

Synthesis and fabrication of wide bandgap semiconductors for high-power electronics

by

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AN ABSTRACT OF A DISSERTATION

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DOCTOR OF PHILOSOPHY

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Abstract

Due to an ever-increasing demand for electricity, it is essential to invest in high-efficiency energy infrastructure. Wide bandgap materials (WBGs) are essential to the development of energy production, storage, transportation, and usage. WBGs (with bandgaps exceeding ~ 2 eV) typically have high breakdown fields, low voltage leakage in high electric fields, high maximum operating temperatures, ability to interact with high energy light, and chemical stability all while being able to maintain high levels of efficiency relative to their moderate bandgap counterparts, leading to significant energy and cost savings. This dissertation explores the development of WBG semiconductors for two applications: Power conversion and storage in beta-voltaic cells and efficient power transportation through diamond photocathodes.

Boron suboxide (B_6O) is a wide bandgap semiconductor with a direct bandgap between 1.8 – 3.0 eV and has garnered interest due to its ability to heal from radiation damage, its high neutron capture cross-section, chemical inertness, high-temperature stability, and ultra-hardness of 40 – 67 GPa, making the material ideal for radioisotope batteries. This work employs Density Functional Theory (DFT) to assess these material properties and shows a low diffusion barrier of 0.16 eV for boron diffusion through the lattice, allowing self-healing from Frenkel defects caused by radiation damage. The metal flux method was selected for crystal growth due to its ability to precipitate large-domain, high-purity crystals at atmospheric pressure without a substrate, eliminating crystal strain due to lattice mismatch. DFT results also predict that the synthesis of B_6O from a mixture of B and CuO is thermodynamically favorable in oxygen-deficient environments. Unfortunately, this was not experimentally verified. Analysis of the crystals precipitated from a molten copper flux revealed only mixtures of β -boron and B_2O_3 , indicating kinetic limitations during crystal growth.

The difficulties in B_6O synthesis caused the study to pivot to $C_2Al_3B_{48}$ growth, which is a wide bandgap semiconductor expected to have similar properties to B_6O . $C_2Al_3B_{48}$ crystals up to 7 mm in diameter were grown from an aluminum-boron-carbon flux by varying the carbon concentration. The crystals were characterized using XRD, Raman, and PL. $C_2Al_3B_{48}$ demonstrated a broad band edge between 2.4 – 2.7 eV, which is consistent with its yellow color.

The second project involves vacuum electronics, which offer significant advantages over solid-state devices in high-power, high-frequency applications, but often require bulky cooling systems that prevent miniaturization. Diamond is well-suited for high power electronics due to its extreme hardness, ultrawide bandgap, high carrier mobility, and high electrical breakdown field and for photocathodes in particular due to its negative electron affinity (NEA) when terminated with hydrogen. Silicon carbide (SiC) was initially used to demonstrate photocathode enhancement, which utilized self-assembled Au nanodots to fabricate nanopillars on the cathode substrate using reactive ion etching. SiC devices demonstrated a field enhancement of 205 and a turn-on field of $\sim 6.2 \text{ V}/\mu\text{m}$ when exciting electrons with a 447 nm laser.

The self-assembled Au nanodot fabrication process was transferred to diamond, and this work produced tip widths ranging from 40-460 nm, densities ranging from 0.5-53.5 pillars/ μm^2 , and heights greater than 4.5 μm . The nanodot diameter and density can be tuned using the initial Au film thickness. After fabrication, the pillars were sharpened to tip widths less than 40 nm by annealing in air at 650°C. Finally, diamond was terminated with hydrogen by annealing in forming gas, and the sheet resistance of the diamond films was measured using CTLM.

This work was partially performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, LLNL-TH-2004327.

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Preface

The goal of this dissertation is to advance the use of wide bandgap semiconductors for high power electronic applications. This is realized through two projects. The first is to synthesize boron-rich compounds for use in nuclear batteries. The second is to develop fabrication techniques for diamond photocathodes.

The first two chapters introduce the semiconductors used for these studies as well as common characterization techniques used to analyze these materials.

The first project is detailed through chapters 3, 4, and 5. Chapter 3 discusses the characterization of boron suboxide (B_6O) using density functional theory (DFT), specifically the thermodynamic stability of bulk solids and the ‘self-healing’ capability through atomic diffusion pathways, and was published in *The Journal of Physical Chemistry C*. The exploration of B_6O continues in chapter 4, which discusses the experimental synthesis of boron and boron oxide compounds from a copper flux. Chapter 5 pivots to the precipitation and characterization of the multiple boron-rich Al-B-C compounds that precipitate from an aluminum flux. Each chapter was written in the form of an independent manuscript to be submitted to a journal.

The second project is detailed in chapters 6, 7, and 8. First, photocathode fabrication was applied to SiC in chapter 6 as a ‘proof-of-concept’ before being applied to diamond and optimized in chapter 7, which was published in the *Journal Materials Science in Semiconductor Processing*. Chapter 8 details a surface termination process, which should improve diamond photocathode performance by exploiting the negative electron affinity (NEA) of hydrogen-terminated diamond, and was published in the *Journal of Vacuum Science and Technology A*.

Chapter 9 summarizes both projects and provides recommendations for future work.

Chapter 1 - Introduction and Background for Icosahedral Boron

Compounds

Motivation

Advanced energy infrastructure is essential to maintaining a strong economy and high modern quality-of-life. In 2023, the United States alone consumed 27,500 TWh of energy. This energy consumption drives all aspects of society, such as water and food production, telecommunication, transportation, healthcare, military operations, emergency services, industrial processes and manufacturing, and household appliances. Energy security is a critical concern for future developments due to increasing population, desire to travel, and demand for ever-increasing quality-of-life standards. It's expected that energy consumption increases by 16% - 57% by 2050¹.

Diversification becomes more critical when considering the reduction of energy production via non-renewable resources that produce large amounts of air pollutants, such as petroleum, natural gas, and coal, which made up 83% of energy production in the United States in 2023¹. Therefore, it is necessary to reinforce power infrastructure by diversifying energy production. The diversification leads infrastructure from a centralized power-grid revolving around large power plants to a decentralized power-grid with many integrated energy producers such as nuclear plants, solar panels, and windmills, which require advanced "smart grids" to efficiently distribute power to consumers and various storage banks².

Wide bandgap materials (WBGs) are essential to the development of energy production, storage, transportation, and usage. WBGs (with bandgaps exceeding ~ 2 eV) typically have high breakdown fields, low voltage leakage in high electric fields, high maximum operating temperatures, ability to interact with high energy light, and chemical stability all while being able

to maintain high levels of efficiency relative to their moderate bandgap counterparts^{3,4}, leading to significant energy and cost savings^{5,6} as shown in **Figure 1-1**.

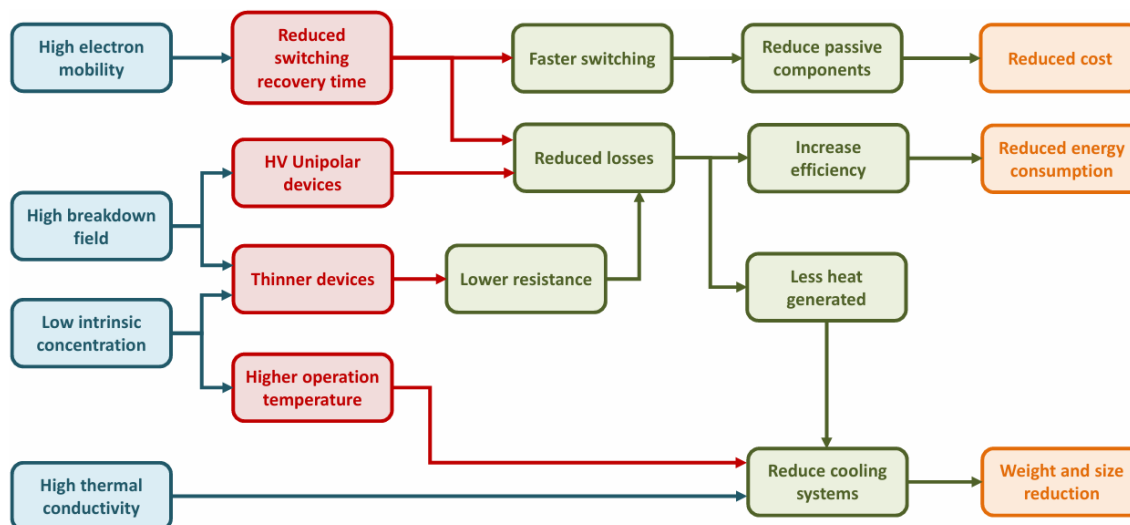


Figure 1-1. WBG semiconductor parameter capabilities (blue); physical properties affected by WBG advantages (red); power electronics characteristics (green); and product benefits (yellow). Figure taken from Ballestín-Fuertes et al. 2021⁶.

The lower energy consumption combined with the reduced weight and complexity of WBG power systems make them ideal for applications including fast-charging systems for electronics and electric vehicles², energy conversion and storage⁷, high power electronics, thin film transistors, optoelectronics, and transparent electronics^{8–10}.

Boron-Rich Compounds for Nuclear Batteries

Icosahedral Boride Structure and Properties

Boron Clusters

Boron-rich compounds (BRCs) have significant applications as wide bandgap semiconductors due to their well-known ability to heal from radiation damage, high neutron capture cross-section^{11–15}, chemical inertness, high temperature stability over 2000°C, and ultra-hardness of 40-67 GPa^{16,17}. These properties make boron-rich compounds ideal candidates for

nuclear applications in extreme environments, such as in neutron detectors or beta-voltaic cells^{11,16,34}. These amazing properties are derived from the unique bonding structure of BRCs. Instead of the typical two-centered bonding where two atoms share two electrons, boron atoms have the capacity for three-centered bonding where three atoms share two electrons in the center of a triangular face^{15,18,19}, as shown in **Figure 1-2**.

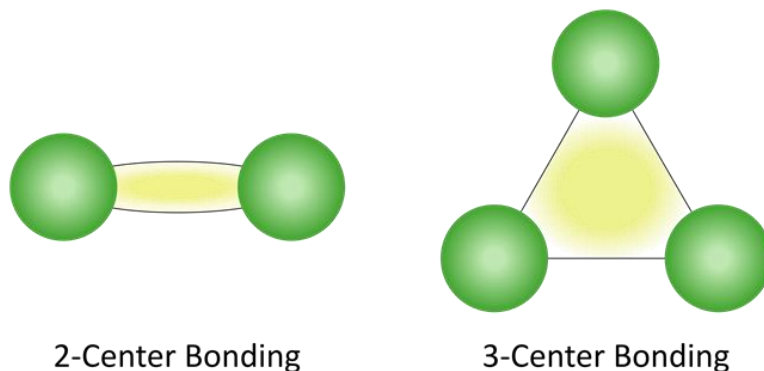


Figure 1-2. Two-centered bonding (left) and three-centered bonding (right) with approximate electron density highlighted in yellow. In both cases, two electrons are shared between all atoms.

This bonding scheme leads to unique crystals structures that revolve around clusters of boron atoms. There are two kinds of boron clusters. Most structures primarily rely on clusters of twelve boron atoms that form a regular icosahedron¹⁵, as shown in **Figure 1-3**. The other cluster formation uses twenty boron atoms in the form of twinned icosahedra. The B₂₀ unit is typically only present in materials based on the β -tetragonal boron allotrope, including many compounds that incorporate aluminum into the crystal structure^{20,21}. Both configurations are electron deficient and require additional atoms to donate electrons to the system^{15,18}.

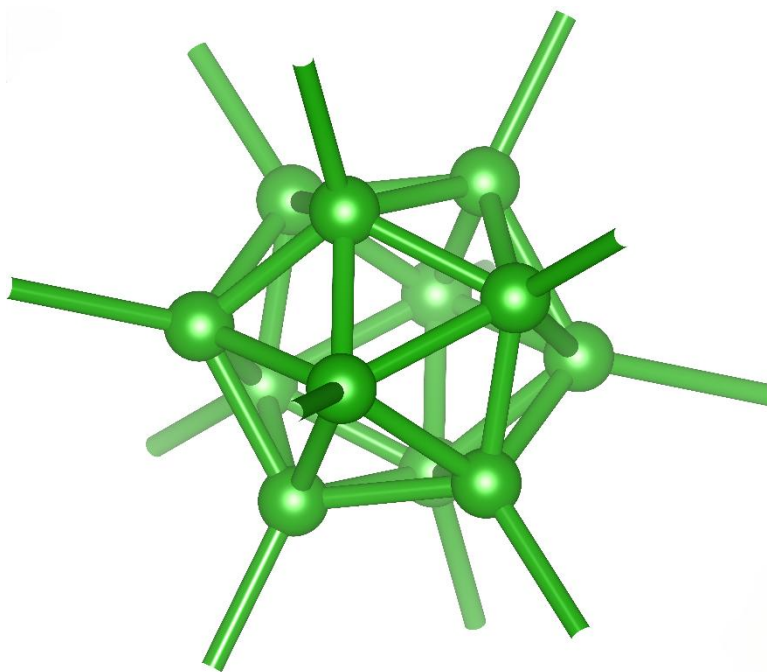


Figure 1-3. The B_{12} icosahedra unit²². Electrons are concentrated in the center of the triangular planes.

Boron Suboxide

Crystal Structure and Properties

Like other icosahedral compounds, boron suboxide (B_6O or $B_{12}O_2$) has garnered interest due to its ability to heal from radiation damage, high neutron capture cross-section^{14,15}, chemical inertness, high temperature stability, wide direct bandgap of 1.83 – 3.0 eV^{11–13}, and ultra-hardness of 40-67 GPa^{16,17}. It is predicted that B_6O specifically can be doped both *n* and *p*-type, which is a major advantage over other wide bandgap semiconductors. It can be doped *n*-type by interstitial Si defects and can be doped *p*-type using substitutional carbon defects on the oxygen sites¹³. These properties make B_6O a promising candidate for semiconductor applications in high radiation environments, such as radioisotope batteries and neutron detectors.

Boron suboxide is also a promising candidate for thermoelectric applications due to its higher-than-average Seebeck coefficients, even relative to other icosahedral boron

compounds^{15,16,18,19}. The stiff bonding structure in these compounds also leads to a surprisingly high thermal conductivity of 285 W/(m K)^{23,24}. The combination of thermoelectric properties, resistance to high temperatures, and chemical stability makes icosahedral compounds ideal for developing thermal management systems for high power electronics.

The unit cell for boron suboxide, as well as several other boron-rich compounds like boron subarsenide (B_2As_{12}) and boron subphosphide (B_2P_{12}), is based on the α -boron structure, a rhombohedron with boron icosahedra centered on the corners of the rhombohedra and interstitial elements in the center of the unit cell. Two-centered covalent bonds connect six boron atoms from each icosahedron directly to neighboring icosahedra. The remaining boron atoms are bonded to the non-boron atoms, which donate electrons to further stabilize the icosahedra^{14,15,18}.

Figure 1-4 illustrates the unit cell for B_6O . However, boron suboxide is a known non-stoichiometric compound with many oxygen deficient structures^{13,17,25–27}.

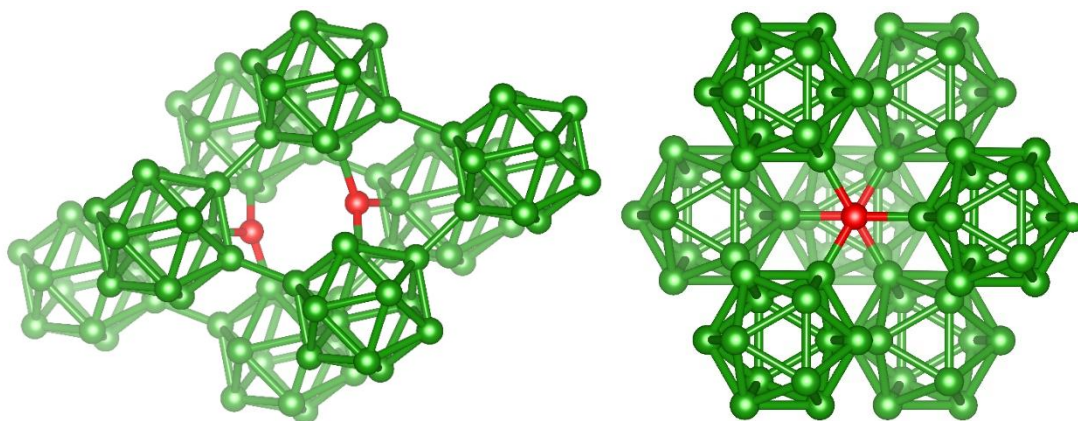


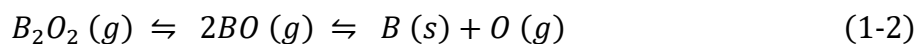
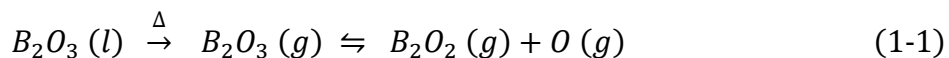
Figure 1-4. Crystal structure of B_6O . The boron atoms (green) are arranged in icosahedra and oxygen atoms (red) link the icosahedra in groups of three. This structure image was generated in VESTA²².

B_6O crystal growth is still in its early stages. Prior reports on its crystal growth required high temperatures and pressures to produce stoichiometric B_6O . Synthesis at lower pressures tends to produce oxygen deficient, non-stoichiometric boron suboxide, drastically changing its

properties^{11,12,17}. This impedes the study of B₆O properties since a pure material with a high degree of crystallinity is needed to further refine these property measurements.

Synthesis: Oxidation of Solid Boron

Three pathways are commonly used in the synthesis of B₆O. The first and most common technique is the direct oxidation of solid boron using boron oxide (B₂O₃). The process has been broken down by Slack *et. al.*¹⁶ using the NIST-JANAF thermochemical tables. B₂O₃ has a low melting point and high vapor pressure and decomposes into several different compounds at temperatures above 1200 K following reactions below¹².



The gaseous BO formed in Eqn. (1-2) behaves as a carrier of oxygen to solid boron, and the partial pressure of BO is more than 8 orders of magnitude higher than monoatomic oxygen formed in Eqn. (1-3). Slack *et. al.*¹² concludes that B₆O formation is thermodynamically favorable at atmospheric pressure above 1200°C. Monoatomic oxygen penetrates the solid boron crystal structure to bind to B₁₂ icosahedra in the solid-state reaction:



The formation of B₆O is expected to proceed slowly due to the low monoatomic oxygen concentration, and the pressure and temperature need to be raised to increase monoatomic oxygen concentration and therefore the rate of formation of B₆O. Low pressure experiments consistently produce oxygen deficient, non-stoichiometric boron suboxide crystals that tend to have small crystal domains that are frequently mixed with amorphous material and B₂O₃^{11,17,26}. The thermodynamic stability of stoichiometric B₆O at ambient pressure indicates that the oxygen

deficiency seen at low pressures is caused by kinetic limitations on the system, and better reaction mediums will need to be explored to maximize the amount of oxygen that can bind with the boron icosahedra at ambient pressures.

Synthesis: Reduction of B_2O_3 with B in a Liquid Flux

If the temperature is increased enough for boron to dissolve into a B_2O_3 melt, then B_6O can be formed through the direct reduction of B_2O_3 in the reaction presented below^{25,28}.



Due to the high vapor pressure of B_2O_3 , the pressure must be increased to maintain a liquid system. Stoichiometric B_6O readily forms at pressures around 5.5 GPa at temperatures between 1200°C-2000°C. However, crystal domains are still typically small, up to approximately 40µm in diameter²⁶. This is likely due to the fact that B_2O_3 does not form a significant eutectic with boron suboxide¹¹. Without a steep eutectic, boron suboxide will precipitate rapidly as the system cools below the saturation point of B_6O in B_2O_3 . Rapid precipitation causes many nucleation points to form, resulting in many crystals with small domains. However, if a low eutectic point is used, a steep solubility curve can be used to control the nucleation rate. Han *et. al.*¹¹ were able to produce B_6O crystals up to 2 mm in diameter by substituting B_2O_3 with boric acid, H_3BO_3 . This was performed at 5.5GPa and 2100°C, where boric acid decomposes into B_2O_3 and water at low temperatures. The addition of water to the system generates a eutectic where B_6O crystals can precipitate from the flux through controlled nucleation, forming large single crystals.

Synthesis: Reduction of Metal Oxides

Metal oxides can similarly be reduced by boron to form boron oxide, provided an appropriate reductant is used. A metal oxide will undergo the following reaction:



Where suitable metals, **M**, could be metals such as nickel, copper, zinc, or magnesium on the condition that their respective oxides have a higher Gibb's energy of formation than the B₆O target compound. However, metals will be left behind as impurities in B₆O that can ideally be removed in post-processing. For this reason, zinc oxide is a popular reactant as zinc and excess boron powder impurities can both be removed using hydrochloric acid^{25,28}.

Unfortunately, this technique still has the drawback of not having a eutectic or notable solubility curve, since B₆O will form solid crystals upon reacting due to its high melting temperature, so nucleation cannot be controlled. Therefore, crystals produced with this method are typically small. A metal flux that forms a eutectic with B₆O could potentially be used to control nucleation in the system and to maximize crystal domain sizes, which is discussed later in this dissertation. No instances of using a metal flux to synthesize B₆O have been reported thus far.

Aluminum Boron Carbides

Crystal Structure

Aluminum and carbon can be used to make boron-rich compounds instead. Due to boron's high affinity for both aluminum and carbon, multiple phases of boron-rich compounds can be precipitated from a carbon-containing aluminum flux to form aluminum-boron-carbon (ABC) compounds. The three primary compounds of interest are alpha aluminum dodecaboride (α -AlB₁₂), beta aluminum boride (C₂Al₃B₄₈) and a third higher carbon-content compound (C₄AlB₂₄). These are all expected to be wide bandgap materials. AlB₁₂ is reported to have a bandgap of 1.9 eV²⁹. Due to the yellow color of C₂Al₃B₄₈, the bandgap is anticipated to be between 2.4-2.8 eV.

Little literature has been published on these materials due to the complex crystal structure making analysis of the materials incredibly difficult. Up through the 1950s-1960s, these carbon compounds were believed to be various structures of the aluminum-boron system, and carbon was not considered as part of the crystal structure. Because of these misunderstandings in the compositional analysis, $C_2Al_3B_{48}$ is often referred to as $\beta-AlB_{12}$ ³⁰ and C_4AlB_{24} is commonly referred to as AlB_{10} ³¹. The boron structure of the AlB_{12} system is considerably more complex than the boron-rich compounds discussed earlier in this report, such as B_6O . This is due to an additional B_{20} configuration which is shaped like two partially merged B_{12} icosahedra. The boron in AlB_{12} is structured in a combination of B_{12} and B_{20} clusters, which is shown in **Figure 1-5**, following the β -tetragonal boron sublattice.

