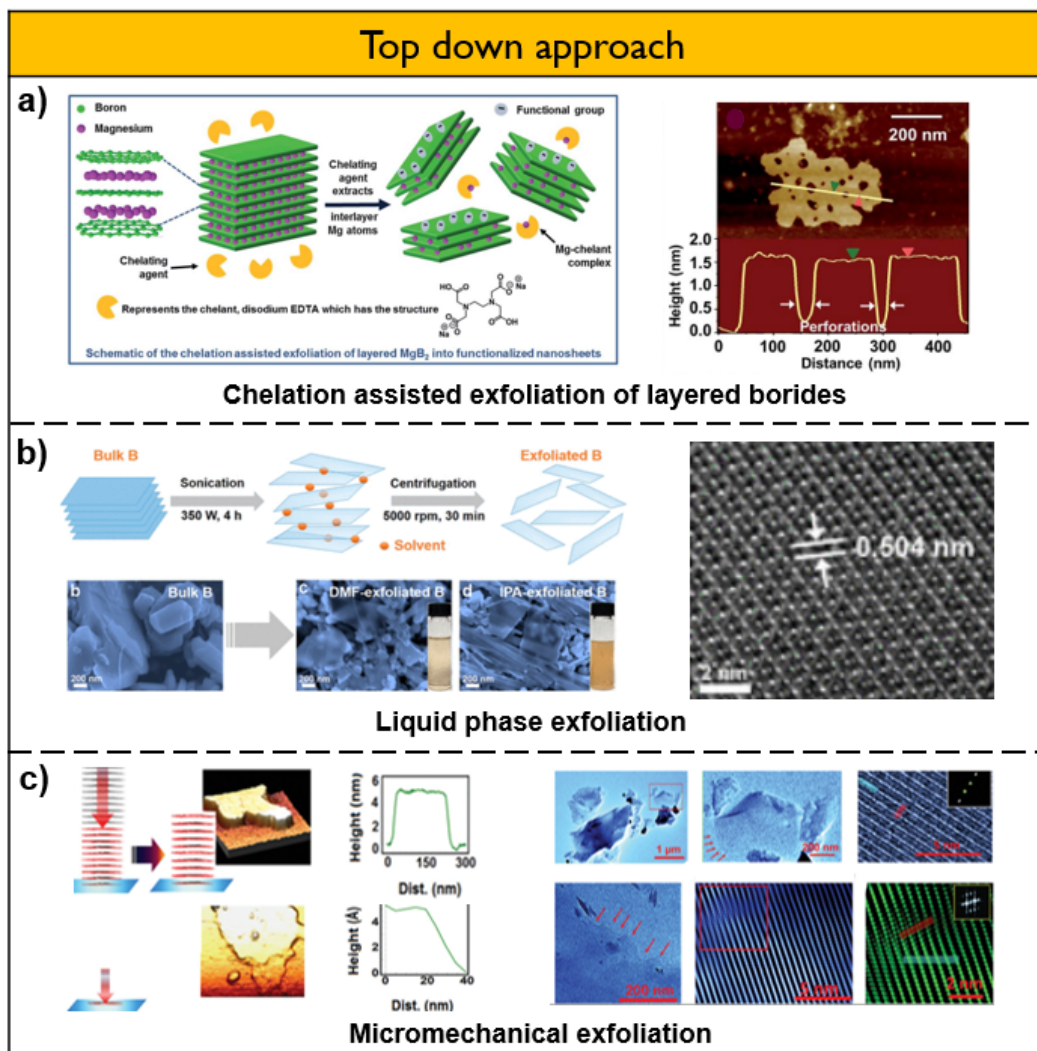


Figure 1.7: The figure illustrates several experimental methods for synthesizing 2D boron through a top-down approach. Figure (a) shows the chelation-assisted exfoliation of metal borides, a technique used to produce boron nanosheets, while Figure (b) demonstrates the liquid-phase exfoliation (LPE) of boron, resulting in the formation of 2D boron sheets. Figure (c) illustrates the micro-mechanical exfoliation process, wherein boron layers are physically separated to produce 2D boron structures. Images adapted with permission Ref. [14, 22, 114]

an average size of approximately 110 nm and an average thickness of around 3 nm. These borophene sheets have demonstrated promising potential for applications in drug delivery systems. Ranjan et al. have demonstrated that borophene sheets, including β_{12} , χ_3 , and intermediate phases, can be synthesized through liquid-phase exfoliation (LPE) and the reduction of borophene oxide (Modified Hummer's method). Their research confirmed the metallic nature of these borophene sheets. Furthermore, they explored the applications of borophene sheets, highlighting their exceptional anchoring capabilities, which are utilized in photo-sensing, gas sensing (e.g., ammonia), molecule sensing (e.g., methylene blue), and strain sensing.

In the modified hummer method procedure $KMnO_4$ and boron powders are mixed mechanically and combined with a cooled sulfuric and phosphoric acid mixture[24]. The solid mixture is then added to the acid mixture in a beaker and stirred under mild heating at 60 °C, causing an exothermic reaction that produces thick smoke and borophene oxide sheets. Reduced borophene oxide is obtained through solvothermal or microwave reduction. Despite defects affecting crystal quality, the process supports scalable production from hundreds of grams to kilograms.

Chahal et al. demonstrated that the successful synthesis of borophene can also be achieved using the adhesive tape exfoliation technique, a cost-effective method for producing monolayer borophene[114]. This approach facilitates the rapid and effective generation of high-quality, phase-pure borophene sheets, which are crucial for developing advanced devices and sensors. Additionally, this method is noted for its simplicity and scalability in synthesizing borophene, making it a practical choice for large-scale production. HRTEM and Raman spectroscopy have confirmed the predominance of the β_{12} and χ_3 phases within these two-dimensional crystals. There are multiple other reports on borophene synthesis by different top-down methods.

1.4.3 Borophene: A Material of Exceptional Potential

Research into borophene has highlighted its exceptional properties, making it a highly promising material for a wide range of applications. Key discoveries include its unique mechanical and electrical characteristics, with Young's modulus reaching up to 398 N/m along the armchair direction, outperforming graphene. Borophene also allows for ultrafast ion transport and energy-efficient ion movement, making it an excellent candidate for use as an anode material in metal-ion batteries. Additionally, it shows strong catalytic abilities[115, 116] in hydrogen evolution[117, 118], oxygen evolution[118, 119], oxygen reduction[119], and CO_2 electroreduction

reactions[120], and has a notable capacity for hydrogen storage[121] due to its lightweight nature and potential for metal decoration[122–128].

Moreover, Borophene has demonstrated significant potential in sensing applications[115, 129], with reports indicating its ability to detect various gases and substances such as ethanol[130], hydrogen cyanide[131], and formaldehyde (HCHO)[132]. The Fullerene and 2-Pmmn phases have shown potential as sensors for carbon monoxide (CO) and nitrogen monoxide (NO)[133, 134]. Additionally, the 2-Pmmn phase has exhibited good adsorption behavior for Ammonia (NH_3), Carbon dioxide (CO_2), and Nitrogen dioxide (NO_2)[134]. Other studies have demonstrated borophene’s ability to detect toxic gases such as Phosgene ($COCl_2$) and Carbon monoxide (CO)[135], as well as Hydrogen sulfide (H_2S)[136]. In the biomedical field, borophene has shown promise in numerous applications[129], such as cancer therapy[23], respiratory sensors[134], toxic gas monitoring[137], DNA sequencing[138], drug biosensing (e.g., metronidazole)[139], glucose electrochemical biosensors[140], bioimaging[141], cancer treatment[142], and modulation of cellular internalization and immune response in macrophages[143]. Borophene is also being explored as a key agent for drug delivery and diverse medical applications[23, 129]. Additionally, it exhibits Dirac fermions characteristics in β_{12} borophene[144], and its various phases show potential for superconductivity[145–149], thereby enhancing its scientific relevance. These attributes suggest extensive and potentially groundbreaking applications of borophene across multiple domains.

1.5 Outline of thesis

Recent advancements in borophene synthesis have been remarkable, yet a comprehensive understanding and practical applications of borophene are still in the nascent stages, necessitating further investigation. This study delves into the interaction dynamics between borophene and gold, elucidating the structural and electronic characteristics of borophene. Additionally, we examine the behavior of clusters on gold surfaces and their interaction with borophene sheets. We also investigate the multiphase characteristics of LPE borophene. Furthermore, we present a novel phase of borophene synthesized via electron beam deposition on a silver (111) substrate, utilizing a powder precursor for the first time in this process.

The initial focus of our research was on the study of the adsorption of LPE borophene on the Au(111) substrate, accompanied by atomic-scale characterization of its structure and electronic properties. The sample was prepared by spin-coating

LPE borophene onto the Au(111) substrate. Using STM and spectroscopy (STS), supported by density functional theory (DFT), we identified the phase as β_{12} and examined the atomic structure of LPE borophene and its interaction with the gold substrate. A significant finding was that LPE borophene yields sheets comparable to those grown by molecular beam epitaxy (MBE) or electron beam deposition, positioning it as a cost-effective alternative to these demanding techniques for producing high-quality borophene sheets.

Upon successfully demonstrating the formation of monolayer flakes of LPE borophene on Au(111) substrates using the spin-coating technique, we observed that the interaction between the borophene monolayer and the Au(111) substrate was sufficiently strong to perturb the substrate's Herringbone reconstruction[150]. In subsequent experiments, repeated spin-coating of LPE borophene on Au(111) led to nearly complete coverage of the substrate with borophene monolayers. In instances where uncovered regions remained, we observed triangular-shaped boron clusters. A third cycle of spin-coating resulted in complete coverage with self-assembled boron clusters, demonstrating the potential for uniform monolayer borophene formation on Au(111). Localized studies using STM helped elucidate the stability, interaction, and behavior of these clusters.

Expanding our investigation, we analyzed the crystallographic phases found in LPE borophene. Recognizing the urgency to develop a deeper understanding of these phases, we conducted detailed electron imaging (atomically resolved HRTEM) of sonochemically exfoliated borophene in IPA solvent. We identified the chemical phase purity of exfoliated borophene using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and conducting atomic force microscopy (CAFM). By comparing the correlation length in two distinct directions and the areal density of periodic units in the borophene lattice, we distinguished various crystallographic phases. Additionally, density functional theory (DFT) calculations of band structures for prominent phases (α , β_{12} , χ_3 , and striped) of borophene, along with axial translational moiré phases, revealed phase-dependent electronic characteristics.

My final project centered on the synthesis of borophene utilizing electron beam deposition on an atomically flat Ag(111) substrate. This work led to the successful deposition of a previously unreported phase of borophene. To further understand the behavior of this phase, we subjected the sample to a series of annealing processes at room temperature. The initial annealing induced an evolution of the phase, leading

to noticeable changes in its structure. Upon subjecting the sample to a subsequent annealing cycle, we observed a complete transformation of the phase into distinct clusters, indicating a significant morphological evolution driven by the annealing process.

In summary, this comprehensive study offers crucial insights into the fundamental understanding of the interaction between borophene and gold substrates, the crystallographic phases of LPE borophene, and the novel borophene phase synthesized on Ag(111). These results contribute to a deeper understanding of borophene's behavior and lay the groundwork for future research and technological advancements across a range of applications involving this material.

Chapter 2

EXPERIMENTAL METHODS AND SETUP

2.1 An overview

Several advanced systems were employed in our experimental setups to ensure precise and accurate results. These included Scanning Tunneling Microscopy (STM), high-resolution transmission electron microscopy (HRTEM), electron beam deposition, and a spin coater. Each technology was integral to the experimental process and contributed to different stages of our experimental workflow.

STM and HRTEM, representing modern microscopy's pinnacle, were pivotal for resolving atomic structures with exceptional precision. STM provided atomic-level surface imaging, offering critical insights into the electronic properties of the materials under investigation. Its ability to probe surfaces at such a fine scale allowed for the detailed characterization of electronic behaviors and surface phenomena.

HRTEM, renowned for its unmatched resolution, enabled the visualization of atomic arrangements within samples. This capability was crucial for examining structural details with exceptional clarity, allowing us to observe and analyze the precise positioning of atoms. The atomic resolution capacity of HRTEM facilitated a deeper understanding of the material's structural integrity and defects at the atomic scale.

The sample preparation process was equally critical, supported by the spin coater and electron beam deposition systems. The spin coater ensured the uniform deposition of thin films by spinning the substrate at high speeds, achieving consistent and even coatings essential for subsequent analyses. electron beam deposition allowed for high-precision thin film fabrication, enabling controlled deposition of material layers with nanometer-scale accuracy. This precision in film fabrication was vital for maintaining the integrity of the samples and ensuring reliable experimental results.

These advanced systems formed the backbone of our experimental setups, each contributing to the high-resolution imaging and precise sample preparation necessary for our investigations.

2.2 Scanning tunneling microscopy (STM)

The development of STM represents one of the most significant advancements in condensed matter physics. This groundbreaking technique revolutionized nanoscale imaging and manipulation, enabling scientists to visualize and manipulate individual atoms and molecules and to understand local electronic behavior through spectroscopy. However, the history of the STM is quite interesting: Gerd Binnig and Heinrich Rohrer, the founders of STM, initially aimed to conduct localized spectroscopy on areas smaller than 100 Å in diameter. Their primary goal was not to invent a new type of microscope but to explore localized spectroscopy at these tiny scales. This theoretical concept remained unexplored until Seymour Keller directed their attention to vacuum tunneling experiments using the positionable tip by W. A. Thompson (Thompson and Hanrahan, 1976). Binnig and Rohrer realized that their idea could evolve beyond a localized spectroscopic probe. By integrating scanning mechanisms, they could produce both spectroscopic and topographic images, effectively creating a new form of microscopy. This method closely resembled stylus profilometry (Williamson, 1967; Guenther et al., 1984), with a significant distinction: instead of a mechanical contact between the tip and the surface, a small gap of a few Å was maintained and controlled by the tunneling current between the tip and the sample.

Binnig and Rohrer discovered a paper in which an instrument shared fundamental similarities with our STM's operational principles by R. Young et al. (1972) describing a field-emission microscope known as the "topografiner." However, a notable distinction was present: its tip had to maintain a significant distance from the surface, operating at high voltage to induce field emission currents rather than tunneling currents. Consequently, this setup yielded a lateral resolution comparable to that of an optical microscope. The principal challenge for the system involved achieving vibration-free operation and sub-nanometer precision in the movement of the tip. This was addressed by implementing vibration isolation techniques and piezoelectric elements, which were optimized through tunneling experiments. Due to the finite size of atoms, the tip's surface is inherently rough, resulting in the formation of minitips. The tunnel current's extreme sensitivity to the tip-sample separation favors the minitip that is closest to the sample.

Binnig et al. demonstrated the technical feasibility of vacuum tunneling with externally controllable tunnel distance, achieving this even at room temperature and under non-ultrahigh vacuum conditions[151, 152]. This achievement marked

the initial step towards developing STM. Subsequently, they illustrated that STM provides a true three-dimensional topography of surfaces at an atomic scale, offering a resolution significantly superior to that of Scanning Electron Microscopy (SEM). Their work successfully resolved monoatomic steps of the (110) surfaces of CaIrSn_4 and Au[153]. Further, it improved the understanding of 7×7 reconstruction of the Si(111) surface which was one of the most interesting problems in surface science[154].

Simultaneously, the development of vacuum tunneling has seen significant contributions over the years[155]. Initially, U. Poppe reported on vacuum tunneling in 1981, focusing on tunneling spectroscopy of exotic superconductors[152]. This work was subsequently complemented by E. C. Teague, who, in his thesis, presented $I(S)$ curves that were not widely available in contemporary literature[156]. The scanning tunneling spectroscopy (STS) method was initially conceptualized by fixing the probe tip laterally and varying the bias voltage between the tip and the sample while maintaining a constant tunnel current. This procedure was intended to generate an S-V curve, which reflects the separation between the tip and the sample and reveals the spectrum of surface states over the applied voltage range. Initially, Binnig et al. employed this technique to study metal surfaces, where they identified plateaus in the S-V curves at high voltages exceeding 4 V[155, 157]. These plateaus were ascribed to field-emission resonances, whereas features observed at lower voltages were attributed to the image state in a separate study[158]. Lozanne et al. were the first to use low-temperature STM to visualize spatial variations in superconductivity with a resolution as fine as 13 nm[159]. In parallel, Becker et al. demonstrated the correlation between spectral features and electronically derived surface states by studying the Si(111) 7×7 surface[160]. Over the years, the STM technique has evolved significantly, demonstrating its profound utility in surface science, materials science, and physics. STM enables the investigation of both topographical and local electronic properties with atomic-scale precision. Unlike other techniques such as X-ray diffraction (XRD) and low energy electron diffraction (LEED), which provide structural information indirectly, STM offers direct real-space imaging of the surface. Although scanning electron microscopy (SEM) also provides real-space images, its resolution is limited compared to STM. HRTEM is another direct method capable of resolving atomic structures; however, STM uniquely combines atomic resolution with the ability to probe local electronic properties around the Fermi energy with high energy resolution.

2.2.1 Theoretical foundation of STM and STS

STM and STS are fundamentally based on the principles of quantum tunneling. This section will begin with a theoretical discussion of the core concepts of tunneling. We will first consider the electron potential within the framework of classical mechanics, described by the potential $V(x)$.

$$\frac{p^2}{2m} + V(x) = E, \quad (2.1)$$

where m = mass of electron and E = Energy.

In the classical regime, an electron cannot penetrate a potential barrier if energy $E < V(x)$. However, in quantum mechanics, electrons can tunnel through potential barriers. To illustrate this phenomenon, we will first consider a one-dimensional model of the tunneling junction. Following this, the discussion will be extended to the application of this concept to the case of a Scanning Tunneling Microscope (STM) tip will be explored.

One-dimensional tunneling

Tunneling of electrons from the tip to the sample is a case similar to a potential barrier. In quantum mechanics, an electron traveling under the effect of potential can be described as a wave function $\Psi(z)$ and the time-independent Schrodinger equation as

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \psi(z) + V(z)\psi(z) = E\psi(z) \quad (2.2)$$

The potential $V = 0$ for regions I and III, so the Equation and solutions :

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \psi(z) = E\psi(z) \quad (2.3)$$

$$\psi_I(z) = Ae^{ikz} + Be^{-ikz} \quad (2.4)$$

$$\text{where, } k = \sqrt{\frac{2mE}{\hbar^2}} \quad (2.5)$$

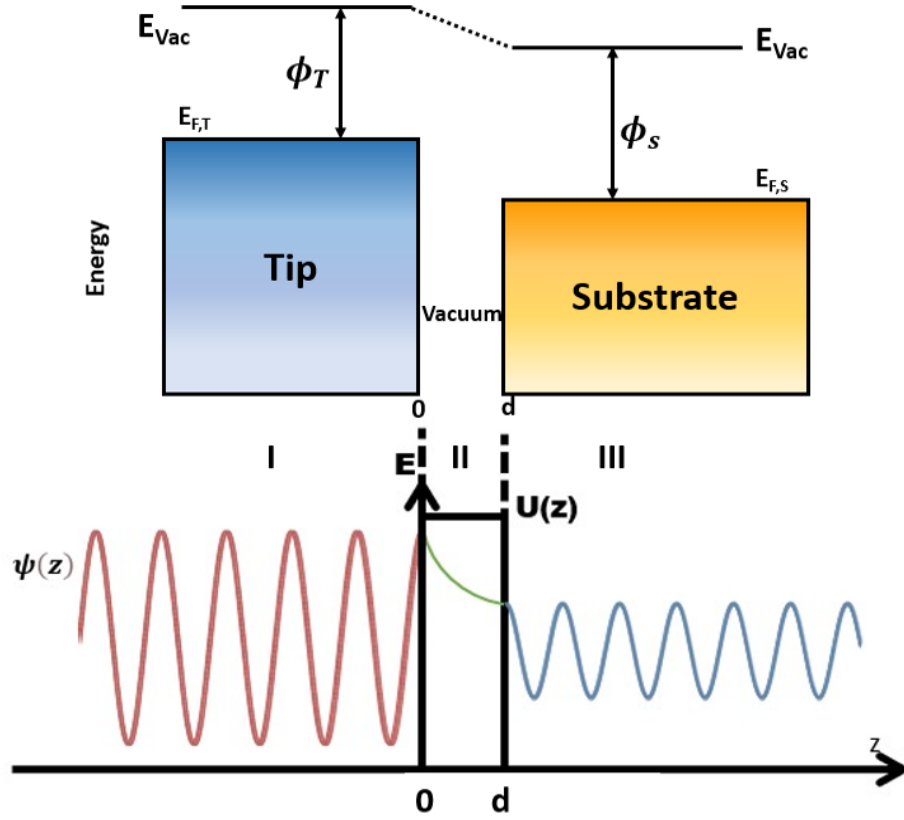


Figure 2.1: The image depicts a one-dimensional tunneling junction, featuring barrier height U and width d , along with the corresponding wave functions in each of the three regions.

The wave is only moving to the right so the solution in region III is :

$$\psi_{III}(z) = E e^{ikz} \quad (2.6)$$

The potential $V = U(z)$ for regions II, so the Equation and solutions are

$$-\frac{\hbar^2 k^2}{2m} + U(z) = E \quad (2.7)$$

$$\psi_{II}(z) = C e^{-k'z} + D e^{k'z} \quad (2.8)$$

$$\text{where, } k' = \sqrt{\frac{2m}{\hbar^2} [U - E]} \quad (2.9)$$

Compiling all the results

$$\psi(z) \begin{cases} \psi_I(z) = Ae^{ikz} + Be^{-ikz} & z < 0 \quad \text{region I} \\ \psi_{II}(z) = Ce^{-k'z} + De^{k'z} & 0 \leq z \leq d \quad \text{region II} \\ \psi_{III}(z) = Ee^{ikz} & z > d \quad \text{region III} \end{cases} \quad (2.10)$$

The Transmission coefficient is the ratio of the probability current density of the transmitted wave to the incident wave.

$$T = \frac{E^2}{A^2} \quad (2.11)$$

Applying the boundary conditions at $z = 0$ and $z = d$,

$$T = \frac{4k^2k'^2}{(k^2 + k'^2)^2 \sinh^2(kd) + 4k^2k'^2} \quad (2.12)$$

If the barrier potential $U \gg E$, which corresponds to a very high potential barrier, the parameter $kd \gg 1$, so the transmission coefficient :

$$T \approx \frac{16k^2k'^2}{(k^2 + k'^2)} e^{-2kd} \quad (2.13)$$

$$T \approx \frac{16E(U - E)}{U^2} e^{-2kd} \quad (2.14)$$

$$I \propto T \propto e^{-2kd} \quad (2.15)$$

Metal-insulator-metal (MIM) tunneling spectroscopy

Bardeen developed a theoretical framework for analyzing (MIM) tunneling junctions[161]. Instead of solving the Schrödinger equation for the combined system, he examined the two individual components separately. Using time-dependent perturbation theory, Bardeen quantified the transmission rate of electrons through the tunneling barrier.

He showed that the amplitude of electron transfer, or the tunneling matrix element M , is determined by a surface integral of the unperturbed wave functions of the two subsystems at the separation surface. it does not impact the results, significantly. Additionally, if $|M|$ remains nearly constant within the energy range of interest, the

tunneling spectrum is given by the product of the density of states (DOS) of the two electrodes.

The tunneling spectrum between two electrodes A and B, having the density of state ρ_A and ρ_B , respectively :

$$I \propto \int_0^{eV} \rho_A(E_{FA} - eV + \epsilon) \rho_B(E_{FB} + \epsilon) d\epsilon \quad (2.16)$$

According to Bardeen's formula as in Eqn. 2.16, the electronic structures of the two electrodes are symmetrically incorporated into the equation. In calculating the tunneling current, the density of states (DOS) of both electrodes, A and B, contribute equally to the determination of the tunneling current. When both electrodes are metallic, the I-V (current-voltage) curve is linear. In contrast, if one of the electrodes is superconducting, the I-V curve exhibits a threshold behavior. If both electrodes are superconducting, the I-V curve displays two distinct thresholds, separated by a region of negative differential conductance.

Asymmetry in tunneling spectrum

Electronic states are occupied up to the Fermi energy (E_F) in both the tip and the sample. No tunneling current is observed when the electrostatic potentials on either side of the tunnel junction are equal (i.e., tunnel applied voltage is 0). Electrons do not encounter any unoccupied states on the opposite side of the barrier, so there is no effective current.

When a voltage (V') is applied, the Fermi levels of the tip and sample shift relative to each other, enabling tunneling processes within the energy interval (eV') which results in a flow of current. The magnitude of the tunnel current is influenced not only by the barrier height and width but also by the number of available electronic states. This relationship is characterized by the density of states (DOS), which quantifies the number of electronic states within a specific energy range. Consequently, the electronic density of states $\rho(E)$ on both sides of the tunnel junction is also a critical factor in determining the tunnel current.

$$I \propto \int_0^{eV'} \rho_S(E_{FS} + \epsilon) \rho_T(E_{FT} - eV' + \epsilon) d\epsilon \quad (2.17)$$

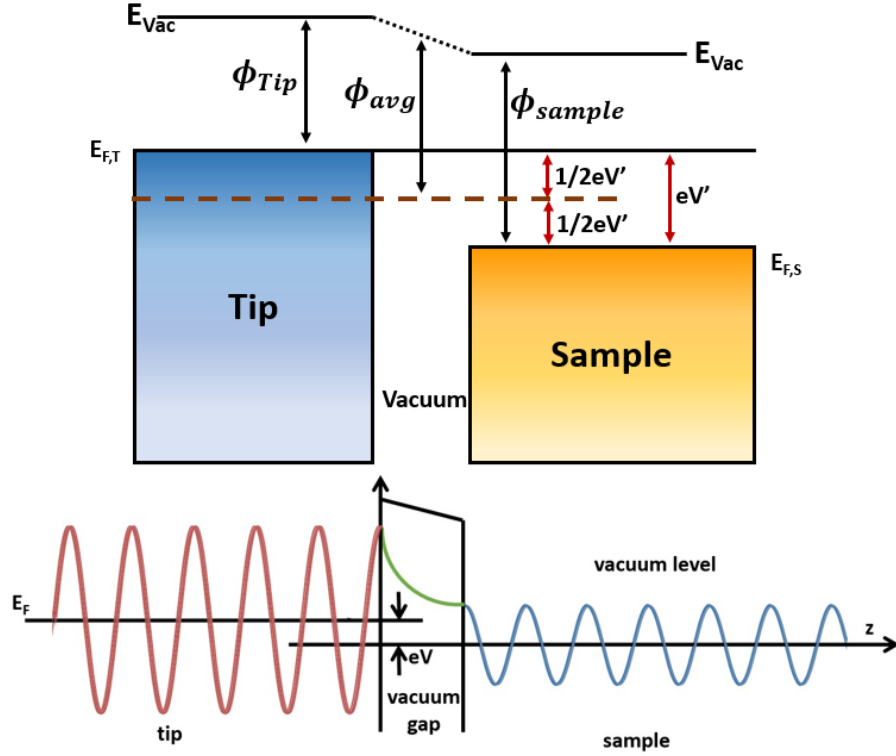


Figure 2.2: Schematic Representation of shifting in fermi level due to applied potential and asymmetry in tunneling junction.