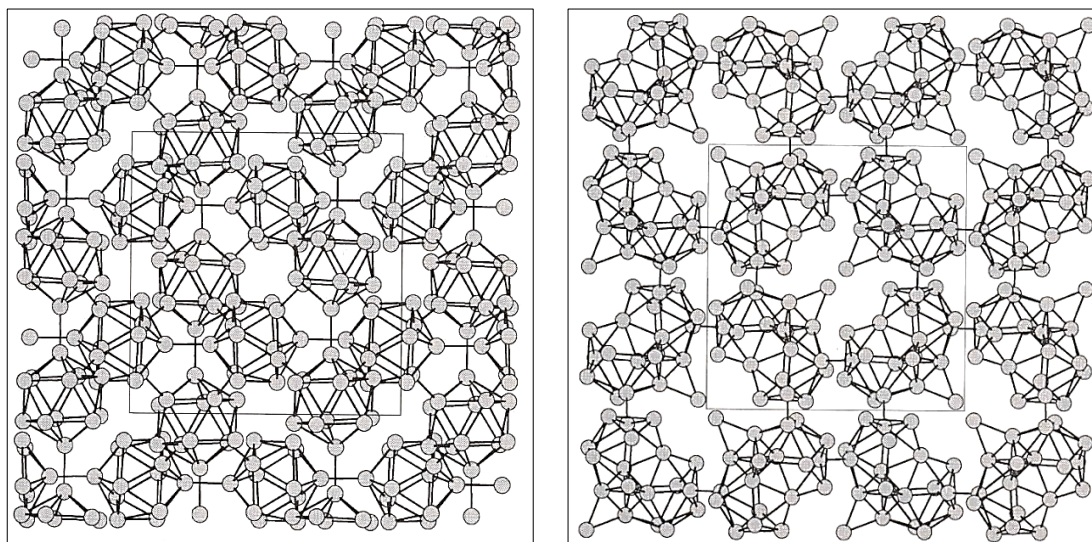


Figure 1-5. Arrangement of B_{12} icosahedra (left) and B_{20} clusters (right) of $\alpha-AlB_{12}$ as seen along the c axis²⁰.

The addition of carbon to the lattice stabilizes the α -tetragonal boron sublattice. It consists of four B_{12} icosahedron with an additional atom in the center to cross link them, as shown in **Figure 1-6**. This boron phase is highly controversial, and some researchers insist that impurities such as carbon or nitrogen are required to substitute the central atom position to

stabilize the structure³². In the case of $C_2Al_3B_{48}$, the central atom is substituted by a carbon atom and aluminum interstitial atoms exist throughout the structure. Aluminum seems to be statistically distributed throughout the boron lattice, as all aluminum sites are partially occupied^{30,33}.

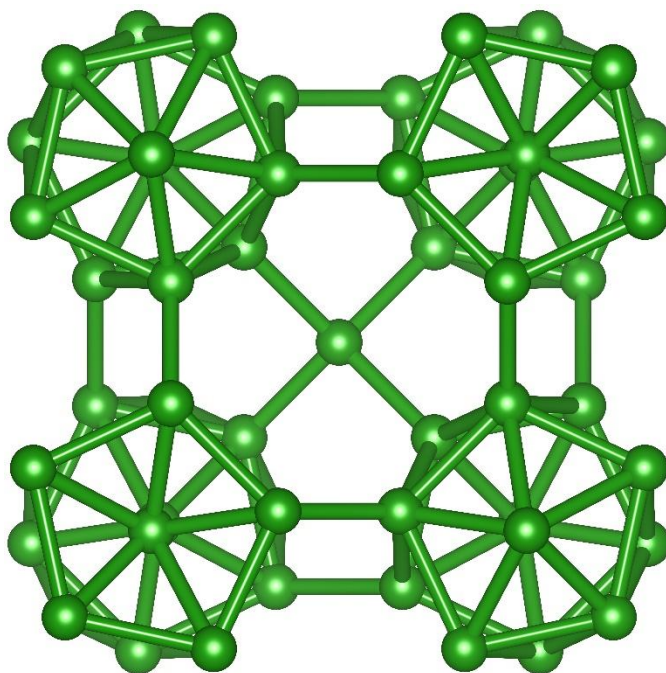


Figure 1-6. α -tetragonal boron sublattice, consisting of four B_{12} icosahedron crosslinked by a central interstitial atom²⁷. This is the boron sublattice for $C_2Al_3B_{48}$.

As more carbon is added to the system to form $C_2Al_3B_{48}$ and C_4AlB_{24} , the boron configuration follows the β -tetragonal boron sublattice, shown in **Figure 1-7**, which is typically only seen at high pressures^{21,33–35}. Like $C_2Al_3B_{48}$, the aluminum interstitial sites are only partially occupied^{33,36}.

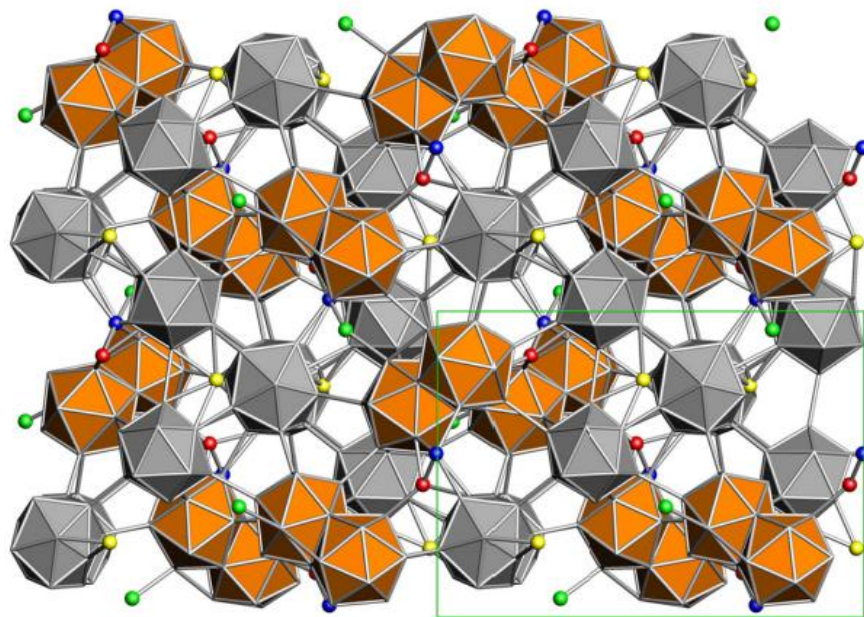


Figure 1-7. Crystal structure of β -tetragonal boron, which makes up the basis lattice for C_4AlB_{24} ²¹. Grey objects represent B_{12} clusters and orange objects represent B_{20} clusters.

Synthesis

Few studies on synthesis methods have been published. Most studies utilize an aluminum solvent to dissolve either boron and carbon or boron carbide to precipitate these ABC compounds. Some papers suggest a temperature dependence on the system. At temperatures less than 1400°C, C_4AlB_{24} was more likely to form as a fraction of the phases present, even when only enough carbon to form $C_2Al_3B_{48}$ was used in the initial flux³⁷. $C_2Al_3B_{48}$ also has a temperature dependent phase transition: At temperatures exceeding 850°C, the compound exists in a tetragonal lattice whereas it turns into an orthorhombic lattice at lower temperatures^{30,33}. This phase transition is not homogenous, leading to twinning in the crystal lattice at lower temperatures. Therefore, an annealing treatment or slowly cooling through the phase transition temperatures might benefit the crystal quality of crystals produced through the metal flux method. Other phases in the ABC system are still being identified, such as the direct bandgap

semiconductor $\text{Al}_{2.69}\text{B}_{50}$ and $\text{C}_2\text{AlB}_{12}$, and these phases will be better identified as more studies are produced on the ABC system^{38,39}.

There have also been studies on reactive sintering of either boron or boron carbide with aluminum to form ABC compounds, but results were largely unsuccessful with low yields, low purity, and small crystal domains. Pure boron worked best as a starting material. Other boron sources such as B_4C and B_2O_3 are not reactive enough to produce ABC compounds with high yields, and often produce materials with considerable impurity content that proves difficult to remove^{40–46}.

‘Self-Healing’ from Radiation Damage

Boron-rich icosahedra are also well known for their unique ability to resist nuclear radiation damage due to their three-centered bonding^{7,14,47}. As a boron atom is displaced from an icosahedra due to high energy electron or ion bombardment, one of its valence electrons is left in the icosahedra, forming an electron-rich B_{11} icosahedra and an electron deficient boron ion, which are known as Frenkel defect pairs^{14,15,48}. The electromagnetic force between the ions allows for quick recombination into a complete structure, as shown with the self-healing of a Frenkel defect in the B_{12}P_2 structure in **Figure 1-8**. This ‘self-healing’ property of boron icosahedra makes these compounds particularly enticing for nuclear applications, where radiation would quickly degrade other semiconducting compounds^{7,47,49}. This self-healing property drastically extends the lifetime on electronic devices that rely on radiation, such as beta-voltaic cells, or devices in high radiation environments like nuclear reactors. This “self-healing” property is further described using density functional theory calculations in Chapter 3 - Structure, Stability and Electronic Properties of Boron Suboxide: A Density Functional Theory Study.

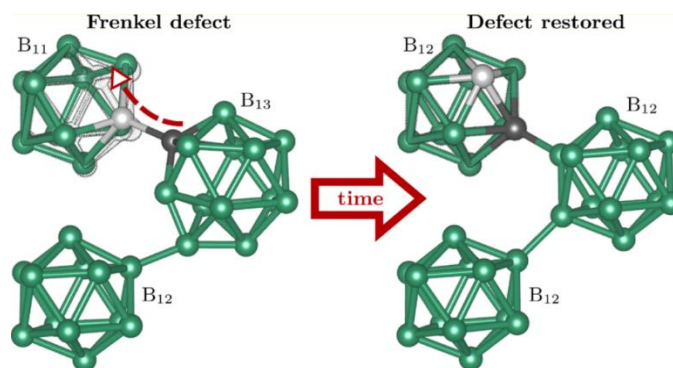


Figure 1-8. Partial structures of boron subphosphide 'self-healing' from a Frenkel defect in the $B_{12}P_2$ structure. The displaced atom is shown in black and a mediating atom is shown in gray⁴⁸.

This mechanism was tested by Carrard¹⁴ and Emin¹⁵ by bombarding icosahedral boron compounds like $B_{12}P_2$ with high-energy electrons and ions. Enough energy was applied to the ion bombardment to displace each boron atom several times, enough to render most other materials amorphous. The sample defects were monitored using transmission electron microscopy (TEM), which failed to observe defect clusters or amorphization of the boron-rich materials, as shown in **Figure 1-9**.

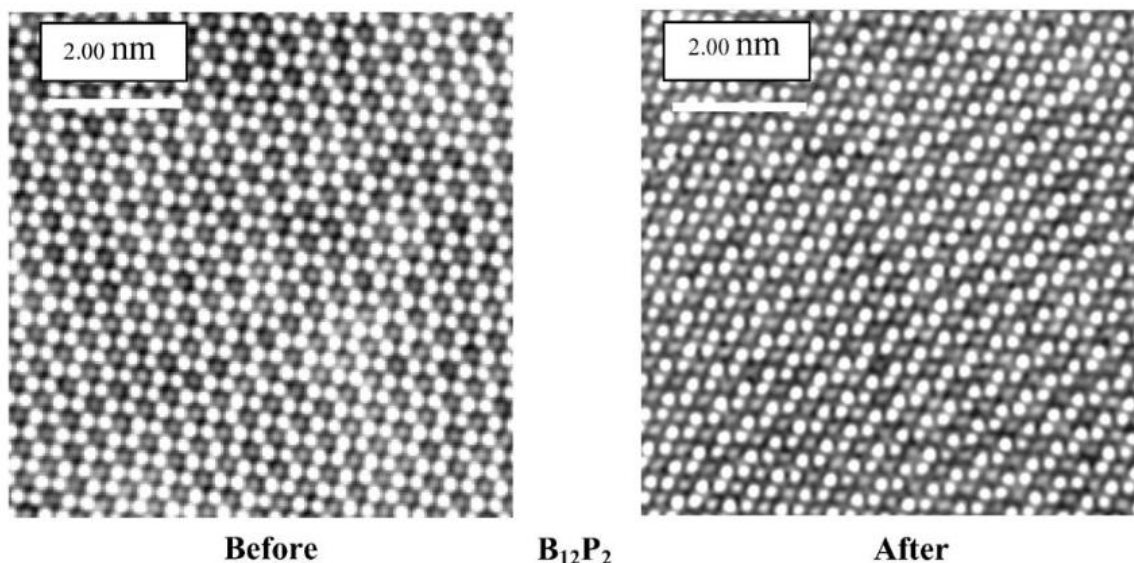


Figure 1-9. High-resolution TEM shows no damage to the icosahedral boron compound $B_{12}P_2$ after intense bombardment (10^{18} electrons/cm²s) by 400 keV electrons to a net dose of 10^{23} electrons/cm². The TEM did not observe any significant damage to the crystal structure¹⁵.

Applications of Icosahedral Boron Compounds

Power conversion devices, such as beta-voltaic cells, are a potential application of boron-rich materials. Traditional batteries are limited to a oxidation-reduction reaction within a liquid medium, rendering them bulky with a low power density and short lifetime¹⁹. A beta-voltaic cell utilizes a radioisotope as an energy source. Solid-state nuclear batteries have several benefits over traditional liquid ion batteries, including a high energy density, long working-life, potential for miniaturization, and stability in extreme environments. The miniaturization and high energy density of nuclear batteries leads to direct applications in micro-electro-mechanical systems (MEMS), implantable medical devices, drones, and spacecraft in harsh environments^{50,51}. **Figure 1-10**⁵² demonstrates the superior energy density of nuclear batteries, which can be 2 – 6 orders-of-magnitude higher than other traditional power methods such as lithium ion batteries.

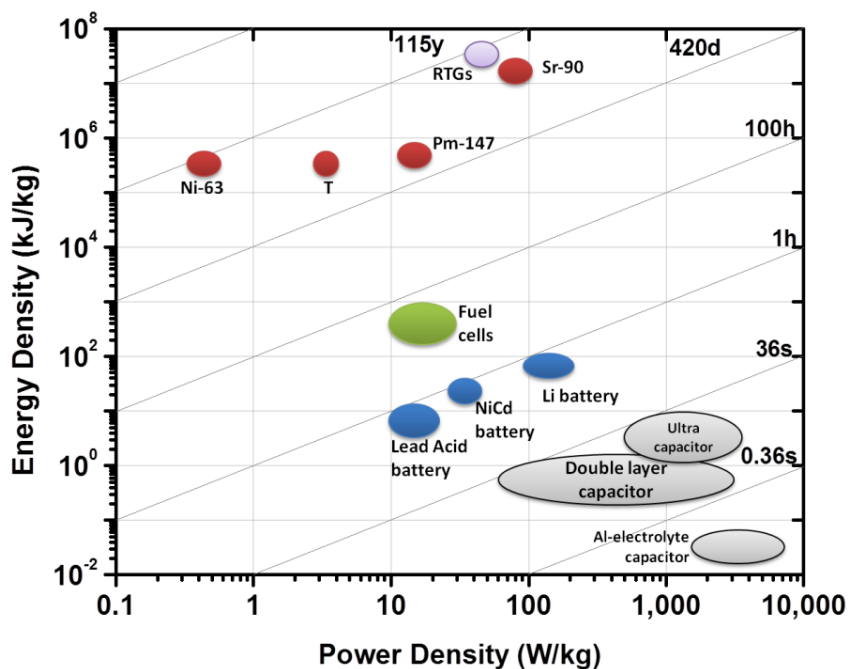


Figure 1-10. Ragone plot showing nuclear batteries of various radioisotopes (red) compared to radioisotope thermoelectric generators (RTGs), chemical batteries (blue), fuel cells (green), and capacitors (grey)⁵².

In beta-voltaic cells, the radioisotope emits beta-particles that create electron-hole pairs (EHPs) at a p-n junction made from a solid-state semiconductor material, generating a current following the electron-voltaic effect^{53,54}, as shown in **Figure 1-11**.

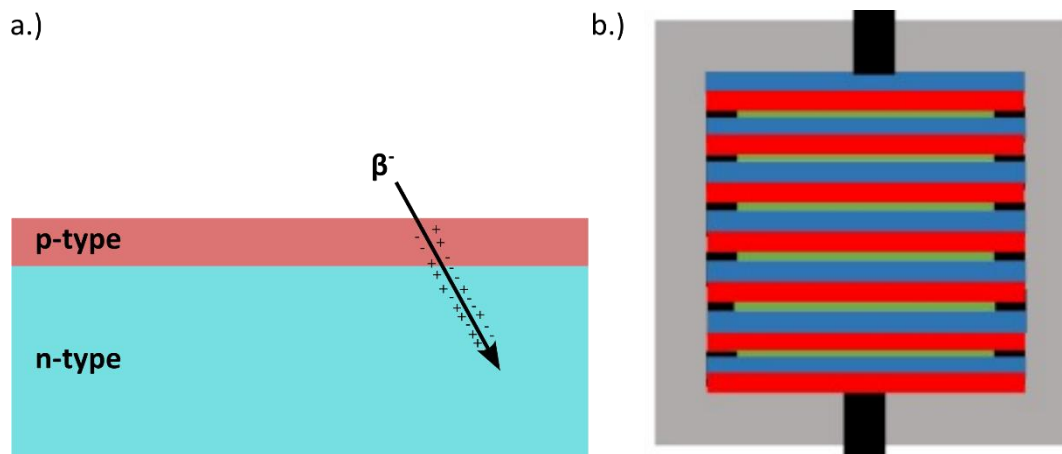
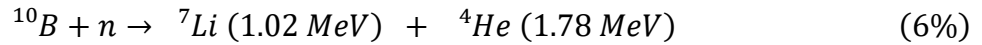
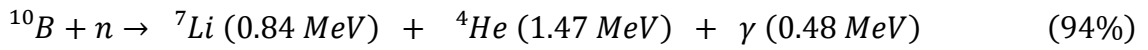


Figure 1-11. (a) Schematic of a p-n junction beta-voltaic device. (b) The layout of a beta-voltaic cell. *p*-type material (blue) and *n*-type material (red) are connected in series by conductive material (black). In-between the *p-n* junction layers is a radioisotope (green) that generates beta-particles⁷.

Unfortunately, nuclear bombardment rapidly deteriorates most materials, drastically decreasing the lifetime and power density of modern beta-voltaic cells. However, boron-rich semiconductors have an excellent combination of properties to overcome these issues. Self-healing from nuclear radiation may increase the lifespan and power output potential of beta-voltaic cells. Furthermore, chemical inertness at high temperatures and a wide bandgap for maximized battery efficiency are ideal properties for applications in energy conversion devices^{7,15,19,47}, making boron-rich compounds promising candidates for future energy storage.

Neutron detection is another nuclear application where materials with high radiation-hardness are desirable. Currently, ^3He is the most prominent element used for neutron detectors due to its very large thermal neutron cross-section (5330 barns)^{19,47}. However, ^3He is primarily

produced as a by-product from the maintenance of nuclear warheads, which has declined drastically since the end of the Cold War in the late 1980s. Therefore, other materials are needed to replace ^3He , the most promising of which contain either ^6Li or ^{10}B . As an element, ^{10}B has a large thermal neutron capture cross-section of 3840 barns, orders of magnitude larger than most elements, and it's not sensitive to gamma and x-ray radiation due to the low electron cloud density surrounding boron atoms, making boron-rich semiconductors an ideal material for neutron detection^{19,47,55,56}. ^{10}B undergoes two nuclear reactions with thermal neutrons¹⁹:



In typical solid-state neutron detectors, the reaction between an atom and neutron form electron-hole pairs. The electrons then move towards a positive contact and holes are effectively transferred to a negative contact, creating an electric signal that can be used to measure the radiation interactions. The neutron interacting with ^{10}B causes orders of magnitude more electron-hole pairs than traditional gas filled ^3He detectors. Combining this with its high neutron capture cross-section, boron is expected to be a very high efficiency material for neutron detectors⁵⁷. However, previous attempts to synthesize B_6O resulted in small crystal domains with high impurity concentrations, resulting in high charge trap densities. To improve the electrical properties, sensitivity, and efficiency of these devices, large, high purity, low defect single crystals are needed.

Metal Flux Synthesis Method

To improve the synthesis of boron-rich compounds at low pressure, a flux medium that can dissolve high concentrations of reactants at around 1500°C and facilitate a chemical reaction is used in a technique called the metal flux method. This is a conceptually simple crystal growth technique, where a molten metal flux is heated beyond its melting point, saturated with the

source materials for boron-rich compounds, and slowly cooled down. As the temperature decreases, the flux becomes supersaturated and begins precipitating crystals as shown in **Figure 1-12**^{58,59}.

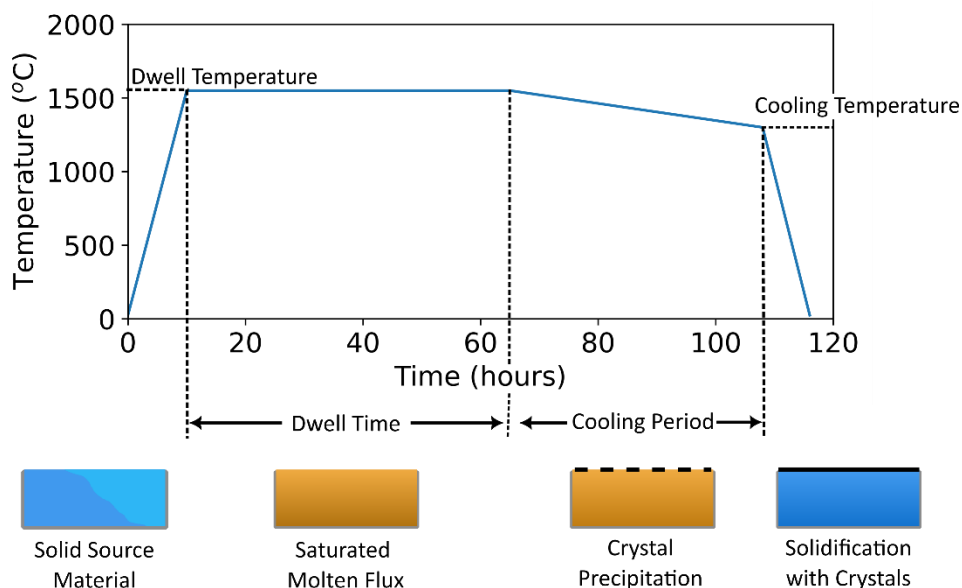


Figure 1-12. Diagram demonstrating the metal flux method process. Solid source materials are heated up to high temperature, around 1500°C, and left to dwell to fully dissolve the boron. The flux is then slowly cooled, causing the supersaturated flux to precipitate crystals.

There are several benefits to using the metal flux method. First, the liquid medium can help retain oxygen compounds essential to the reaction, potentially relieving the system of some kinetic limitations and lowering the pressure required for high quality crystal growth. The temperature required to grow large crystals can also be decreased to well below the high melting point of boron by dissolving the boron in a suitable flux. A liquid growth medium is also beneficial to B₆O growth because of its unique crystal structure, as there will be no thermal or crystallographic mismatch that may occur with techniques that require substrates, such as chemical vapor deposition (CVD) or molecular beam epitaxy (MBE)⁵⁹. The metal flux has the additional benefit of trapping impurities in the flux instead of the precipitating crystals⁵⁸. The

combination of these traits leads to crystals grown from a metal flux having low strain, minimal crystal defect densities, and low impurity concentrations^{55,58,59}.

Several parameters need to be optimized for crystal growth using the metal flux method. The dwell temperature must be high enough to dissolve the necessary source materials into the flux and to satisfy thermodynamic and kinetic requirements for the desired chemical reaction to occur. The dwell time needs to be long enough to completely dissolve source materials and saturate the flux. The most important parameters are typically the ramp down rate (i.e., the cooling rate) and the flux composition^{19,49,58}. The ramp down rate must be slow enough to inhibit nucleation as much as possible. Rapid nucleation results in many small-domain crystals, but a slow cooling rate allows for large single crystals by focusing crystal precipitation into (ideally) a single nucleation point¹⁹.

Reactive sintering has been the primary synthesis method for previous BRC studies^{11,26,28}. However, the metal flux technique has successfully been applied towards the synthesis of other boron-rich compounds such as boron subarsenide ($B_{12}As_2$). In this case, a nickel flux was used to dissolve boron powder at 1150°C while a separate source of arsenic powder was heated to 600°C to create an arsenic atmosphere. The arsenic then dissolved into the nickel flux and reacted with the boron to form $B_{12}As_2$. The crystals precipitated upon cooling at a rate of 3.5°C/hr down to 900°C^{19,49}. The resulting crystals grew upwards of 15mm across depending on the cooling rate. Raman, SIMS, and defect selective etching showed high crystallinity and low impurity concentrations¹⁹. This provides good precedence for using the metal flux technique to grow other boron-rich compounds.

Diamond Photocathodes

Photocathode Requirements

Despite rapid development of solid-state electronics in the past several decades, vacuum electronic devices (VEDs) remain superior for high-frequency, high-power electron transport due to the absence of electron scattering in the transport media and the high critical field of vacuum^{60,61}. This lends itself to applications in wireless communication, electron microscopy, radar, x-ray sources, remote sensing and imaging, cancer treatment, and energy conversion^{61–63}. As such, researchers are developing photocathodes to efficiently inject electrons into vacuum using the photoelectric effect. VEDs rely on a cathode that emits electrons that are transported across the vacuum, as shown in **Figure 1-13**.

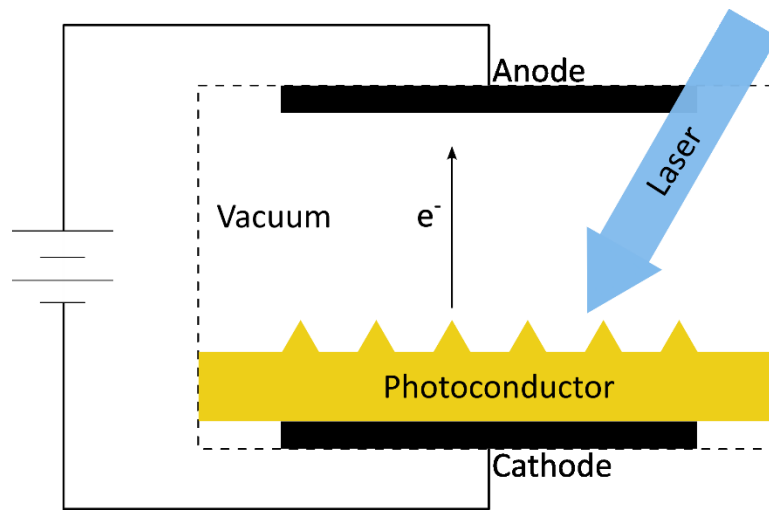


Figure 1-13. Diagram of a photocathode. A voltage bias is applied across a vacuum, where the photoconductor acts as the cathode. As the laser excites electrons into the conduction band, the electrons are emitted into the vacuum towards the anode.

Photocathodes are typically either metals or semiconductors. Metal photocathodes can operate at low vacuum requirements and have longer lifetimes but have a low photoelectric response to light. Semiconductor photocathodes have significantly higher photoelectric yield but have stringent vacuum requirements and are more sensitive to trace concentrations of impurities,

lowering device lifetimes. Therefore, current research in literature is interested in developing semiconductor photocathodes with high environmental robustness, lowering the vacuum requirements for device packaging and extending the device operating lifetime^{62,64}. To achieve this, the photocathode material must demonstrate high quantum efficiency (QE), the ability to emit electrons in response to excitation by photons, as well as improved environmental inertness.

Nitrogen-doped diamond has exceptional properties that make it a promising material for many electronic applications. Moreover, nitrogen-doped ultrananocrystalline diamond has significantly lower switching losses compared to traditional semiconductors such as SiC⁶⁵. Hydrogen-terminated diamond possesses a negative electron affinity (NEA)⁶⁴. These properties make diamond an ideal candidate for photocathodes. Prior studies focused on maximizing the electron emission density from polycrystalline diamond. This is typically done by increasing the density of grain boundaries, which are electrically conductive channels that readily bring electrons to the photocathode surface and emit them to vacuum. However, there is still need to develop high-power photocathode devices with low dark current leakage, which can be done using single crystalline diamond.

Diamond Structure and Properties

Bulk structure and properties

Diamond is a semiconductor material that is highly prized for its mechanical, electrical, and optical properties. It has an ultra-wide bandgap of 5.47eV, hardness greater than 60 GPa, optical transparency, high breakdown field, high dielectric strength, high carrier mobility and thermal conductivity, radiation hardness, and chemical inertness that are all being explored for device applications in high power electronics and optoelectronics, especially in extreme

operating conditions^{66–68}. The amazing properties of diamond are due to its sp^3 structure, producing short, high energy bonds⁶⁹ as shown in **Figure 1-14**.

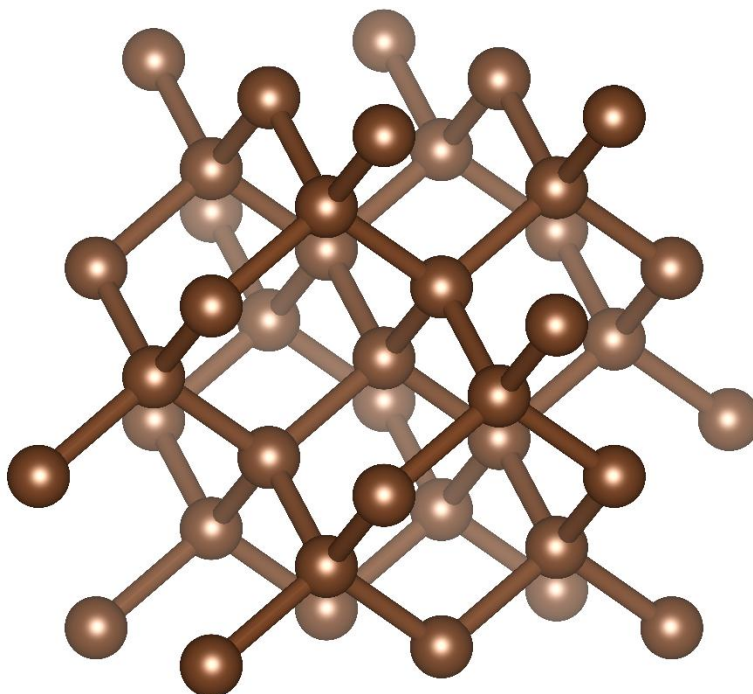


Figure 1-14. Illustration of the diamond crystal structure.

Unlike single-crystal diamond, which is an electrical insulator, nanocrystalline diamond is electrically conductive. This is due to the sp^2 hybridized (graphitic) carbon bonding found at the diamond grain boundaries. The conductivity at the grain boundaries translates into a high QE, resulting in a high photocurrent density in polycrystalline diamond photocathodes^{64,70,71}.

Surface termination

Dangling bonds on diamond surfaces are typically terminated with either hydrogen or oxygen, resulting in significant differences in surface properties. **Figure 1-15** shows the configuration for both terminations across the (100) plane. In hydrogen-terminated diamond, each surface carbon atom is occupied by a hydrogen atom. In oxygen-terminated diamond, oxygen atoms form bridge structures between the carbon atoms⁷².

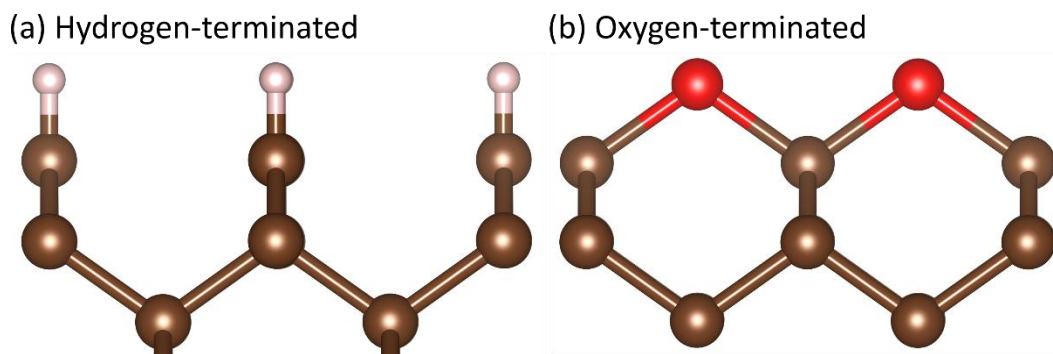


Figure 1-15. Illustration of the (a) H- and (b) O-terminated (100) diamond surfaces. Carbon atoms are brown, hydrogen atoms are white, and oxygen atoms are red.

Oxygen-terminated diamond is insulating, has a positive electron affinity (PEA), and is hydrophilic due to the negatively charged surface. This termination is typically achieved by exposure to an O_2 plasma, thermal oxidation in air, or treatment in strong acids^{72–74}. Oxygen-terminations are preferred for applications requiring electrical insulation and is also common for diamond electrochemical electrodes or biological applications.

Hydrogen-terminated diamond is electrically conductive, hydrophobic, and has a negative electron affinity (NEA). The conductivity is induced by a 2-dimension hole gas (2DHG), which is formed by the interaction between the dipole on the carbon-hydrogen (C-H) bond and adsorbates from the atmosphere, as explained by the surface transfer doping model^{72,75–77}, as shown in **Figure 1-16**. A hole layer forms on the diamond surface and an electron layer forms at the first monolayer of adsorbates. Adsorbates with low conduction band minimums produce denser hole gasses^{77–79}.

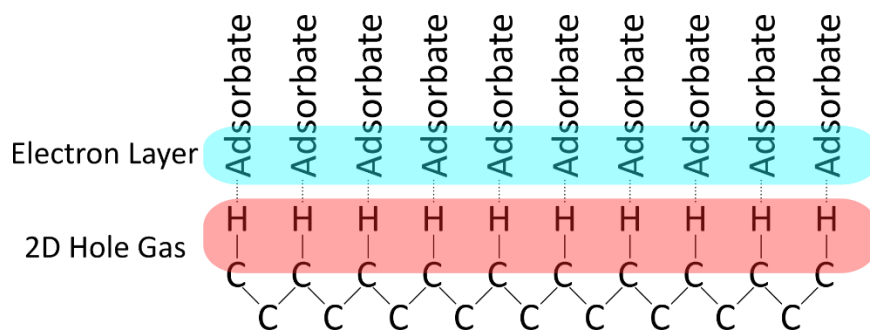


Figure 1-16. Illustration of transfer doping on the surface of hydrogen-terminated diamond. The C-H bond dipole interacts with adsorbates with low conduction band minimums, leaving behind a positively charged hole gas (red) on the surface of the diamond. The electrons consolidate on the first monolayer of adsorbates (teal).

Diamond formed by MP-CVD is hydrogen-terminated since the primary plasma constituent is hydrogen. Diamond can also be hydrogen-terminated by annealing in hydrogen or exposure to a hydrogen plasma^{80,81}. Due to the negative electron affinity, which promotes the release of electrons from the diamond surface into a vacuum, hydrogen-terminated diamond is commonly used in photocathode applications for VEDs. The conductive surface and fast response time also makes diamond perfect for high-power electronics such as high-quality field effect transistors (FETs)⁸²⁻⁸⁴.

Nitrogen Doping

Photoconductivity is an essential property for developing photocathodes, and this property is typically achieved by doping wide bandgap semiconductors with deep-level donors. The absorption of light increases the electrical conductivity of a photoconductive material by exciting electrons from a trapped donor level into the conduction band, as shown in **Figure 1-17**. This effect is present in nitrogen-doped diamond. Nitrogen acts as a substitutional donor with a donor energy level 1.7eV below the conduction band⁶⁸.

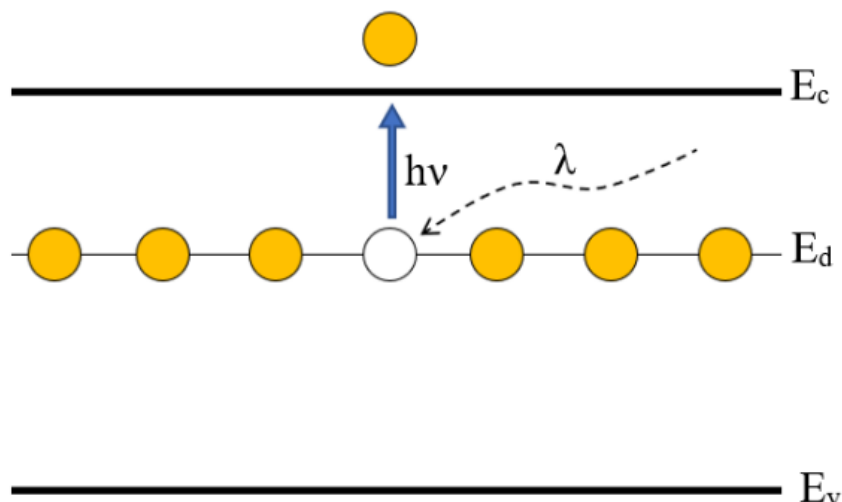


Figure 1-17. Generalized diagram demonstrating photoconductivity. Electrons (yellow) are trapped in a donor band within the bandgap of a material and are excited into the conduction band upon interacting with light.

Diamonds are commonly classified by impurity and defect type. Type I diamond contains nitrogen and has either aggregated (Type Ia) or isolated defects (Type Ib)⁸⁵. Type Ia diamonds have a broad energy band edge due to the large variety of possible defect clusters, including even-numbered nitrogen aggregates, odd-numbered nitrogen aggregates, optically active nitrogen-vacancy pairs, or a combination thereof. Type Ib diamond is ideal for electrical applications as the isolated point defects do not interact with other point defects, such as vacancies or adjacent nitrogen sites. The uniformity of the nitrogen defects in Type Ib diamond results in >10x magnification in quantum efficiency from diamond photocathode devices, as shown in **Figure 1-18**⁶⁸.

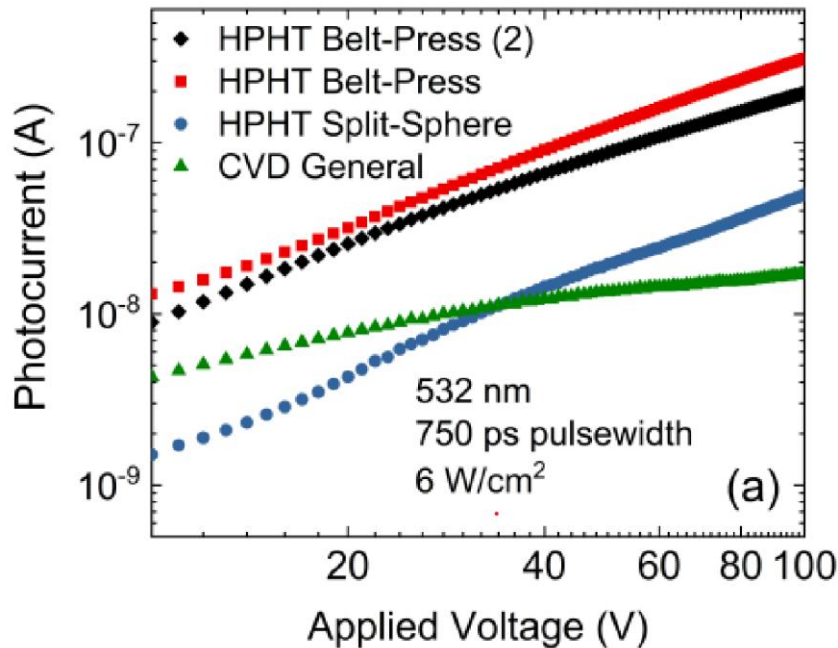


Figure 1-18. Photocurrent as a function of applied voltage⁶⁸. Green is Type Ia diamond. Red is Type Ib diamond, which shows an order of magnitude higher current.

Diamond Chemical Vapor Deposition

There are two common methods of diamond synthesis; plasma chemical vapor deposition (P-CVD) and high temperature, high pressure synthesis (HTHP). This dissertation will focus primarily on diamond CVD. Microwaves excite a mixture of hydrogen and methane into a plasma. The carbon ionized from the methane then deposits onto a diamond seed at temperatures between 700°C-1000°C, which allows for diamond growth at low pressures of around 100Torr⁸⁶⁻⁸⁹. A diamond seed is essential for diamond synthesis, otherwise only graphite would form. As the reaction proceeds, the hydrogen plasma quickly reacts with any graphite, leaving only high purity diamond. A diagram demonstrating the CVD system is shown in **Figure 1-19**⁹⁰.

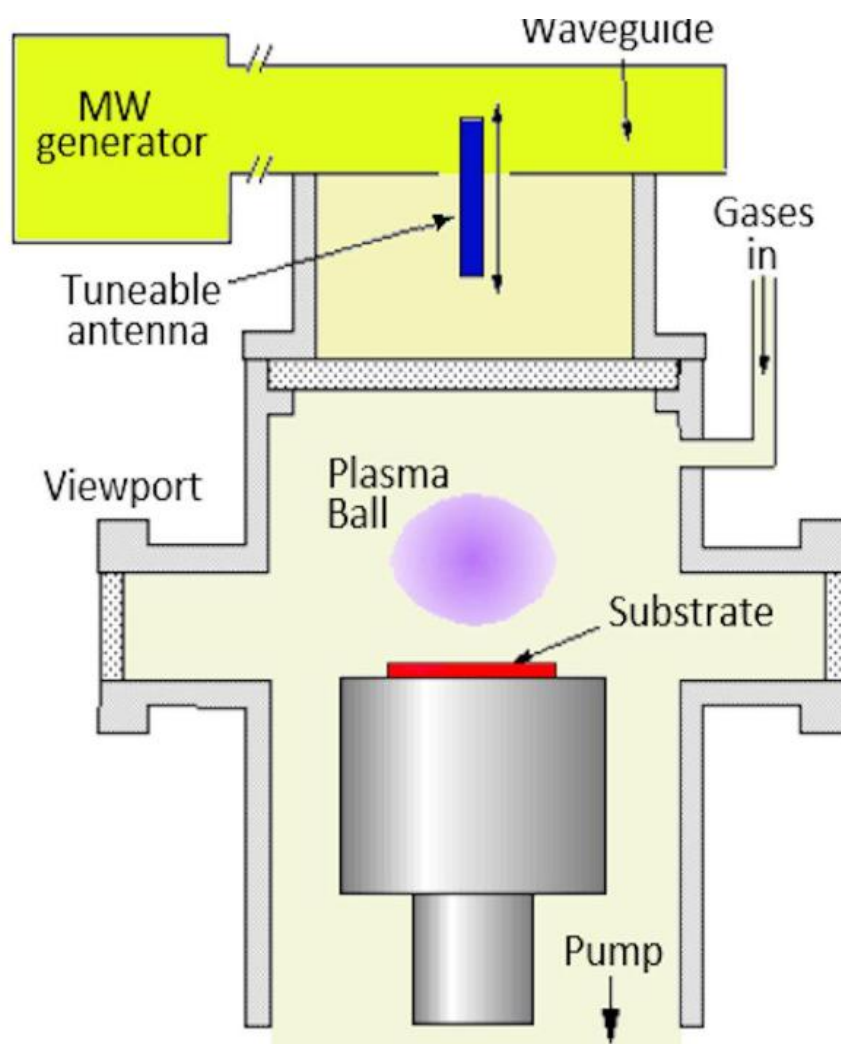


Figure 1-19. A plasma CVD system⁹⁰. A hydrogen and methane plasma ball deposits carbon onto a diamond substrate.

Nitrogen is commonly used to greatly accelerate the diamond growth rate⁹¹. Nitrogen lowers the activation energy for hydrogen removal at the dangling bonds on the diamond surface, which inhibits bonding of additional carbon^{92,93}. However, the impact of the nitrogen on the growth rate is dependent on the crystal facet, growth temperature, and pressure of the system^{86–96}. **Figure 1-20** shows the logarithmic relationship between nitrogen content in the plasma and the growth rate of diamond films⁸⁶. Since nitrogen defects are essential to diamond photoconductivity, it is important to pair this with the nitrogen incorporation into the diamond lattice, shown in **Figure 1-21**.

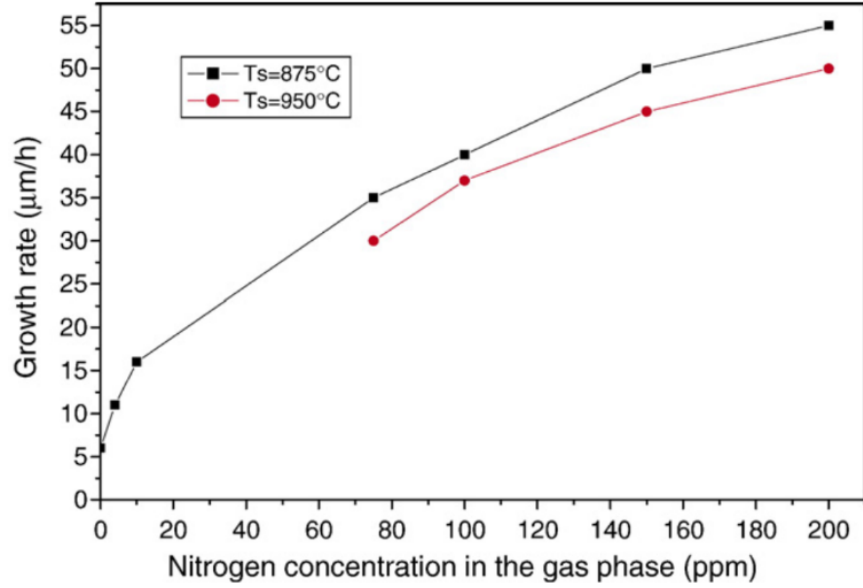


Figure 1-20. Diamond growth rate as a function of nitrogen flow rate at different substrate temperatures⁸⁶.