Where ρ_S represents the densities of states (DOS) of the sample and ρ_T for the tip. E_{FS} is fermi energy corresponds to the sample and E_{FT} for tip.

Assuming that the density of states within the energy interval (eV) remains approximately constant,

$$I \propto V e^{-2kd} \quad (2.18)$$

According to the energy diagram of the tip and sample junction, the Fermi level of the sample is lower than that of the tip by eV' . To simplify the analysis, an average work function Φ_{avg} is introduced, representing the energy difference from the vacuum level to the midpoint between the two Fermi levels. The tunneling current (I) can be expressed as :

$$I = \frac{4\pi e}{\hbar} \int_{-1/2eV'}^{1/2eV'} \rho_S(E_{FS} + 1/2eV' + \epsilon) \rho_T(E_{FT} - 1/2eV' + \epsilon) |M(\epsilon)|^2 d\epsilon \quad (2.19)$$

Where, $|M(\epsilon)|$ is tunneling matrix defined by Bardeen.

$$|M(\epsilon)| = |M(0)| \exp\left(\frac{K_0 \epsilon s}{2\phi'}\right) \quad (2.20)$$

Putting the value of $|M(\epsilon)|$ from eqn. 2.20

$$I = \frac{4\pi e}{\hbar} \int_{-1/2eV'}^{1/2eV'} \rho_S(E_{FS} + 1/2eV' + \epsilon) \rho_T(E_{FT} - 1/2eV' + \epsilon) |M(0)|^2 \exp\left(\frac{K_0 \epsilon s}{\phi'}\right) d\epsilon \quad (2.21)$$

The exponential factor results in a greater contribution from the positive half of the bias interval compared to the negative half. As the main contribution is coming from $\epsilon \approx eV'/2$. So,

$$\frac{dI}{dV} \approx \rho_S(E_{FS} + eV') \rho_T(E_{FT}) \quad (2.22)$$

Applying a positive bias voltage (V) causes the tunneling current to be proportional to the sample's density of states (DOS) at the energy $E_F + eV$ if the tip's DOS is effectively concentrated at the Fermi level. Conversely, when a negative bias is applied, electrons tunnel from the occupied states of the sample to the unoccupied states of the tip, making the tip's energy spectrum a crucial factor in the tunneling process. So, assuming a constant DOS for the tip, the differential conductivity is directly proportional to the density of states of the sample.

$$\frac{dI}{dV} \propto \rho_S(E_{FS} + eV) \quad (2.23)$$

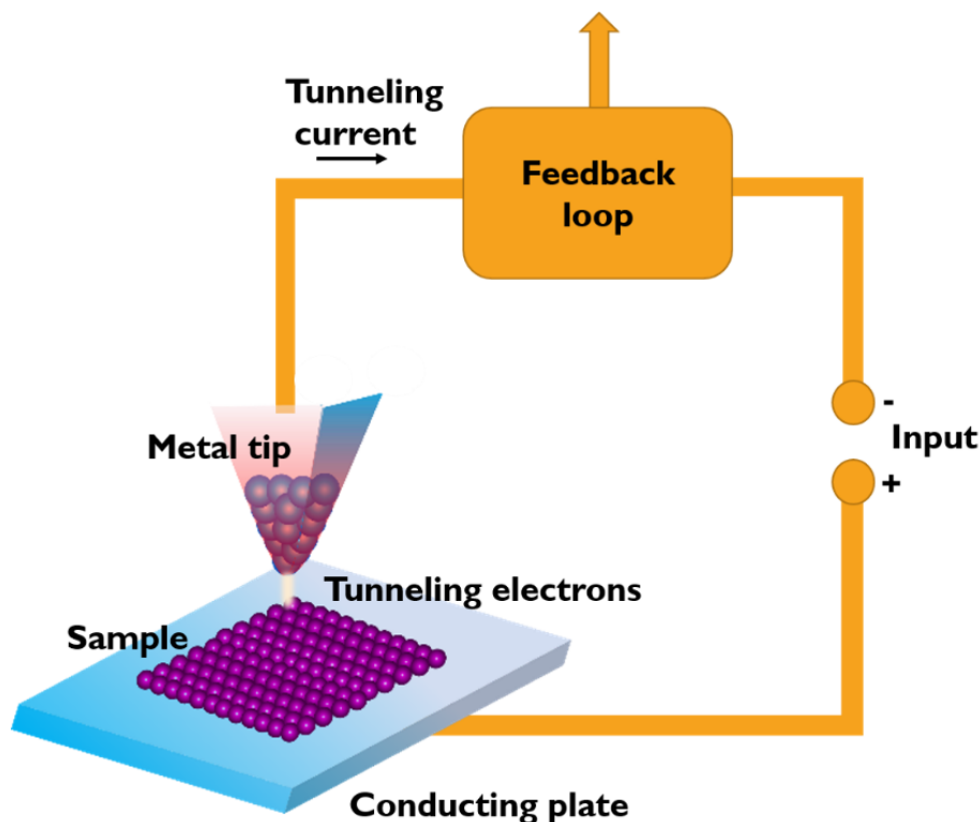


Figure 2.3: Schematic Representation of Scanning Tunneling Microscopy working

2.2.2 Operational principle of STM

The fundamental operation of a scanning tunneling microscope (STM) is illustrated in Figure 2.3. The STM utilizes piezoelectric crystals to maneuver a sharp metallic tip across the sample surface under investigation. A tunnel voltage, typically ranging from millivolts to volts, is applied between the atomically sharp tip and the sample. The current that varies with the distance between the tip and the sample is then measured, providing data on the surface topography.

The scanning tunneling microscope (STM) operates in two primary modes: constant current mode and constant height mode. In constant current mode, the STM employs a feedback control system to regulate the distance between the tip and the sample, maintaining the tunneling current at a predetermined setpoint. Conversely, in constant height mode, variations in tunneling current are used to map

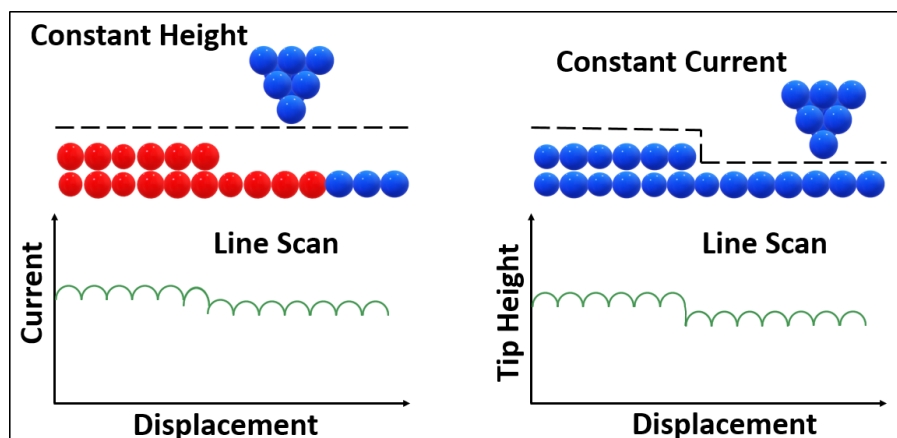


Figure 2.4: a) illustrates the schematic of constant height mode b) illustrates the schematic of constant height mode.

changes in the sample surface topography as the tip remains at a fixed height. Assuming a uniform density of states across the sample surface, the scanning tunneling microscope (STM) tip will perfectly replicate the topography of the surface. For a detailed discussion, let us delve further into these operational principles.

Constant Current mode

The Constant Current Mode is the predominant technique employed for acquiring STM images. In this mode, the STM tip scans across the sample surface while maintaining constant current and voltage. To ensure a constant tunneling current at a given voltage, the feedback system continuously adjusts the vertical position of the tip by modulating the voltage V_Z applied to the z-piezoelectric element. This approach enables the tip to accurately trace surfaces with varying topographies. In an ideal scenario where the surface exhibits uniform electronic properties, a constant current mode ensures that the tip-to-surface distance remains consistent throughout the scan. This condition enables the tip to accurately map the surface topography. As a result, the z-piezoelectric voltage directly correlates with the height of each surface element, yielding a topographical map of the surface based on the tip's position, $Z(x, y)$. In this operational mode, the STM image in real space is constructed by mapping the height variations relative to the lateral displacement during scanning. A key advantage of this mode is that the STM tip follows the topography of the surface, minimizing the risk of tip-sample contact or damage, as the feedback loop actively maintains the system's stability.

Constant height mode

In constant height mode, the scanning is performed with the tip maintained at a fixed voltage V_Z applied to the z-piezoelectric element, while the tunneling current I is recorded as a function of the tip's position. The voltage V between the tip and the sample is held constant, and the feedback mechanism of the servo system is disengaged. Consequently, any surface irregularities are indicated by variations in the tunneling current as the tip encounters these features. This mode facilitates faster scanning compared to the constant current mode because the servo system is not required to adjust for surface features continuously. This advantage is particularly significant for real-time observations of dynamic processes, such as during STM video recordings. The main challenge when conducting experiments in this mode is that if the surface roughness surpasses the preset gap between the tip and the surface, it may lead to the tip making contact with the surface. It is compounded by the difficulty in accurately obtaining topographical information. Figure 2.4, illustrates the operation in both constant current mode and constant height mode.

2.2.3 Ultra high vacuum & Low Temperature Scanning Tunneling Microscope (UHVLT STM)

All the experiments described in this thesis were conducted using a Low-Temperature Scanning Tunneling Microscope (LT-STM) produced by Omicron Nanotechnology, now known as ScientaOmicron. The system consists of two main components: Low-Temperature Scanning Tunneling Microscope (LT-STM) chamber for conducting measurements, and the preparation chamber for substrate preparation. Let's explore the system in detail:

Figure 2.5 illustrates the low-temperature scanning tunneling microscopy (LT-STM) chamber is configured with an Ultra-High Vacuum (UHV) chamber enclosed within a bath cryostat. This bath cryostat comprises two concentric dewars: the outer dewar is designated for liquid nitrogen (LN_2), while the inner dewar is designed for both liquid nitrogen (LN_2) and liquid helium (LHe). Within the UHV chamber, the primary stage is supported by spring suspensions to mitigate vibrational disturbances as shown in Figure 2.6 (b). This main stage provides designated areas for the placement of the tip and sample during experimental measurements. This Scanning Tunneling Microscope (STM) system is designed to perform measurements at three specific temperatures: 4.2 K, achieved using liquid helium (LHe); 77 K, facilitated

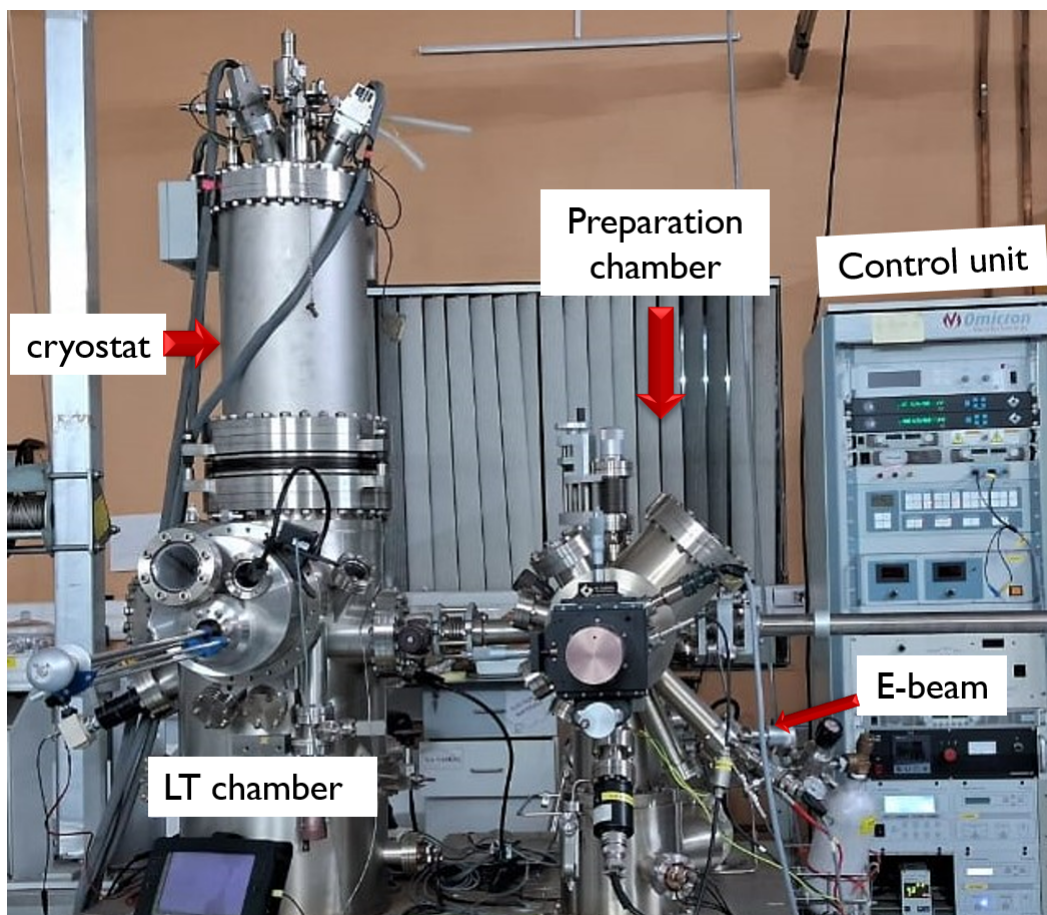


Figure 2.5: Image illustrates the complete STM system.

by liquid nitrogen (LN_2); and 300 K, corresponding to room temperature. When the inner dewar is filled with (LN_2), the system can sustain a temperature of 77 K for approximately three days on a single (LN_2) refill, allowing for extended uninterrupted experiments. Alternatively, when filled with LHe, the system maintains a temperature of 4.2 K for over two days.

The entire scanning tunneling microscope (STM) stage can be vertically adjusted via the knob located at the upper section of the cryostat. The stage is elevated and positioned to establish direct contact with the liquid helium (LHe) dewar for effective cooling. Cooling is achieved through thermal contact with a bath cryostat, which simultaneously cools both the STM tip and the sample. This ensures that the tip and the sample maintain the same temperature during measurements, significantly reducing thermal noise, which is crucial for accurate spectroscopy. The low temperature of the tip enhances the stability of STM images by minimizing the thermal diffusion of the apex atom.

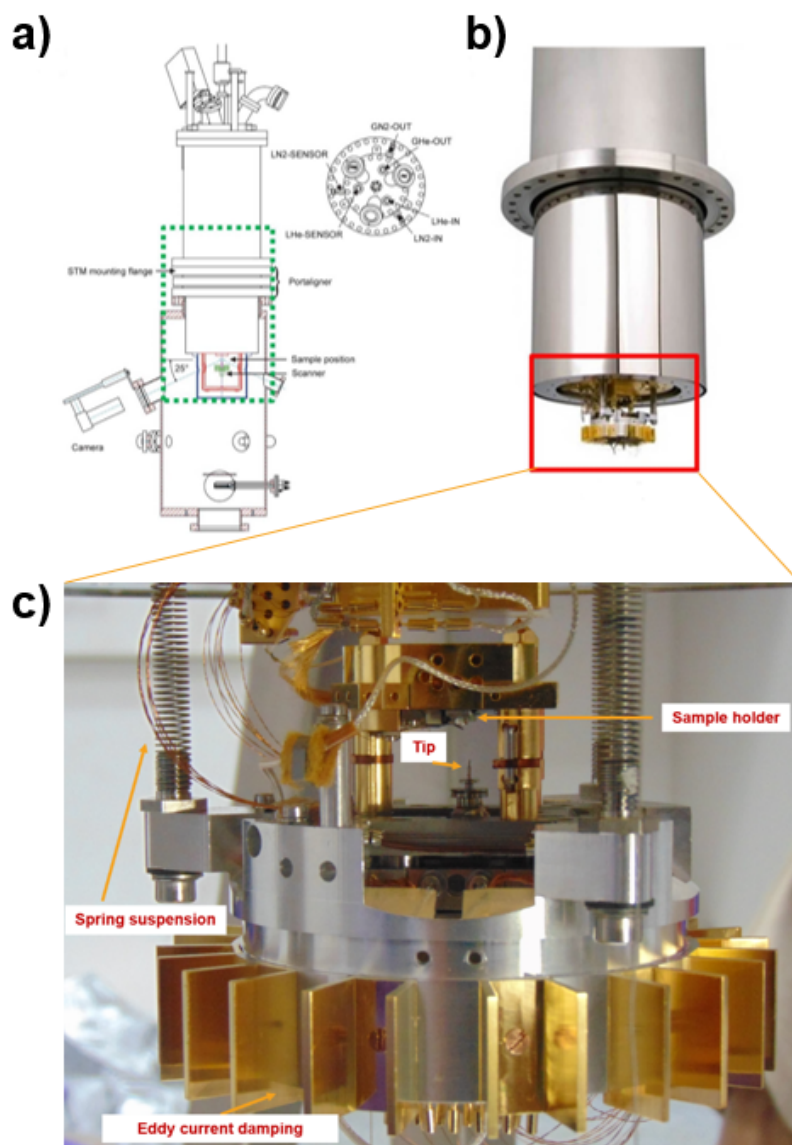


Figure 2.6: (a) The schematic of the LT chamber, (b) Image of the opened LT chamber, which shows the main stage attached by spring suspension, (c) Closeup image of the LT STM main stage.

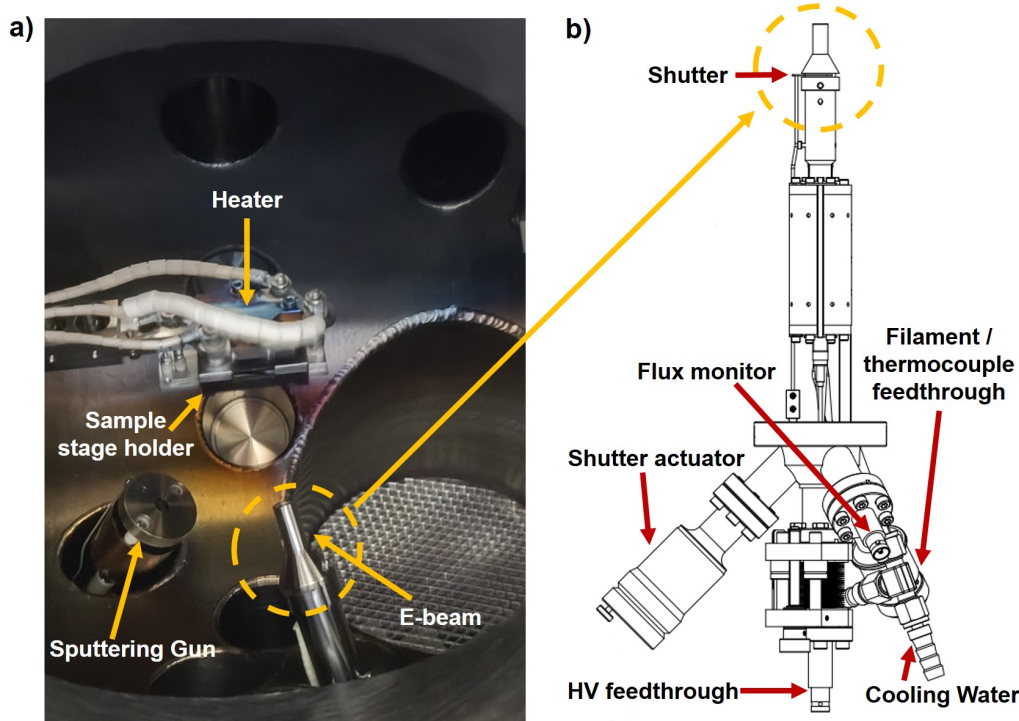


Figure 2.7: a) The image illustrates an internal view of the chamber, where its constituents such as electron beam, heater, sample stage holder, and sputtering ion gun are marked. b) The image showing the schematic of the E-beam evaporator. The circularly marked section in image (b) represents the corresponding marked area in image (a)

The experimental stage is designed to be suspended using three springs, which effectively attenuate vibrations during experiments. The stage is suspended in a manner that allows it to hang freely, without physical contact with the liquid helium dewar or the surrounding sidewalls. This configuration minimizes mechanical vibrations and reduces thermal losses associated with contact with ambient temperatures. Additionally, noise is further mitigated through the incorporation of an eddy current damping unit. The main experimental stage is shown in Figure 2.6 (c).

Preparation chamber

The preparation chamber is also a UHV chamber for sample preparation and cleaning, depicted in Figure 2.5, it achieves a base pressure on the order of 10^{-10} mbar. Figure 2.7 provides a detailed internal view of the chamber, with its components clearly labeled. The chamber is equipped with the following substrate preparation tools: (i) a high-temperature resistive heater, (ii) an Ar^+ ion sputtering system, (iii)

an in-situ crystal cleaver, and (iv) an electron beam evaporator.

The resistive heater is meant to anneal or clean samples. It was also utilized during the growth of borophene to sustain a temperature of 500°C for the Ag(111) substrate. The Ar^+ ion is employed for surface cleaning of samples, while a cleaver is utilized specifically for the cleaving of layered van der Waals materials. The electron beam evaporator, depicted in the accompanying figure, is integrated with the preparation chamber. The evaporator's length is adjustable, allowing for modification of the distance between the source and the substrate. It contains a single crucible, which can be covered with a metal sheet. Additionally, the evaporator is equipped with a water cooling system to manage its temperature during operation.

2.3 High-Resolution Transmission Electron Microscope (HRTEM)

The transmission electron microscope (TEM), invented by Ernst Ruska and Max Knoll in 1931, has evolved significantly while retaining its core principles. TEM operates by using electromagnetic lenses to direct an electron beam, produced by a thermionically heated filament, through a high-voltage field.

When an electron wave interacts with a sample, it creates a diffraction pattern that reveals the sample's structural details. By examining both the diffraction pattern and the image, insights can be gained into grain sizes, precipitates, their orientation relative to the matrix, and superstructures. The energy-dispersive X-ray attachment allows for qualitative and quantitative analysis of elemental compositions through characteristic X-ray spectra.

High-resolution transmission electron microscopy (HR-TEM) extends the principles of conventional transmission electron microscopy (TEM) to achieve superior resolution, allowing for the detailed examination of crystal structures and lattice defects in advanced materials. HR-TEM produces high-resolution interference images that reveal atomic-scale features by utilizing both transmitted and scattered electron beams. The technique delivers phase contrast images with resolutions comparable to the unit cell dimensions, enabling direct observation of local structural features and atomic-level anomalies. This capability makes HR-TEM an essential tool in condensed matter physics and materials science. It plays a vital role in the analysis of structural defects and their effects on material properties. HR-TEM is widely employed in fields such as crystallography, materials science, life sciences, and mineralogy, facilitating the study of both crystalline and amorphous materials, phase

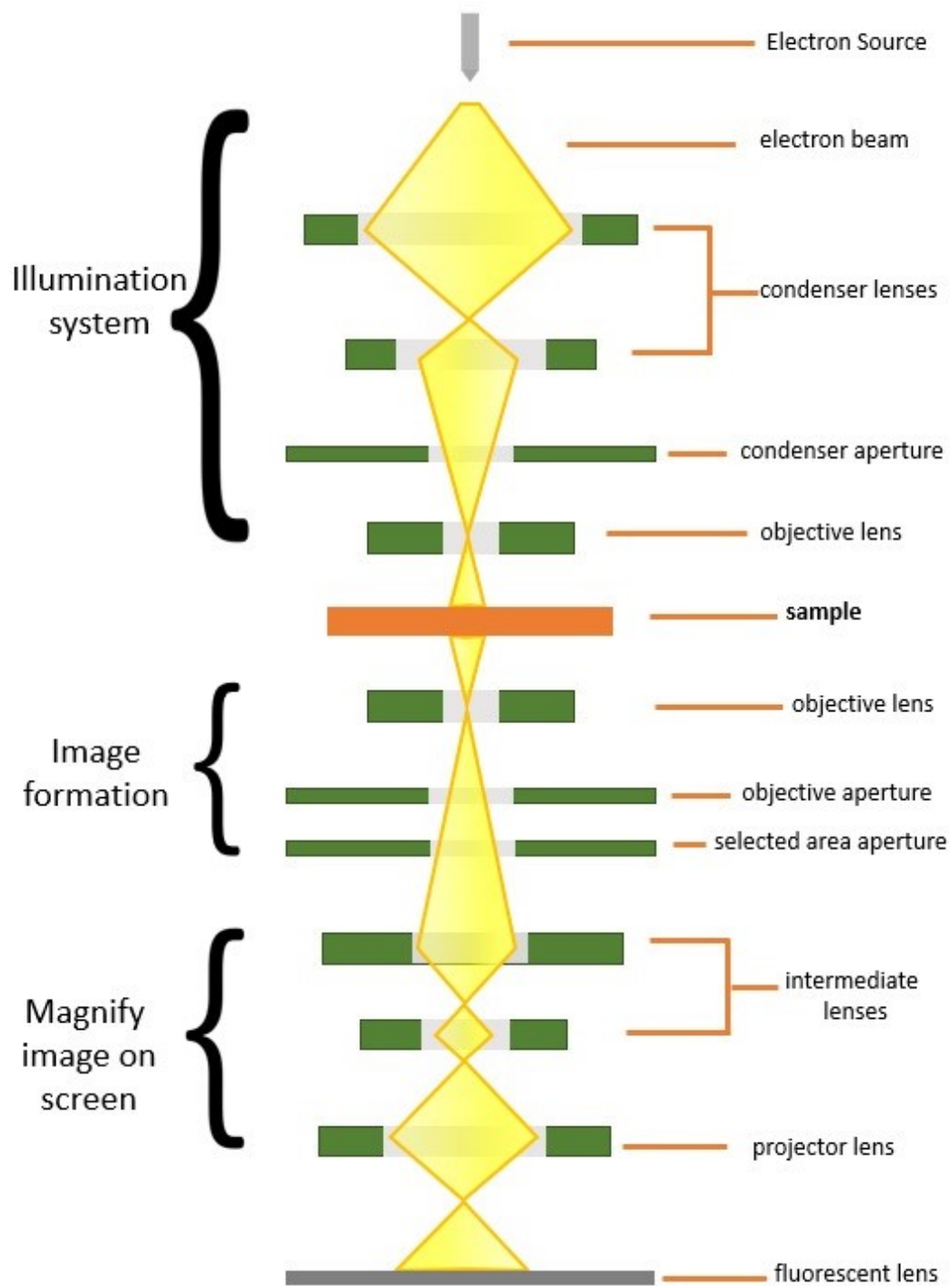


Figure 2.8: The image illustrates the schematic of the HRTEM.

transitions, internal interfaces, and dynamic processes like crystal growth and defect formation.

The combination of HR-TEM with electron diffraction (ED) and crystallographic image processing (CIP) has advanced the resolution of crystal structures. Notably, in 1949, Vainstein and Pinsker utilized ED for structure determination. Wenk et al. achieved a significant milestone in 1992 by reconstructing a 3D structure of the mineral staurolite from 2D HR-TEM images, resolving individual atoms with a resolution of 0.138 nm. Recent advancements continue to enhance structure analysis, with Convergent Beam Electron Diffraction (CBED) proving crucial for detailed information on lattice parameters and crystal symmetry, particularly in thick crystals with small unit cells.

2.3.1 Working principle of HRTEM

The transmission electron microscope (TEM) operates on a principle similar to that of light microscopes, with the primary distinction being the type of radiation used. While light microscopes utilize visible light rays to concentrate and form an image, TEM employs a beam of electrons to focus on and generate an image of the specimen. In TEM, an electron gun located at the top of the instrument generates a stream of monochromatic electrons. This electron stream is initially focused into a coherent beam by the condenser lenses 1 and 2. The first condenser lens is responsible for adjusting the spot size of the electron beam on the specimen, while the second condenser lens refines this beam into a precise, well-defined point from its initial broad, diffused state.

Subsequently, the beam is further refined by the condenser aperture, which blocks electrons that deviate significantly from the optical axis. The portion of the beam that successfully traverses the specimen is then focused into an image by the objective lens. Optional apertures, such as the objective and selected area apertures, are employed to enhance image contrast and isolate specific diffraction patterns. The objective aperture improves contrast by excluding high-angle diffracted electrons, whereas the selected area aperture facilitates the analysis of diffraction patterns arising from ordered atomic structures.

As the image progresses through intermediate and projector lenses, it undergoes magnification and is ultimately projected onto a phosphor-coated screen. When the electron beam interacts with the sample and subsequently strikes the screen, it generates light. Areas of low electron transmission appear darker due to increased

sample thickness or density, while regions of high transmission appear brighter, indicating lesser thickness or density. Data acquired from electron scattering—both elastic and inelastic—provides comprehensive insights into the sample. Elastic scattering produces diffraction patterns that preserve the incident beam's energy, while inelastic scattering modifies the intensity of transmitted electrons, revealing details about dislocations, grain boundaries, and second-phase particles.

In this research thesis, HRTEM was used to determine and classify the atomic arrangement of different borophene polymorphs. The HRTEM data were acquired at a beam energy of 200 keV.

2.4 Atomic force microscopy (AFM)

Atomic Force Microscopy (AFM) is a high-resolution scanning probe technique that uses a sharp tip to scan the surface of a sample, measuring atomic-scale interactions to generate detailed 3D topographical maps[162, 163]. In addition to topography, AFM can evaluate local physical properties such as electrical, mechanical, functional, and tribological characteristics at the nanoscale. One of its key advantages is its ability to scan both conducting and non-conducting surfaces, making it an exceptionally versatile tool. This versatility enables AFM to image a wide range of materials, including polymers, ceramics, composites, glass, and biological specimens.

2.4.1 Working principle

The AFM (Atomic Force Microscope) utilizes a cantilever with a very sharp tip that is mounted on a piezoelectric actuator. The interaction between the sharp tip and the sample generates forces that cause the cantilever to deflect, following the principles of Hooke's law. The deflection of the cantilever is measured using a low-power laser, which is reflected off the back of the cantilever and onto a position-sensitive photodetector. The detector then records the position of the reflected laser spot, providing precise measurements of the cantilever's deflection. A feedback mechanism is integrated into the system to continuously adjust the position of the AFM tip in response to changes in the forces acting on it. This ensures that the tip remains in the optimal position relative to the sample surface, allowing for accurate measurements of surface features at the nanoscale. The feedback system also replicates the changes in force along the scan line, enabling precise topographic mapping of the sample surface. AFM operates in two main scanning modes: static and dynamic. In the static mode, the cantilever remains stationary as the tip scans

across the surface. In dynamic mode, the cantilever oscillates, and there are two specific sub-modes: intermediate (tapping) mode and non-contact mode.

Contact mode

In this mode, the AFM tip maintains continuous physical contact with the sample surface as it scans. The cantilever is deflected by the forces between the tip and the surface, which may include repulsive forces at close distances. This deflection is measured in real-time, and the feedback system adjusts the tip's position to maintain a constant force between the tip and the surface. Contact mode is particularly useful for imaging hard, flat surfaces, as it provides high-resolution topographic data. However, it can be damaging to softer samples because the tip maintains continuous contact with the surface, which may result in scratching or deformation.

Tapping mode

It is also known as intermediate mode, In which the cantilever oscillating at its resonant frequency, with the tip making intermittent contact with the sample surface. This mode is useful for imaging softer surfaces, as it minimizes damage to the sample while maintaining high-resolution topography.

Non-contact mode

it keeps the cantilever oscillating just above the surface without making physical contact, which operates exclusively in the attractive force regime between the tip and sample to detect surface features. This mode is typically used for ultra-sensitive measurements of surface properties.

In this research thesis, AFM was employed to characterize the topography of both Au(111) surfaces and two-dimensional boron sheets. It was also used to determine the step height of these sheets. The data was taken in the tapping mode by Nanosurf Easyscan 2 system. The force constant of the tips was 48 N / m, while the resonant frequency was 190 kHz.

2.4.2 Conductive Atomic Force Microscopy (C-AFM)

C-AFM is a specialized mode of Atomic Force Microscopy (AFM) used to map local variations in electrical conductivity at the nanoscale while simultaneously capturing the surface topography of a sample. This technique is particularly valuable for investigating electrical properties at high spatial resolution. In C-AFM, a sharp,

conductive probe is brought into direct contact with the sample surface. As the probe scans across the surface, a bias voltage is applied between the AFM tip and the sample. This applied voltage induces a current flow between the two, and the corresponding current is measured at each point during the scan. The collected data is used to generate high-resolution conductivity or current maps, revealing nanoscale electrical characteristics of the material under study. C-AFM operates similarly to Scanning Tunneling Microscopy (STM) in that both techniques measure electrical properties at the nanoscale. However, the key distinction lies in the nature of the current being measured. While STM relies on quantum tunneling current and requires a conductive or semi-conductive sample, C-AFM measures the actual electrical conductivity at a given point of contact. This fundamental difference makes C-AFM more versatile, as it can analyze a wider range of materials, including insulating or poorly conductive samples, which are challenging to study using STM.

In this research thesis, C-AFM was employed to investigate the electronic behavior of borophene spin-coated on Au(111). C-AFM data was obtained by the Asylum Research MFP 3D Scanning Probe Microscope system.

2.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful imaging technique widely used in material science, physics, biology, and other scientific fields. It provides high-resolution images of a sample's surface morphology, texture, and microstructure by scanning it with a focused beam of electrons. SEM is particularly valued for its ability to analyze both conductive and non-conductive materials[164].

2.5.1 Working Principle

SEM works in a manner similar to an optical microscope but uses electrons instead of visible light. In an optical microscope, light waves are focused using glass lenses to illuminate and magnify a sample. Similarly, in SEM, a beam of electrons is focused using electromagnetic lenses to scan the sample. Instead of detecting transmitted or reflected light, SEM collects signals such as secondary electrons, backscattered electrons, and characteristic X-rays to generate images and compositional information. Secondary Electrons (SE): Used to produce high-resolution images of surface topography. Backscattered Electrons (BSE): Provide compositional contrast based on atomic number differences. Characteristic X-rays: Generated when the electron beam excites atoms in the sample, allowing for elemental analysis using energy-dispersive X-ray spectroscopy (EDXS).

2.5.2 Key Components of an SEM

Electron Gun: Produces the electron beam, typically using a thermionic emitter (e.g., tungsten filament) or field-emission source. Electromagnetic Lenses: Focus and control the electron beam. Scanning Coil: Rasterizes the electron beam across the sample surface. Detectors: Capture signals (SE, BSE, X-rays) for image generation or compositional analysis. Vacuum System: Maintains a high-vacuum environment to ensure the electron beam is not scattered by air molecules.

In this research thesis, FESEM was employed to characterize the two-dimensional boron sheets's topography and elemental analysis. FESEM data were acquired using the Zeiss ultra plus SEM system. For energy-dispersive X-ray spectroscopy (EDS), beam energy of 3 keV was chosen to enhance the sensitivity to boron.

2.6 Methods used for Sample Preparation, and Characterization

Now we briefly review the remaining supplementary systems or methods utilized throughout this research thesis, outlining their specific roles and contributions to the study.

2.6.1 Liquid-Phase Exfoliation (LPE) Borophene

Two-dimensional boron sheets were obtained by using the Liquid-Phase Exfoliation (LPE) method, a technique that utilizes specific liquids to efficiently exfoliate crystals into two-dimensional nanosheets.

Free-standing borophene sheets were synthesized using sonochemical approach. In this process, 150 mg of boron was dispersed separately in 40 ml of isopropyl alcohol. The dispersions were placed in an ultrasonic bath (Cole Parmer, 40 kHz) and subjected to ultrasonication for up to 24 hours. To monitor the formation of borophene sheets, samples were extracted from isopropyl alcohol at regular 2-hour intervals until 24 hours. The collected fluids were then centrifuged (Remi, R-24) at 5000 rpm for 3 minutes[24].

2.6.2 Spin-coating

Borophene was deposited on Au(111) using the spin coating method, a technique that employs centrifugal force to uniformly distribute a liquid solution across a surface, resulting in the formation of a thin film. In this technique, a droplet of the solution is introduced to the substrate, which is then rapidly rotated to ensure even coverage. Spin coating is especially advantageous for producing uniform thin films on flat surfaces. The sample for STM measurement was prepared by spin coating at

2000 rpm on Au (111) substrate.

2.6.3 Electron-beam deposition system

The electron beam deposition system was employed to deposit borophene onto an Ag(111) substrate using boron powder as the source material. In this process, an electron beam is accelerated to high kinetic energy and precisely directed towards the boron powder. The kinetic energy of the electrons is converted into thermal energy, which elevates the temperature of the boron powder. This increase in temperature causes the boron to evaporate, and the resulting vapor is then deposited onto the Ag(111) substrate

2.6.4 XPS

X-ray Photoelectron Spectroscopy (XPS) was employed to characterize the chemical composition of two-dimensional boron sheets, where elemental spectra of boron were studied. This surface analysis technique provides quantitative insights into the atomic composition and chemical states, with a sampling depth ranging from approximately 50 to 100 Å. X-ray Photoelectron Spectroscopy (XPS) data was obtained with a Thermo Scientific, *K – ALPHA*⁺.

LIQUID PHASE EXFOLIATED BOROPHENE ON AU(111)

3.1 Introduction

In the field of condensed matter physics and material science, boron is prominently utilized as a p-type dopant in silicon-based electronic devices due to its unique electronic properties. Boron exists in various crystalline forms, including rhombohedral and tetragonal structures, which are significant in different applications. The electronic configuration of boron is denoted as $1s^2, 2s^2, 2p^1$, which highlights the presence of a single unpaired electron in its p-orbital. Due to the electron-deficient p orbitals and the small covalent radius of ~ 85 pm boron is known to form B_{12} icosahedral units[87, 165].

Recent theoretical predictions have introduced several novel boron allotropes, including two-dimensional borophene sheets[25, 91, 166, 167]. These borophene structures exhibit interesting electronic properties, with the potential to function either as metallic conductors or semiconductors, depending on their specific structural configurations and bonding characteristics. The formation of boron nanotubes is initiated by the triangular or hexagonal patterns in which boron atoms are arranged within borophene sheets. These specific atomic arrangements serve as the foundational structures or precursors from which boron nanotubes develop[92, 168]. While the research field of 2D materials took off with the discovery of graphene in 2004, the first 2D allotrope of boron, known as borophene, was realized experimentally in 2015 [98, 99]. Borophene is anticipated to exhibit exceptional properties, including the potential to host Dirac fermions, which are fundamental to its electronic behavior[144]. It is also predicted to exhibit superconductivity, adding to its versatile nature[146, 169]. Additionally, borophene's ability to adopt a variety of crystalline forms enhances its structural flexibility[115, 170]. These attributes collectively pave the way for a wide range of promising applications, positioning borophene as a highly interesting material in advanced research and technological development.

The fabrication of two-dimensional borophene from its natural form can be classified into two primary approaches: bottom-up and top-down methods: bottom-up and top-down [171]. The bottom-up approach involves the growth of borophene through techniques such as electron-beam-assisted evaporation of boron onto single

crystal metal substrates or utilizing Molecular Beam Epitaxy (MBE)[98, 99, 103, 170, 172–175]. In contrast, the top-down approach focuses on breaking down bulk boron into smaller sheets. Due to the complex chemistry of boron, which does not naturally form a van der Waals layered crystal, mechanical exfoliation for borophene production presents significant challenges. However, alternative top-down methods, including ball milling, LPE, ion intercalation, and chelation-assisted exfoliation, have been explored. Among these, LPE is the most widely adopted technique due to its simplicity, high yield, and cost-effectiveness[14, 22–24, 114, 176]. Among these, LPE is the most widely adopted technique due to its simplicity, high yield, and cost-effectiveness.

LPE has been effectively validated as a proficient technique for the exfoliation of other non-van der Waals (non-vdW) materials such as monoclinic tungsten trioxide (α - WO_3) crystals[15], olivine type LiFePO_4 , and spinel type LiMn_2O_4 . Other examples include α - Fe_2O_3 (Hematene) [17], Si[18, 19], Sn[20], B_4C [21] and β -boron[22–24]. The sheets generated through this cost-effective and high-yielding method facilitate a wide range of applications across various fields, including electronics, where they can be utilized in components and devices; energy storage and conversion, where they contribute to more efficient and scalable systems; sensing technologies, enhancing the accuracy and functionality of detection systems; and biomedical applications, where they provide innovative solutions for diagnostics and therapeutic interventions[113, 115].

Theoretical investigations have proposed a range of potential applications for borophene, highlighting its versatility and promising characteristics[115]. Notably, borophene has been suggested as a material for advanced gas sensors due to its high sensitivity and selectivity. In the realm of energy storage, it holds potential for use in alkali metal ion batteries, offering improvements in capacity and performance. Additionally, borophene's unique properties make it an attractive candidate for hydrogen storage, potentially enhancing storage efficiency and capacity. Its high surface area and electrical conductivity also suggest promising applications in supercapacitors, where it could improve charge storage and power delivery. Furthermore, borophene's catalytic abilities have been explored, positioning it as a valuable material in various catalytic processes. However, it is imperative to thoroughly characterize and understand the adsorption behavior of LPE-exfoliated borophene on various surfaces to fully realize its potential in these applications. Despite its importance, this aspect of LPE borophene has been largely overlooked both at

macroscopic and microscopic scales, creating a significant gap in the investigation and utilization of LPE borophene. To address this research gap, our study meticulously investigates the adsorption of Liquid Phase Exfoliated (LPE) borophene on the Au(111) substrate, with a focus on the atomic-scale characterization of its structure and electronic properties. Employing a combination of experimental techniques, including STM along with Spectroscopy (STS) supported by the theoretical insights from Density Functional Theory (DFT), we have identified the phase of borophene as β_{12} . This research delves into the atomic structure of LPE borophene and the nature of its interaction with the gold substrate. Furthermore, a significant observation is that LPE borophene produces sheets with deposition control on metallic substrate comparable to those grown by Molecular Beam Epitaxy (MBE), offering an economical alternative to the more demanding MBE techniques for the production of high-quality borophene sheets.

3.2 Methods

Boron powder, consisting of approximately $\sim 20 \mu\text{m}$ size sheets and purchased from the American Elements with a remarkable purity of 99.99%, underwent a meticulous sonochemical exfoliation process in a range of solvents. These solvents included dimethylformamide (DMF), isopropyl alcohol (IPA), ethylene glycol (EG), and water. The method used was bath sonication and it was performed in 2-hour cycles for a total duration of 24 hours at 40 kHz. Each solvent was carefully selected to investigate and compare their efficiency and effectiveness in exfoliating the boron sheets under precisely controlled conditions, ensuring a thorough evaluation of their potential for producing high-quality exfoliated boron[24].

Sample preparation for the STM measurements included a gold (Au) film with a thickness of $2000 \text{ \AA}$, deposited on mica substrates sourced from Sigma-Aldrich. Further, it underwent a flame annealing process in an ambient atmospheric environment to ensure an atomically clean and smooth surface.

The annealed Au(111) sample was subjected to Atomic Force Microscopy (AFM) to assess whether it exhibited the characteristic planar steps of the Au(111) surface. Following this, STM analysis was performed, revealing the presence of herringbone reconstruction in the STM images, which confirmed the pristine nature of the Au(111) surface.

Following the annealing, LPE borophene dispersed in IPA was carefully spin-coated onto the gold-coated mica substrate at a rotation speed of 2000 revolutions

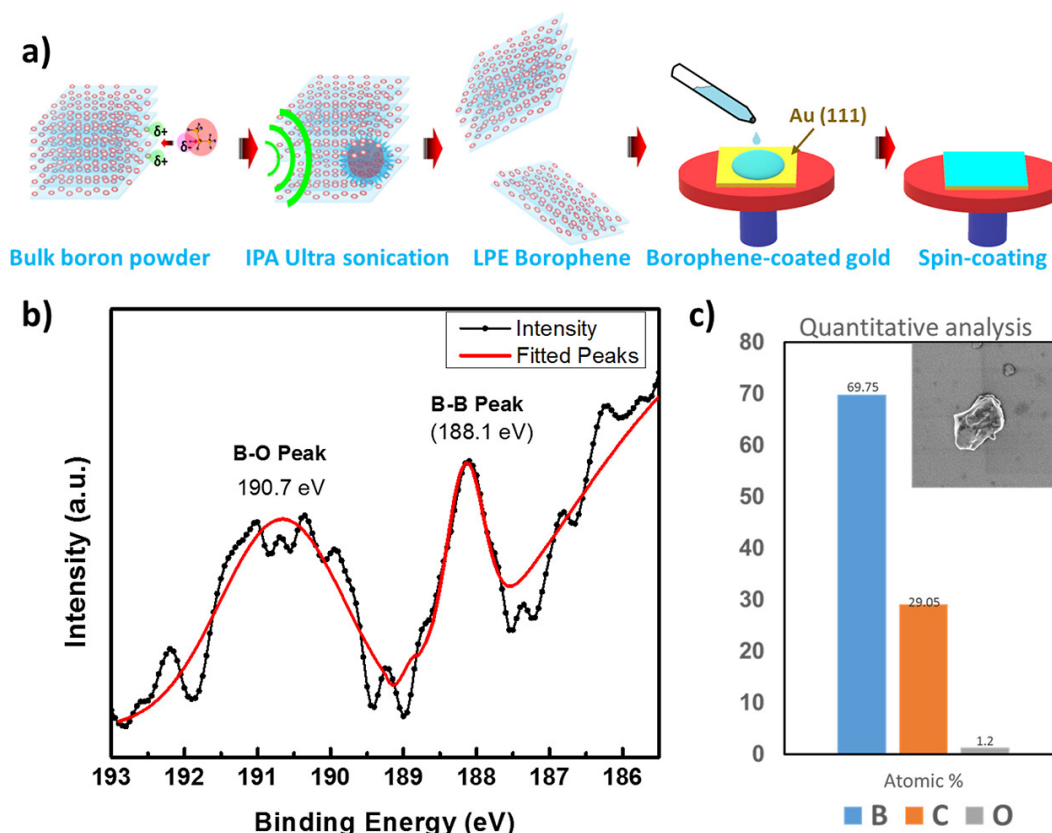


Figure 3.1: Figure presents a comprehensive analysis of the sonochemical exfoliation process and subsequent characterization of borophene. a) The schematic illustrates the sonochemical exfoliation process, beginning with the electrostatic interaction between isopropyl alcohol (IPA) molecules and boron atoms on the borophene surface. This interaction is followed by the ultrasonic cavitation of IPA bubbles, which ultimately leads to the exfoliation of borophene sheets. The subsequent step involves the spin coating of LPE borophene onto an Au(111) substrate, as depicted in the accompanying illustration. b) the X-ray photoelectron spectroscopy (XPS) spectra of the spin-coated borophene on Au(111) are presented, with fitted peaks corresponding to B–B and B–O bonds, confirming the chemical composition of the material. c) The image shows the energy-dispersive spectroscopy (EDS) analysis of a borophene flake, as depicted in the inset, which verifies the presence of boron, carbon, and oxygen elements. The EDS data provides the atomic percentage composition of these elements. Reproduced with permission from Ref. [150]

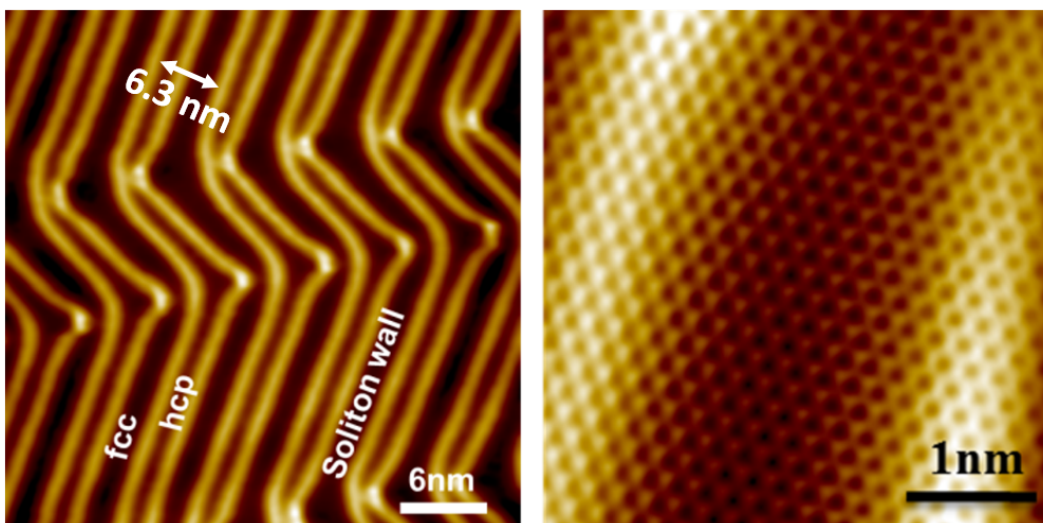


Figure 3.2: The figure presents a STM image of an Au(111) substrate: a) the image shows the Herringbone reconstruction on the pristine Au(111) surface, highlighting the characteristic structural pattern; (b) the image provides a high-resolution atomic resolution of the Au(111) surface. Images adapted with permission Ref[177]

per minute (rpm) to achieve a uniform and well-adhered borophene layer on the prepared Au surface, thereby facilitating subsequent STM analysis. To optimize the density and deposition of boron flakes, the spin-coating process was methodically repeated for two and three cycles, respectively. This approach was carefully designed to ensure uniform distribution and adequate coverage of the boron flakes on the substrate. Following the spin-coating process, the samples underwent STM measurements to evaluate the effects of the varying cycles on the surface morphology and flake distribution, providing critical insights into the optimization of the deposition process.

STM imaging was performed using a commercial low-temperature STM (LT-STM) system (Scienta Omicron) operated under ultra-high vacuum (UHV) conditions with a base pressure maintained at 5×10^{-11} mbar. The imaging was conducted at a cryogenic temperature of 77 K. The Tungsten tip, which was electrochemically etched to achieve high precision, was employed for imaging purposes. The imaging procedure was carried out in constant current mode to ensure consistent image quality. For the spectroscopy measurements, an alternating current (AC) modulation voltage of 10 mV was applied at a frequency of 652 Hz, superimposed on the tunneling voltage (V). The typical voltage sweep for tunneling spanned a range of ± 1 V, during which the variation in the tunneling current (I) was meticulously recorded to

generate a dI/dV spectrum. Post-imaging, all acquired images were processed and analyzed using dedicated image analysis software SPIP 6.3.6 (Image Metrology) to extract and interpret the relevant data.

The identical sample, which was spin-coated, underwent chemical analysis using X-ray Photoelectron Spectroscopy (XPS) with a Thermo Scientific, *K – ALPHA*⁺. This analysis involved a detailed surface examination to characterize the chemical composition of the sample.

Borophene flakes were subjected to comprehensive imaging and analysis utilizing advanced characterization techniques, specifically X-ray Photoelectron Spectroscopy (XPS) and Energy-Dispersive X-ray Spectroscopy (EDS). As depicted in Figure 3.1 (b), the XPS spectra exhibit distinct and well-defined peaks: one corresponding to the B-B interaction at 180.1 eV and another to the B-O interaction at 190.7 eV. The spectral pattern observed in our data exhibits a striking resemblance to those reported for borophene synthesized via electron beam deposition [98] and molecular beam epitaxy (MBE) grown borophene [99, 178]. Specifically, the peak observed at 190.7 eV is likely a consequence of the sample's exposure to the ambient environment before the acquisition of the X-ray Photoelectron Spectroscopy (XPS) data.

The sample for Field Emission Scanning Electron Microscopy (FESEM) was prepared by drop-casting LPE borophene onto a gold-coated mica sheet. FESEM imaging was conducted using the Zeiss Ultra Plus system to analyze the sample. For energy-dispersive X-ray Spectroscopy (EDS), a beam energy of 3 keV was selected to optimize the sensitivity for detecting boron[179].