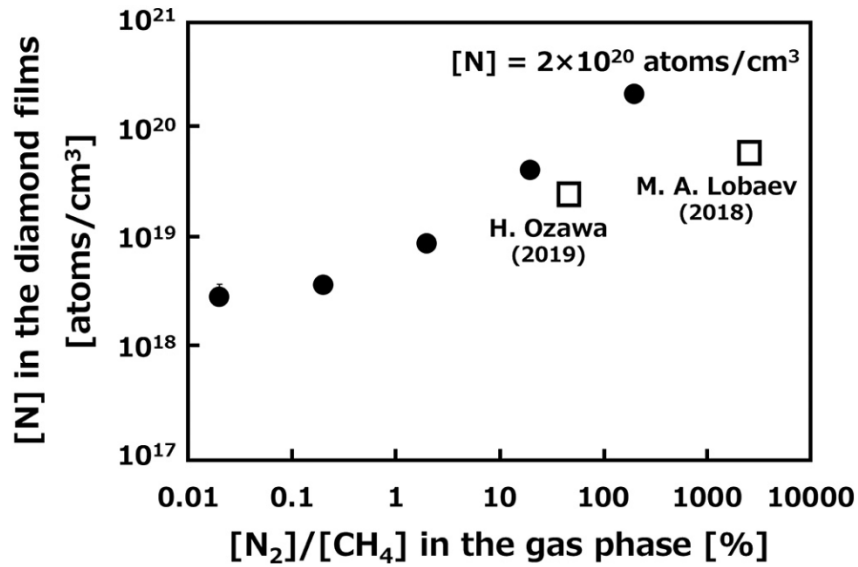


Figure 1-21. Nitrogen incorporation into CVD grown diamond in the (111) facet as a function of nitrogen/methane ratio in the gas phase at 800°C and 225 Torr⁹¹.

Diamond Etching and Fabrication

Developing a reliable etching technique is important for making diamond-based devices and will be explored throughout this dissertation. The most promising processing methods for

diamond devices use oxygen/argon or sulfur hexafluoride (SF₆) plasma to dry-etch the diamond surface^{97–99}, each with different effects. SF₆ has significantly higher etch rates. However, they are prone to creating V-shaped features in the diamond surface. Oxygen-based etching processes are much slower but are highly anisotropic and can create nearly vertical walls, at least in the (001)-plane. **Table 1-1** below lists some data on etching parameters using both etchants⁹⁸.

Table 1-1. Diamond plasma etch rates using various gas compositions, powers, bias voltages, and temperatures⁹⁸.

Gas, Flow [sccm]	Pressure [Pa]	RIE Power [W]	Temperature [°C]	Bias [V]	Etch Rate [μm h ⁻¹]
SF6, 10	6.67	30	300	200	3.6
SF6, 10	5.33	30	300	200	3.6
SF6, 10	0.133	40	300	300	5.2
Ar/O2 1:1	4	30	150	220	0.36
Ar/O2 9:3	6.7	50	200	300	0.7

Few studies have looked at etching rates as a function of nitrogen content, and none have investigated anisotropic behavior. Khokhryakov and Palyanov¹⁰⁰ investigated the impact of nitrogen content on the etch rate of the (111) face using a potassium nitrate melt at 700°C and found a parabolic relationship between etch rate and nitrogen concentration, shown in **Figure 1-22**.

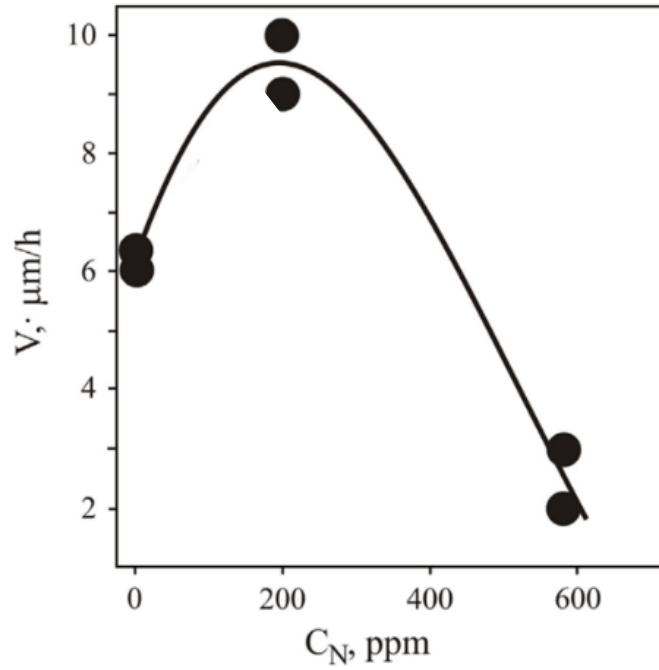


Figure 1-22. Etch rate of diamond as a function of nitrogen concentration using a potassium nitrate melt at 700°C, modified from Khokhryakov and Palyanov (2015)¹⁰⁰.

Chapter 2 - Common Characterization Techniques

Boron-Rich Compounds

Raman Spectroscopy

Raman spectroscopy can be used to identify different boron-rich compounds, as well as assess the crystal strain present in specific samples. Boron structural chemistry is complex, leading to many observed vibrational modes. First-order Raman spectra of boron-rich compounds can be broken into three sections: Interstitial element bond vibrations, inter-icosahedral bond vibrations, and intra-icosahedral bond vibrations. **Figure 2-1** below shows the first- and second-order Raman vibrational modes for B_6O ^{34,101–103}.

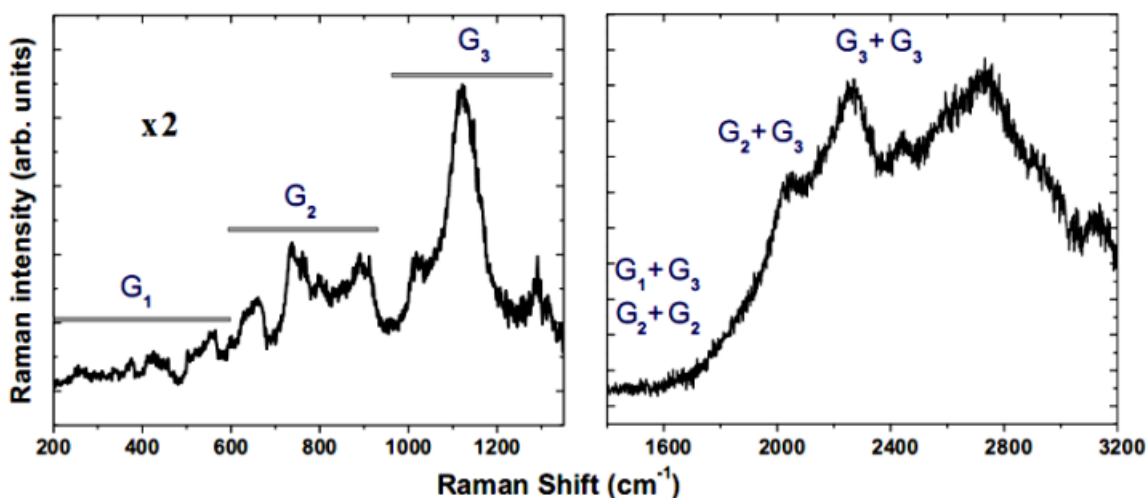


Figure 2-1. (Left) First- and (right) second-order Raman spectra of B_6O ¹⁰¹. Spectral band G_1 is assigned to vibrational modes involving oxygen atoms. Spectral band G_2 is assigned to intra-icosahedral (B-B) bonds. Spectral band G_3 is assigned to vibrational modes between icosahedra.

Spectral band G_1 , from 200 – 500 cm^{-1} , is assigned to B-O and O-O bond vibrations. The interaction between oxygen atoms in the B_6O crystal complex is very weak, so the O-O chain vibration at 373 cm^{-1} is barely visible. The peak complex just above 500 cm^{-1} is related to the motion of the B_{12} icosahedra about the oxygen atom¹⁰².

Spectral band G_2 , from $500 - 950\text{ cm}^{-1}$, is assigned to intra-icosahedral vibrational modes, and is similar between different boron-rich compounds. The most prominent peak is typically between $750 - 820\text{ cm}^{-1}$ and is attributed to the external three-centered bonds, which become compressed when two-centered bonds are stressed. The broadness of this peak is typically attributed to internal crystal strain³⁴.

Spectral band G_3 , from $950 - 1300\text{ cm}^{-1}$, is assigned to inter-icosahedral vibrational modes¹⁰¹. It is similar for most compounds based on the α -B crystal structure, such as B_6O , $B_{12}P_2$, and B_4C , and differs from compounds based on other boron structures, such as β -B. For example, the E_g and A_{1g} peaks ($1000 - 1200\text{ cm}^{-1}$) should be more prominent in B_6O than it is in β -B.

In both the G_2 and G_3 spectral bands, both the peak positions and intensities are strongly influenced by the metal dopants. For example, in vanadium-doped β -B, a strong peak develops at 1060 cm^{-1} and a peak at 1100 cm^{-1} splits. Since this work uses the metal flux method to grow boron compounds, this is an important impact to consider.

$C_2Al_3B_{48}$ is based on the tetragonal boron structure and is more complex than B_6O . However, there are many parallels between the Raman spectra, such as peaks around 800 cm^{-1} representing three-center bond vibrations. The strong peaks between $950 - 1300\text{ cm}^{-1}$ are attributed to inter-icosahedral bond vibrations. An example of Raman taken of $C_2Al_3B_{48}$ is presented in **Figure 2-2**³⁴.

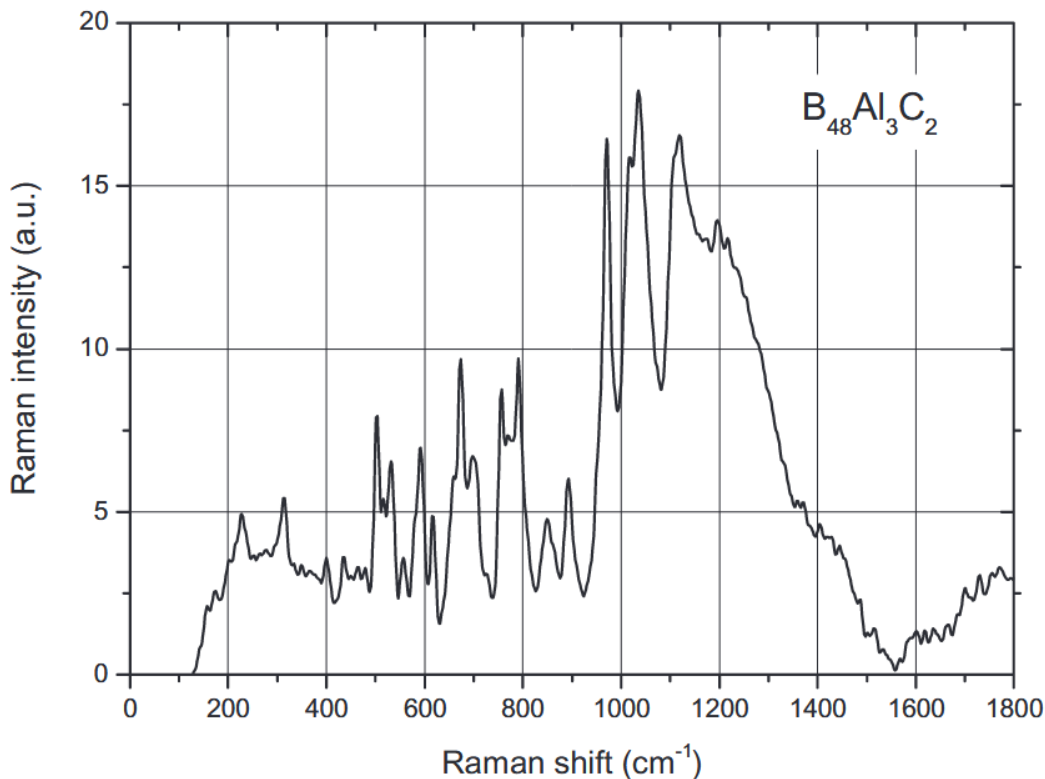


Figure 2-2. Raman spectrum of $C_2Al_3B_{48}$.³⁴

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is advantageous for identifying B_6O because the incorporation of oxygen into a boron lattice creates an easily identifiable set of peaks. Pure boron shows a peak at ~ 187.5 eV, boron oxide (B_2O_3) creates a single peak at ~ 192.5 eV, while B_6O generates a set of three peaks at 187.5 eV, 189 eV, and 193.5 eV^{104,105}, as shown in **Figure 2-3**. Charging effects can shift the relative positions of the three peaks associated with B_6O , with the high-energy peak at 192 eV shifting more than the two lower energy peaks.

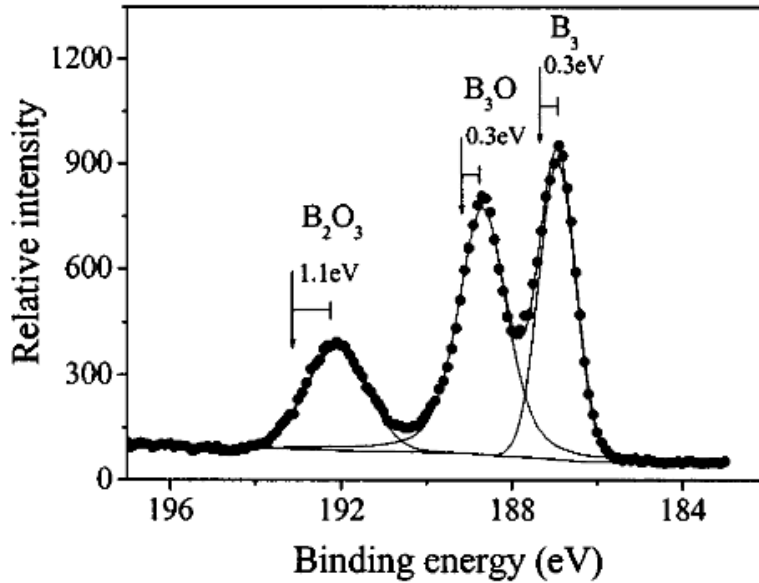


Figure 2-3. XPS B 1s spectrum of B₆O with intentional negative surface charging¹⁰⁴. The number above each peak indicates the peak shift due to the negative surface charging.

The three B₆O peaks are associated with different types of boron chemical bonds. The B₃ peak is associated with icosahedral boron bonding. The B₃O peak is associated with the trigonal oxygen bond linking boron icosahedra together. Finally, the B₂O₃ peak is associated with grain boundary impurities, which is evidenced by the depletion of the B₂O₃ peak by sputter-etching¹⁰⁴.

Diamond

Raman Spectroscopy

Raman spectroscopy is commonly used for structural analysis of diamond. There are two peaks most commonly addressed during Raman analysis of diamond; the “D-peak” at 1332 cm⁻¹ and the “G-peak” at 1580 cm⁻¹, as shown in **Figure 2-4**. The D-peak is related to sp³ hybridization, which is found in the bulk. The G-peak is related to sp² hybridization, which occurs at grain boundaries and certain defect sites^{71,106}.

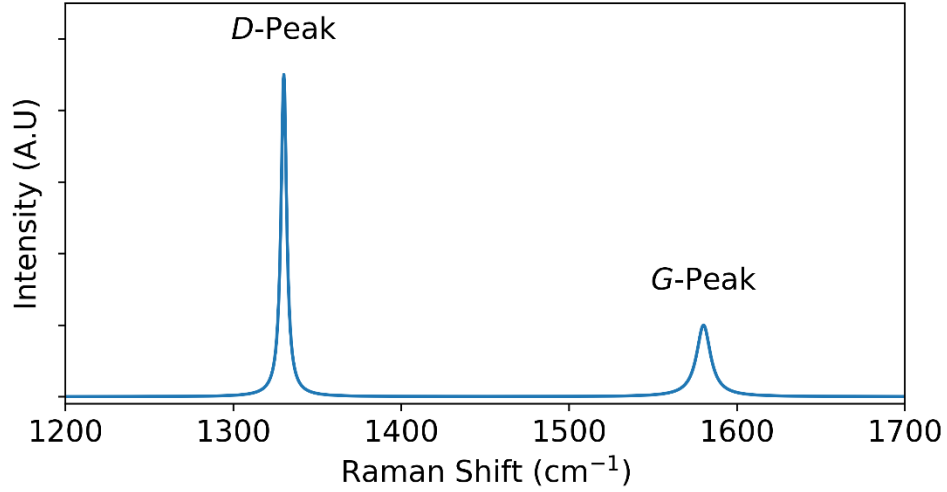


Figure 2-4. Simulated Raman spectra of diamond showing the “D-peak” and “G-peak” at 1332 cm^{-1} and 1580 cm^{-1} respectively.

Since the D-peak is related to the bulk intrinsic crystal structure, it can be used to assess crystallinity by measuring the full width at half maximum (FWHM). A Lorentzian curve (Cauchy distribution) is fit to the peak using Eqn. (2-1),

$$\text{Signal} = I \frac{\gamma^2}{4(x - x_o)^2 + \gamma^2} \quad (2-1)$$

where γ is the FWHM, x_o is the peak position, I is the peak intensity, and x is the Raman shift.

Smaller FWHM values indicate better crystallinity and reduced strain.

The ratio of the D-peak to the G-peak intensities indicate the relative presence of defective structures in the system. In polycrystalline diamond, the relative crystal grain size is calculated by the following figure of merit¹⁰⁷,

$$\beta_{D/G} = \frac{I_D}{I_G} \quad (2-2)$$

where I_D is the intensity of the D-peak and I_G is the intensity of the G-peak. A higher $\beta_{D/G}$ indicates larger bulk diamond grains, while a lower value indicates an increased density of structural defects.

Fourier-Transform Infrared Spectroscopy

Accurate analysis of the nitrogen concentration is essential to advance diamond technology. Fourier-transform infrared spectroscopy (FTIR) is a straightforward, simple, and reliable method of nitrogen analysis. FTIR is measured from 950cm^{-1} to 2700cm^{-1} , and Eqn. (2-3) is used to determine the nitrogen concentration in the diamond film¹⁰⁸:

$$N = 911.85 \left(\frac{S_N}{S_0} \right)^{0.9919} \quad (2-3)$$

where N is the nitrogen concentration in ppm, S_N is the peak area in the range $950\text{--}1450\text{ cm}^{-1}$ (related to nitrogen content), and S_0 is the peak area in the range $1500\text{--}2700\text{cm}^{-1}$ (intrinsic to diamond). This is illustrated using different types of diamond in **Figure 2-5**.

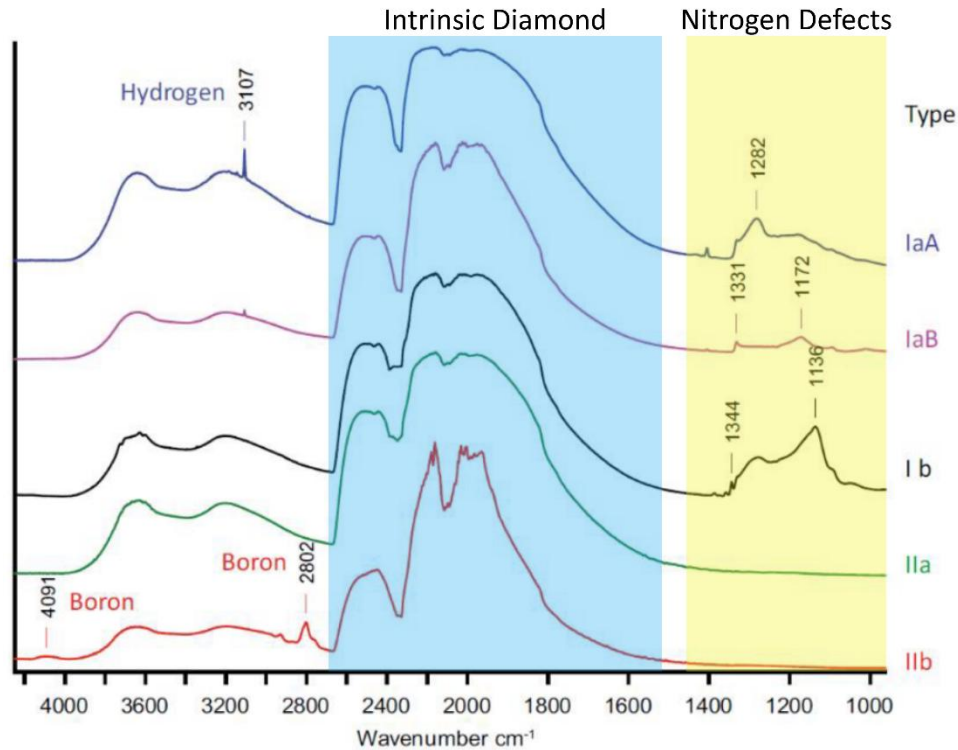


Figure 2-5. FTIR of diamond with various dopants. The intrinsic diamond peak range is highlighted in blue. The signal correlated with nitrogen defects is highlighted in yellow. This figure is modified from Martynova et al.¹⁰⁸.

Since the different defect centers present distinct spectra, FTIR is the common method for identifying the diamond type. Type II diamond has nitrogen content below the detection level. The clustering of diamond shifts FTIR peak positions, allowing Type Ia and Type Ib diamond to be distinguished under careful analysis^{108,109}. Isolated nitrogen defects (Type Ib) typically have peaks at 1136 cm^{-1} and 1344 cm^{-1} . Nitrogen clustering (Type Ia) shifts the resulting peaks. Two-nitrogen clusters (Type IaA) produces a peak at 1282 cm^{-1} . Four-nitrogen clusters (Type IaB) produces a peak at 1175 cm^{-1} . These small differences are significant in modelling the optical and electrical properties of the diamond defect centers.

Electrical Measurement Techniques

Circular Transmission Line Measurements

Circular transmission line measurements (CTLM) are used to calculate the surface resistance of a semiconductor and the contact resistance between a semiconductor and metal contact. A metal contact is deposited onto the material being measured. Rings of the material to be measured, with variable gap spacing (g) and internal radius (r), are exposed, creating an ohmic contact pad in the center of the ring and an ohmic contact surrounding the ring, as shown in **Figure 2-6**.

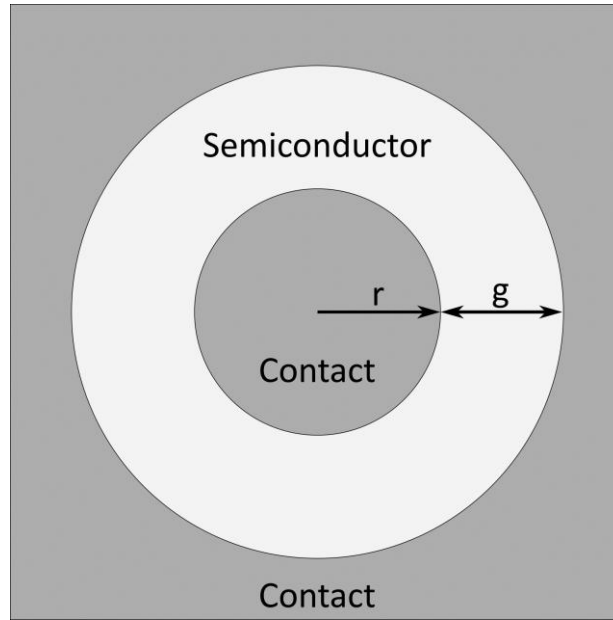


Figure 2-6. Circular transmission line measurement ring setup. There should be several exposed semiconductor rings with the same internal radius (r) but with variable gap spacing (g).