In the inset of Figure 3.1 (c), a Field Emission Scanning Electron Microscopy (FESEM) image reveals the morphology of the borophene flakes. Meanwhile, the accompanying histogram in Figure 3.1 (c) presents Energy Dispersive Spectroscopy (EDS) data, offering a detailed depiction of the elemental composition and emphasizing the relative presence of boron, carbon, and oxygen. The detected carbon in the EDS analysis is likely due to contributions from the solvent, Isopropyl Alcohol (IPA), or may result from electron beam-induced hydrocarbon formation, as discussed by Hugenschmidt et al. [180]. Despite this, both X-ray Photoelectron Spectroscopy (XPS) and EDS analyses converge in demonstrating that boron is the predominant element in the sample.

All the computational calculations were performed using density functional theory (DFT), as implemented in Vienna Ab-initio Simulation Package (VASP)[181]. The plane wave basis set and projector augmented wave (PAW) potentials [182] were used with $2s^2, 2p^1$ electrons as valence states for B, and $6s^1, 5d^{10}$ electrons as valence states for Au. The electron exchange-correlation energy was calculated by the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional[183]. The electronic kinetic energy cut-off for the plane wave basis was set at 420 eV, and geometry was optimized using the conjugate gradient approach. The unit cell parameters and atomic positions were fully relaxed until the energy converged to within 10^{-6} eV and the atomic force dipped below 0.01 eV/Å. A $2 \times 3 \times 1$ supercell with four layers of Au(111) planes was used in the calculations. A vacuum layer of 15 Å in between adjacent layers was used to avoid the physical interaction between images due to the periodic boundary condition along the c-axis. Brillouin zone integration was carried out using Monkhorst-Pack special k-point[184] mesh of Γ -centered $8 \times 10 \times 1$ for the geometry optimization, electronic structure, and adsorption energy calculations. The Tersoff-Hamann approximation[185] was used for STM simulation, and the integration of partial density of states (PDOS) was done at ± 1 eV around the Fermi energy E_F . The visualization of STM images was done using HIVE-STM software[186].

3.3 Observation of scattered borophene flakes

The deposition of LPE borophene onto an Au(111) substrate was achieved through spin-coating. During the spin-coating process, the centrifugal force effectively expels excess liquid and more substantial LPE sheets, resulting in the selective retention of only the planar LPE borophene sheets on the Au(111) substrate. This selective adherence illustrates the efficiency of the spin-coating method in ensuring that only the desired planar borophene sheets remain adhered to the substrate. The simplified relation for the spin coating process relating to different parameters given by, [187, 188]

$$h \propto \left(\frac{\mu}{\rho \cdot t \cdot \omega^2} \right)^{\frac{1}{2}} \quad (3.1)$$

where, h is the thickness of the coated layer which depends on the fluid viscosity μ , the fluid density ρ , the angular velocity ω , and the spin time t , the duration of rotation of the sample. The low viscosity of the IPA solvent enhances the adherence

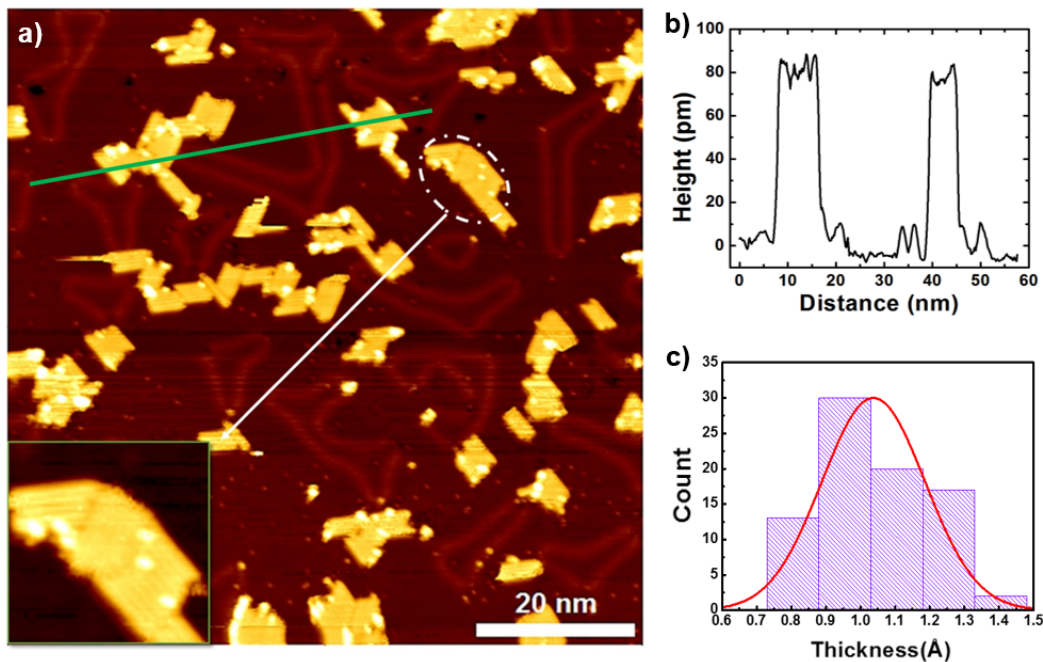


Figure 3.3: a) The STM image shows the β_{12} phase borophene sheets dispersed on the Au(111) terrace, captured with imaging parameters of $V_{bias} = -3$ V and $I_{set} = 20$ pA. The inset offers an enlarged view of the flakes inside the white dotted oval, showing that within the flakes, parallel stripes are present, and the flakes themselves have varying orientations. b) The histogram represents the measured thickness of different borophene sheets observed in several STM images, with an average thickness of $1.04 \pm 0.15 \text{ \AA}$. Images adapted with permission Ref. [150]

of smaller particles to the substrate, while larger particles are expelled with the IPA due to the centrifugal force generated by high angular speed. A high spin coating speed, combined with adequate time, ensures the uniform distribution of smaller particles across the substrate.

The STM was used to characterize the LPE Borophene spin-coated sample. The STM image, depicted in Figure 3.3 (a), encompasses a region of $80 \text{ nm} \times 80 \text{ nm}$, providing detailed insights into the spatial arrangement of borophene sheets distributed across the Au(111) substrate. The image reveals that each borophene sheet covers an area of several tens of square nanometers, with the sheets exhibiting elongated stripes that measure approximately $(3.6 \pm 0.4) \text{ nm}$ in length. The inset in Figure 3.3 (a) provides a detailed close-up view of the sheet highlighted by the white oval. In this close-up, it is evident that the stripes within the sheet exhibit various orientations, aligning in distinct patterns across the surface.

To further determine the feature parameters and phase characteristics of borophene,

we employed highly resolved STM images. These images revealed that the unit cell parameters for the borophene stripes are $4.7 \pm 0.3 \text{ \AA}$ and $3 \pm 0.1 \text{ \AA}$, as illustrated in Figure 3.5 (a). The observed topography and unit cell parameters correspond well with the predicted β_{12} phase ($\nu_{1/6}$). This is the ground state predicted by the CE method of computation[29].

The quasi-planar borophene structures exhibit a greater tendency to adsorb onto the Au(111) surface, with the adsorption energy of the planar β_{12} phase being notably lower compared to other borophene phases[29]. This preference is supported by our STM measurements, which consistently reveal the presence of the β_{12} phase on Au(111). These observations affirm the accuracy of the predictions made by the coordination environment (CE) method, highlighting its reliability in forecasting the behavior of borophene phases in adsorption studies.

The average thickness of the borophene flakes, determined from multiple measurements across various sheets using STM images, is $1.04 \pm 0.15 \text{ \AA}$. This measurement closely aligns with the previously reported value for borophene grown on copper substrates [101].

The observed planarity and thickness of these flakes correspond to the monolayer β_{12} phase, which is a significant observation for substrate-supported LPE non-van der Waals (vdW) sheets. Although LPE borophene is anticipated to exhibit a range of phases with varying sheet sizes and thicknesses [24], only the β_{12} phase has been consistently detected across all experimental runs, demonstrating a uniform and consistent height throughout

3.4 Perturbation of herringbone reconstruction

The STM image illustrates distinct wavy structures in the background of the adsorbed borophene on the Au(111) surface, which are identified as the herringbone reconstruction (HBR) patterns inherent to the Au(111) surface. Herringbone reconstructions manifest as multiple parallel, strip-like structures resembling bones on the pristine Au(111) surface. This phenomenon is attributed to a 4.34% compression of the top layer in the close-packed (110) direction, wherein 23 atoms in the topmost layer align with 22 atoms in the underlying layer. Such surface compression results in a periodic arrangement of regions stacked in face-centered cubic (FCC) and hexagonal close-packed (HCP) configurations, separated by soliton walls. Notably, the distance between adjacent soliton walls remains consistently reported as 6.3 nm in the pristine Au(111), except when altered by external factors[189, 190].

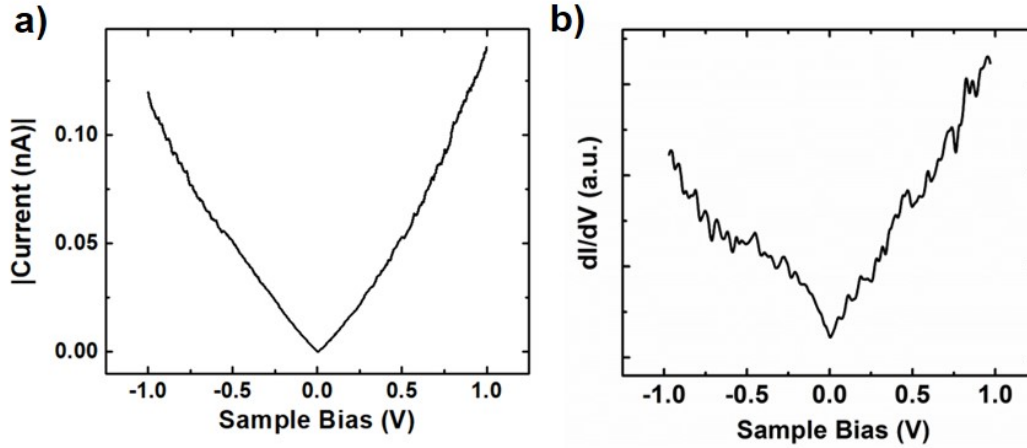


Figure 3.4: a) The figure illustrates the current-voltage (I-V) curve for the β_{12} phase of borophene b) The differential conductance (dI/dV) curve of borophene is shown with spectra recorded at a current of 100 picoamperes (pA) and a voltage of 700 millivolts (mV), with the feedback loop being open during the measurement. Images adapted with permission Ref. [150]

The introduction of adsorbates, such as atoms, clusters, or molecules, prompts relaxation of the Au(111) surface, leading to modifications in the original HBR configuration. Consequently, the shape and spacing of the soliton boundaries within the HBR pattern are affected, reflecting the influence of the adsorbed borophene [191, 192]. The extent of modification observed in the herringbone reconstruction of Au (111) serves as an indicator of the interaction strength between the Au (111) surface and the adsorbate. As illustrated in Figure 3.3 (a), the herringbone reconstruction displayed represents a significant deviation from the unperturbed soliton wall structure, which maintains a separation of 6.3 nm. This pronounced alteration suggests that the β_{12} phase exerts a strong interaction with the Au (111) substrate.

3.5 Confirmation of metallicity in LPE Borophene

We have observed that the adsorbed LPE borophene on Au(111) exhibits metallic behavior, which contrasts with the insulating nature typically associated with bulk boron, as documented in previous studies [39, 174]. This deviation from bulk boron's insulating properties has also been reported for borophene sheets synthesized through electron beam deposition [98, 174] and Molecular Beam Epitaxy (MBE) methods [178].

By employing STS measurements, we have explored the electronic nature of borophene sheets on Au(111), where the dI/dV spectrum reveals a gapless profile,

indicative of metallic characteristics. This metallicity emerges from the interaction between the electron sea of Au(111) and the occupied states of the β_{12} phase of borophene. Such modulations in the β_{12} phase open up potential applications, particularly as metallic interconnects or as templates for one-dimensional channels in nanoscale device architectures.

3.6 DFT calculations

To understand the stability of borophene sheets on Au(111) substrate DFT calculations have been carried out. DFT provides insight into the energetic and thermodynamic aspects of borophene-Au interactions by calculating adsorption energies and chemical potentials per boron atom. Charge redistribution analysis and Bader charge analysis further elucidate electronic interactions, which helps to understand the bond strength between the β_{12} phase and the Au substrate. The stability of the borophene sheets on Au substrate is compared in terms of adsorption energy E_{ad} and the chemical potential μ_B per boron atom. Adsorption energy per boron atom is calculated using the following formula [193] $E_{ad} = (E_{Au-B} - E_{Au} - E_B)/n_B$, and the chemical potential per boron atom is calculated using $\mu_B = (E_{Au-B} - E_{Au})/n_B$ where E_{Au-B} is the energy of the B-adsorbed Au system, E_{Au} is the energy of Au(111) surface without any B layer on it, E_B is the total energy of free-standing borophene sheet, and n_B is the number of boron atoms. The chemical potential of all the prominent borophene structures with different vacancy concentrations ν on Au(111) substrate is compared. The results show that the borophene structure with a vacancy concentration of $\nu_{1/6}$ has a minimum chemical potential of -7.3112 eV/atom with adsorption energies and E_{ad} of -1.0391 eV/atom in β_{12} phase. % Here, u is the density of the interlayer bonds, defined as $u = b/B$, where B is the number of boron atoms in the triangular lattice, and b is the number of boron atoms forming the interlayer bonds.

The charge redistribution due to borophene sheet adsorption on Au(111) was studied by calculating the difference between the charge density of the B-adsorbed Au(111) surface and the charge density sum of the Au(111) surface and B, i.e., $\Delta\rho = \rho_{Au-B} - \rho_{Au(111)} - \rho_B$ where $\rho_{B-adsorbed}$, $\rho_{Au(111)}$, and ρ_B are the charge density values of B-adsorbed Au substrate, Au substrate, and B, respectively. To get more insight into the stability of these structures on Au substrate, Bader charge analysis was done to determine the interfacial charge transfer[194]. The charge transfer taking place between β_{12} phase and Au substrate is $0.0095 \text{ e } \text{\AA}^{-2}$. The higher charge

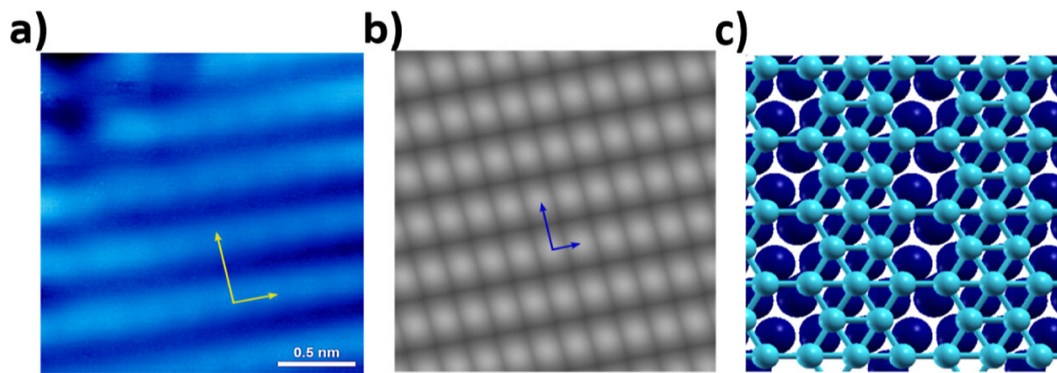


Figure 3.5: a) The STM image of the β_{12} phase was captured at a bias voltage of $V = -0.7$ V and a current of $I = 1$ nA. b) Corresponding, DFT-simulated image of β_{12} borophene is presented. c) Top view of the relaxed structure of the β_{12} phase on Au(111) is shown, with gold atoms represented in dark blue and boron atoms depicted in light blue. Images adapted with permission Ref. [150]

transfer between the borophene and Au(111) suggests stronger interaction between the β_{12} phase with the Au substrate. This matches with the experimental finding of modified herringbone reconstruction attributed to the enhanced interaction between borophene and Au(111).

Figure 3.5, presents a comparative analysis between the STM image and simulated image for the β_{12} phase. Figure 3.5 (a) is the STM image acquired at a voltage (V) of -0.7 V and a current (I) of 1.0 nA, while Figure 3.5 (b) showcases the simulated image at an energy level of 1 eV. In both images, the unit cell is distinctly marked. Simulated results perfectly match the experimentally observed results. Figure 3.5 (c) provides a top view of the relaxed structure of the β_{12} phase on Au(111). Notably, the parameters of the observed borophene phase β_{12} in the STM image (4.7 ± 0.3 and 3 ± 0.1 Å) correspond well with the results obtained throughout the simulation (5.06 and 2.92 Å). The simulated findings presented herein effectively explain the experimental observations and provide a comprehensive understanding of the structural characteristics of the β_{12} phase of LPE borophene when adsorbed on the Au(111) substrate.

3.7 Conclusions

LPE borophene has been successfully deposited onto the Au(111) surface using a spin-coating technique. Detailed characterization through high-resolution STM revealed that the borophene adsorbed is the β_{12} phase, which was further confirmed

to exhibit metallic properties via STS measurements. The observed perturbation in the herringbone reconstruction of the Au(111) surface provides compelling evidence of the strong interaction between the β_{12} phase borophene and the underlying gold substrate. Complementary Density Functional Theory (DFT) calculations further validate the presence of the β_{12} phase and indicate significant charge transfer between the borophene layer and the Au(111) surface. This substrate-supported borophene holds promise for various applications, particularly in the design of interconnects or catalysts, owing to its strong substrate interaction. Moreover, the modulations within the β_{12} phase can serve as "strain inducers," making this material highly suitable for flexible and stretchable wearable electronics. The adoption of our low-cost, scalable Liquid-Phase Exfoliation (LPE) approach to deposit borophene on selected substrates via spin-coating offers a viable pathway toward the economical development of boron-based materials for advanced technological applications.

LIQUID-PHASE EXFOLIATED BORON FLAKES AND CLUSTERS: A COMPREHENSIVE ANALYSIS

4.1 Introduction

Boron, a group 13 element, is renowned for its diverse chemistry and multiple allotropes, attributed to its electron deficiency. Boron possesses only three valence electrons, yet it demonstrates a fascinating capability to engage in electron-sharing through various mechanisms, resulting in the formation of two-electron, multicenter (2e-nc) bonds. This unique electron-sharing ability enables boron to exist in multiple allotropes, each with distinct structural characteristics. Notably, boron forms several well-known allotropes, including α -rhombohedral, β -rhombohedral, α -tetragonal, β -tetragonal, and γ -orthorhombic phases. Each of these allotropes is fundamentally structured around icosahedral clusters, which serve as the building blocks of their respective crystalline forms.

The stability of individual icosahedral boron structures has been a subject of significant research interest. Studies by Kawai et al. (1991) revealed an inherent instability in these structures[86]. However, both theoretical and experimental studies indicate that the corresponding quasi-planar Boron clusters composed of 12 boron atoms exhibit stability[25, 26]. This stability in the quasi-planar structures, as opposed to the 3D icosahedral configurations, arises due to their electron deficiency. Notably, these quasi-planar structures demonstrate significantly lower energy states compared to their 3D counterparts.

The exploration of boron cluster stability is pivotal for understanding the feasibility of borophene, a 2D allotrope of boron. Discoveries regarding the stability of quasi-planar boron structures have catalyzed research into whether these clusters could form stable 2D or 3D configurations with increasing atoms. Structural stability assessments for boron clusters have been conducted for sizes up to 100 atoms, revealing a preference for planar or quasi-planar (2D) conformations in clusters containing fewer than 28 atoms[90]. As the cluster size increases, boron clusters transition from planar/quasi-planar to cage-like configurations. Multiple boron

cages were investigated and the B_{80} cluster was found to be the most energetically favorable cage[195]. Jun Ni reported that the alpha phase sheet by unfolding the B_{80} cage is the most stable borophene phase[27].

Theoretical studies have demonstrated the stability of different boron clusters when supported on metallic substrates, and these clusters extend to form borophene and serve as foundational elements for various borophene polymorphs[28, 196]. Free-standing Bropehene's energy is higher than Bulk Boron's, so it was expected to be stable on the substrate. In search for suitable substrates, Zhang et al. explored multiple substrates like Au, Ag, Cu, and Ni and determined the preferable structures of Borophene for individual substrates [29]. The experimental observation of boron B_{36} planer crystal with hexagonal vacancies enhances the possibility of experimentally synthesized Borophene[97].

The first experimental observation of planar borophene was on Ag(111) having polymorphic borophene phases[98]. Experimental observations revealed a characteristic feature in forming borophene, wherein boron clusters are formed initially followed by borophene formation[98, 99, 103]. In a report by Lan Chen, they observed that during borophene bilayer growth on the monolayer of the β_{12} phase, boron clusters B_5 covalently bind to the monolayer at specific sites. With an increase in the density of these clusters, a transition in the structure occurred, leading to the gradual formation of a bilayer boron configuration[197]. The adsorption of the B_5 cluster on specific sites remains intact even after annealing at 800 K, It confirms that the adsorption is very strong and stable. these clusters have lateral dimensions have 5 ± 0.5 Å and height of around 60 pm.

In the previous chapter, we demonstrated the successful formation of monolayer flakes of LPE borophene on Au(111) substrates using the spin-coating technique, which effectively disrupted the substrate's herringbone reconstruction due to the strong interaction between the borophene monolayer and the Au(111) surface.[150]. Building on this, we carried out repeated spin-coating of LPE borophene onto Au(111). We achieved nearly complete substrate coverage with the borophene monolayer. In instances where small uncovered areas remained, we observed the presence of triangular boron clusters. A third spin-coating cycle resulted in complete coverage by self-assembled boron clusters atop the borophene monolayer, suggesting that the borophene monolayer serves as a template for the self-assembly of these clusters. Further insights into the stability, interaction, and behavior of these clusters

will be provided through localized STM studies.

4.2 Method

Freestanding borophene was synthesized through liquid-phase exfoliation (LPE) of boron powder in isopropanol (IPA), as described in prior studies[24, 150]. For STM investigations, the LPE-derived borophene was spin-coated onto an Au(111) substrate, following the procedure outlined in earlier reports[24, 150].

Initial STM observations indicated a sparse distribution of the boron layer on the substrate, prompting further investigation into the effects of multiple spin-coating cycles. The application of two spin-coating cycles notably enhanced the coverage, resulting in a complete borophene self-assembled layer on the Au(111) substrate. Upon implementing a third spin-coating cycle, the self-assembly of boron clusters was observed, covering the whole substrate.

4.3 Observation of full coverage of β_{12} flakes

The deposition of borophene through a single cycle of spin coating has been previously documented, revealing the presence of scattered borophene flakes with unit cell lattice parameters of $4.7 \pm 0.3 \text{ \AA}$ and $3 \pm 0.1 \text{ \AA}$ [150]. In this study, we enhance the concentration of borophene flakes by implementing an additional spin-coating cycle. Figure 4.1 displays large-area STM images of borophene deposited on Au(111) after two spin-coating cycles. Generally, we observed complete coverage of the borophene flakes without discontinuities, as illustrated in Figure 4.1. However, in rare instances, it is found that some areas of the Au(111) substrate are free of borophene but it exhibits scattered triangular-shaped boron clusters, as depicted in Figure 4.2(b).

In Figure 4.2 (a), the central region of the image reveals faint wavy lines corresponding to the perturbed herringbone reconstruction, which is more clearly visible in the inset image. The unit cell parameters for the borophene stripes, illustrated in both Figure 4.2(a) and Figure 4.2(b), are measured as $4.7 \pm 0.3 \text{ \AA}$ and $3 \pm 0.1 \text{ \AA}$, consistent with the previously reported data for the β_{12} phase. So the monolayer self-assembly corresponds to the $\beta_{12} (\nu_{1/6})$ phase, similar to the scattered flakes reported previously. it was the first report having only β_{12} phase marking the previous chapter as the first report of this phase of polymorphic boron on Au(111). This phase is consistently observed in all trials of 1-cycle and 2-cycle depositions for all samples in our STM measurements. Our STM data exclusively reveal the β_{12} monolayer phase on Au(111).

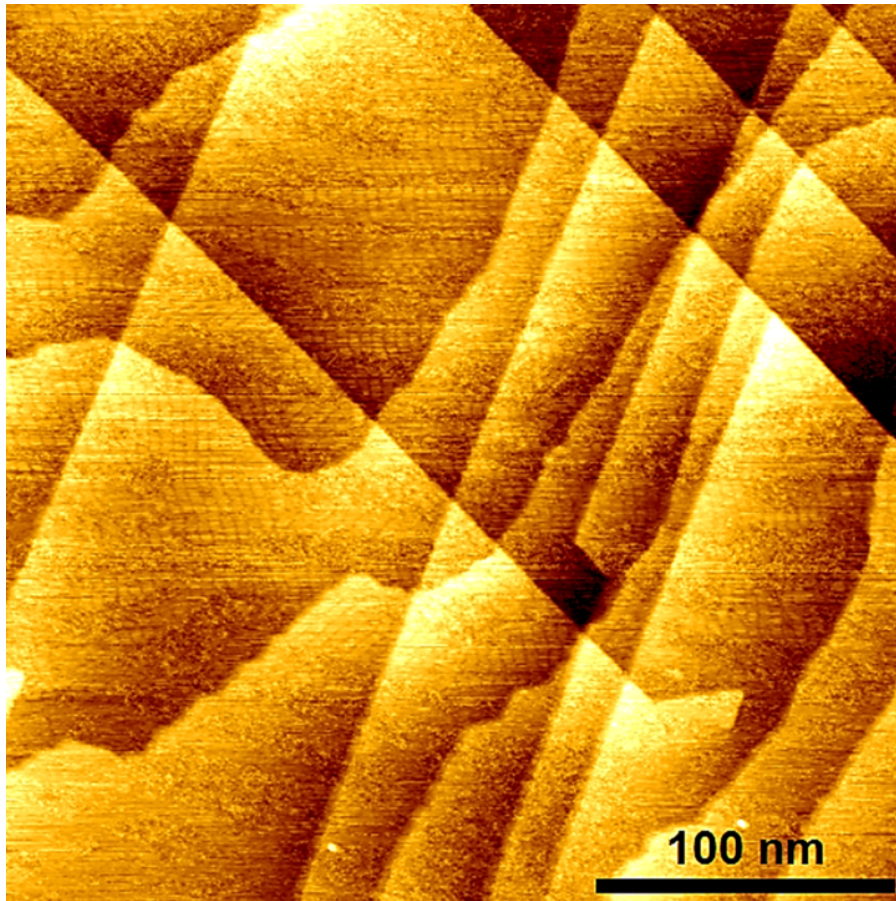


Figure 4.1: a) The large-size ($300\text{nm} \times 300\text{nm}$) STM image reveals complete coverage of the Au(111) surface by self-assembly of the β_{12} phase, image was taken at a bias voltage of 1 V and a current of 40 pA

Figures 4.2 (a) and (b) reveal that the area of individual sheets is approximately a few nm^2 . The elongated stripes comprising the sheets measure approximately (3.6 ± 0.4) nm in length. Sheets of different sizes are oriented at $(59 \pm 7)^\circ$ or $(120 \pm 9)^\circ$, as marked in Figure 4.2 (a). This confirms a preferential alignment of the borophene sheets along the symmetry directions of the Au(111) substrate. Such coverage demonstrates the large-scale planarity and stability of the borophene sheets for a spin-coated liquid sample.

We have previously discussed the Herringbone reconstruction, which is an inherent property of an annealed Au(111) surface. In this reconstruction, 23 atoms in the topmost layer align with 22 atoms in the layer beneath, causing compression in the top layer. This compression creates a periodic array of fcc-stacked and hcp-stacked regions, separated by soliton walls. In the absence of external perturbations,

the distance between two adjacent soliton walls remains constant, and this distance is widely reported and accepted to be 6.3 nm. The adsorption of any foreign object can lead to perturbation of the shape or distances between the soliton boundaries of the herringbone reconstruction as seen in our previous chapter. Figure 4.2(a) displays the parallel lines characteristic of the herringbone reconstruction, highlighted by black dotted lines, with a measured spacing of 7.8 nm. This observed spacing indicates that the borophene flakes are interacting with the substrate, resulting in a modification from the unperturbed herringbone reconstruction spacing of 6.3 nm [189–191].

In the previous chapter, it was noted that the Modified Herringbone reconstruction within the distributed borophene flakes exhibited significant perturbations [150]. However, the images presented in Figure 4.2 reveal that only the spacing between the layers is altered, indicating that the perturbations are limited in comparison when considering the scattered borophene flakes. A qualitative inference from this direct observation is that the interaction of the self-assembled borophene domains with the Au(111) substrate is weaker concerning the borophene scattered flakes of borophene sheets. This explains why herringbone reconstruction is strongly perturbed in the previous chapter as compared to the current data. In Figure 4.2, where herringbone reconstruction is seen to be weakly perturbed, it can be inferred that there is an interaction among the closely packed sheets. Which results in the weakening of the interaction of the sheets with the substrate. Thus we infer that the modification of herringbone reconstruction depends on the coverage of borophene sheets over Au(111) due to the interaction of borophene sheets to the substrate.

4.4 Clusters self-assembly

The growth of bilayer borophene was first demonstrated by Liu et al. [174] on Ag(111) using electron beam evaporation of a boron rod and later by Chen et al. [178] on Cu(111) via molecular beam epitaxy (MBE). Both achieved bilayer borophene through precisely controlled extended growth following the formation of a single atomic layer. Liu et al.'s work on Ag(111) resulted in bilayer borophene with a structure identified as bilayer α -borophene. This phase grows through covalent bonding between the α -phase ($\nu_{1/9}$) and monolayer boron sheets.

In contrast, the bilayer borophene grown by Chen et al. on Cu(111) exhibited a structure similar to the β_{12} -like configuration, with boron atoms arranged in zigzag rows. Chen's results also indicated that excess electrons are transferred from the

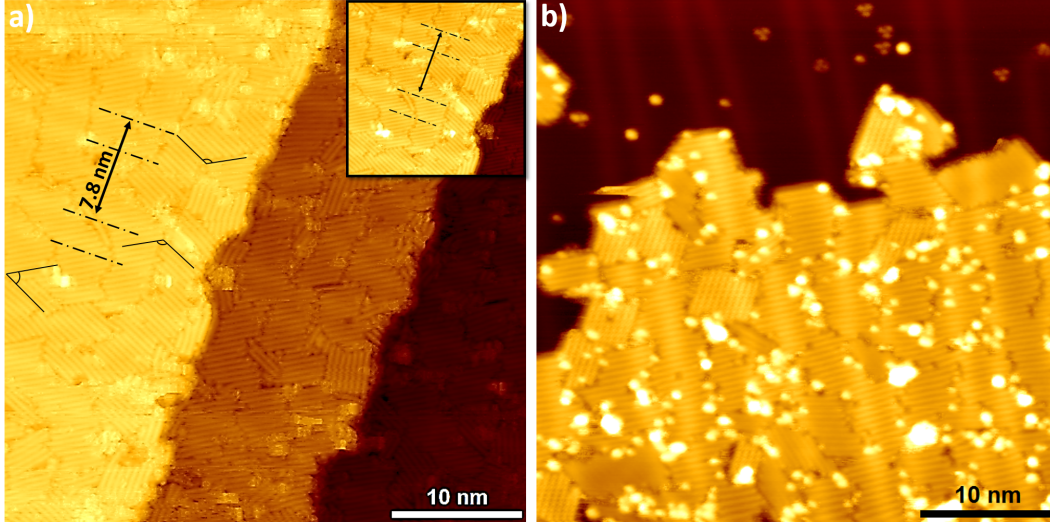


Figure 4.2: High-resolution STM images of borophene spin-coated onto atomically flat Au(111) reveal detailed features of the borophene sheets. a) illustrates that after two spin-coating cycles, a 40 nm $\times$ 40 nm scan demonstrates complete coverage of borophene sheets, which exhibit striped borophene phase on the Au(111) substrate. The inset highlights the stripes more clearly, with a herringbone reconstruction spacing of 7.8 nm. The borophene sheets align at specific angles, as indicated on several sheets. Imaging parameters are $V = 2.0$ V and $I = 0.5$ nA. b) Image shows the self-assembled domain coverage of borophene sheets on Au(111), including several triangular-shaped boron clusters. Imaging parameters are $V = -3.0$ V and $I = 0.1$ nA. Images adapted with permission Ref. [198]

first boron layer to the second, leading to a redistribution of in-plane electrons in the bilayer borophene. This electron redistribution is advantageous for the growth of the bilayer boron sheet.

Similar to the case of monolayer borophene, where theory results carved out pathways to realize borophene experimentally, predictions for bilayer borophene were made right from the bilayer being a host to topologically nontrivial Dirac nodal line [199–201], to anode material in lithium-ion battery[202]. Inspired by these predictions, we conducted an additional spin-coating cycle to investigate whether a new phase would emerge or if the same β_{12} phase would be retained during a third spin-coating cycle.

The outcome of conducting three spin-coating cycles produces very interesting results. To investigate the structural characteristics of borophene after these coating cycles, we performed STM imaging, with the images depicted in Figure 4.3. The images reveal a periodic lattice with a unit cell dimension of (4.8 ± 0.2) Å $\times$

(4.8 ± 0.2) Å. These results suggest that the self-assembly process covered the substrate completely. The herringbone reconstruction is faintly visible, showing a hint of deformation and irregularity, in contrast to the previously reported wavy lines[150] or the parallel lines typically observed in β_{12} monolayer borophene full coverage, as shown in Figure 4.2. These observations imply that the structure resembles the α phase described by Liu, closely matching the BL- α borophene configuration but displaying parameters consistent with those reported for bilayer borophene by Chen et al.

The self-assembly we observed resembles to the reported growth of bilayer α phase structures, though there are minor variations in the parameters. Upon closer inspection, we observed that the clusters are organized differently, with parameters differing by approximately 1 Å, which indicates a distinct arrangement of well-ordered boron clusters.

The self-assembly of boron clusters demonstrates a crystalline-like organization within certain regions. However, the majority of the areas exhibit protrusions in their arrangement. This observation reinforces the concept of self-assembly. Additionally, numerous individual clusters, varying in configuration, are seen positioned above the self-assembled borophene monolayer. These clusters, which exhibit similar parameters, are depicted in Figure 4.2 (b), where a triangular configuration of three clusters is visible. Figure 4.4 (a) illustrates more loosely packed self-assembly, where individual clusters are discernible. While in Figure 4.4 (c) demonstrates that the clusters are densely packed, resulting in a top surface composed of these clusters that feature pronounced protrusions rather than a flat profile. This indicates that the observed sheet is composed of these individual clusters. As observed in our experiment, the individual clusters have the potential to self-organize into a structure that closely resembles the alpha phase, given that they achieve precise alignment during the self-assembly process. The monolayer appears to play a crucial role as a template for this self-assembly process that supports the organization of clusters and guides their arrangement.

Multiple boron clusters have been predicted and experimentally explored in various studies. Recently, an article on bilayer growth in borophene reported the observation of boron clusters during the growth process, identifying these clusters as B_5 [197]. These clusters exhibit a selective affinity for specific sites on MLB, forming a covalent boron–boron bond, resulting in a periodic arrangement. This phenomenon can be attributed to the charge distribution and electron delocaliza-

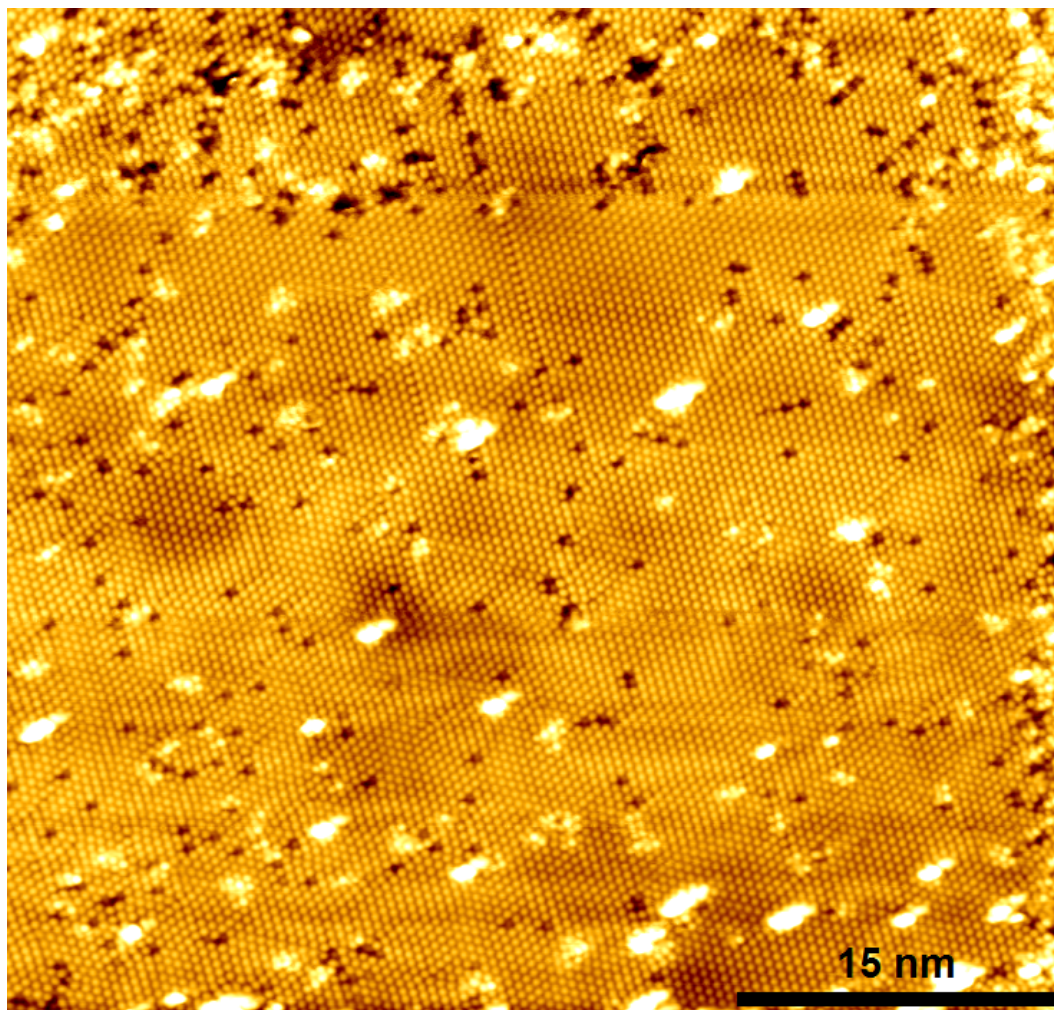


Figure 4.3: High-resolution STM image of boron clusters after three cycles of spin-coating over atomically flat Au(111). Imaging parameters are $V = -3.0$ V and $I = 0.5$ nA. Image adapted with permission Ref. [198]

tion characteristics of MLB, which also prevent the co-adsorption of additional B_5 clusters in the vicinity. Further adsorption of these clusters leads to the formation of bilayer borophene. In our case, the size of the clusters matches the parameters reported in that study. This prompted us to conduct a theoretical analysis to identify the possible clusters of self-assembly over the β_{12} monolayer. This analysis aims to provide a deeper understanding of the underlying mechanisms driving the formation of these clusters and their arrangement during the self-assembly process.

We aimed to characterize the modified herringbone reconstruction across various coverage levels of borophene and clusters. Previous studies have shown that

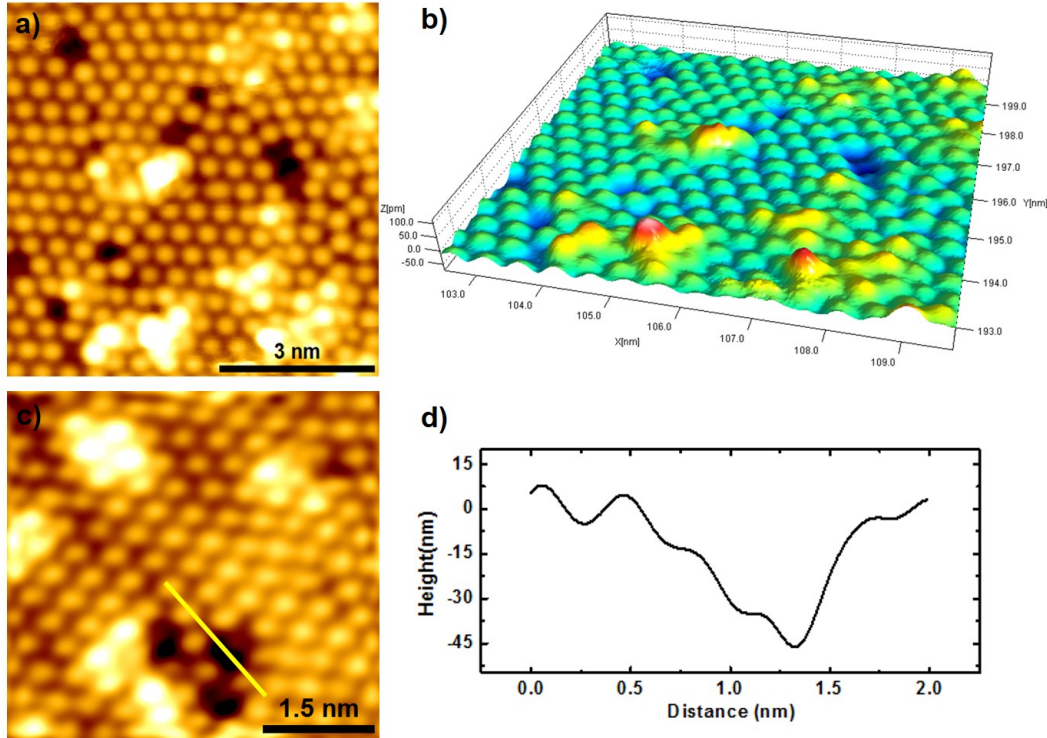


Figure 4.4: a) Atomic resolved STM image showing loosely packed boron clusters, Imaging parameters are $V = -3.0$ V and $I = 1$ nA. b) Corresponding 3D image of (a). c) High-resolution STM image showing tight packing forming surface protrusions. d) Height profile of the missing clusters along the line marked in (c). Imaging parameters are $V = 3.0$ V and $I = 1$ nA. Image(a) adapted with permission Ref. [198]

when the borophene flakes do not fully cover the imaged area, the degree of herringbone modification is significantly higher[150]. In contrast, as illustrated in Figure 4.2, full coverage of borophene flakes results in a consistent herringbone pattern with parallel lines, although the spacing between the soliton walls increases. This suggests that perturbations are less pronounced in uniformly distributed flakes compared to scattered flakes, likely due to the influence of their packing density.

A qualitative analysis of this observation suggests that the interaction between smaller domains of striped borophene sheets and the Au(111) substrate is stronger, leading to a pronounced perturbation. Conversely, for full coverage, the herringbone reconstruction is weakly perturbed, indicating that the interaction among closely packed sheets is stronger, thereby weakening the interaction between the sheets and the substrate. Consequently, it can be concluded that the modification of herringbone reconstruction depends on the coverage of borophene sheets on the Au(111) surface.

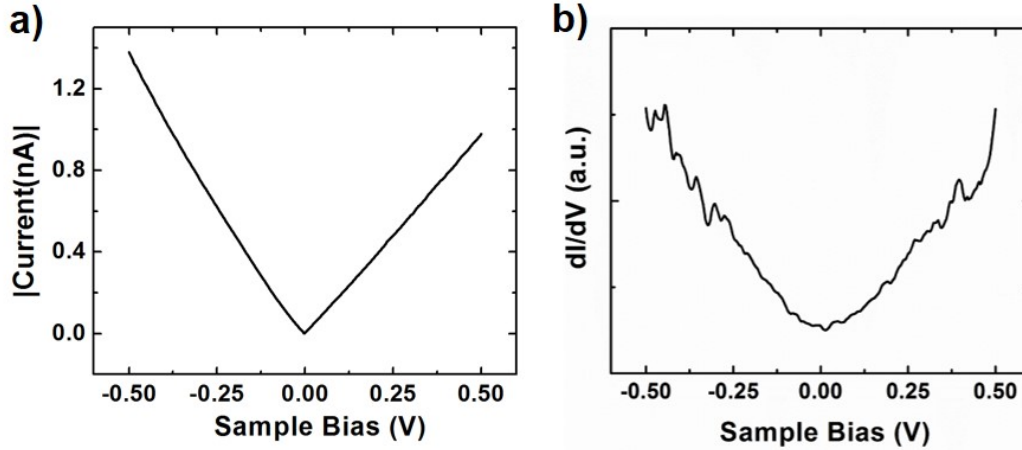


Figure 4.5: IV and dI/dV taken of the self-assembly of the boron clusters. These graphs indicate the boron clusters are metallic in nature. Graphs adapted with permission Ref. [198]

This effect may be attributed to the electron deficiency of borophene flakes being compensated at higher coverage levels. In the case of boron clusters, there is a subtle indication of the herringbone reconstruction. This observation, depicted in Figure 4.3, shows that the herringbone pattern is significantly altered. This pronounced modification of the herringbone structure could result from the combined charge transfer within the monolayer and the boron clusters.

We also carried out STS measurements for this sample. The spectra are shown in Figure 4.5. The I-V curve shows a linear response between $\pm 0.5V$. The dI/dV curve confirms that the boron clusters and their self-assembly are metallic. This highlights the role of dimensionality in tuning the electronic properties of 2D boron because bulk boron is insulating [39]. The boron clusters achieved through spin-coating represent a novel observation, as boron clusters and their self-assembly via the LPE method have not been previously documented. This study also elucidates the electronic properties of the clusters and their interaction strengths. Furthermore, it demonstrates that boron clusters can self-assemble into uniform coverage, opening up various applications for these clusters. This method underscores the cost-effectiveness of spin-coating combined with the economical LPE process for producing borophene and boron clusters. It establishes a robust mechanism for facilitating the scalable production of substrate-supported monolayers and boron clusters. This approach provides a straightforward yet precise strategy for engineering application-specific, customized production of borophene and boron clusters.

4.5 Conclusions

We have investigated LPE borophene and boron clusters deposited on an Au(111) surface via spin coating. By varying the number of spin coating cycles, we successfully achieved both a fully covered monolayer and boron cluster deposition of LPE borophene on Au(111). High-resolution STM and STS were employed to characterize the resulting structures. Our analysis revealed that the monolayer phase corresponds to β_{12} , while the exact configuration is unknown till now. Additionally, the self-assembled clusters exhibited a diverse array of configurations, as observed in the STM images.

Our findings revealed that the full-coverage borophene monolayer perturbs the herringbone reconstruction of Au(111) to a lesser extent, indicating a reduced interaction between the borophene flakes and the Au(111) substrate. Conversely, the boron clusters exhibited self-assembly on the borophene monolayer, suggesting that the monolayer acts as a template for this process. Density Functional Theory (DFT) calculations further confirmed charge transfer between the β_{12} borophene monolayer and the Au(111) surface, as well as between the boron clusters, the borophene monolayer, and the Au(111) substrate. These calculations also confirmed the metallic nature of the boron clusters.

This study deepens our understanding of borophene and boron clusters, particularly their interactions with gold surfaces, revealing their inherent affinity for substrates. These findings suggest that borophene and/or boron clusters exhibit a strong interaction with Au(111). Therefore, it is highly likely that borophene and/or boron clusters may also demonstrate strong interactions with other elements, surfaces, gases, and more, offering valuable insights into their potential applications in catalysis, battery technology, hydrogen generation, sensors, and broader materials science.

POLYPHASY OF 2D BORON

5.1 Introduction

Borophene, an atom-thin boron sheet is a metallic Dirac material and remains amongst the least explored Xenes [98]. While pristine graphene [1, 203], lacks metallicity (needed for energy storage and electrocatalytic applications), its zero-band gap and lack of effective charge carriers have restricted its dream applications in electronic, optoelectronic, and spintronic chips. Several Xenes such as semiconducting phosphorene [204, 205], germanene[206], silicene[207] etc and metallic goldene[208], molybdenene[209] and berylline[210] have been invented and developed in past decade. One of the common hurdles in implementing these quantum materials in practical devices is their oxidation under an ambient environment. In contrast to all these Xenes, borophene is the lightest Dirac material with pronounced crystallographic anisotropy[211]. While borophene is metallic for both β_{12} and χ_3 phases with excellent electronic mobility, thermal conductivity as well as Young's modulus[212], anisotropic stretchability, especially along the ridgelines[213]. Regardless of earlier myths regarding its instability in ambient conditions which made it a very elusive material, significant literature has surfaced indicating it to be a next-generation wonder material, especially for flexible electronics, plasmonics, ultrafast sensing, energy storage, and catalysis[114, 214–217].

Since crystallographic phases determine borophene's physical and chemical properties, it is essential to understand its phase evolution. While the epitaxy of bottom-up ALD/MBE grown borophene with underlying metallic (silver, gold, etc) catalyst surface determines their crystallographic phases[218], polyphasy in liquid phase exfoliated borophene has remained a mystery till date. Parent boron crystals available in precursor powder usually result in the corresponding crystallographic phase of borophene in liquid-phase exfoliated samples [22, 24]. However, the crystalline quality of borophene is severely impacted by strain in the lattice. The solvent-solute interactions' role is deemed the key parameter in efficient exfoliation without fragmentation. Solvents with higher Hansen parameters such as NMP and DMF are told to help exfoliate better. There is, however, a dearth of detailed studies

on the evolution of various phases in the same solvent, partly due to a lack of focused efforts in this direction and also due to poor quality of HRTEM images.

Considering the urgency to develop a deeper understanding of crystallographic phases found in liquid phase exfoliated borophene, herein, we carried out detailed electron imaging (atomically resolved HRTEM) of sonochemically exfoliated borophene in IPA solvent. The chemical phase purity of exfoliated borophene was identified by Raman and X-ray photoelectron spectroscopy, Atomic force microscopy (AFM), and conducting atomic force microscopy (CAFM). Correlation length in two distinct directions and the areal density of periodic units in the borophene lattice were compared to distinguish various crystallographic phases. Density functional theory calculation of band structures for prominent phases (α , χ_3 , β_{12} and striped) of borophene along with axial translational moire phases have been carried out to reveal phases dependent electronic character.

5.2 Methods

The borophene sample for HRTEM was prepared by drop-casting LPE borophene, synthesized via a sonochemical method, as explained earlier, and its schematic is shown in Figure 5.1(a). The characterization of the HRTEM samples was conducted independently of the spin-coated sample preparation. it included SEM which confirmed successful exfoliation, revealing sheet-like structures with lateral dimensions of 100-500 nm (Figure 5.1(a)). Raman spectroscopy verified phase purity with peaks at $\sim 811\text{ cm}^{-1}$ and 679 cm^{-1} , corresponding to the β_{12} and χ_3 phases (Figure 5.1(b)). XPS analysis indicated minimal oxidation of borophene, as evidenced by the B 1s peak appearing at around 187.8 eV. (Figure 5.1(c)).

Atomic force microscopy (AFM) revealed sheets with thicknesses of 8-10 monolayers and lateral dimensions of 100-150 nm (Figures 5.1(d) and (e)), with histogram analysis showing the impact of sonication duration (Figure 5.1(f)). Conductive atomic force microscopy (CAFM) confirmed uniform electrical properties, with I-V characteristics indicating good conductivity across the sample (Figures 5.1(g), (h) and (i)).