A current-voltage (I-V) curve is measured across the semiconductor by pressing electrical leads onto the metal contacts. The total resistance (R_T) is calculated using Ohm's Law.

$$R_T = \frac{V}{I} \quad (2-4)$$

Since the contacts are concentric circles, there is a higher current density at the interior of the ring than at the exterior of the ring. To account for this, a correction factor must be applied to the calculated total resistance across the ring. Once resistance is calculated for several rings of variable gap spacings, a linear model of total resistance as a function of gap spacing can be fit to the data, as shown in **Figure 2-7**.

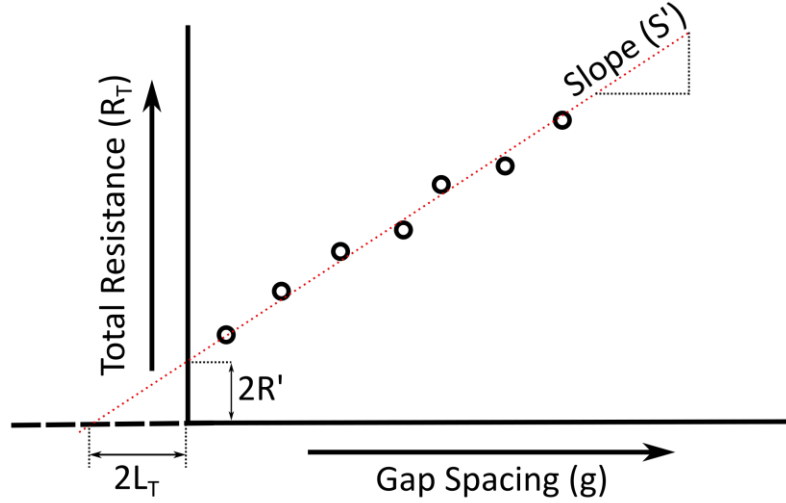


Figure 2-7. Total resistance as a function of gap spacing. Using ohmic contacts should produce a linear fit. From these model parameters, sheet resistance, contact resistance, and transfer length can be calculated.

A linear model should be fit to the total resistance (R_T) as a function of gap spacing (g).

The sheet resistance (R_{sh}) is calculated using the slope (S'), as shown in Eqn. (2-5).

$$R_{sh} = S' * 2\pi r \quad (2-5)$$

The contact resistance (R_c) is calculated by taking half the y-intercept, since there are two points of contact, and multiplying by the contact area, as in Eqn. (2-6).

$$R_c = R' * 2\pi r \quad (2-6)$$

The transfer length, (L_T), which is the distance required for the majority of the voltage drop underneath a metallic pad, is half the x-intercept, again because there are two points of contact. The transfer length is directly correlated to specific contact resistivity (ρ_c) using Eqn. (2-7).

$$\rho_c = \frac{L_t^2}{R_{sh}} \quad (2-7)$$

With these parameters, engineers can characterize materials for use in ever-shrinking devices in micro- and nanoelectronics. Next, we will assess how current emission is characterized for electron emission applications.

Fowler-Nordheim

Field electron (FE) emitters are commonly characterized using the Fowler-Nordheim (FN) plots, which are measured as I-V curves. The Fowler-Nordheim equation is given in Eqn. (2-8),

$$J = \frac{A\beta^2 E^2}{\phi} \exp\left(-\frac{B\phi^{\frac{3}{2}}}{\beta E}\right) \quad (2-8)$$

where J is the current density, ϕ is the work function of the emitter material, E is the applied electric field, β is the field enhancement factor, and A and B are the FN constants (1.546×10^{-6} A V^{-2} and 6.83×10^7 eV $^{-3/2}$ V cm $^{-1}$, respectively¹¹⁰). FN-plots are developed from the form below.

$$\ln\left(\frac{J}{E^2}\right) \text{ vs. } \frac{1}{E} \quad (2-9)$$

An example of an FN-plot is given in **Figure 2-8**. The linear region (Region I) represents an ideal FN emitter where current is limited by FN-tunneling. As voltage increases (Region II), emission will be limited by carrier concentration in the semiconductor material. As such, Region II is sensitive to temperature or incident light intensity, which excite additional carriers in a semiconductor. At the highest electric fields (Region III), impact ionization begins in the depletion zone, resulting in another linear segment¹¹¹.

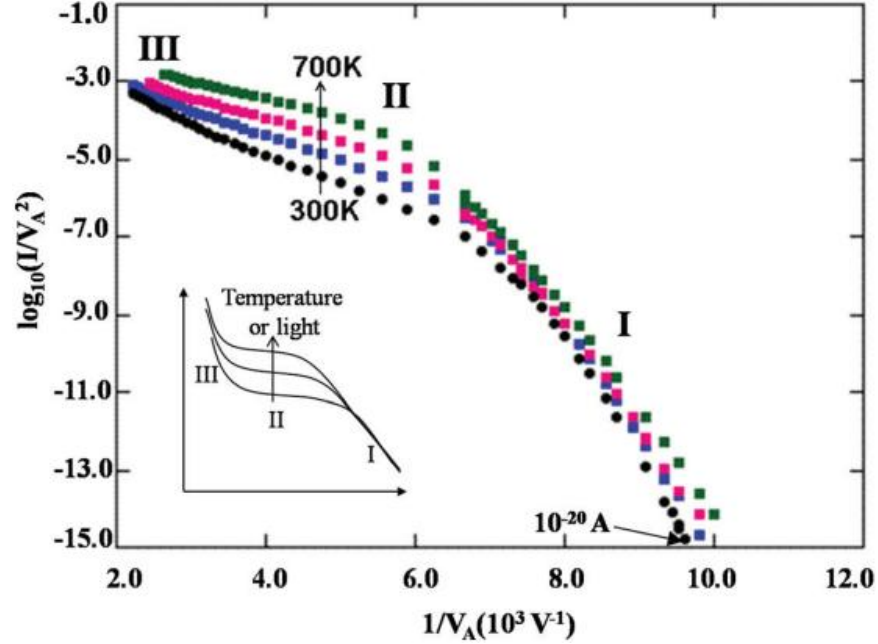


Figure 2-8. Fowler-Nordheim plot of a SiC nanowire single-emitter¹¹¹. Region I exhibits standard linear FN behavior. Region II is limited by carrier concentration. Region III is associated with ionization of the depletion zones at high electric fields.

For this work, the field enhancement factor β will be experimentally determined for large-area emitter arrays. β has two contributions, the enhancement due to local emitter geometry and the global enhancement related to the distribution of emission centers across the emitter surface¹¹². β is derived from the slope (S') of Region I of the FN-plot, shown in Eqn. (2-10).

$$S' = -\frac{B\phi^{\frac{3}{2}}}{\beta} \quad (2-10)$$

For maximum field emission, low density emission centers consisting of sharp, high aspect-ratio structures is preferred. These structures often look like arrays of tall pillars with refined, sharp tips from which electrons can be emitted.

Chapter 3 - Structure, Stability and Electronic Properties of Boron

Suboxide: A Density Functional Theory Study

Abstract

Boron suboxide (B_6O) is a boron-rich compound derived from the α -rhombohedral boron lattice with extreme hardness and unusual semiconducting properties. In this work, Density Functional Theory (DFT) was used to show that unit cell volume, mechanical strength, bandgaps, and thermodynamic stabilities of B_6O are influenced by the interstitial elements and point defects at the icosahedral sites. While the hexagonal unit cell volume (HUCV) varies with interstitial occupancy, it is the icosahedral defects that weaken the intrinsic bulk modulus of B_6O . Using the hybrid HSE functional, we confirmed that the perfect B_6O bulk is a p-type semiconductor with a direct bandgap of 1.8 – 3.0 eV. Furthermore, by screening the α -boron compounds systematically, we found that a simple octet rule may offer a consistent explanation for the variations in the computed electronic structures. The formation free energies calculated over a wide range of temperatures (0 - 2500 K) and pressures (0 - 80 GPa) predict that formations of interstitial defects become favorable only at higher temperatures (ca. 1800 K) in bulk B_6O lattices. The nudged elastic band (NEB) method was employed to identify the minimum energy pathways for the diffusions of dislocated B and O atoms. The diffusion of icosahedral B atoms has an energy barrier of 0.16 eV. More complex B diffusion paths involving the reorganization of icosahedral boron atoms incur higher barriers (> 1 eV). In contrast, the diffusion of interstitial O atoms is facile, with a barrier of 0.4 eV. Lastly, successive O insertions into the α -B lattice were performed using DFT to generate a basic understanding of the oxidation process. These calculations provide fundamental atomistic insights into the growth of B_6O crystals and control of its point defects.

Introduction

Since Weintraub¹¹³, B₆O has become one of the most studied α -boron compounds due to its unusual physical behaviors^{114–116} and untapped potentials in high-temperature thermoelectrics¹¹⁷, transparent electronics¹¹⁸, and photovoltaics¹¹⁸. Boron suboxide (B₆O) is a chemically stable and hard refractory material^{15,119–121}. The microhardness of B₆O is as high as 55 GPa^{12,23,119,122,123}, placing B₆O among the top superhard materials such as cubic boron nitride (cBN) and diamond^{121,123}. Like B₁₂P₂^{124,125} and B₁₂As₂^{125,126} the lattice of B₆O is derived from the α -rhombohedral boron (α -B), in which the B₁₂ icosahedra are packed in a primitive rhombohedral cell¹²⁷. For these compounds, the O, P, and As atoms occupy the center of the triangle formed by three neighboring icosahedra. While the adjacent P and As in B₁₂P₂ and B₁₂As₂ also form pairs with P-P and As-As inter-atomic bonds, these are absent in B₆O.

Many fascinating properties exhibited by B₆O can be traced to the twelve-atom icosahedra, with their chemical bonding comprehensively discussed in literature^{15,23}. The B–B bond lengths in α -B were determined by Bolmgren and coworkers¹¹⁶ using X-ray powder diffraction data and vary in the range of 1.56 ~1.84 Å. Each B₁₂ icosahedra can provide up to 36 valence electrons (i.e., 2s² 2p¹). Specifically, a majority of electrons (26 in total) participate in the three-center intra-icosahedral bonding, six for the two-center inter-icosahedral covalent bonding, and the remaining four for the inter-icosahedra three-center bonds¹⁸. Overall, the icosahedron in α -B is electron-deficient¹⁵. An interstitial O atom combines its six valence electrons (2s² 2p⁴) with the two electrons from the three-center inter-icosahedral bond, forming three two-center B–O bonds. Thus, the octet rule is satisfied by the O atom.

Several boron-rich icosahedral semiconductor compounds, including B₁₂P₂ and B₁₂As₂, have been confirmed to be *p*-type¹². It is believed that B₆O may also qualify as a promising *p*-

type transparent conducting oxide (TCO). The direct bandgap of the B₆O single crystal is predicted to be 2.8 eV¹²⁸. With a hole effective mass of ~ 0.6 ¹¹⁸, the charge carrier mobility shall be high compared to current TCO standard bearers such as CuAlO₂ and SrCu₂O₂. Akashi and coworkers¹¹⁷ demonstrated that B₆O also displays *p*-type conductivity using hot-pressed (30 MPa and 1400°C) samples. Varley *et al.*¹³ suggested that the *p*-type behavior possibly originates from the H- or C-substituted complexes at the O site using the many-body perturbation method.

Nevertheless, the relationship between *p*-type doping and conductivity is not established. This issue is further complicated by the lack of synthesis methods to control the crystal stoichiometry. The B₆O crystals obtained from hot pressing often contain amorphous phases¹²⁹. High-temperature, high-pressure solid-phase reactions between boron and boron oxide (B₂O₃) consistently yield higher quality B₆O single crystals^{17,114,116,123}. By dissolving boron into the B₂O₃ flux, crystals over 100 μm in size formed from the B₆O–B₂O₃ eutectic melt at 5.5 GPa and 2100°C¹³⁰. To aid synthesis, understanding the underlying chemistries responsible for vacancy formation and remediation is fundamental to revealing the intrinsic properties of B₆O. B-substituted at the interstitial **O_i** site (B antisites) produces *p*-type B₆O¹².

The α -boron compound family accommodates a large variety of interstitial elemental species (e.g., C, O, P, As). Varley *et al.*¹³ pointed out that removing an interstitial O from the B₆O lattice is energetically feasible. On the other hand, replacing the interstitial O with a B atom requires a higher energetic cost. The occupancy of interstitial elements also engenders variations in the physical properties of the α -boron compounds. Slack and Morgan showed that a correlation of O vacancy (**v_O**) concentrations with the hexagonal unit cell volume (HUCV) exists¹². In principle, the stoichiometric B₆O lattice yields the smallest HUCV because the B atom is significantly larger than O in diameter. Hence, it is possible to deduce the stoichiometries

of boron suboxide samples based on the measured HUCV. For instance, Bills and Lewis¹³¹ estimated that up to 40% of the $\mathbf{O}_v$ could be filled by B atoms.

The energetic costs to create defects (e.g., $\mathbf{v}_B$) in the icosahedra are much higher than oxygen vacancies. The high stability in B_{12} icosahedra justifies that α -boron compounds can withstand damage upon extensive irradiation, making it a promising candidate suitable for high-power beta-voltaic applications¹⁵. Huber and coworkers⁴⁸ found that the activation energy in the diffusion pathways for B atoms displaced from the icosahedra recombining with a $\mathbf{v}_B$ (a Frenkel defect pair) in the $B_{12}P_2$ lattice can be as low as a few milli-electron volts. Hence, the ability of B_{12} icosahedra to quickly repair their $\mathbf{v}_B$ also plays a role in the self-healing phenomena of several other α -boron compounds¹⁴.

In this work, Density Functional Theory (DFT) calculations were performed to understand how cell volume, bulk modulus, and band structures are affected by defects and structural variations at the lattice O (i.e., interstitial) and icosahedral sites of the α -phase B_6O (simply as B_6O). The formation energies were obtained to reveal the relative thermodynamic stabilities of various point defect structures, which is essential to control these structure-dependent physical and electronic properties for future applications. Moreover, nudged elastic band (NEB) calculations were performed to identify the minimum energy pathways (MEPs) and energy barriers encountered during the repair of interstitial O and icosahedral B defects. Lastly, the reaction energetics and structures from atomic O insertions were extracted from DFT to mimic the oxidations of the α -B lattice.

Computational Methods

Density Functional Theory (DFT)

All geometries optimizations and electronic structure calculations were performed using the Kohn-Sham DFT implemented in the Vienna *Ab Initio* Simulation Package (VASP)¹³². The projector augmented wave (PAW) method was employed to treat the core electrons¹³³. The total energies were computed using an energy cutoff up to 520 eV. The generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) functional (GGA-PBE) was employed for geometry optimizations and total energy calculations¹³⁴. A $(6 \times 6 \times 6)$ k -point mesh generated using the Monkhorst-Pack scheme was used to relax crystal lattices and obtain the electronic structures¹³⁵. Tests on the B₆O lattice using a much denser mesh $(12 \times 12 \times 12)$ confirm that both energy and structure have converged at the current setting. The criterion for the wavefunction convergence is 1×10^{-5} . The ionic relaxation is stopped when all forces are less than 0.02 eV/Å. The tetrahedron method with Blöchl corrections was adopted to compute the total energies of the materials¹³⁶. Bulk structures were optimized by allowing the primitive cell volume, shape, and atoms to relax. The energy bandgaps reported in the main text were calculated using the HSE06 functional¹³⁷ with a range-separation parameter (HFSCREEN) of 0.2 and a mixing parameter (AEXX) of 0.25.

Lattice vibrations and phonon calculations

The vibrational contribution to the free energy was estimated under the quasi-harmonic approximation. Here, phonon dispersions were calculated using PHONOPY¹³⁸. The phonon modes of B₆O and its defect structures were calculated using their $(2 \times 2 \times 2)$ supercells. The vibrational entropy takes the form of Eqn. (3-1):

$$S_{\text{vib}}(T) = \frac{1}{2T} \sum_{qj} \hbar \omega_{qj} \coth \left[\frac{\hbar \omega_{qj}}{2k_B T} \right] - k_B \sum_{qj} \ln \left[2 \sinh \left(\frac{\hbar \omega_{qj}}{2k_B T} \right) \right] \quad (3-1)$$

where k_B and $\hbar$ are the Boltzmann and the reduced Planck's constants. ω_{qj} is the phonon frequency of phonon mode (q, j). Moreover, the zero-point energy (ZPE) corrections were also obtained directly from PHONOPY.

Mechanical and thermodynamic properties

The thermodynamic properties of bulk crystals were calculated as functions of pressure and temperature. First, the pressure dependence of the free energies is described according to the 4th-order Birch-Murnaghan (BM4) equation of state (EOS) as in Eqn. (3-2):

$$E(V) = a + bV^{-\frac{2}{3}} + cV^{-\frac{4}{3}} + dV^{-2} \quad (3-2)$$

The coefficients in the BM4 EOS for each compound were determined by compressing and expanding the unit cell within 10% of the equilibrium cell volume. The bulk moduli (**Table 3-1**) were calculated using Eqn. (3-3):

$$B(V) = V \frac{\partial^2 E}{\partial V^2} \quad (3-3)$$

The Fermi-Dirac distribution, Eqn. (3-4), is used to calculate $S_{el}(T)$ according to Eqns. (3-5):

$$f(\varepsilon, T) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1} \quad (3-4)$$

$$S_{el}(T) = -\gamma k_B \int n(\varepsilon) [f \ln f + (1 - f) \ln(1 - f)] d\varepsilon \quad (3-5)$$

where γ is 1 for spin-polarized calculations, $n(\varepsilon)$ represents the electronic density of states (DOS), and $f(\varepsilon, T)$ is the Fermi distribution function expressed by Eqn. (3-4), where ε_f and μ are the Fermi energy and the electronic chemical potential, respectively. These parameters ensure that the Fermi function yields the correct total number of electrons corresponding to the specified temperature.

The configurational entropy (S_{config}), as expressed in Eqn. (3-6), can stabilize defect formation energies¹³⁹:

$$S_{\text{config}} = k_B \ln \frac{N!}{(N - n_v)! n_v!} \quad (3-6)$$

where N represents the number of available sites in the lattice, and n_v represents the number of defects (vacancy) in the unit cell. The values of N and n_v were determined based on the symmetry of each defect structure. For $\text{B}_{6.5}\text{O}_{0.5}$, N and n_v assume the values of 2 and 1, respectively. Nevertheless, it should be noted that N increases rapidly with the unit cell volume. The lack of symmetry due to defects boosts S_{config} , as shown in **Appendix Figure A.1** using larger N values.

For pure boron compounds, van Setten et al.¹⁴⁰ showed that the zero-point energy (ZPE) influences the energetic ordering. Hence, the ZPE term is included in all thermodynamic calculations. Then, the free energies, $G(V, T)$, as a function of cell volume and temperature, are calculated according to Eqn. (3-7)

$$G(T, V) = E(V) + ZPE - T(S_{\text{vib}} + S_{\text{el}} + S_{\text{config}}) \quad (3-7)$$

summing over the DFT total energies, and the S_{vib} , S_{el} , and S_{config} terms. The relative thermodynamic stability was evaluated based on the formation energies (ΔG_f) defined by Eqn. (3-8),

$$\Delta G_f = G_{\text{def}} - \frac{n_B}{12} G_{\alpha-B} - \frac{n_O}{2} \mu_{\text{O}_2} \quad (3-8)$$

where G_{def} represents the free energy of a defect structure. $G_{\alpha-B}$ and μ_{O_2} are the free energy of defect-free α -B and O_2 .

Nudged Elastic Band (NEB) calculations

The atomic diffusion minimum energy paths and energy barriers were identified using the climbing-image NEB method¹⁴¹. Five NEB images linearly interpolated between the optimized endpoints were used. A spring constant of 5.0 eV/Å² was chosen between the images. The conjugate gradient optimizer implemented in VASP (IOPT=2) was used. The default finite difference step size (0.005) and the maximum allowed step size for translation (0.2) were applied for all transition state searches.

Results and Discussion

Bulk α -B and B₆O structures

The rhombohedral primitive cells of α -B and B₆O were initially retrieved from the Materials Project for bulk optimizations²⁷. These cells contain 12 icosahedral B atoms. We reported the optimized lattices (**Table 3-1**) using a pair of hexagonal cell parameters (i.e., *a* and *c*). For α -B (**Figure 3-1a**), the optimized lattice constants with the GGA PBE functional are *a* = 4.90 Å and *c* = 12.55 Å (HUCV = 261 Å³), which agree very well with the X-ray diffraction data¹². For B₆O (**Figure 3-1b**), the lattice constants yielded by the GGA-PBE functional are *a* = 5.39 Å and *c* = 12.32 Å (HUCV = 310 Å³), respectively. The hexagonal cell volume was slightly overestimated compared to the experimental measurements provided by Slack (also listed in **Table 3-1**)¹². The overestimation of HUCV can be corrected by the hybrid HSE06 functional. As summarized in **Table 3-1**, the *a* and *c* parameters from the hybrid functional in this work match quite well with the calculations at the GW and HSE level reported by Varley and coworkers¹³.

B₆O and α -B share the same lattice symmetry (i.e., $R\bar{3}m$). In B₆O, the two interstitial O atoms are arranged along the trigonal [111] direction. The O atoms energetically prefer to bond with three adjacent B_I atoms (**Figure 3-1b**). The B–O bond length is 1.50 Å. For B₁₂P₂, B₁₂P₂,

and B₄C, their interstitial atoms (i.e., P, As, C) occupy similar positions at the interstitial sites. The separation between the O atoms is 3.01 Å versus the distance (3.06 Å) measured by Bolmgren and coworkers¹¹⁶. The inter-atomic distances between the pnictide atoms (i.e., P and As) in B₁₂P₂ and B₁₂As₂ are 2.25 Å and 2.41 Å, respectively. These pnictide P and As atoms form one additional bond by accepting one *p* electron from each other to satisfy the octet rule. By combining the three-centered inter-icosahedral electrons with the O 2s and 2p electrons, the octet rule is already satisfied for the O atoms without forming the O–O bond.

Table 3-1. The hexagonal lattice constants, HUCVs, bulk moduli, bandgaps of α -B, B₆O, and defect structures.