5.3 Results and discussion

Intercalation and ultrasonic cavitation of IPA molecule in between the van der Waals layers of boron crystal (schematic in Figure 5.1(a)) gives rise to successful exfoliation synthesis of borophene. SEM image in the inset of Figure 5.1 (a) shows

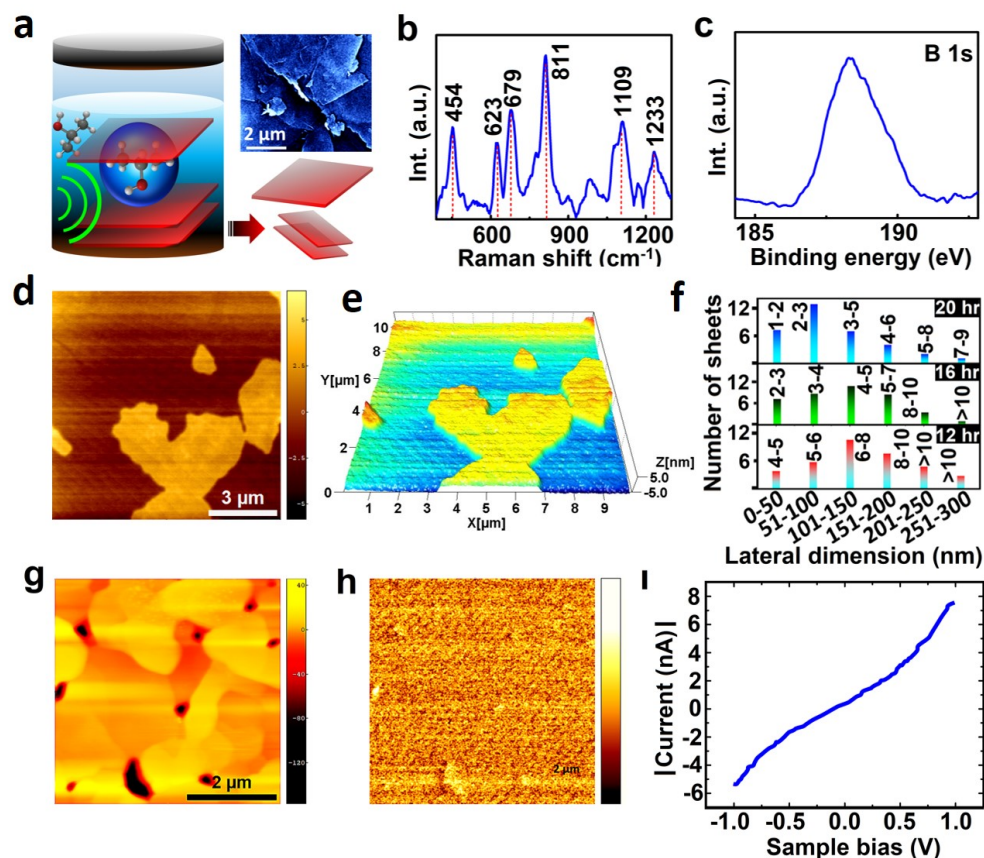


Figure 5.1: a) Schematic of the InterCalation and ultrasonic cavitation of IPA molecule between the boron crystal layers lead to the exfoliation of boron into borophene, inset showing FESEM image of LPE borophene. b) Raman spectra of LPE Borophene. c) XPS Spectra of LPE Porophene. d) AFM image showing LPE Borophene. e) Corresponding 3D view of AFM image, showing borophene flake in 3D form. f) Graph showing Time-dependent exfoliation of sheets. g) AFM image of borophene-coated Au(111). h) C-AFM image corresponding to AFM image. i) IV spectra taken of C-AFM image.

layered sheet-like features with a few ~ 100 -500 nm sheets and some large area ($\sim \mu\text{m}$ scale) sheets. Raman spectroscopy of synthesized borophene samples revealed the pre-dominant existence of both β_{12} (peak $\sim 811 \text{ cm}^{-1}$) and χ_3 (peak $\sim 679 \text{ cm}^{-1}$) phases in the borophene sample (Figure 5.1(b)). The chemical phase purity of synthesized borophene sheets is established by B 1s-resolved peak in XPS at $\sim 187.8 \text{ eV}$ and negligible oxidation, as is evident from the absence of B-O shoulder $\sim 191 \text{ eV}$ (Figure 5.1 (c)). Atomic force microscopy revealed the synthesis of large area $\sim (\mu\text{m}$ scale) ~ 8 -10 monolayers thick sheets as shown in Figure 5.1(d). Corresponding 3D view of the AFM image is shown in the Figure 5.1(e), shown the step height of the 2D sheets around 5 nm. Detailed number of monolayers vs lateral dimensions histogram plot reveals that longer sonication of boron powder in IPA, results in smaller lateral dimension and thinner layers. For example, 12 hours of sonication results in a lateral dimension and thickness distribution with the maximum number of sheets having 6-8 layers and 100-150 nm lateral dimensions (Figure 5.1(f)). In a separate experiment, when 16-hour sonication was carried out on boron dispersion in IPA, lateral dimensions and thickness distributions were witnessed to shift to lower thickness (~ 4 -5 layers) and almost similar lateral dimensions. Further, upon 20 hours of sonication, the size vs thickness distribution plot shifted towards tinnier sheets having lateral dimensions in 51-100 nm and 2-3 monolayered sheets being the majority (Figure 5.1(f)). CAFM (Figure 5.1(h)) carried out on the same location shown in Figure 5.1(g) shows uniformity in current value at a bias of 1 Volt. Interestingly, typical I-V characteristics obtained through CAFM exhibited nA current values (Figure 5.1(I)).

Carbon has a valency of 4 and its allotropes such as amorphous carbon (coal), graphite, charcoal, diamond, etc are naturally occurring materials and abundantly available. Diamond (sp³-hybridized), graphite (sp² hybridized), and diamond-like graphite (DLG) as well as graphite-like diamond (GLD) sp²-sp³ mixed phases form under different sets of thermodynamic (P+T) conditions. The phase diagram for carbon is shown in Figure 5.2(a)). Interestingly, while tungsten has the highest melting point of 3442°C , graphite melts at 3650°C , and diamond melts above 3800°C . Graphite is a naturally occurring van der Waals material, which can easily be exfoliated to graphene. Several top-down exfoliation techniques as well as bottom-up crystal growth techniques have already been established to produce graphene in Kg scale. Graphene is sp²-hybridized and has a perfectly flat hexagonal lattice. Boron, in contrast to Carbon, has 3 valence electrons, however, has the extremely interesting

capability to share electrons in a variety of ways and exhibits 2e-nc bonding. Boron has several allotropes including α -rhombohedral, β -rhombohedral, α -tetragonal, β -tetragonal, γ -orthorhombic, α -Ga as well as amorphous phases (Figure 5.2(b))[219]. Experimental phase diagram of boron shows well-defined boundaries between α , β and γ phases (Figure 5.2(c))[220]. The Advent of 2-dimensionality makes it even more adverse for boron atoms. The absence of a sufficient number of electrons in the valence (2nd) shell in boron atoms restricts them from forming stable flat crystals. This forces boron atoms to form varieties of crystallographic features such as periodic porous structure, periodic 3D protrusion, and their several combinations therein. Polymorphism in borophene is very pronounced[93, 170].

The role of developed local strain, moire phases including various twist angles between atomic sheets, translation (along X, along Y, and both X and Y), and their combinations (twist+translation) in already complicated energetics (due to lack of electrons, 2e-nc bonding) leads to further expansion of the list of crystallographic structural phases in LPE borophene. We observed the evolution of various crystal phases. Especially at the edges, crystalline borophene sheets were witnessed in HRTEM imaging (Original image in Figure A.1 (a) and colored image in Figure A.1(b)). Moreover, monolayers were observed to have local strain locally destructing crystalline order. Due to this effect, amorphous, partly crystalline, and crystalline sections were observed in the same borophene sheet (original image in Figure A.1 (c) and colored image in Figure A.1(d)). Out of all crystal phases of borophene, anisotropic phases are of great significance, as they exhibit enhanced physical and chemical properties in certain ridgeline directions. Ball-stick diagram overlapped over the zoomed-in HRTEM images, 3D views showing clear-cut evidence of ridgelines and FFT showing the central array of bright dots representing ridgelines and a subsidiary array of dim dots on both sides representing an array of underlying atoms between the ridgelines establish β_{12} (Figure 5.2(d-g)), striped (Figure 5.2(h-k)) and χ_3 (Figure 5.2(l-o)) phases in LPE borophene. Average inter-atomic distances along ridgelines were observed to be 0.35 nm, 0.18 nm, and 0.7 nm for β_{12} , striped, and χ_3 phases respectively (Figure 5.2(g,k,o)). Atoms were found to be placed at an average distance of 0.52 nm, 0.5 nm, and 0.7 nm in the direction normal to the ridgelines. Moreover, atoms are mostly equidistant in the direction normal to the ridgelines. Also, line profiles acquired for direction normal to ridgeline clearly show underlying atoms. These crystallographic phases have earlier been reported for ALD and MBE-grown borophene [98, 99]. The role of strain in locally modulating crystal structures

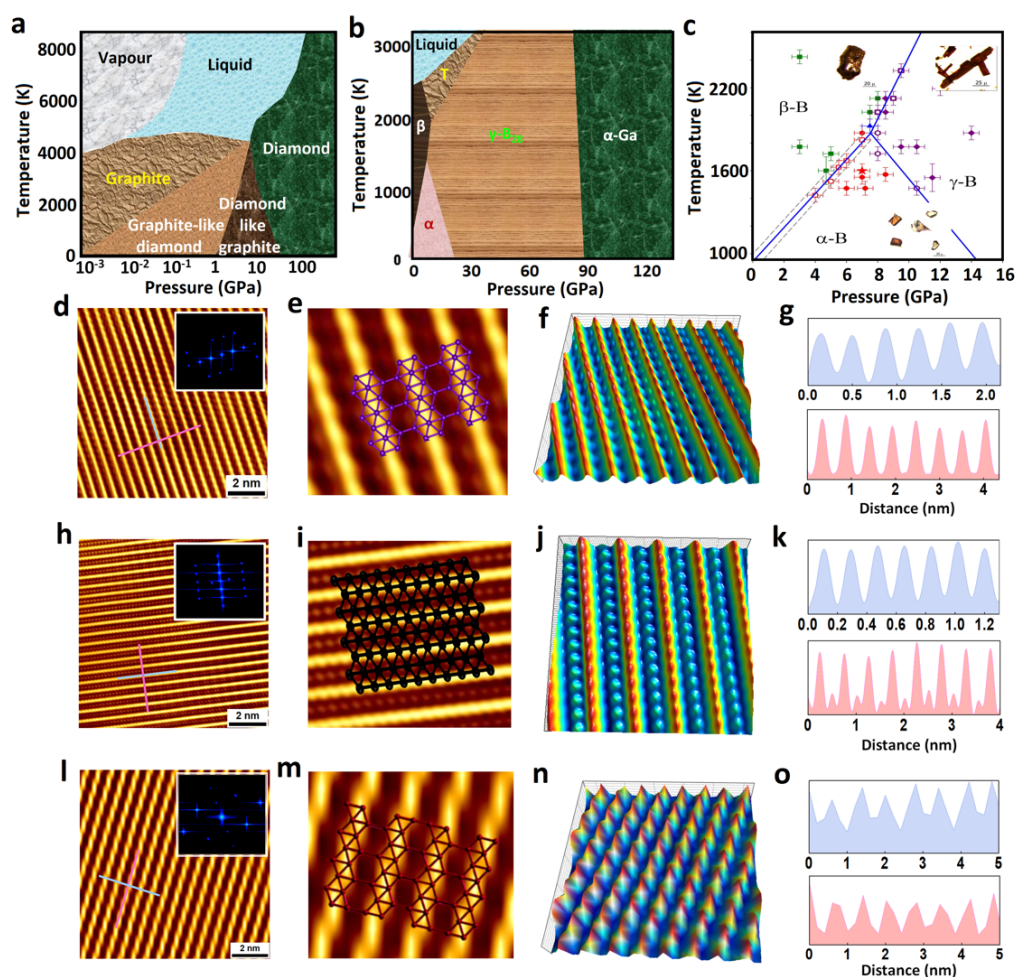


Figure 5.2: a) Allotropes of carbons. b) Image showing the evolution of allotropes of boron under different temperatures and pressure c) Phase diagram showing dependency of Boron Allotropes Stability on Pressure and Temperature. d) Image of β_{12} phase and corresponding FFT in the inset. e) Zoomed and overlaid atomic structure of β_{12} . f) 3D image of the β_{12} phase. g) Line scan on the β_{12} , along the ridge line and perpendicular to it in the respective color. h) Image of stripped phase and corresponding FFT in the inset. i) Zoomed and overlaid atomic structure of stripped phase. j) 3D image of the β_{12} phase. k) Line scan on stripped phase, along the ridge line and perpendicular to it in the respective color. l) Image of χ_3 phase and corresponding FFT in the inset. m) Zoomed and overlaid atomic structure of χ_3 . n) 3D image of the χ_3 phase. o) Line scan on χ_3 , along the ridge line and perpendicular to it in the respective color.

of borophene has been witnessed, as can be seen in Figure A.2, with atomic arrangements being different in the same sheet. 3D view (Figure A.2 (d,h)) clearly shows the distinction. Moreover, while line profiling (Figure A.2 (e, i)) shows different heights of alternate arrays, FFT patterns (Figure A.2 (c,g)) show striking evidence of strain-mediated differences therein. Average inter-atomic distances along ridgelines were found to be 0.18 nm and 0.18 nm and the average distances in normal direction were 0.74 nm and 0.74 nm for the two structural twin phases. Enhanced image quality and material purity obtained by implementing detailed experimental protocols in the present research, show clear evidence of strain-induced structural maneuver. Common to all anisotropic phases is 2-fold symmetry in FFT with a central array of bright spots (representing ridgeline atoms) and subsidiary arrays of dim dots (representing underlying atoms) placed on both sides of the central array.

Crystallographic features with higher (4-fold and 6-fold) symmetry were also obtained in LPE borophene sheets as can be visualized in Figure 5.3. Clear evidence of more than one symmetry direction is observed in Figure 5.3(a-d) having parallelogram (array of elongated atomic clusters having their symmetry directions at angle $\sim 120^\circ$) boron lattice and in Figure 5.3(e-h) exhibiting mostly square (array of spherical atomic clusters having their symmetry directions at angle $\sim 90^\circ$) lattice. As can be evidenced in Figure 5.3(d), the average distances in two symmetry directions were 0.33 nm and 0.27 nm. The average distances however were observed to be 0.3 nm and 0.3 nm in Figure 5.3(h). Overall, both Figure 5.3 (a-d) and Figure 5.3(e-h) represent distinct crystallographic phases with the same structure having certain 4-fold, 6-fold symmetry stretched over a very large area, as can be seen in FFT patterns. However, Figure 5.3(i) and especially zoomed-in 3D view Figure 5.3(k) represent a new phase with symmetry mixing having 6-7 atoms arranged in an array making a ridgeline segment and then its termination followed by another ridgeline segment in the alternate array. The FFT pattern in Figure 5.3(j) shows minor deviations in the array of central bright spots and more pronounced off-line deviations in the arrays of subsidiary arrays. Moreover, line profiles lack symmetry along chosen symmetry directions (Figure 5.3(l)). Average inter-atomic distances in two directions were observed to be 0.24 and 0.24 nm. Figure 5.3 (m) and especially zoomed-in 3D view Figure 5.3(o) shows banana bonds (sharing electrons by forming 3D-protruded bonds). Mixed-fold symmetry is obvious from the FFT pattern (Figure 5.3(n)) for the banana phase. As in atomistic line profiles, height offsets are quite apparent (Figure 5.3(p)).

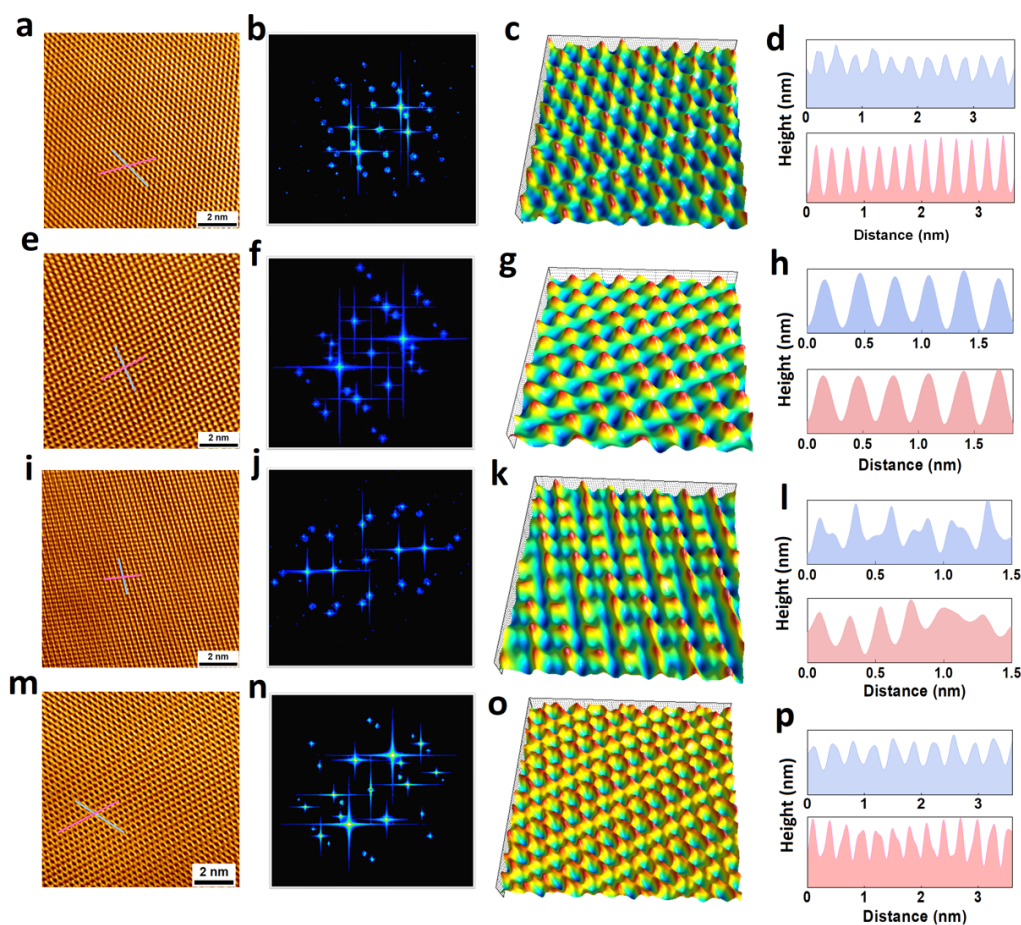


Figure 5.3: a) Image showing β -rhombohedral phase. b) FFT corresponding to β -rhombohedral phase. c) 3D image of the β -rhombohedral phase. d) Line scan on the β -rhombohedral phase, along the ridge line and perpendicular to it in the respective color. e) Image showing isotropic phase f) FFT corresponding to isotropic phase. g) 3D image of the symmetric phase. h) Line scan on the isotropic phase, along the ridge line and perpendicular to it in the respective color. i) Image showing mixed phase. j) FFT corresponding to mixed phase. o) 3D image of the mixed phase. p) Line scan on the mixed phase, along the ridge line and perpendicular to it in the respective color. m) Image showing mixed phase with banana bonds. n) FFT corresponding to mixed phase with banana bonds. o) 3D image of the mixed phase with banana bonds. p) Line scan on the mixed phase with banana bonds, along the ridge line and perpendicular to it in the respective color.

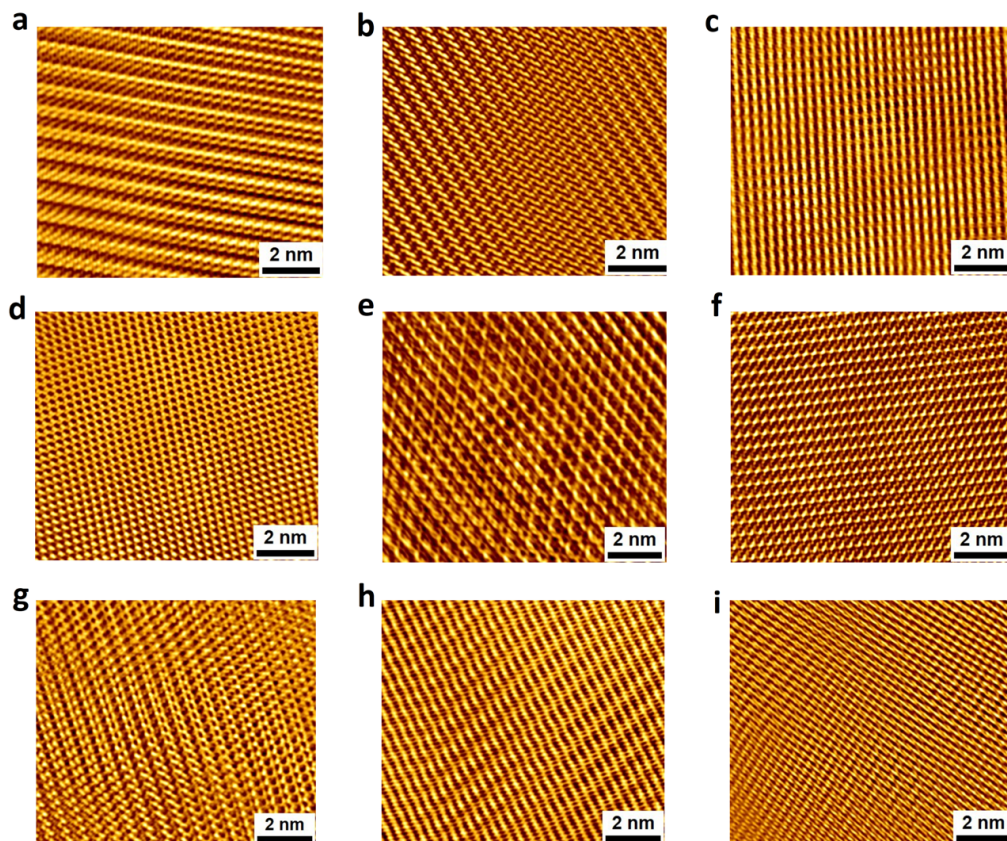


Figure 5.4: The images depict various complex phases of borophene, with the image (c) closely resembling the γ_{28} phase, which has been previously identified through chemical vapor deposition (CVD) techniques.

Apart from anisotropic phases (Figure 5.2 and Figure A.2) and 4-/6- fold symmetry phases (Figure 5.3(a-d) and Figure (e-h)) and mixed-fold symmetry phases (Figure 5.3 (i-l) and Figure 5.3(m-p)), several crystallographic phases with complex geometries such as intertwined, entangled, and woven fabric like structures have also been witnessed (Figure 5.4). Interestingly, even within one image, structures have been found to falter and apparent different geometries were witnessed in two different regions even within the 10 nm X 10 nm image area. For example, the top-left and bottom-left of Figure 5.4(a), top-left and central regions in Figure 5.4 (b), top-left and bottom-left of Figure 5.4(d), top-left, central and bottom-left in Figure 5.4(g) exhibit distinctions in features present therein. Interestingly, the evolution of these crystallographic borophene phases having versatile complex geometries has never been reported for LPE borophene. Clinching experimental evidence of seem-

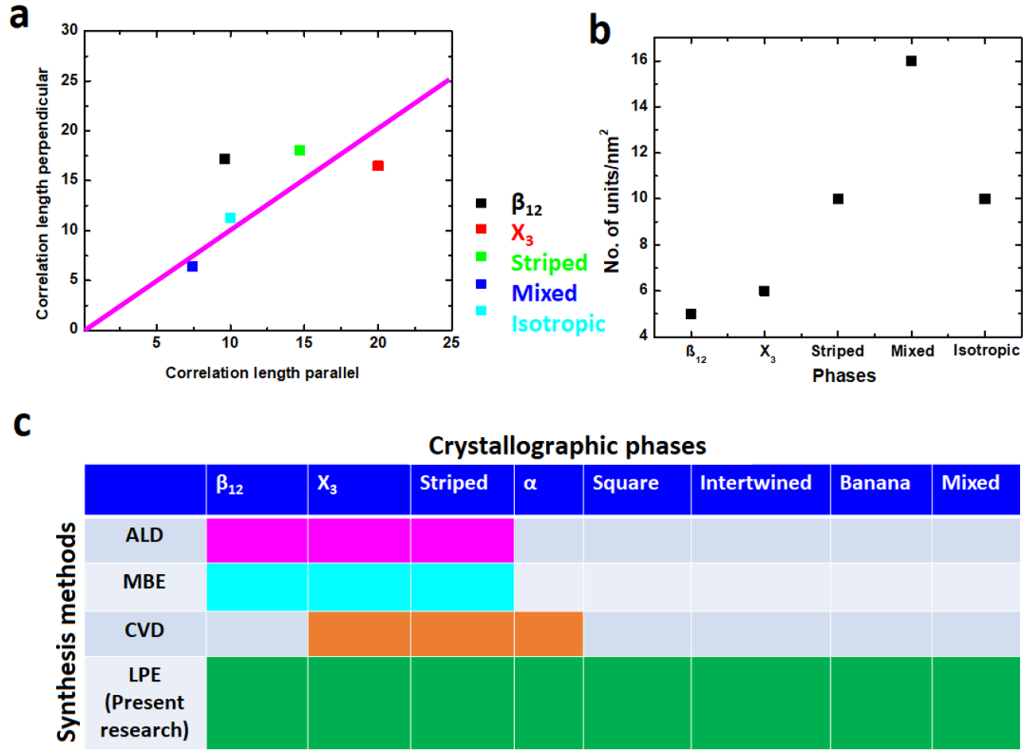


Figure 5.5: a) Plot showing the correlation length of different phases along the ridge line and perpendicular to it. b) Plot showing the density of different phases. c) Illustrated the phase discovered with different methods.

ingly impossible structural phases with a bonding nature unheard till now in LPE borophene is extremely intriguing as further studies are warranted in this direction.

To quantitatively distinguish various crystallographic borophene phases, correlation length values along the ridgeline direction and in the direction normal to it were computed from the obtained HRTEM images. While the χ_3 phase exhibited a correlation length higher in the direction parallel to the ridgeline than that in the direction normal to the ridgeline, other phases including those of β_{12} , striped and isotropic phases exhibited lower correlation along the ridgelines (Figure 5.5 (a)). For the mixed phase, however, correlation lengths in two orthogonal directions were registered to be almost equal. Interestingly enough, β_{12} phase exhibited a correlation length higher in the direction normal to ridgelines (Figure 5.5 (a)). The most striking feature of borophene material, namely anisotropic physical and chemical property such as world record electronic mobility and Young modulus along

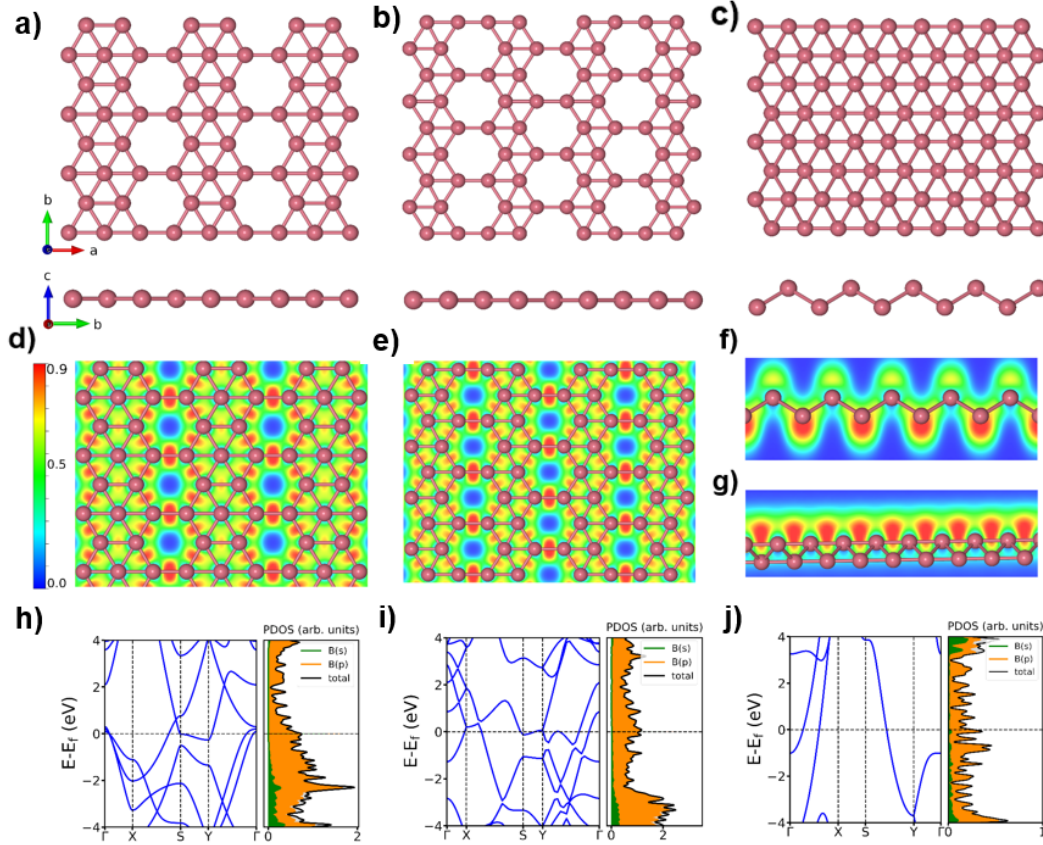


Figure 5.6: The images illustrate the schematics of (a) β_{12} , (b) χ_3 , and (c) the striped phase. The corresponding Electron Localization Function (ELF) is presented in (d), (e), (f), and (g). Meanwhile, the respective band structures and Partial Density of States (PDOS) are depicted in (h), (i), and (j).

ridgeline directions find their origin in the formation of periodically spaced isolated ridgelines with closely spaced atoms constituting ridgelines. Since ridgelines are far apart from each other having an array of underlying atoms (situated relatively far apart), cluster density is minimal for anisotropic β_{12} and χ_3 phases (Figure 5.5 (b)). On the other hand, striped, isotropic, and mixed phases exhibit a higher areal density of clusters (Figure 5.5 (b)). It should be noted that these are not single atoms, but rather clusters of several (6-7) atoms. We confirm that while bottom-up approaches of experimental realization of borophene have been reported to yield limited crystallographic phases (for example, β_{12} , χ_3 and striped phases by ALD as well as MBE; χ_3 , striped and α phases by CVD), LPE synthesized borophene exhibited square lattice, intertwined lattice, banana phase and several other crystallographic phases having mixed-fold symmetries and complicated geometries (Figure 5.5 (c)).

Band gaps value and nature (direct/indirect) of band gaps at various momentum levels (e.g. γ) and DOS determine the electronic and excitonic character of borophene, therefore; band structure calculations were carried out. DFT band structures of major crystallographic phases (β_{12} , χ_3 and striped) demonstrate a clear-cut distinction between the electronic and excitonic characters of these phases (Figure 5.6). While β_{12} , and χ_3 both are metallic, α phase is semiconducting. Layer-dependent DOS is a common feature in borophene. Moreover, the number of pores, the number of edge-exposed boron atoms, and specific crystal geometries present in borophene determine the local electronic character of borophene. The structural evolution of these complex geometries in various experimentally observed phases in the present research article itself needs detailed investigation.

5.4 Conclusion

In conclusion, a detailed investigation of the evolution of crystallographic phases in LPE borophene obtained by sonochemical exfoliation in IPA solvent following detailed experimental protocol has been conducted through atomistic resolution electron imaging. Clinching evidence in the form of clean HRTEM images establishes the presence of β_{12} , χ_3 and striped, isotropic phases and several other phases having complex geometries for the first time. The chemical phase purity of borophene materials was established by Raman and XPS spectroscopies. DFT band structure calculations hint at distinct electronic and excitonic characters of various borophene phases.

Chapter 6

ELECTRON BEAM GROWN BOROPHENE AND ITS EVOLUTION INDUCED BY ANNEALING

6.1 Introduction

The evolution of borophene synthesis represents a significant milestone in materials science, driven by an interplay of theoretical predictions and experimental advancements. Borophene, a monolayer of boron atoms, was first successfully synthesized by Mannix et al., who employed an electron beam evaporator in an ultrahigh-vacuum environment[98]. This achievement was made possible through concurrent progress in theoretical modeling, experimental techniques, and a deeper understanding of boron cluster behavior.

Theoretical studies laid the groundwork for the exploration of borophene. Initial research on boron clusters revealed the potential for 2D boron sheets[26, 28, 87, 89, 90, 97]. In 2012, Penev et al. utilized theoretical modeling to demonstrate borophene's polymorphic nature, highlighting its diverse structural forms [93]. Key to the successful deposition of these 2D boron sheets is the use of a metal substrate with optimal binding strength to boron atoms. This is crucial for overcoming the thermodynamic challenges associated with bulk boron, which makes borophene metastable compared to its three-dimensional counterpart. Liu's 2013 study, based on first-principles calculations, suggested that borophene could be synthesized on metal or metal boride surfaces[94]. The study found that high nucleation barriers on Au or Ag(111) surfaces hinder the formation of three-dimensional boron during deposition, thereby promoting the formation of 2D boron. The weak interaction between borophene and these substrates also facilitates an easier post-growth separation process.

The experimental validation of the planar hexagonal B_{36} cluster further accelerated the pursuit of monolayer boron or borophene, confirming its achievable structure[97]. This configuration allows for the creation of borophenes with varying hole densities and orientations. Zhang et al. expanded on this by examining the interaction of borophene with various substrates, including Au, Ag, Cu, and Ni[29]. Their research indicates that a planar $\nu_1/6$ -sheet configuration of borophene is generally favored on most studied metals. This work underscores the importance of

substrate-boron interactions in the formation of 2D boron structures and suggests a pathway for controlled synthesis through tailored boron-metal interactions.

Atomic-scale characterization via STM revealed two distinct borophene phases. Mannix and colleagues identified a homogeneous phase characterized by atomic chains with periodic vertical buckling of 0.30 nm, and a striped phase with a rectangular lattice structure measuring 0.51 nm ($\pm$ 0.02 nm) and 0.29 nm ($\pm$ 0.02 nm), supported by density functional theory (DFT). Feng et al. demonstrated the synthesis of borophene by utilizing epitaxial techniques to grow boron sheets on Ag(111) substrates. Their study identified two specific configurations of borophene: the β_{12} and χ_3 sheets, both of which displayed triangular lattices with distinct periodic aperture arrangements as visualized through STM.

As research into borophene has progressed, the scope of its synthesis has expanded, encompassing a variety of substrates such as Cu(111/100), Al(111), and Ir(111). This exploration has revealed a diverse array of borophene phases, each dependent on the substrate, which underscores the material's intricate structural and electronic properties. The evolution of borophene research has gradually shifted towards understanding its practical applications and stability, spurring the development of alternative synthesis methods, including chemical vapor deposition (CVD) and top-down approaches like chelation-assisted borophene liquid-phase exfoliation (LPE). These methods not only enhance our understanding of borophene's fundamental characteristics but also unveil its potential for a wide range of advanced technological applications.

Borophene has emerged as a highly promising material, owing to its exceptional properties, such as superior mechanical strength, electrical conductivity, and ultrafast ion transport. These attributes make it particularly suited for applications in metal-ion batteries and catalysis. Furthermore, borophene shows significant potential in sensing various gases and substances, as well as in biomedical fields, including cancer therapy, biosensing, and drug delivery. The unique phases of borophene also exhibit interesting properties, such as Dirac fermions and potential superconductivity, which further enhance its appeal for cutting-edge technological innovations.

However, the stability of borophene, especially in ambient environments, remains a critical factor that influences its practical utility. The exposure of monolayer and bilayer borophene to oxygen and air has been extensively studied, as it plays a crucial role in determining the material's viability for real-world applications.

Mannix et al. demonstrated that single-layer (SL) borophene oxidizes and degrades significantly when exposed to oxygen or air, highlighting the material's vulnerability under ambient conditions[98]. Liu et al. demonstrated edge oxidation of borophene even under a limited oxygen supply in ultra-high vacuum (UHV) conditions[221]. However, Wu et al. provided a contrasting perspective by showing that boron sheets remain stable with limited oxygen exposure[222]. Their findings indicated that oxidation primarily occurs at the edges, while the boron sheet itself exhibits a degree of stability against oxidation. However, research conducted by Chen et al. and Li et al. revealed that bilayer borophene demonstrates a higher oxidation resistance [178, 223].

In our study, we examine the impact of prolonged room-temperature annealing on the stability of borophene. Our results demonstrate that, over an extended period, borophene experiences substantial evolution, transforming from a crystalline-like structure into a non-crystalline configuration. Further annealing at room temperature induces additional changes, leading to the formation of cluster-like structures. These observations provide new insights into the dynamic nature of borophene and its tendency to evolve under ambient conditions, highlighting the importance of understanding its stability for potential applications.

6.2 Methods

The borophene sample preparation via electron beam deposition was carried out on an Ag(111) substrate. Before deposition, the Ag(111) crystal underwent a thorough cleaning process involving multiple cycles of sputtering and annealing to ensure an atomically clean and smooth surface. Once the substrate was adequately prepared, the borophene deposition process commenced under ultra-high vacuum conditions. The base pressure within the deposition chamber was maintained at approximately 10^{-8} mbar, ensuring minimal contamination during the growth process. The substrate temperature was precisely controlled and maintained at 500°C throughout the deposition.

The boron flux was maintained in the range between 14.1 nA and 21.5 nA. The deposition process was sustained for 40 minutes, allowing sufficient time for the deposition of sufficient boron required to form a borophene layer on the Ag(111) substrate. STM image of the Ag(111) surface is shown in Figure 6.1(a), and its inset shows the atomic resolution of the Ag(111). The corresponding IV and the

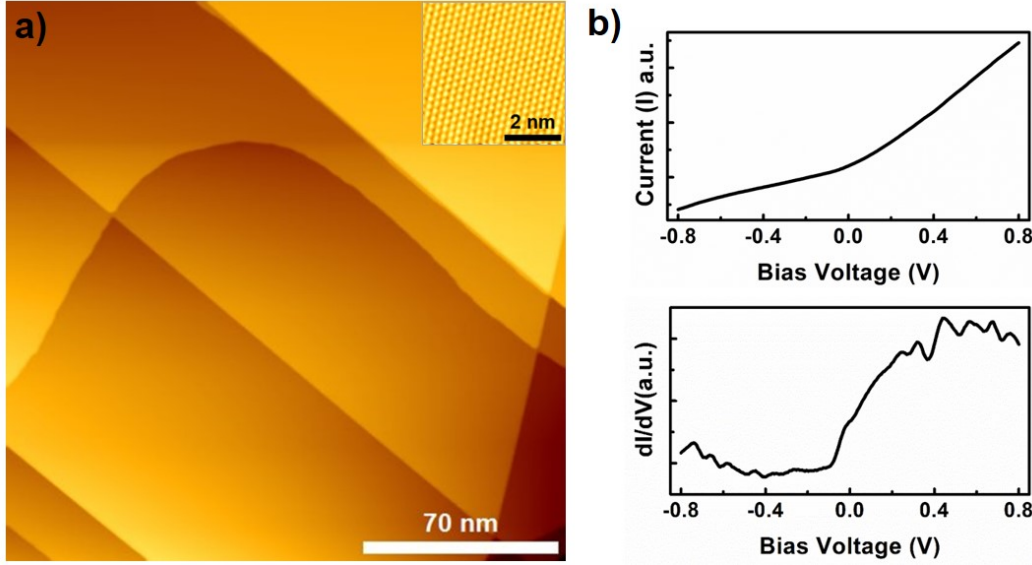


Figure 6.1: a) The figure presents a STM image of an Ag(111) substrate. b) The graphs showing IV and dI/dV spectra of Ag(111)

differential conductance (dI/dV) spectra, presented in Figure 6.2(b), capture the electronic properties of the Ag(111) surface. Notably, the dI/dV spectra reveal the characteristic surface states of the Ag(111) substrate, which are indicative of the localized electronic states confined at the surface.

6.3 Observation of a New Phase in Borophene Growth: Configuration and Key Insights

In our study, we achieved successful growth of borophene on an Ag(111) substrate utilizing electron beam deposition. This deposition process yielded borophene sheets with dimensions spanning just a few square nanometers. In addition to the formation of these borophene sheets, our observations also revealed the emergence of single atomic boron chains and some irregular clusters scattered across the substrate. Notably, several of these atomic chains appeared to originate from the edges of the borophene sheets, presenting an interesting growth pattern.

The borophene sheets we observed exhibited orientation along three distinct directions, indicative of a preferential growth aligned with the symmetry directions of the Ag(111) substrate. The phases we observed are influenced by the bias polarity applied during the experiments. The borophene sheets manifest with a negative height relative to the substrate when a positive bias is applied, while they exhibit an elevation above the substrate under a negative bias. This effect is illustrated

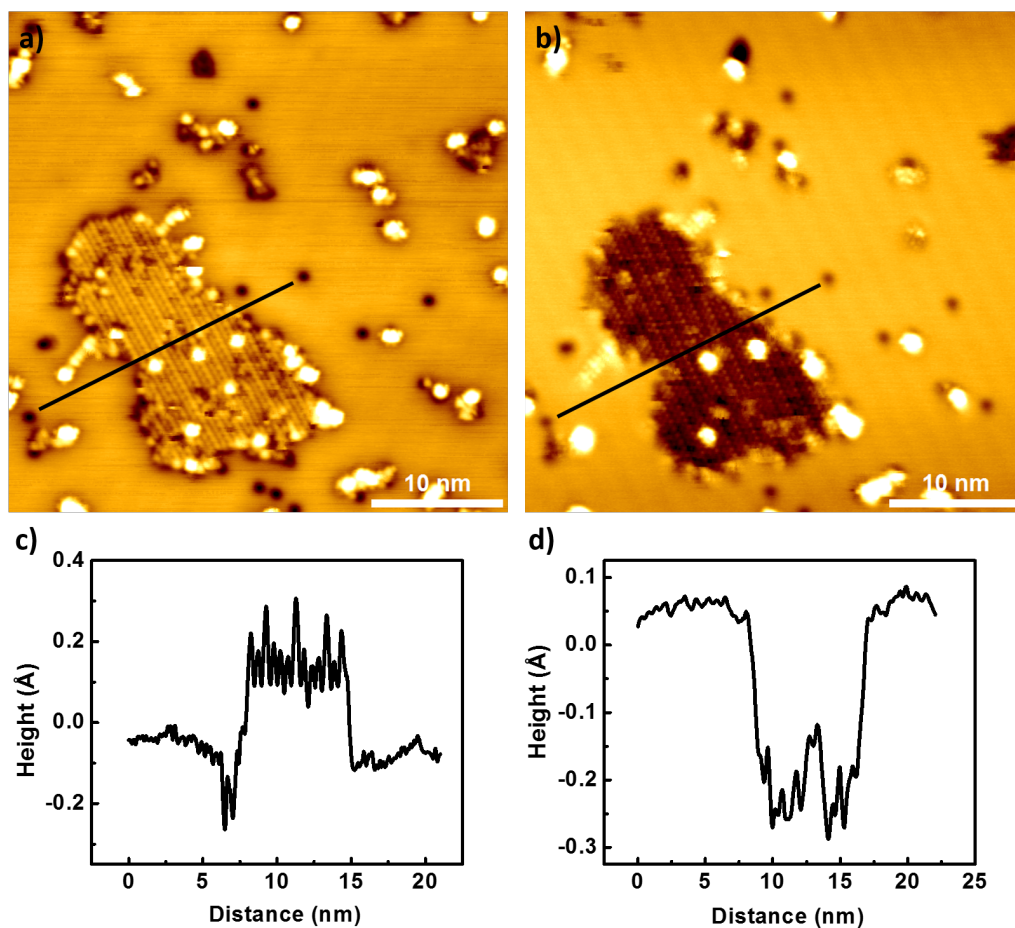


Figure 6.2: STM images showing the borophene phase via electron beam growth. a) The image was taken with a negative bias showing the sheet elevated to the substrate. The bias voltage of $V = -0.8$ V and current of $I = 50$ pA. c) The image was taken with a positive bias voltage showing the sheet at depth relative to the substrate. The bias voltage of $V = 0.8$ V and current of $I = 50$ pA. c) Image showing the height profile along the line marked in a). d) Image showing the height profile along the line marked in b).

in Figure 6.2, where Figure 6.2(a) shows the sheet elevated above the substrate when a negative bias is applied, and Figure 6.2(c) depicts the borophene sheet at a negative height relative to the substrate with a positive bias. To achieve a clearer understanding of the borophene sheet's elevation relative to the Ag(111) substrate, the height profile shown in Figure 6.2(c) corresponds to the line traced along the borophene sheet in Figure 6.2(a) under negative bias. In contrast, to visualize the depth of the borophene sheet relative to the Ag(111) substrate under positive bias, the height profile depicted in Figure 6.2(d) corresponds to the line marked along the borophene sheet in Figure 6.2(b).

The borophene phase we obtained is completely different from the previously documented β_{12} , χ_3 , or striped borophene phases observed on Ag(111) surfaces[98, 99, 224]. Contrary to these polymorphic phases, our results reveal a single-phase borophene structure. Figure 6.3 displays atomically resolved STM images: panel (a) shows the STM image at a negative bias, while panel (b) presents the image at a positive bias. The corresponding height profiles are depicted in panels (c) and (d), respectively, along the line marked on the borophene sheet. These high-resolution atomic-scale STM images further clarify the polarity-dependent characteristics of the borophene sheet. To accurately characterize this observed phase, we are conducting density functional theory (DFT) calculations, which are expected to provide a detailed understanding and validation of the borophene phase identified in our experiments.

The contrast variation in borophene sheets observed, depending upon the polarity of the applied bias, can be understood through the integrated density of states (DOS). When a negative bias is applied, there is a sufficient density of states available, allowing electrons to tunnel effectively. Conversely, when a positive bias is applied, the integrated density of states is significantly reduced, thereby limiting the availability of electronic states for tunneling. This disparity in the density of states under different bias polarities explains the observed contrast variation of the borophene sheet.

6.4 Surface State Evolution of Ag(111) due to Borophene

It has been reported that borophene when grown on the Ag(111) substrate, exhibits metallic characteristics, a notable contrast to the non-metallic behavior observed in its three-dimensional (3D) boron counterparts. This pronounced deviation highlights a significant departure from the typical electronic properties of bulk boron

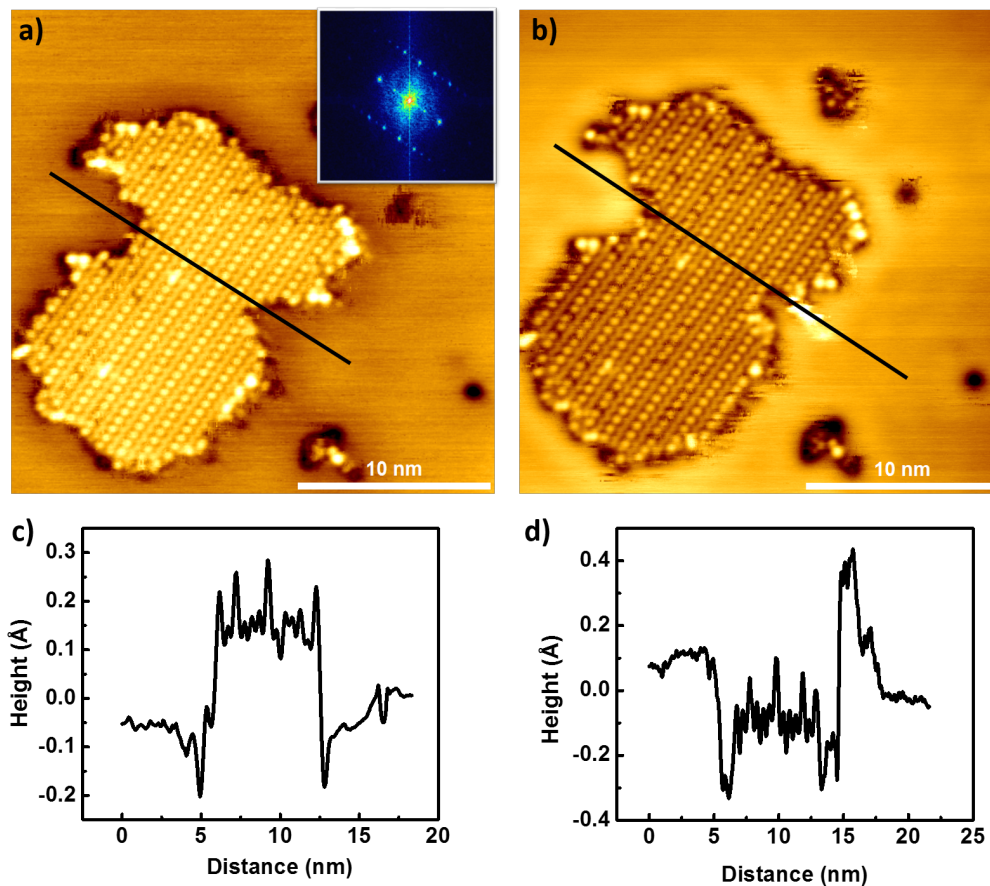


Figure 6.3: a) High-resolution STM images of borophene acquired at a negative bias voltage of $V = -0.2$ V and a tunneling current of $I = 10$ pA reveal the material's structural details. The fast Fourier transform (FFT) of the image, presented in the inset, corroborates the crystalline nature of the borophene. b) High-resolution STM images of borophene at -ve Bias. The bias voltage of $V = -0.2$ V and current of $I = 10$ pA. c) Image showing the height profile along the line marked in a). d) Image showing the height profile along the line marked in b).

structures, which do not exhibit the same metallic traits[98, 101, 170].

Despite the recognition of borophene's metallic properties on silver substrates, there is a notable absence of comprehensive studies investigating how the presence of borophene sheets affects the surface electronic states of the Ag(111) crystal. The specific influence of borophene on the electronic structure of the silver substrate remains largely unexplored. The current lack of detailed reports on this interaction implies that, although the metallic nature of borophene on silver is well-established, the underlying modifications or effects on the surface states of the silver substrate have not been thoroughly examined.

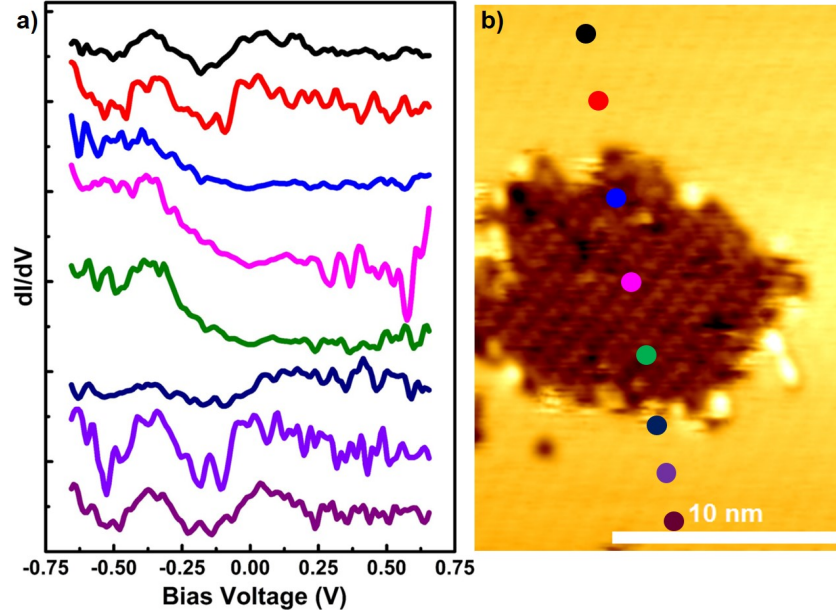


Figure 6.4: a) STS measurements were conducted at various specific locations within the image, as indicated by the markings (These spectra are vertically shifted for clarity). b) Each colored dot in the image corresponds precisely to the position where the spectra were acquired, with the color of the dot matching the color of the corresponding spectrum as shown in (a). The scanning parameters of the image were, Bias voltage(V) = 1 V and Current (I) = 40 pA.

To address this gap in the literature, we have undertaken an in-depth investigation using line spectra measurements to explore how borophene influences the electronic structure of Ag(111). Our approach involved capturing line spectra along a specific path: beginning with measurements at two points on the silver substrate, moving through three distinct points on the borophene layer, and finishing with additional measurements at three more points on the silver substrate. This method enabled us to systematically trace and analyze the changes in surface states across different regions, thereby providing valuable insights into the interactions between borophene and the silver surface. By examining the changes in electronic properties as the spectra moved from silver to borophene and back, we aimed to uncover potential modifications induced by the borophene layer and enhance our understanding of the fundamental interactions between these materials.

The STS measurements were carried out at various specified locations within the image, as indicated by the distinct markings in the inset. Each colored dot within the image corresponds precisely to the exact position where the spectra were obtained, with the color of the dot directly matching the color of the corresponding

spectrum. This methodical mapping is instrumental in facilitating a clear and direct comparison of the electronic properties at these different locations, thereby offering insights into the spatial variations present across the studied surface. The marked positions, along with their associated spectra, play a critical role in enhancing our understanding of the local electronic structure of the material under investigation.

Through this detailed analysis, we can distinctly observe the progression of the spectra associated with the silver substrate, specifically focusing on the initial two spectra and the final three spectra, all of which correspond to the Ag(111) surface. Under conventional conditions, the surface state of clean Ag(111) is reported to be at around 70 meV[225, 226]. However, in this particular instance, we detect significant alterations in these states, which can be attributed to the interaction between boron atoms and the silver surface.

A particularly noteworthy aspect of this analysis is the presence of a distinct kink observed within the voltage range of 0.35V to 0.45V. This kink is a feature that also appears in the spectra of borophene, suggesting a pronounced influence of boron incorporation on the electronic structure of the silver substrate. The appearance of this kink indicates a significant modification in the electronic properties of Ag(111) due to the presence of boron.