Methods	a (Å)	c (Å)	HUCV (Å ³)	Bulk modulus (GPa)	Bandgap (eV)	References
α-B						
GGA-PBE	4.90	12.55	261	206	1.4 (indirect)	This work
HSE06	4.88	12.50	258		2.0 (indirect)	This work
B₆O						
GGA-PBE	5.39	12.32	310	230	2.1 (direct)	This work
HSE06	5.36	12.26	305		2.8 (direct)	This work
G0W0, GGA	5.39	12.32				Varley et al. ¹³
HSE (32%)	5.35	12.26				Varley et al. ¹³
Experimental	5.40	12.31				Kurakevych, Solozhenko ¹²²
	5.31	12.36	302			Slack and Morgan ¹²
				314		Chen et al. ¹⁴²
Defect structures						
B ₆ O _{0.5}	5.20	12.45	291	187	3.3 (indirect)	This work
B _{5.5} O	5.39	12.31	310	165	metallic	This work
B _{6.5} O _{0.5}	5.56	12.26	328	186	metallic	This work
B _{5.5} O _{1.5}	5.29	12.81	310	174	metallic	This work

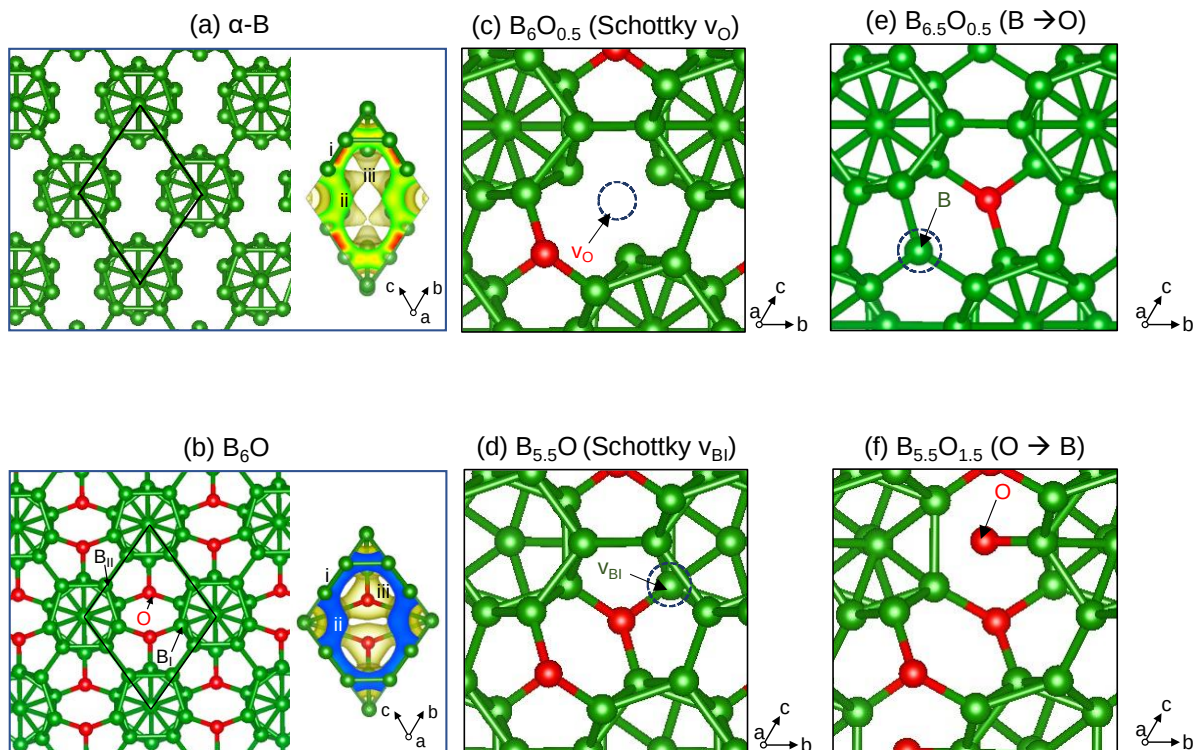


Figure 3-1. (a) α -B (b) Bulk B_6O structure in the rhombohedral unit cell. The B_I and B_{II} atoms in B_6O are labeled in (b). (c-d) $B_{12}O$ and $B_{11}O_2$ with Schottky point defects (dashed circles and arrows indicate B and O point defects); (e) $B_{13}O$ with a substitutional B (i.e., B antisite); and (f) $B_{11}O_3$ with one icosahedral B replaced by O (indicated by the arrow). Red: O; green: B. The total charge densities are plotted for α -B and B_6O as inset figures in (a) and (b), respectively. Vesta²² was used to visualize charge density iso-surfaces (iso-surface level = 0.0805).

The inter-icosahedral and intra-icosahedral distributions of the total charge density were plotted for α -B and B_6O crystals (inset figures of Figure 3-1a-b). As expected, the charge accumulates along the inter-icosahedral B–B bonds (labeled as i). Charge accumulation is also observed by cutting through the triangular face of the icosahedron (labeled as ii), confirming the existence of the intra-icosahedral three-center bonds^{15,143}. Moreover, charge accumulates at the vacancy sites of α -B (labeled as iii), originating from the four second-shell electrons contributed by the 12 icosahedral B atoms. In B_6O , similar high charge densities occur along the B–B bond and across the icosahedral face. In addition, charges are also accumulated at the O occupation site.

Defective B₆O and properties

Four defect structures were considered: Schottky-type O and B vacancies (Figure 3-1c-d), a B antisite (Figure 3-1e), and one icosahedral B atom substituted by O (Figure 3-1f). To reflect the B and O occupancy, fractional stoichiometries were adopted to represent the defect structures such as B₆O_{0.5}, B_{5.5}O, B_{6.5}O_{0.5}, and B_{5.5}O_{1.5} relative to B₆O. For instance, a stoichiometry of 0.5 in B₆O_{0.5} indicates only 50% of the O sites are occupied, and the system is O-deficient. The same interpretation applies to B when its stoichiometry is different from 6. The B_I and B_{II} atoms are not all chemically equivalent. The total energy calculations suggest that it is energetically favorable to remove or replace the B_I atom, which directly bonds with O, to form B_{5.5}O and B_{5.5}O_{1.5}. The phonon dispersions were calculated to verify if the defect structures were stable. As shown in **Appendix Figure A.2**, B₆O, B₆O_{0.5}, and B_{6.5}O_{0.5} are dynamically stable at 0 GPa. These results are expected since O-deficient B₆O compounds have been confirmed experimentally¹³¹. However, B_{5.5}O and B_{5.5}O_{1.5}, which contain a vacancy at the B_I site (denoted as ν_{B_I}), display negative phonon frequencies, indicating that icosahedral defects are unstable.

By occupying the inter-icosahedral sites of α -B, the unit cell volumes increase. In practice, the HUCV values are an indicator of the crystal stoichiometries and compositions¹³¹. As shown in **Figure 3-2a**, the HUCV of α -B expands from 261 Å³, to 291 Å³ for B₆O_{0.5}, and then to 310 Å³ (B₆O). HUCV also depends on the atom type at the interstitial site. In **Figure 3-1a**, the largest HUCV value corresponds to B₁₃O, where the interstitial O is replaced by a B atom (a boron anti-site), whose diameter is approximately 50% larger¹². This trend can be extended to B₁₂P₂ and B₁₂As₂. The reported HUCV values for these compounds are 367.7 Å³ and 389.1 Å³, respectively¹². The point defects in the icosahedra do not seem to affect the cell volume. The HUCVs of B_{5.5}O and B_{5.5}O_{1.5} remain unchanged (310 Å³) from B₆O.

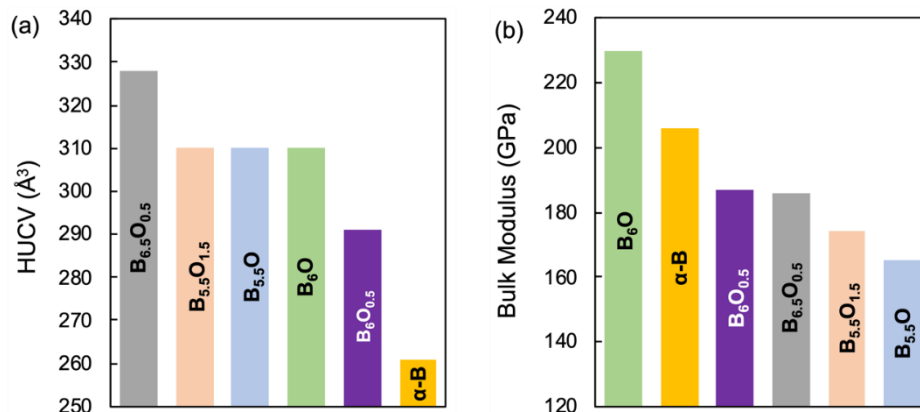


Figure 3-2. (a) Hexagonal unit cell volumes (HUCV, Å³) and (b) bulk moduli (GPa) of α -B, (b) organized in decreasing order. Yellow: α -B; green: B_6O ; purple: $B_6O_{0.5}$; blue: $B_{5.5}O$; grey: $B_{6.5}O_{0.5}$; and orange: $B_{5.5}O_{1.5}$.

The α -boron compounds are generally incompressible due to the short, strong intra-icosahedral B–B bonds. Slack and Morgan¹² pointed out that the addition of B–O bonds, which are stronger than B–B, makes B_6O even less compressible than pure α -B. As shown in **Figure 3-2b**, the bulk moduli of B_6O and α -B are 230 GPa and 206 GPa, respectively. The bulk moduli of all defective structures are lower. The bulk modulus of $B_6O_{0.5}$ reduces to 187 GPa, closely followed by $B_{6.5}O_{0.5}$, with one interstitial O replaced by B. The imperfect interstitial site occupation significantly impacts the bulk modulus to such an extent that non-stoichiometric B_6O becomes more compressible than α -B. Defects in icosahedra, both hetero-atom substitution ($B_{5.5}O_{1.5}$) and point vacancy ($B_{5.5}O$), further reduce the bulk modulus.

Many α -boron compounds are wide bandgap semiconductors. Their energy bandgaps generally fall between 2 to 4 eV¹². The band structures and energy bandgaps of α -B and B_6O presented in **Figure 3-3a-b** and **Table 3-1** were determined with the hybrid HSE06 functional as the benchmark. α -B has an indirect bandgap of 2.0 eV, versus a direct bandgap of 2.8 eV for B_6O , both in good agreement with the bandgaps calculated using the G_0W_0 method¹³. The band structures are susceptible to point defects in the B_6O lattice. B_6O with an interstitial v_O has an

indirect bandgap of 3.3 eV (**Figure 3-3c**). Otherwise, the bandgaps vanish entirely if the icosahedron contains a Schottky v_{B_I} defect (**Figure 3-3d**) or the O heteroatom (**Figure 3-3e**). Our calculations suggested $B_{6.5}O$ also becomes metallic when one interstitial O is replaced by B (**Figure 3-3f**).

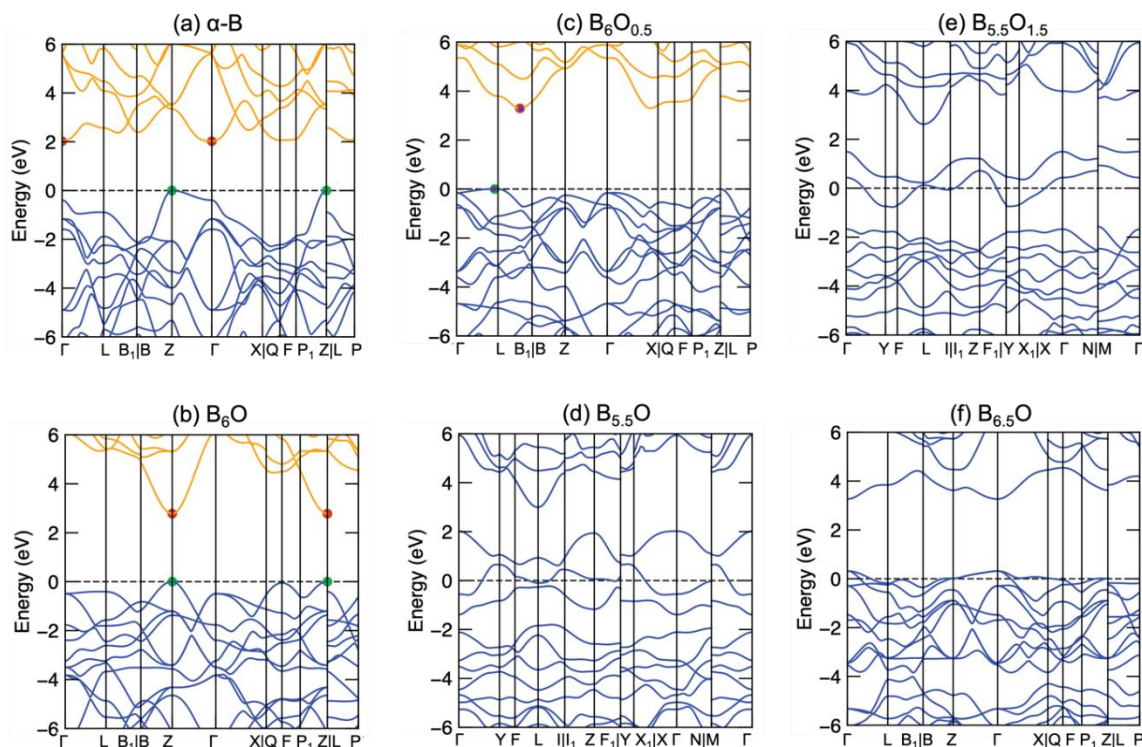


Figure 3-3. Band structures of (a) α -B, (b) B_6O , (c) $B_6O_{0.5}$, (d) $B_{5.5}O$, (e) $B_{5.5}O_{1.5}$, and (f) $B_{6.5}O$ generated using the hybrid HSE06 functional. The band edges (green: valence band maximum; red: conduction band minimum) are labeled for α -B, B_6O , and $B_6O_{0.5}$ that possess an indirect or direct bandgap. All band structures were automatically generated with the *sumo* package¹⁴⁴.

To better interpret the variations in the mechanical and electronic properties of defective B_6O , we selected α -boron compounds with their interstitial sites occupied by other main group elements X (X = C, N, P, S, As, and Se), denoted as $B_{12}(X-X)$ (or $B_{12}(X-X-X)$), $B_{12}(O-X)$, $B_{12}(X-B-X)$, and $B_{12}(B-X)$. Using the characteristic HUCV of these compounds as a descriptor, we first attempted to establish the relationship with their bulk modulus values (**Appendix Figure A.4a**), which decrease as HUCV increases. However, α -B and $B_6O_{0.5}$, which miss or consist of

no interstitial atoms, disobey the general trend. The bulk moduli of the compounds from the group of $B_{12}(B-X)$ are all lower than the predictions by the linear regression based on the actual HUCV. The calculated HUCV and bulk modulus for each compound are listed in **Appendix Table A.1**.

The electronic band structures and energy band diagram for the semiconductor materials among the chosen compounds to identify their electronic identities. These band structures (**Appendix Figure A.3**) are organized based on the interstitial atoms and their positions in the periodic table. The compounds remain as semiconductors when the same type of atoms occupy their interstitial sites except for $X = N$. For other interstitial pnictide atoms (i.e., P and As), the compounds are expected to be *p*-type semiconductors. Varley *et al.*¹³ discussed the possible roles of interstitial atoms (e.g., H, N) acting as electron donors or acceptors within the bandgap. Unlike $B_{12}P_2$, $B_{12}As_2$, or even $B_{12}AsP$, the two interstitial N atoms in $B_{12}N_2$ lack the inter-atomic N–N bonding. Hence, each atom carries one unpaired 2p electron and becomes an acceptor. The same rule can be applied to B_6ON , the only compound exhibiting the metallic character. We also predicted that all $B_{12}(X-B-X)$ and $B_{12}(B-X)$ compounds containing a B atom at their interstitial sites are metallic. Like B_6ON , the interstitial atoms in these compounds are electron acceptors. The only exception is $B_{13}N_2$, in which the B atom sandwiched between two N atoms carries a lone electron and is a donor.

Understanding the broad trend of the electronic structures will help discover the ideal α -boron compounds for specific applications. Structures like B_6OC and B_6ON are relevant because the substitutions of interstitial O by C or N impurities are thermodynamically favorable. Varley *et al.*¹³ suggested that an N and H rich environment could even destabilize the growth of B_6O due

to the formation of the NH complex. Carbon is another common impurity that interferes with the crystallization of α -rhombohedral boron¹⁴⁵.

Thermodynamic stability

The dependence of formation energies on temperature and pressure ($\Delta G_f(T, p)$) are shown in **Figure 3-4** to reveal the thermodynamic conditions favoring the formation of specific point defects. The stable form of α -B and O₂ was used in Eqn. (3-8) as the reference for elemental B and O, respectively. **Figure 3-4a** plots $\Delta G_f(T, p)$ as a function of temperature (0~2500 K) at their equilibrium volume (i.e., 0 GPa). Thermodynamically, the lowest ΔG_f corresponds to the stoichiometric B₆O, while ΔG_f for all other defective structures are higher. Below 500 K, B_{5.5}O_{1.5} and B_{5.5}O are thermodynamically favored, even though the phonon dispersions suggest that both compounds are dynamically unstable. The formation energy of B_{5.5}O_{1.5} remains lower over other systems up to 1800 K due to a higher number of the strong B–O bond. This trend will reverse and shifts the thermodynamic favorability toward the O-deficient structures (e.g., B₆O_{0.5}) only at much higher temperatures (i.e., > 1800 K) so that the formation of B–O bonds will be penalized due to high O₂ entropy cost. At 2500 K, **Figure 3-4a** also shows that the ΔG_f of B_{6.5}O_{0.5}, with an even less O content than B₆O_{0.5}, becomes lower than B_{5.5}O_{1.5} and B_{5.5}O.

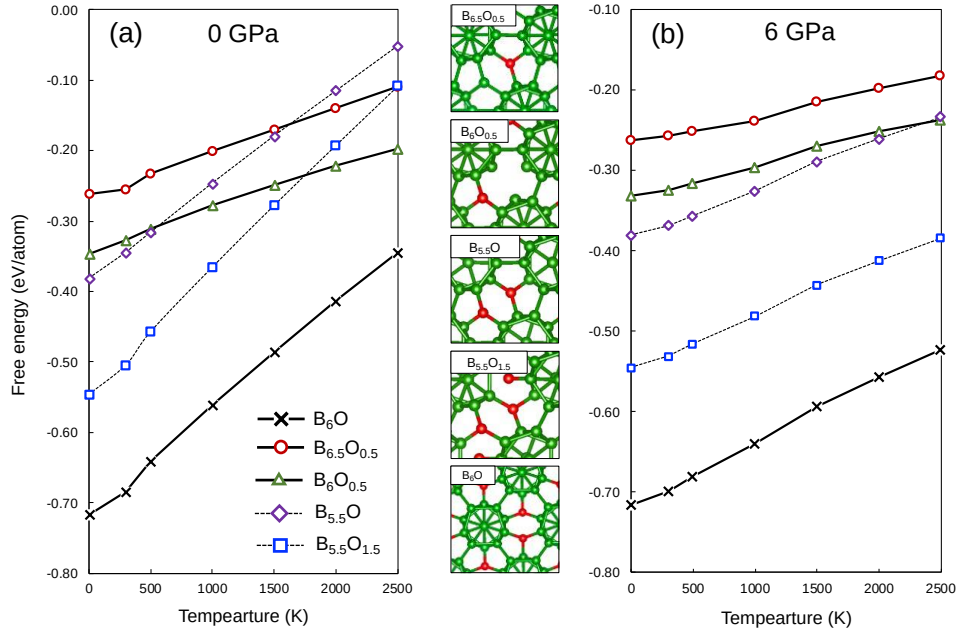


Figure 3-4. Formation energies (ΔG_f in eV/atom) of B_6O , $B_6O_{0.5}$, $B_{5.5}O$, $B_{6.5}O_{0.5}$, and $B_{5.5}O_{1.5}$, plotted as a function of temperature (0-2500 K) at (a) 0 GPa, and (b) 6 GPa. The pressure corresponds to the lowest defect formation energies for each system. Cross: perfect B_6O ; square: $B_{5.5}O_{1.5}$; diamond: $B_{5.5}O$; triangle: $B_6O_{0.5}$; circle: $B_{6.5}O_{0.5}$.

A broad range of pressure conditions was also considered in this work. Here, the ΔG_f evaluated at 6 GPa (i.e., $\sim 1\%$ isotropic compression of the unit cell) were chosen for discussion (**Figure 3-4b**) since most high-pressure B_6O syntheses are carried out under similar pressures. As shown in **Figure 3-4b**, the thermodynamic ordering related to defect formations remains identical to that at 0 GPa and low temperatures. In contrast, the ordering remains unchanged except at extreme temperatures at 6 GPa. At 2500 K, the ΔG_f of $B_6O_{0.5}$ becomes lower than that of $B_{5.5}O$ due to a shortening of intra-icosahedral B–B bonds which compensate for the intra-icosahedral defects when compressed at high pressures. ΔG_f also becomes less dependent on the temperature as the additional stabilization cancels some O_2 entropic penalties.

The variations of ΔG_f for all defect structures do not vary monotonically with pressures. As shown in **Appendix Figure A.5**, the ΔG_f minimum exists for each temperature. The trends

corresponding to other pressures are also shown (**Appendix Figure A.6**). Overall, the same trend is retained at elevated pressures. However, it is interesting to note that, at 80 GPa, ΔG_f increase abruptly at 1000 K. At 1250K, the thermodynamic ordering changes as the ΔG_f of $B_6O_{0.5}$ is lower than that of $B_{5.5}O_{1.5}$. Calculations of ΔG_f suggest that the defect formations can be thermodynamically challenging for a lattice with low defect concentrations. In addition, high temperature and lower pressure may shift the thermodynamic favorability toward certain types of defect formation, such as $B_6O_{0.5}$, over the other defects.

The contributions from S_{el} and S_{config} in systems with high symmetry or low defect concentrations are relatively small compared to S_{vib} . Nevertheless, ΔG_f can be significantly lowered with S_{config} for mixed or defective materials. Here, the DFT calculated ΔG_f at 6 GPa is corrected using S_{config} calculated by assuming $N = 15$. As a result, ΔG_f for all defect structures decrease along with increasing temperatures. At approximately 1400 K, defect formation (i.e., $B_{5.5}O_{1.5}$) is favored over the formation of the stoichiometric B_6O , as shown in **Appendix Figure A.7** in the Supporting Information. At even higher temperatures, the other defect structures also display similar behavior. At 1500 K and 6 GPa, the formations of $B_6O_{0.5}$ and $B_{6.5}O_{0.5}$ are competitive against the stoichiometric B_6O (**Appendix Figure A.7**).

Migrations of B and O atoms within B_6O lattice

Upon high energy radiation, atoms (i.e., B or O in B_6O) can be displaced from their equilibrium positions. Hence, defect structures such as the Frenkel pair are frequently encountered⁴⁸. Although there is a strong thermodynamic driving force for the recombination of displaced B or O with the vacancy site, the energy barrier along the diffusion pathway may still impede or even halt the healing process. Here, atomic migrations within the B_6O lattice containing Frenkel pairs based on the nudged elastic band (NEB) calculations will be discussed.

For all NEB calculations, the initial state configurations represent structures with the Frenkel defects that were relaxed to the local potential energy minima, whereas the final state configurations (FS) represent the *healed* structures. A $(2 \times 2 \times 2)$ supercell consisting of eight icosahedra was used to prevent the displaced atom from interacting with its periodic image. Five intermediate images were used to probe the minimum energy pathway (MEP). The climbing image technique is applied in NEB calculations to ensure that the highest image is pushed to the saddle point¹⁴¹.