The spectrum identified as the third from the end, which is marked in a deep blue color, demonstrates the least deviation when compared to the other spectra of Ag(111) in the series. This particular spectrum, despite being positioned closest to the borophene sheet, retains a resemblance to the spectrum associated with the Ag(111) surface itself. While this spectrum shows the characteristics of the Ag(111) surface, still it reveals a very faint indication of a kink within the voltage range of 0.35 to 0.45 volts. This subtle kink, although present, suggests that the influence of the boron on the spectrum is relatively minor. As a result, the spectral features observed are primarily determined by the properties of the underlying silver substrate rather than by the borophene layer. This observation underscores the fact that the spectral characteristics are predominantly governed by the inherent properties of the Ag(111) surface, with minimal impact from the borophene layer. In contrast, for other spectra, a notable impact of boron is observed in altering the surface states of Ag(111).

6.5 Borophene Phase evolution via Room-Temperature Annealing

The specific phase of borophene grown on a silver (Ag) (111) substrate has remained undetermined up to this point. Consequently, there is a lack of references regarding the stability of this particular phase. Various reports have documented the stability characteristics of borophene, revealing that monolayer borophene is susceptible to oxidation, particularly starting from the edges, while bilayer borophene has demonstrated notable stability against oxygen. Despite these findings, there are no existing studies that have systematically evaluated the stability of the borophene phase through extended annealing processes.

To address this gap, we investigated to assess the stability of the borophene phase under prolonged annealing conditions. Specifically, we conducted experiments to assess how the grown borophene phase responds to annealing at room temperature for 3 weeks. This investigation aims to provide new insights into the long-term stability of borophene and contribute to the broader understanding of its behavior under prolonged room temperature exposure.

Initially, we subjected the sample to a gradual increase in temperature, starting from 77 K and reaching room temperature (300 K). This elevated temperature was maintained continuously for a period of 3 weeks. Following this, we then cooled the sample back down to 77 K in preparation for subsequent scanning. The results were very interesting, we observed a complete phase transformation of the borophene into an entirely new structural phase. Additionally, this transformation was accompanied by a notable increase in the density of boron clusters within the sample, highlighting a profound alteration in its structural and compositional characteristics.

The phase modification and the substantial increase in the density of boron clusters, as depicted in Figure 6.5 (a), reveal significant changes in the system. This enhancement in cluster density can be comprehensively attributed to the migration of boron atoms from the subsurface regions of the Ag(111) substrate to its surface. This migration phenomenon leads to an accumulation of boron clusters at the surface, which generates an excess of such clusters. This accumulation could be pivotal in driving the phase evolution of the system.

The transformation of the phase can be attributed to two main factors: the accumulation of excess boron clusters and the shift toward a phase with higher thermodynamic stability. The surplus clusters impose significant strain on the borophene phase, which in turn drives the transition to a more stable phase. This shift is driven by the thermodynamic advantage offered by the new phase. As

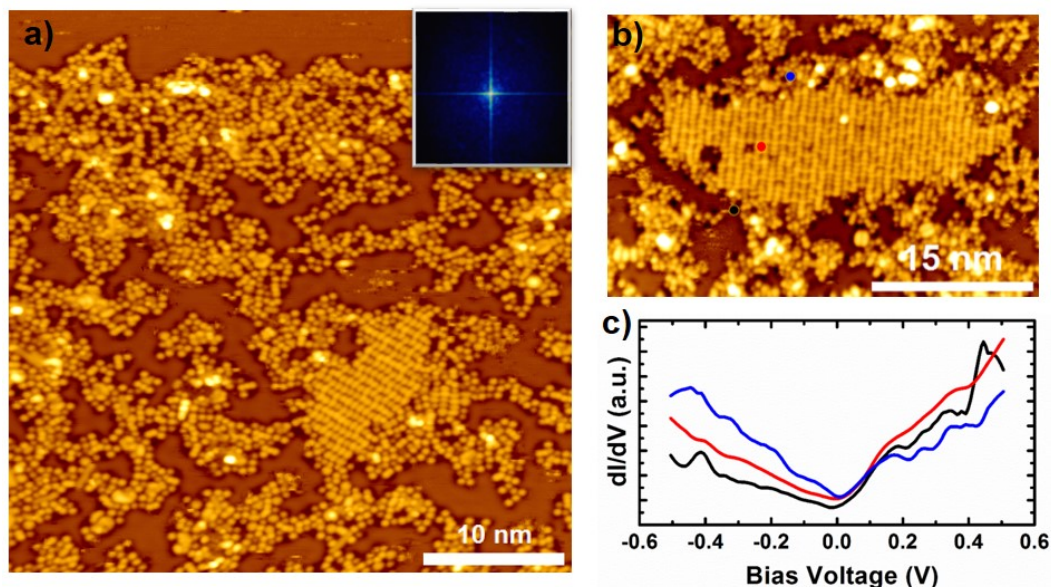


Figure 6.5: a) The image depicts the phase evolution of the material post-annealing at room temperature. The accompanying Fast Fourier Transform (FFT) displayed in the inset corroborates the material's non-crystalline characteristics. b) The image illustrates the specific locations where STS measurements were conducted, as indicated by the markings. Each colored dot precisely denotes the position at which the spectra were acquired. c) The STS spectrum is presented with dot colors corresponding to the respective points indicated in the image (b). The scanning parameters of images were, Bias voltage (V) = 1 V and Current (I) = 40 pA

the system overcomes the energy barrier associated with the previous phase, the transition becomes more pronounced and energetically advantageous. Thus, the process underscores a shift towards a more stable and energetically favorable phase, facilitated by the reorganization and increased density of the boron clusters. The determination of the phase and DFT analysis of thermodynamical stability will be very crucial to understanding the exact reason behind the phase evolution.

The STS analysis of the evolved phase demonstrates its metallic characteristics, as depicted in Figure 6.5(b). This analysis reveals a complete transformation of the Ag(111) and borophene surface states. The Ag(111) substrate is nearly obscured, with the majority of its surface covered by the borophene phase or its clusters.

Line spectra measurements were conducted in the remaining vacant regions on the Ag(111) substrate adjacent to the borophene sheet, on the borophene sheet itself, and again on the silver substrate. Notably, the differential conductance (dI/dV) spectra obtained from these areas did not exhibit distinctive features characteristic

of either Ag(111) or borophene. The spectra displayed minimal variation between the borophene and Ag(111) regions, suggesting that the surface state of Ag(111) has been effectively quenched. Consequently, what is observed is an integrated surface state that encompasses contributions from both the borophene and the Ag(111) substrate.

6.6 Phase transformation into Clusters: Insights into Structural Transformation

We decided to do a third room temperature annealing cycle, our objective was to investigate the effects of introducing a third annealing cycle on the material, with a specific focus on how this additional thermal treatment would influence the structural transformations. In this experiment, we modified the duration of the annealing process, reducing it to 4 days, in contrast to the 3 weeks employed in previous cycles.

The rationale behind incorporating a third annealing cycle was to explore whether this additional thermal exposure would lead to further structural evolution or significant changes in the material's properties. The decision to shorten the annealing time for this cycle was based on the hypothesis that even a brief period of thermal treatment might still significantly affect the material's phase and structure.

Upon completing the 4-day annealing cycle, we conducted a thorough analysis to observe and document the transformations that occurred in the material. The results revealed a complete phase transition from the initial structure to a new, clustered configuration. This transition is indicative of a fundamental change in the material's phase, driven by the formation of clusters.

The formation of these clusters may potentially be attributed to their higher thermodynamic stability relative to the original phase. This clustering effect suggests that, under the specific conditions imposed by the third annealing cycle, the material might undergo a phase transformation that tends to favor the formation of clusters, possibly due to their lower energy state and inherent stability. It underscores the significant potential influence of both the duration of the annealing process and the cumulative number of cycles on the material's phase behavior, and structural evolution.

Through a series of repeated STM imaging of a specific region, an interesting phenomenon was observed: the clusters within this area exhibited rotatable behavior. This observation became increasingly evident as successive scans revealed that the

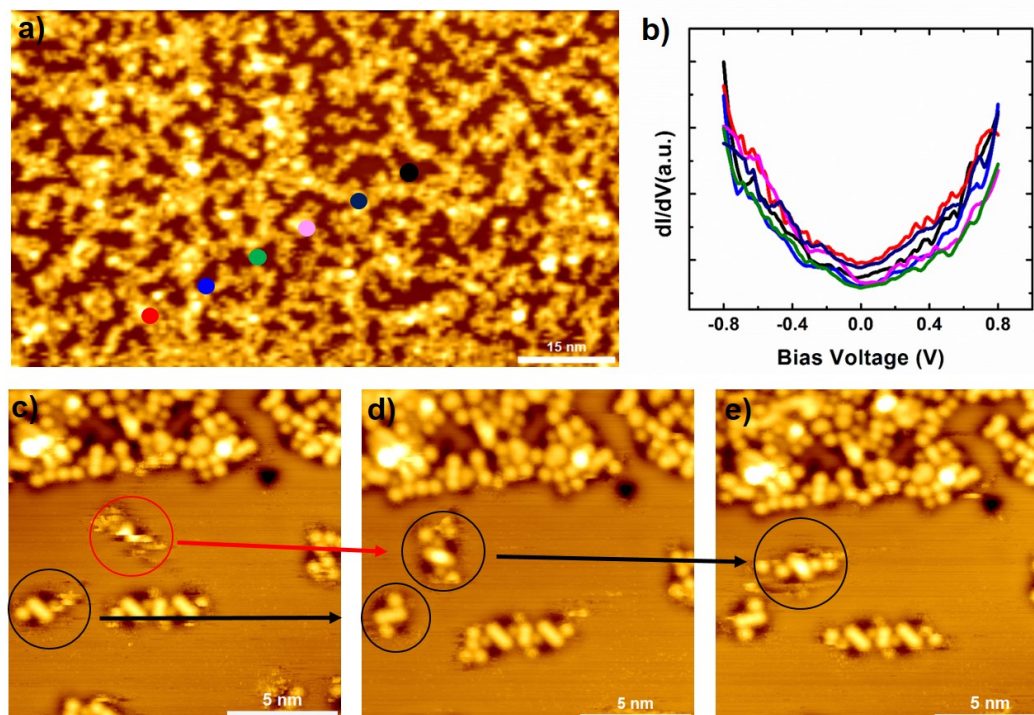


Figure 6.6: a) The image illustrates the phase evolution of the material following 2nd annealing cycle at room temperature. b) STS measurements were performed at selected locations within the image (a), each colored dot in the image corresponds precisely to the position where the spectra were acquired, with the color of the dot matching the color of the corresponding spectrum. The scanning parameters of images were, Bias voltage (V) = 0.6 V, and Current (I) = 100 pA. Images (c), (d), and (e), illustrate the rotation and formation of the boron clusters.

clusters changed orientation. This dynamic behavior suggests an interactive process between the STM tip and the molecules within the clusters.

The rotational movement of the clusters is likely attributed to the interaction between the STM tip and the molecular structures during the scanning process. As the STM tip traverses the area, it imparts energy to the molecules, which disrupts their stable positions and induces rotation. This interaction implies that the clusters are not rigidly fixed but loosely bound to the underlying silver (Ag) substrate.

The relatively weak binding of the clusters to the substrate imparts them with notable rotatability, allowing them to rotate with ease. This weak adhesion facilitates their ability to shift orientation, highlighting both their flexibility and the dynamic nature of their interaction with the substrate.

In addition to this rotational behavior, a significant observation is the emergence

of clusters within the scanned area. These clusters manifest as distinct, localized groupings of particles or structures that aggregate in specific regions. The dynamics of cluster rotation and formation are comprehensively depicted in Figure 6.6 (a), (b), and (c). It illustrates clusters at various rotation stages, with each rotating cluster encircled by black circles. Black arrows mark the initial and final positions of these rotating clusters, detailing their rotational behavior. The formation of new clusters is also highlighted within black circles and indicated by red arrows, providing a thorough visual account of both the rotational behavior and the formation process.

6.7 Conclusion

We have successfully identified a novel single phase of borophene, synthesized through electron beam deposition using boron powder, and confirmed its metallic properties. Our detailed observations reveal that the initial crystalline structure of borophene undergoes significant transformations when subjected to annealing at room temperature. This annealing process induces a phase transition, transforming the borophene from its original sheet-like form into discrete clusters.

In the first step annealing triggers the transformation of borophene into a sheet with a modified structure, concurrently leading to the formation of clusters. The observation that the differential conductance (dI/dV) spectra on Ag(111) and borophene sheets remain unchanged indicates that the surface states have been quenched. During a subsequent annealing phase, these sheets are further transformed into discrete clusters. These clusters exhibit rotational mobility and exhibit minimal interactions with the underlying substrate.

These clusters are observed to rotate and exhibit weak interactions with the underlying substrate. This transformation underscores the dynamic nature of borophene and its sensitivity to ambient conditions. Understanding these structural changes is essential for harnessing the material's potential effectively and ensuring its stability in various applications.

Chapter 7

CONCLUSION

The current study presents an in-depth exploration of two distinct types of borophene samples: liquid-phase exfoliated (LPE) borophene and electron beam-grown borophene phases on Ag(111). The characterization of LPE borophene involved both Scanning Tunneling Microscopy (STM) and HRTEM, whereas the electron beam-grown borophene was exclusively analyzed using STM. The findings from these analyses significantly deepened our understanding of the intrinsic properties of borophene.

The investigation began with the deposition of LPE borophene onto an Au(111) substrate via the spin-coating technique. High-resolution STM imaging revealed that the deposited borophene primarily exhibited the β_{12} phase, a configuration identified as metallic through STS. Notably, the strong interaction between the β_{12} borophene phase and the Au(111) surface was evidenced by disturbances in the characteristic herringbone reconstruction of the Au(111) surface. Density Functional Theory (DFT) calculations provided additional insights, corroborating the experimental observations and revealing significant charge transfer between the β_{12} phase and the Au(111) substrate. These theoretical findings were consistent with the STM and STS results, providing a cohesive and robust understanding of the material's behavior.

The implications of these results are substantial. The β_{12} borophene, when supported by the Au(111) substrate, exhibits promising potential for advanced applications, particularly in the development of interconnects and catalysts due to its strong interaction with the substrate. Furthermore, the observed modulations within the β_{12} phase suggest its utility as an effective "strain inducer," making it particularly attractive for flexible and stretchable wearable electronics applications. The LPE method for borophene deposition via spin-coating also emerges as a scalable and cost-effective approach, offering a practical pathway for economically developing boron-based materials tailored for advanced technological applications.

By varying the number of spin-coating cycles, the study successfully achieved both a fully covered monolayer and the deposition of boron clusters of LPE borophene on Au(111). High-resolution STM characterization of these structures revealed that the monolayer phase corresponded to the β_{12} configuration. Additionally, the self-

assembled boron clusters exhibited a diverse array of configurations, as captured in the STM images. STS measurements confirmed that both the monolayer and the clusters retained their metallic properties, consistent with the characteristics observed in sparsely distributed borophene flakes.

The study further demonstrated that the full-coverage borophene monolayer perturbed the herringbone reconstruction of Au(111) to a lesser extent, indicating a relatively reduced interaction between the borophene flakes and the Au(111) substrate. In contrast, the boron clusters tended to self-assemble on the borophene monolayer, suggesting that the monolayer acts as a template for this organization. DFT calculations reinforced these findings, confirming charge transfer interactions not only between the β_{12} borophene monolayer and the Au(111) substrate but also between the boron clusters, the borophene monolayer, and the substrate. These calculations further affirmed the metallic nature of the boron clusters, thereby enriching our understanding of the intricate interactions within these complex systems.

Following this the increased no of coating cycle results in full coverage of borophene and boron clusters. Further, our investigation delved into the crystallographic evolution of LPE borophene synthesized through sonochemical exfoliation in an IPA solvent, followed by detailed atomistic resolution electron imaging. High-Resolution Transmission Electron Microscopy provided unequivocal evidence of the presence of β_{12} , χ_3 , and striped isotropic phases, as well as other complex geometries within the borophene samples. The chemical purity of these phases was confirmed using Raman and X-ray Photoelectron Spectroscopy (XPS), while DFT calculations offered insights into the distinct electronic and excitonic properties of the various borophene phases, highlighting their potential for diverse applications.

In addition to the LPE borophene, we also identified a novel single phase of borophene synthesized through electron beam deposition using boron powder. This phase, confirmed to be metallic, undergoes significant structural transformations upon annealing at room temperature. The annealing process initially induces the evolution of borophene into a sheet-like structure with transformed properties, accompanied by the formation of discrete clusters. A subsequent annealing phase further transforms these sheets entirely into isolated clusters, which exhibit rotational mobility and weak interactions with the underlying substrate. These clusters, observed to rotate and interact minimally with the substrate, underscore the dynamic and sensitive nature of borophene, particularly in response to ambient conditions.

This study provides critical insights into borophene and boron clusters, demon-

strating their significance for the development of next-generation material technologies. The strong interfacial interaction observed between β_{12} borophene and the Au(111) substrate highlights its potential for integration into nanoscale interconnects and catalytic systems, where charge transfer dynamics can be harnessed to optimize functional performance. Additionally, the modification of the Au(111) herringbone reconstruction upon borophene deposition suggests its capacity to induce localized strain, presenting opportunities for strain-engineered electronic device applications. The scalability and economic viability of the spin-coating method for liquid-phase exfoliated (LPE) borophene deposition further reinforce its suitability for industrial implementation. By precisely controlling the number of coating cycles, this study achieved both monolayer and clustered configurations, demonstrating the tunability of surface coverage across different borophene phases. These varied structural arrangements offer a unique platform for investigating phase-dependent electronic properties, with potential applications in nanoelectronics and sensing technologies.

Comprehensive structural and chemical characterization of LPE borophene, including the identification of β_{12} , χ_3 , and striped isotropic phases, highlights the material's structural polymorphism. The coexistence of multiple borophene phases suggests that targeted synthesis strategies could enable precise tuning of material properties for specific technological applications. Additionally, this study reports the synthesis of a novel single-phase borophene via electron beam deposition on Ag(111), broadening the scope of borophene research. The observed structural evolution of this phase under ambient annealing conditions underscores borophene's susceptibility to thermal and environmental factors, a critical consideration for its stability and long-term device performance. These insights contribute to a deeper understanding of borophene's structural and electronic properties, highlighting its potential for applications in nanotechnology and providing valuable insights into its use in catalysis, battery technology, hydrogen generation, hydrogen storage, sensors, and materials science. Additionally, its prospects in energy storage and flexible electronics further demonstrate its wide-ranging potential. Future research should focus on refining deposition techniques, systematically exploring substrate interactions, and assessing stability under operational conditions to fully unlock borophene's functional capabilities for practical applications.

Moreover, this research provides a deeper understanding of the various coexisting phases of borophene and explores the stability and evolution of these phases into clusters. Understanding these behaviors is essential for developing more stable

borophene phases, which are crucial for its predicted applications. The investigation of structural changes is key to effectively harnessing borophene's potential in advanced applications, ensuring stability and functionality across diverse environments. Our findings offer critical insights into borophene's behavior, paving the way for new applications in nanotechnology, materials science, and biomedical sciences.

Appendix A

SUPPLEMENTARY IMAGES FOR HRTEM

The complex energetics of LPE borophene, already complex due to electron deficiency and two-electron multicenter bonding, are further influenced by the presence of developed local strain and moiré phases. These phases arise from varying twist angles between atomic sheets, translations along the X and Y axes, and their combinations (twist+translation), which collectively contribute to an expanded array of crystallographic structural phases. Notably, the evolution of multiple crystal phases was observed, with crystalline borophene sheets distinctly visible at the edges in HRTEM imaging. Refer to the original image in Figure A.1(a) and the corresponding color-marked image in Figure A.1(b) for enhanced clarity. To facilitate identification, distinct phases have been highlighted using different colors.

Furthermore, monolayers of borophene exhibited localized strain, which disrupted the inherent crystalline order. This disruption resulted in a coexistence of amorphous, partially crystalline, and crystalline regions within individual borophene sheets (as shown in the original image in Figure A.1(c) and the colored image in Figure A.1(d)).

The impact of strain on the local modulation of borophene's crystal structures is clearly demonstrated in Figure A.2, which illustrates variations in atomic arrangements within the same sheet. A three-dimensional perspective (Figures A.2 (d) and (h)) provides a clear visualization of these structural differences. Additionally, line profiling (Figures A.2 (e) and (i)) highlights variations in the heights of alternating arrays, while fast Fourier transform (FFT) patterns (Figures A.2 (c) and (g)) offer compelling evidence of strain-induced structural variations. Measurements of average interatomic distances along the ridgelines were found to be 0.18 nm, with perpendicular distances measuring 0.74 nm for the two distinct structural twin phases. The enhanced image quality and material purity achieved through the meticulous experimental protocols employed in this study further support the observed strain-induced structural modifications.

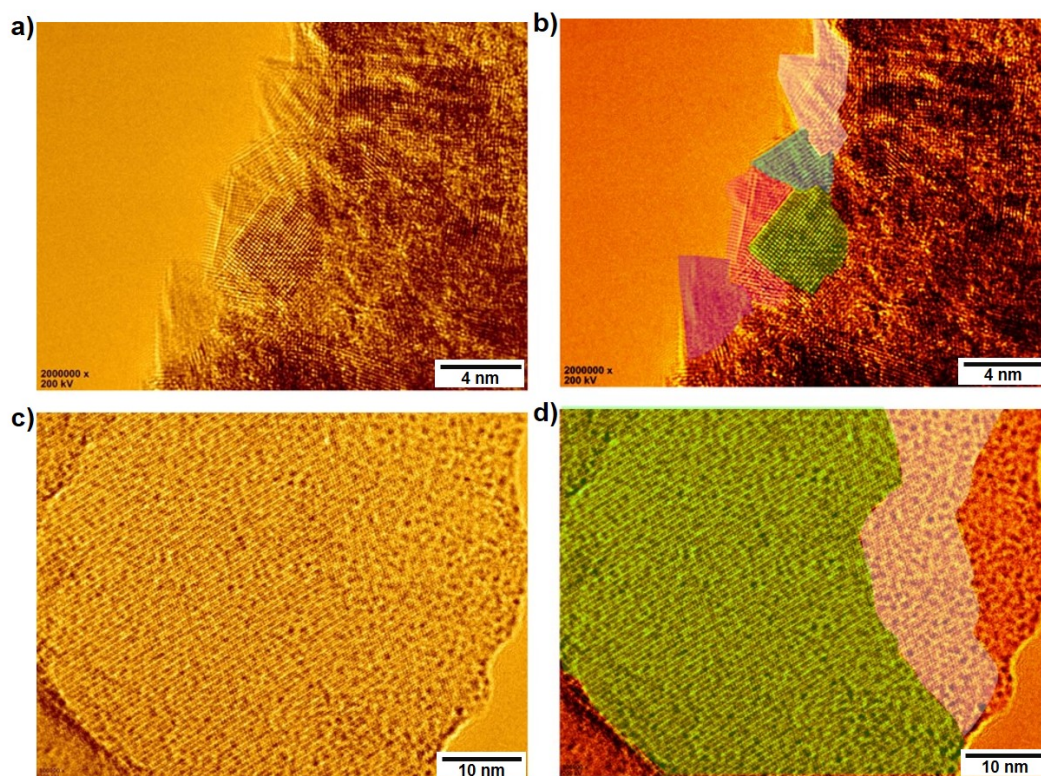


Figure A.1: The images (a) and (c) illustrate regions within the same borophene sheet, displaying a combination of amorphous, partially crystalline, and crystalline structures. The evolution of these phases is highlighted using different colors in the corresponding images (b) and (d).

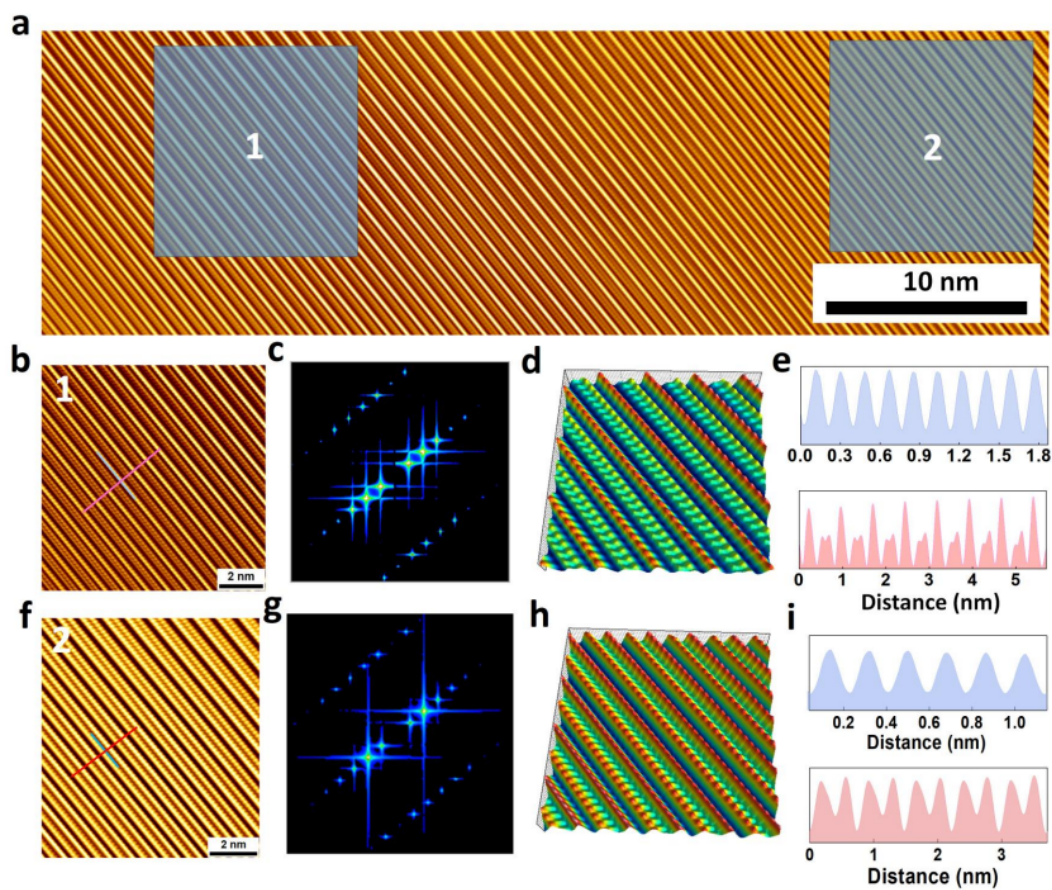


Figure A.2: The influence of strain on the localized modulation of borophene's crystal structure is evident where variations in atomic arrangements are observed within the same sheet.

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