The MEP with the lowest diffusion energy barrier for the displaced B in B₆O is illustrated in **Figure 3-5a**. Initially, a B_{II} atom (**Figure 3-1b**) is relocated to the nearby void forming five B–B bonds with three adjacent icosahedra (excluding the icosahedron where it originally belongs). This configuration is metastable and approximately 6 eV higher in potential energy than the defect-free state. Also, the icosahedron retains its shape despite missing the B atom. Due to the proximity to the vacancy, the diffusion pathway to repair this B Frenkel defect is short, with an overall barrier of only 0.16 eV. Other Frenkel pair configurations involving displaced B atoms were considered. As shown in **Figure 3-5b**, the displaced B_{II} atom forms four B–B bonds with three adjacent icosahedra (including the icosahedron where it originally belongs). The initial structure is 7 eV higher in potential energy than the FS. However, the energy barrier for recombining the displaced B with the vacancy remains low, at 0.40 eV. In both cases, small displacements of B atoms and the well-maintained icosahedral lattice ensure that the Frenkel-type defect will self-heal quickly due to the negligible energy barriers.

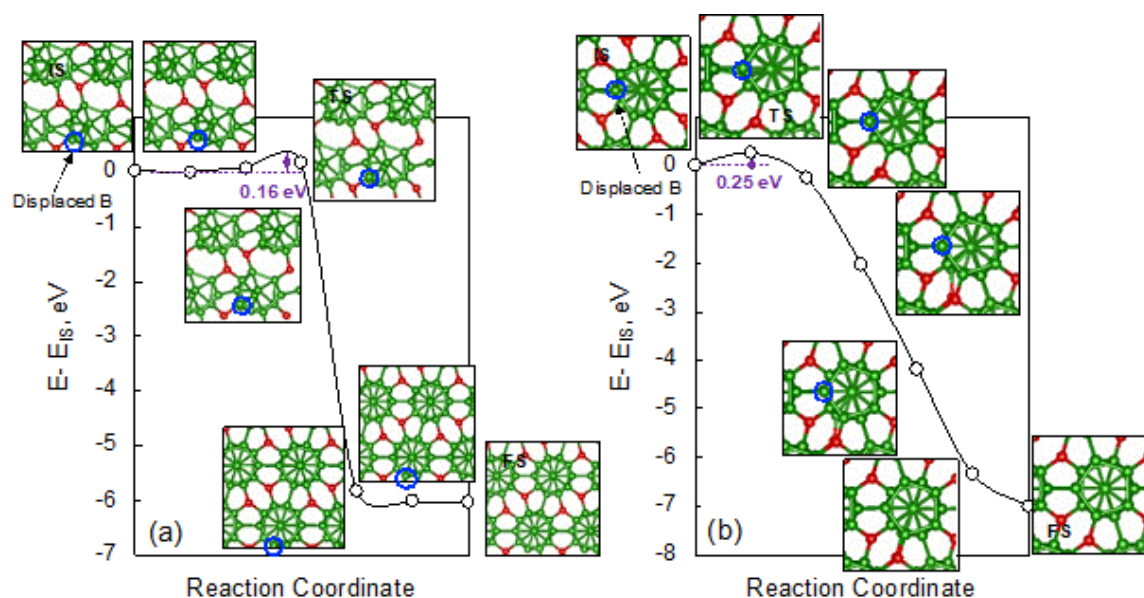


Figure 3-5. Potential energy surfaces depicting different migration pathways (a and b) of a displaced B atom (highlighted by the blue circles). In these pathways, the B₁₂ icosahedral structures are not affected by the Frenkel pair. The inset figures illustrate the IS, FS, and interpolated images along each MEP. The energy barriers are also labeled.

Other more complex B diffusion pathways involve B₆O in lattices containing more significantly distorted icosahedra. For instance, a B_{II} atom displaced from one icosahedron is incorporated into a neighboring icosahedron to form a metastable B₁₃ (see **Figure 3-6a**). In this case, the energy cost is much higher at approximately 11 eV. Realistically, a stronger incident energy source shall be required to produce such an IS. The energy barrier to repairing such a B_{IV} vacancy is 1.25 eV. Expectedly, the potential energy surface displays a more complex landscape. Besides the energy barrier, the diffusion process also includes an energy valley (a local energy minimum) associated with the lattice restructuring of B₁₃. The numerous bond cleavage and formations help explain the apparent higher barrier. Note that the eventual B atom that repairs the Frenkel defect may not necessarily be the original displaced atom. A similar process, with a comparable energy barrier (1.39 eV), was observed in **Figure 3-6b**.

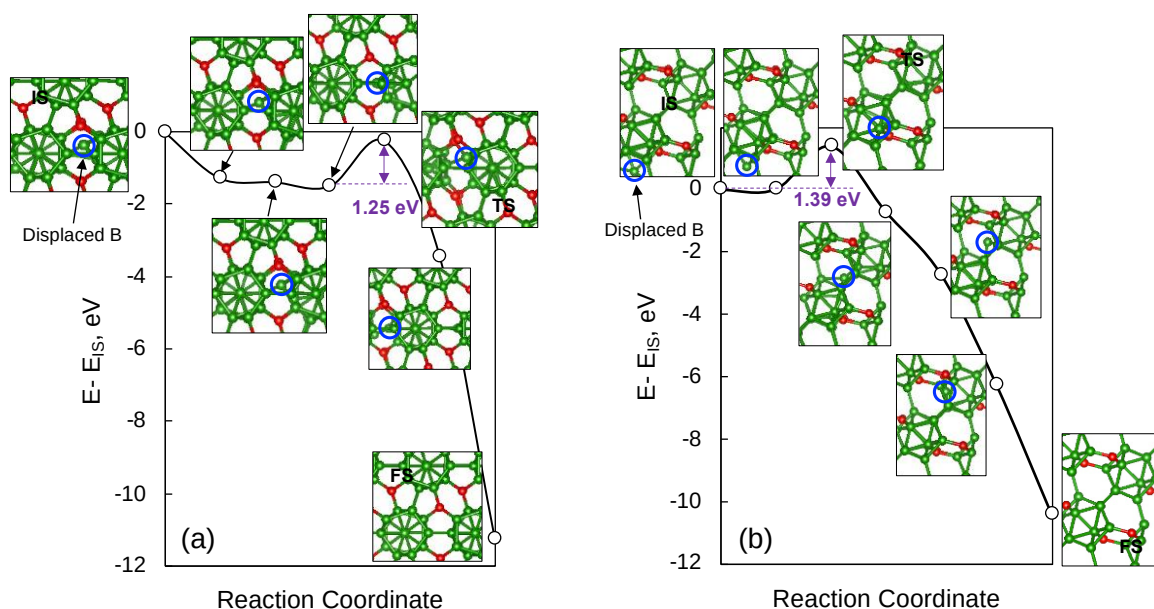


Figure 3-6. Potential energy surfaces depicting different migration pathways (a and b) of a displaced B atom (highlighted by the blue circles). In these pathways, the B_{12} icosahedral structures are initially distorted. The B atoms in these icosahedra reorganize in the diffusion pathways. The inset figures illustrate the IS, FS, and interpolated images along each MEP. The energy barriers are also labeled.

One possible migration pathway of interstitial O is illustrated in **Figure 3-7**. The diffusion of O species is a relevant process for boron oxidation reactions. Initially, the O atom is relocated to a bridge site between the B_{II} atoms. This metastable Frenkel defect is more than 10 eV higher than the FS. NEB calculations showed that O migration could be spontaneous because the overall potential energy surface can be characterized by an energy downhill, except for a small energy barrier of 0.4 eV. Hence, a small perturbation of the initial configuration could be sufficient for O to return to the original lattice site.

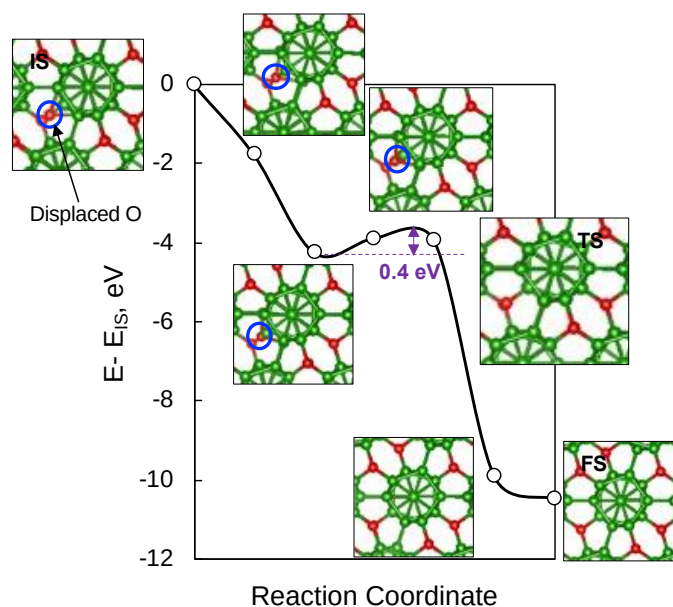
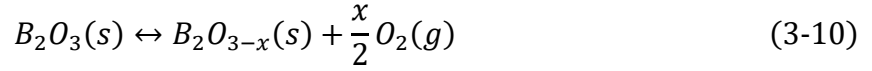
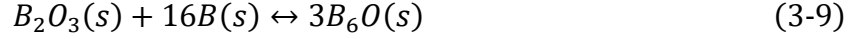


Figure 3-7. Potential energy surfaces depicting different migration pathway of a displaced O atom (highlighted by the blue circles). The inset figures illustrate the IS, FS, and interpolated images along each MEP. The energy barriers are also labeled.

Oxidation of boron

The overall process for B_6O formation via hot press and sintering of B and B_2O_3 can be expressed by Eqn. (3-9)^{17,130}. Thus far, a detailed description of the B_6O formation chemistries is still lacking. It is possible that the process was composed of two stages: (i) decomposition of B_2O_3 to release O species (Eqn. (3-10)), and (ii) the incorporation of O atoms into the pure B lattice (i.e., the oxidation as in Eqn. (3-11)). B_2O_3 is thermodynamically stable (b.p.: up to 2130 K). In the trigonal phase (**Appendix Table A.2**), each B atom has three B–O bonds in an sp^2 configuration. This strong B–O bonds must be broken to initiate the reaction. DFT calculations yield the reaction energy to remove the first O as 5.14 eV, which is highly endothermic. Hence, a high temperature is necessary to drive the enthalpic process for Eqn. (3-10). Afterward, a B–B bond forms spontaneously to fill the v_O . Deep decompositions of B_2O_3 finally produce a network formed by sp^2 B–B bonds (see **Appendix Figure A.8**).



For the oxidation process described by Eqn. (3-11), α -B was used due to the lattice similarity ($R\bar{3}m$) to that of B_6O (see **Table 3-1**). We employed a hexagonal unit cell that can accommodate a maximum of six O atoms. The O atoms were successively inserted into the open interstitial sites. Structure optimizations showed that the O atoms always prefer the 3-fold inter-icosahedral site throughout the process. Between α -B and B_6O , each intermediate configuration represents a unique partial O occupancy, i.e., 0.17, 0.33, 0.5, 0.67, and 0.83. At the O occupancy of 0.17, the B_I - B_I interatomic distance increases from 2.01 Å (in α -B) to 2.37 Å. Note that the interatomic distances in the remaining occupied sites are also elongated by ~ 0.08 Å. The lattice expansion continues with each O addition. As shown in **Figure 3-8a**, HUCV varies almost linearly with the O occupancy (0~1). The energy profiles (**Figure 3-8b**) for the oxidation of α -B were plotted at 0 K, and 2500 K, 6 PGa. As shown in the previous section, the diffusion energy barriers for interstitial O are small. Hence, the activation steps were omitted. The thermodynamic profile at high temperatures will become less energy downhill due to the entropy loss of the O element. Nevertheless, a higher pressure will compensate for some entropy costs.

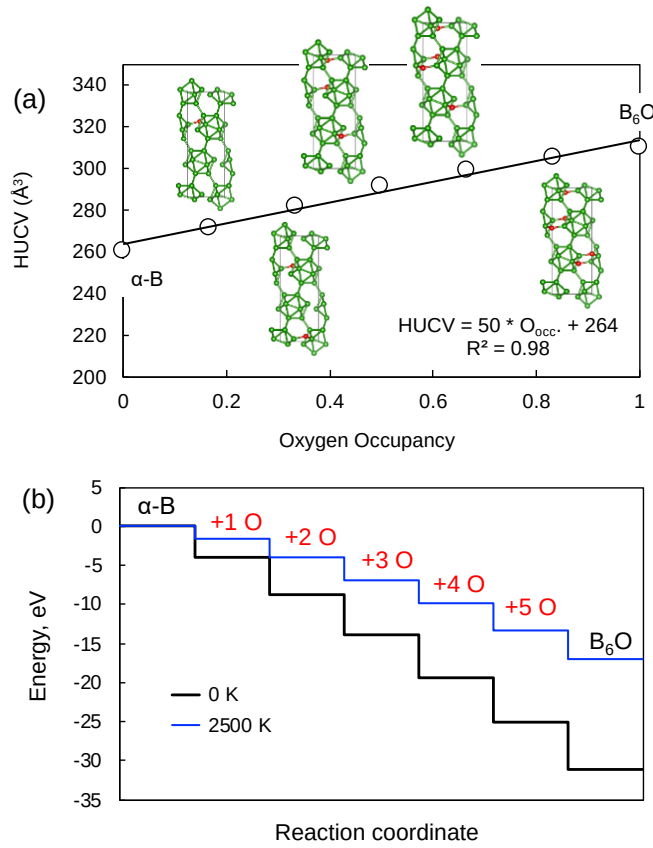


Figure 3-8. (a) Variations of HUCV with O occupancy (O_{occ}) for the process α-B oxidation. (b) Energies changes for successive O insertions into the α-B lattice. The free energies (blue) were estimated at 6 GPa and 2500 K.

Our analysis can reconcile the DFT calculations with the sintering practice to prepare B₆O crystals. High-temperature, high-pressure conditions (4-6 GPa) favor the growth of stoichiometric B₆O^{17,114,130}, whereas yields at low pressures are often O deficient (B₆O_{1-x}, x ≤ 0.28)^{116,146}, due to incomplete filling of the O positions. The oxidation steps should be facile. Therefore, the overall process could be more likely impeded by the generation of the oxidant species and diffusive mass transfer of O species into the interior of the B lattice.

Conclusions

The primary focus of this work is to examine how the lattice and cell volumes, the bulk modulus, and electronic structures vary with the defects residing at the interstitial and

icosahedral locations of B_6O using DFT. We demonstrated that the quantum mechanical methods yielded accurate and consistent descriptions of bulk α -B and B_6O crystals. Hence, we are able to conclude that although the occupation of the interstitial site expands the unit cell volume predictably, the bulk modulus may deteriorate in the presence of the structural defect. The most severe detriment occurs at the icosahedral sites. We also confirmed that B_6O exhibits a p -type semiconductor character, resembling that of $B_{12}P_2$ and $B_{12}As_2$, but with a direct energy bandgap. Furthermore, a systematic screening of the α -boron compounds revealed that the atomic type and composition at the interstitial site may alter the electronic properties of the bulk crystal. The simple octet rule may offer a consistent explanation for the variations observed.

In this work, extensive DFT calculations were performed to compute the thermodynamic stability of solid bulk crystals. The dependence of formation free energies on a wide range of temperature and pressure variables pertaining to various defect structures suggests that interstitial defect formation is more likely at higher temperatures than the icosahedral formation. Nevertheless, this trend can be easily disrupted in systems with higher configurational entropies.

The CI-NEB method was employed to identify the MEPs to describe the diffusion pathways of dislocated B and O atoms in the B_6O lattice. Multiple diffusion pathways are possible for the icosahedral B atoms with energy barriers as low as a few meV. The diffusion of interstitial O atoms is much more facile. Lastly, successive O insertion into the α -B lattice was performed using DFT to generate a basic understanding of the oxidation process. These calculations can be used to acquire fundamental atomistic insights to understand the growth of B_6O crystals and to control the defects.

Chapter 4 - Boron Suboxide (B_6O) Crystal Growth from a Molten Copper Flux

Abstract

First-principles calculations were used to explore the synthesis and crystal growth of B_6O from a metal flux at atmospheric pressure. Experimentally, the successful synthesis of stoichiometric B_6O has only been reported at very high pressures (>5 GPa) and high temperatures ($1700 - 1800^\circ\text{C}$), which limit the crystals that can be grown. At ambient pressures, non-stoichiometric boron suboxide is formed, typically as poorly crystallized powders with small grain sizes ($<10\ \mu\text{m}$). As such, development of ambient pressure techniques to grow stoichiometric B_6O is necessary to increase the size and quality of B_6O crystals. After comparing the stabilities of transition metal (M) oxide compounds in metal-boron-oxygen systems to that of B_6O , copper was identified as the best candidate for metal flux growth of B_6O due to the thermodynamic low stability of CuO at high temperatures, high boron and oxygen solubility, and relatively low cost. DFT calculations predict that the synthesis of B_6O from a mixture of B and CuO is thermodynamically favorable in oxygen-deficient environments. Unfortunately, this was not experimentally verified. Analysis of the crystals precipitated from a molten copper flux revealed only mixtures of β -boron, likely containing copper interstitial defects, and B_2O_3 . This indicates that the system is kinetically limited, where the trigonal B_2O_3 bonds form overwhelmingly faster than the complex B_6O structure from dissolved B. This should be tested in future work by extending the time at which the flux is supersaturated with B, and thus B_{12} icosahedra are pre-formed and available for bonding with oxygen.

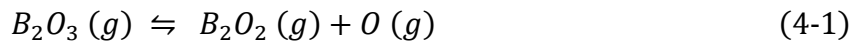
Introduction

Boron suboxide (B_6O , also described as $B_{12}O_2$) has garnered interest due to its ability to heal from radiation damage, its high neutron capture cross-section^{14,15}, chemical inertness, high-temperature stability, wide direct bandgap of 1.8 – 3.0 eV^{11–13}, and ultra-hardness of 40-67 GPa^{16,17}. Both *p* and *n*-type dopants have been predicted for B_6O , which is a major advantage it has over other wide bandgap semiconductors^{13,147}. These properties make B_6O a promising candidate for semiconductor devices that operate in high radiation environments, such as radioisotope batteries and neutron detectors. Boron suboxide is also a promising candidate for thermoelectric applications due to its high Seebeck coefficient (500 $\mu V/K$)^{16,117}. The combination of thermoelectric properties, resistance to high temperatures, and chemical stability makes it, like many boron-rich icosahedral compounds, ideal for developing thermal management systems for high-power electronics.

The unit cell for B_6O is based on the α -boron structure, with boron icosahedra centered on the corners of the rhombohedra and interstitial oxygen in the center of the unit cell. Two-centered covalent bonds connect six boron atoms from each icosahedron directly to neighboring icosahedra. The remaining boron atoms are bonded to the oxygen atoms, which donate electrons to further stabilize the icosahedra^{14,15,18}. However, B_6O is a known non-stoichiometric compound with many oxygen deficient structures^{25–27}.

B_6O synthesis and crystal growth is still in its early stages. In prior reports, B_6O was primarily synthesized by directly oxidizing solid boron using boron oxide, B_2O_3 . Its crystal growth required high temperatures ($>1700^\circ C$) and pressures (>5 GPa) to produce stoichiometric B_6O ^{11,23}. Synthesis at lower pressures tends to produce oxygen deficient, non-stoichiometric suboxides, drastically changing its properties^{11,12,17}. This is due to the complex chemical

decomposition of B₂O₃ required to form compounds that can interact with the icosahedral boron structure, represented by the decomposition reactions below¹⁴⁸:



The gaseous BO formed in Eqn. (4-2) behaves as a carrier of oxygen to solid boron, and the partial pressure of BO is more than 8 orders of magnitude higher than monoatomic oxygen. Slack *et. al.*¹⁴⁸ concludes that B₆O formation is thermodynamically favorable at atmospheric pressure above 1200°C. Monoatomic oxygen penetrates the solid boron crystal structure to bind to B₁₂ icosahedra following Eqn. (4-4):



The formation of B₆O is expected to proceed slowly due to the low monoatomic oxygen concentration, and the pressure and temperature need to be raised to increase monoatomic oxygen concentration and therefore the rate of formation of B₆O. Low pressure experiments consistently produce oxygen deficient, non-stoichiometric boron suboxide crystals that tend to have small crystal domains that are frequently mixed with amorphous material and B₂O₃^{11,17,26}. The thermodynamic stability of stoichiometric B₆O at ambient pressure indicates that the oxygen deficiency seen at low pressures is caused by kinetic limitations on the system, and better reaction mediums will need to be explored to maximize the amount of oxygen that can bind with the boron icosahedra at ambient pressures.

In this study, a new method to synthesize B₆O using the metal flux method was explored using first-principles calculations, followed by experimental crystal growth. The metal flux can dissolve both boron and oxygen, allowing high concentrations of oxygen to readily incorporate

into the boron structure, reducing reaction barriers in the B₆O reaction pathway at atmospheric pressure. Prior first-principles studies on B₆O focused primarily on structural analysis and prediction of mechanical, optical, and electronic properties^{13,24,128,149–152}, but have not been applied to synthesis pathways. This study will compare the relative stabilities of B₆O, B₂O₃, non-stoichiometric suboxides, and precursor compounds to determine the best metal for flux growth of B₆O. After validating the thermodynamic model, boron and metal oxides were dissolved in a molten metal flux and slowly cooled to precipitate crystals to test the method predictions.

Methods

Computational

Potential transition metal solvents for B₆O synthesis and crystal growth were screened using the Materials Project Database²⁷ by comparing the energies of different compounds in the metal-boron-oxygen (M-B-O) ternary phase system at 1773 K. The thermodynamics of the Cu-B-O system were thoroughly explored using density functional theory (DFT) in the *Vienna ab Initio Simulation Package* (VASP)¹⁵³ program, analyzing the energy level of multiple configurations of each relevant compound to develop Gibb's free energy models. A projector augmented wave approximation Perdew-Burke-Ernzerhof functional (GGA-PBE)¹³⁴ was applied in geometry and energy calculations. A (4 × 4 × 4) k-point mesh was generated using the Monkhorst-Pack scheme to relax crystal lattices and to obtain the electronic structures¹³⁵.

Energy minimizations were performed over a range of volumes for Cu, CuO, B₂O₃, B₆O, and several oxygen-deficient suboxides. These energies were fit to the Birch-Murnaghan equation of state (Eqn. (4-5)), resulting in an equation for energy as a function of volume for each compound.

$$E(V) = a + bV^{-\frac{2}{3}} + cV^{-\frac{4}{3}} + dV^{-2} \quad (4-5)$$

The system pressure as a function of volume is determined by taking the derivative of the Birch-Murnaghan equation with respect to volume.

$$P(V) = -\frac{dE}{dV} \quad (4-6)$$

To predict the stability of the various compounds, the system energy must be calculated as a function of both pressure and temperature. Eqn. (4-5) and Eqn. (4-6) were combined to predict the energy as a function of pressure, $E_f(P)$. The vibrational entropies, as a function of temperature, were calculated using PHONOPY¹³⁸. This procedure was repeated at different pressures to produce the vibrational entropy as a function of temperature and pressure, $S_v(T, P)$. The zero-point energy (ZPE) can also be obtained from PHONOPY. The Gibb's energy is calculated using Eqn. (4-7).

$$G(P, T) = E_f(P) + ZPE - T * S_v(T, P) \quad (4-7)$$

Experimental

Experiments to synthesize B_6O crystals were conducted in a single-zone tube furnace at atmospheric pressure. A 10-gram mixture of Cu, boron, and CuO was placed in an alumina boat. Enough boron was added to the flux to saturate the Cu at elevated temperatures. Oxygen concentrations were varied in an attempt to form B_6O without forming B_2O_3 . The oxygen-to-boron atomic ratio was varied from 0.17 - 0.5. This flux was heated to either 1300°C or 1500°C in an inert Ar atmosphere and slowly cooled at a rate of 2°C/hour for 150°C before the system was quenched, as shown in **Figure 4-1**. Alternately, an atmosphere containing 0.1-0.2 vol% O_2

in Ar was flowed over a Cu-boron flux containing no oxide sources. Crystals were recovered by using nitric acid to dissolve the metal ingot.

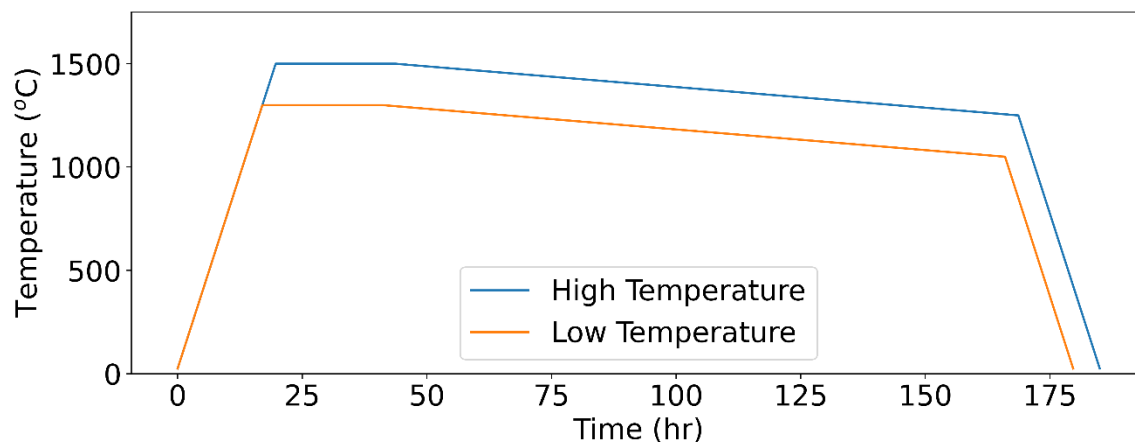


Figure 4-1. Standard metal flux method temperature profile program. The blue line is for high temperature programs held at 1500°C. The orange line is for low temperature programs held at 1300°C.

Raman spectra were measured from 200 cm^{-1} to 1400 cm^{-1} using a 532 nm excitation wavelength. X-ray photoelectron spectroscopy (XPS) was taken over the boron (180 to 196 eV), oxygen (525 to 545 eV), and carbon (279 to 298 eV) energy ranges. XPS shifts were calibrated against the C 1s peak at 284.8 eV. Precipitated icosahedral boron compounds were compared to a β -B standard purchased from Ceradyne, a 99.99% pure B_2O_3 standard purchased from Shanghai Maikun Chemical Co., and a B_6O standard reported by Han et. al¹¹. Finally, a precipitated icosahedral boron sample was analyzed using powder X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation over a 2θ range of 5° to 90°.

Results and Discussion

Solvent Selection

Figure 4-2 shows different behaviors expected from different transition metal solvents. Some metals oxidize readily, such as Fe or Cr, hindering B–O bond formations. Metals such as

Ni or Zn interact strongly with B and form ternary M-B-O compounds, inhibiting pure B_6O growth. A few metals, such as Cu or Pt, react weakly with oxygen, readily dissolve B, and do not form stable ternary compounds. These metals are the ideal candidates for B_6O synthesis.

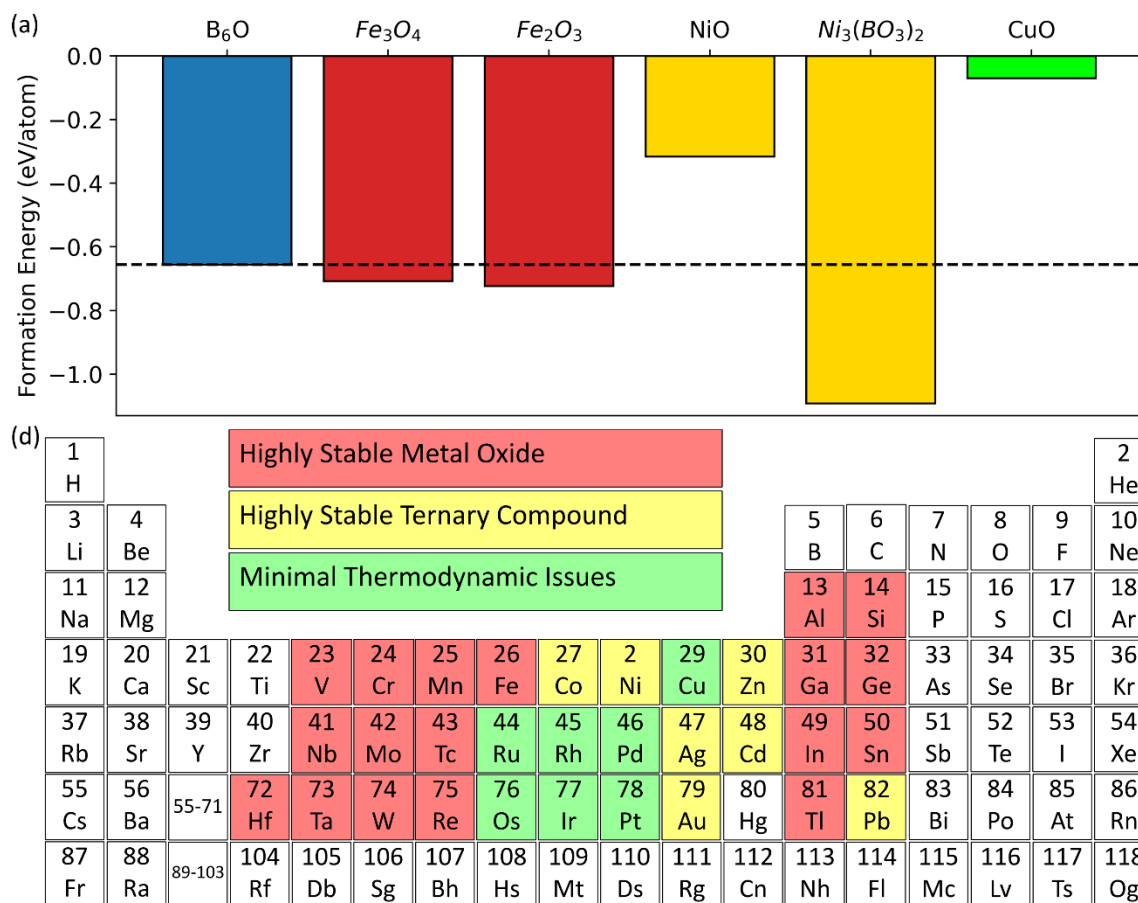


Figure 4-2. Formation energies of Fe, Ni, and Cu oxides relative to B_6O . (b) Color coded periodic table with potential solvents for B_6O crystal growth. The dashed line is the formation energy of B_6O . Elements highlighted in green have minimal thermodynamic issues. Elements highlighted in red have very stable oxides, which will interfere with the B-O reaction. Elements highlighted in yellow have stable ternary compounds (containing the metal, boron, and oxygen), which may interfere with B_6O synthesis.

Figure 4-2b is a highlighted periodic table color-coded to visualize the results from different M-B-O systems. Red, yellow, and green highlighted elements follow the trends in **Figure 4-2a**. The green elements were considered for experiments. The ideal candidate has high boron and oxygen solubility at high temperatures. For this reason, Cu was selected as the metal

flux, with CuO as the oxygen source. Previous studies have reported Cu as a flux for B crystal growth¹⁵⁴. Furthermore, Cu is significantly more economical than metals such as Pt, making it ideal for potential upscaling. The Cu flux is also known to have significant O solubility at high temperatures, substantially higher than that of metals such as Ni and Fe, even at significantly lower temperatures^{155,156}. The high oxygen solubility in Cu at temperatures between 1300°C - 1500°C suggests the possibility for B₆O crystal growth at low temperatures, reducing energy costs during synthesis.

DFT Phase Stability

To validate the DFT equation of state methodology, Gibb's energies were calculated first for different boron allotropes, α -B, β -B, and γ -B. This model was compared to published theoretical boron phase diagrams^{35,157,158}. **Figure 4-3** shows the energy difference between α -B and β -B and γ -B, which was done for ease of visualization.

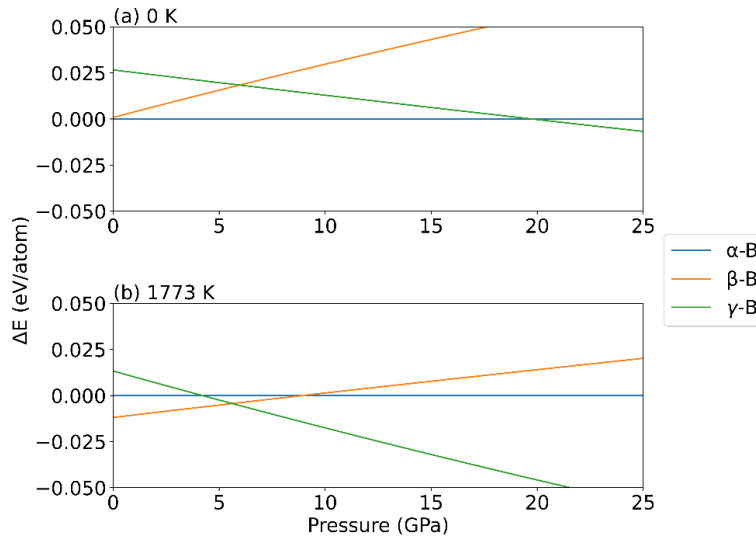


Figure 4-3. Gibb's formation energy difference (eV/atom) between β -B and γ -B from α -B at 0 K and 1773 K. At low temperatures, α -B is stable up to 20 GPa, then γ -B becomes more stable at higher pressures. At high temperatures, β -B is most stable until 5.6 GPa, then γ -B becomes most stable at higher pressures.

A common source of error in DFT-simulated boron phase diagrams is that, at low temperatures and pressures, the relative stability of β -B to α -B is underestimated¹⁵⁷. This issue is still present in this work, likely due to the complexity of the β -B crystal unit, which is significantly larger than either α -B or γ -B crystal units. There is also deliberation in the literature regarding the exact structure of the β -B crystal structure, which can contain either 105 or 106 atoms, or that the true ground state should be the twinned τ -B structure based on the β -B crystal unit¹⁵⁹. These discrepancies explain the elevated energies of β -B at low pressures and temperatures.

The equilibria points among the α , β , and γ phases match the established literature well. There is a large pressure envelope at low temperatures where α -B is most stable, which is also observed in published experiments^{35,158}. At 0 K, γ -B becomes the stable phase at pressures exceeding 20 GPa. At elevated temperatures, the α -B phase envelope disappears. At 1773 K, the β -B phase is most stable up to 5.6 GPa, and γ -B is most stable at higher pressures. These trends indicate that the equation of state simulation is accurate for the complex boron-rich systems involved in the synthesis of B_6O .

Figure 4-4 shows the energy difference between various boron oxides and α -B. B_6O remains more stable than any non-stoichiometric suboxide compound at all temperatures and pressures. However, B_2O_3 is significantly more stable than B_6O until high pressures are achieved. This equilibria point is dependent on the system temperature. The B_2O_3 - B_6O equilibrium point is at 20 GPa at 0 K, increasing to 29 GPa at 1773 K.

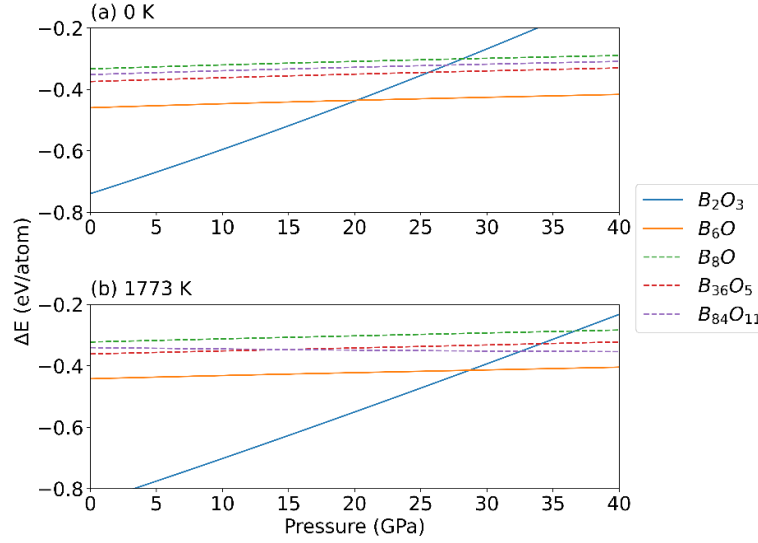


Figure 4-4. Gibb's formation energy difference (eV/atom) between boron oxides and α -B at (a) 0 K and (b) 1773 K. Non-stoichiometric suboxide structures are shown as dashed lines. The pressure at which B_2O_3 becomes less stable than B_6O is smaller at lower temperatures.

To fully understand the proposed Cu-B-O reaction system, CuO and Cu were added to the equation of state models. **Figure 4-5** shows the Gibb's energies of reaction for both B_6O and B_2O_3 synthesis and were simulated using the following reactions based on the direct oxidation of boron:



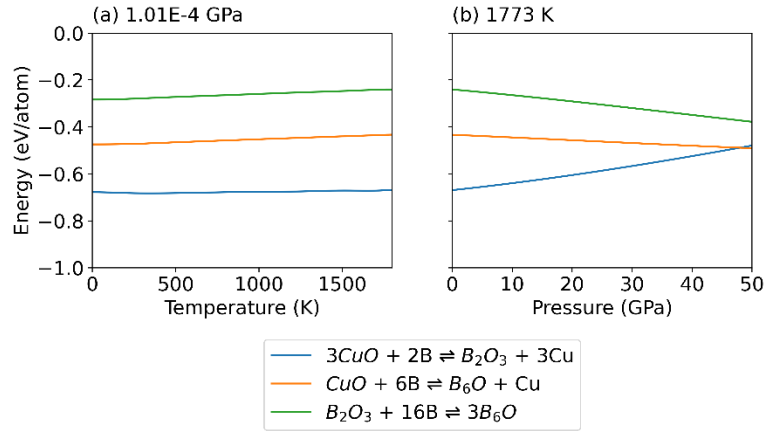


Figure 4-5. Gibb's energy of reaction (eV/atom) for the formation of B₂O₃ and B₆O (a) as a function of temperature and (b) as a function of pressure.

The formation of B₂O₃ from CuO and B (Eqn. (4-8)) is predicted to be the most favorable reaction in the system at all temperatures and at pressures below 48 GPa, which is expected due to the high stability of B₂O₃. The moderate pressure dependence is explained by the trigonal structure of B₂O₃, which is more susceptible to deformation than the stiff bonds of icosahedral boron structures. The formation of B₆O from CuO and B (Eqn. (4-9)) is predicted to be more favorable than the reaction between B₂O₃ and B (Eqn. (4-10)).

All three reactions have a negative associated energy and are predicted to be spontaneous. This agrees with experimental reports. Heating a mixture of boron powder and either B₂O₃^{28,160} or metal oxide^{11,28} is a traditional way to synthesize B₆O. However, this always results in microcrystalline, highly defective, non-stoichiometric boron suboxide when performed at atmospheric pressure due to the kinetic limitations of monoatomic oxygen penetrating a solid boron complex¹². Because of this, and the complex formation of the B₁₂ icosahedra, it is reasonable to assume that B₂O₃ formation (Eqn. (4-8)) will occur rapidly, whereas B₆O formed from the reduction of CuO (Eqn. (4-9)) occurs slowly. The formation of B₆O from the reduction of B₂O₃ (Eqn. (4-10)) is expected to be the slowest reaction due to the complex decomposition

of B_2O_3 . Therefore, the resulting products after growing crystals from a Cu-CuO-B flux is expected to be a mixture of B_2O_3 and B_6O .

Experimental

Attempts to grow B_6O from a Cu flux using a CuO oxygen source were unsuccessful using an oxygen-to-boron atomic ratio between 0.17 and 0.5 at both 1300°C and 1500°C. Two types of crystals were primarily synthesized; beta-phase boron (β -B) and fully oxidized boron (B_2O_3), shown in **Figure 4-6**. The icosahedral boron crystals were grey, opaque crystals with either rectangular or trapezoidal facets. B_2O_3 precipitated from the Cu flux in the shape of white needles.



Figure 4-6. Images of (a) β -B and (b) B_2O_3 precipitated from a Cu-CuO-B flux. B_2O_3 crystals only precipitated from experiments that used high concentrations of oxygen. The scale bars are 1 mm.

Raman spectra was collected from the crystals shown in **Figure 4-6a** and compared to a boron and B₆O sample standard, shown in **Figure 4-7**. Most significantly, the experimental sample is missing the prominent E_g and A_{1g} double-peaks found between 1000 – 1200 cm⁻¹ in crystals with an α -B sublattice, such as B₆O. However, there are many similarities between Raman derived from the precipitated crystals and the β -B standard. The Raman frequencies associated with intra-icosahedral bonding, 500 – 950 cm⁻¹, are attributed to the stretching of the three-center bonds found within boron icosahedra. These peaks are significantly sharper than the peaks presented by the β -B sample standard, indicating a higher degree of crystallinity and lower crystal strain.

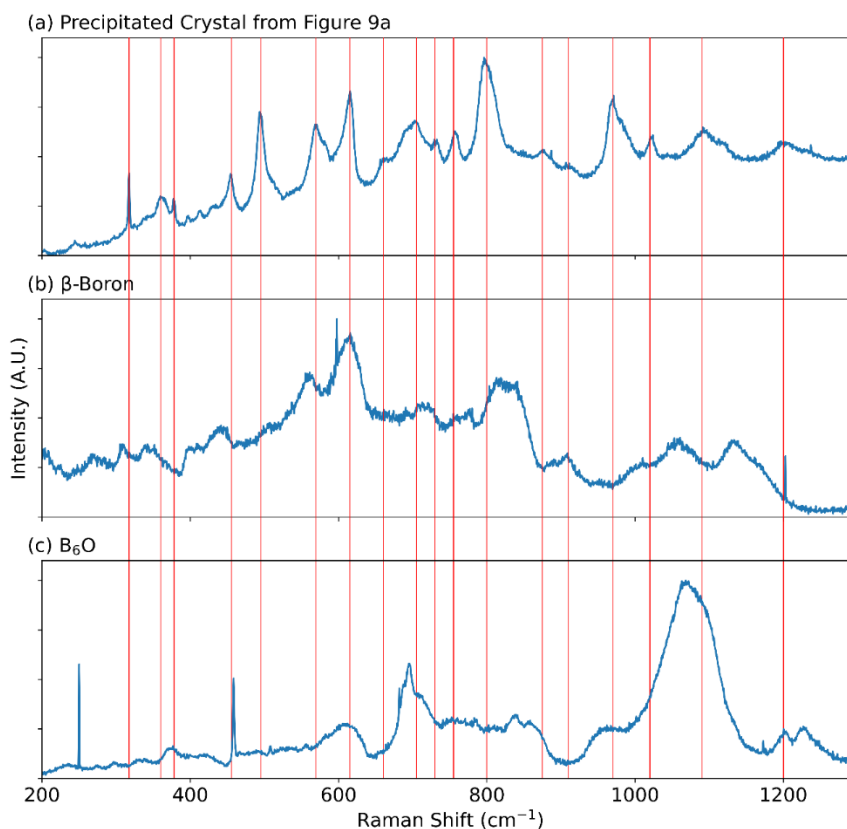


Figure 4-7. Raman of (a) Precipitated black crystals precipitated from a Cu flux, (b) a β -Boron standard, and (c) a B₆O standard. Red lines mark the major peaks on the experimental sample boron-rich crystals.

There are differences in the peak positions and intensities between the precipitated crystal and the β -B standard. Furthermore, some peaks are present in spectra from the precipitated crystal but in neither sample standard, such as the peaks at 495 cm^{-1} and 1020 cm^{-1} . This could be readily explained by interstitial copper defects in a β -B crystal lattice. Raman spectra from β -B is highly susceptible to change from metal interstitial defects. For example, a strong peak develops at 1060 cm^{-1} in vanadium-doped boron, and peak intensity ratios between $500 - 1150\text{ cm}^{-1}$ shift significantly³⁴. Cu, being a slightly heavier element than V, would be expected to impact the vibrational modes of boron in similar ways. Based on this Raman analysis, it is most probable that the icosahedral crystals precipitated from these experiments are Cu-doped β -B. The same results were found for all icosahedral boron compounds precipitated from a Cu flux, regardless of oxygen concentration.

Rietveld analysis from XRD, shown in **Figure 4-8**, also indicates that the structure of the boron-rich crystals is primarily that of β -B without significant concentrations of oxygen. Another structure, $\text{Al}_{2.7}\text{Cu}_{2.34}\text{B}_{105}$, was determined to coincide with the XRD spectra. The structure of this compound is β -B with metal atom inclusions in the crystal lattice, and it is assumed that this indicates Cu interstitial defects in the crystals grown from the Cu flux. The aluminum may originate from the alumina boat used to contain the flux.

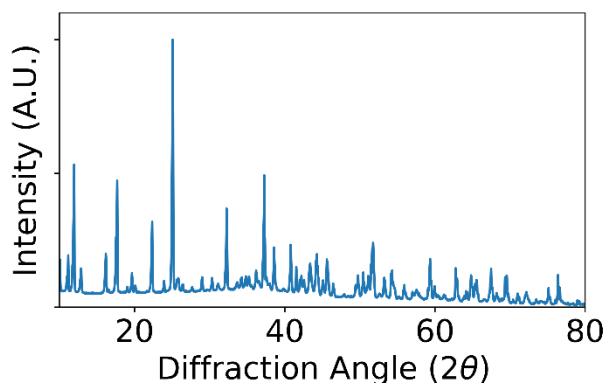


Figure 4-8. XRD of β -B crystals precipitated from a Cu flux.

XPS data collected on both the white needles and the boron-rich compound were compared to data collected on known standards of B_2O_3 and B_6O . XPS is advantageous for identifying boron-oxygen compounds because the incorporation of O into a B lattice creates an easily identifiable set of peaks. Pure B shows a peak at ~ 187.5 eV, B_2O_3 creates a single peak at ~ 192.5 eV, while B_6O generates a set of three peaks at 187.5 eV, 189 eV, and 193.5 eV¹⁰⁴.

Figure 4-9 shows the differences in XPS spectra between the boron-rich crystals precipitated from the Cu flux, the white powder appearing at higher O concentrations, and a known B_6O standard. These results clearly show that the white needles produced in high oxygen environments are B_2O_3 , as the XPS spectra are a close match. They also indicate that the opaque crystals are boron without a significant amount of oxygen incorporation into the bonding structure, as the binding energies do not indicate the presence of B-O bonds.

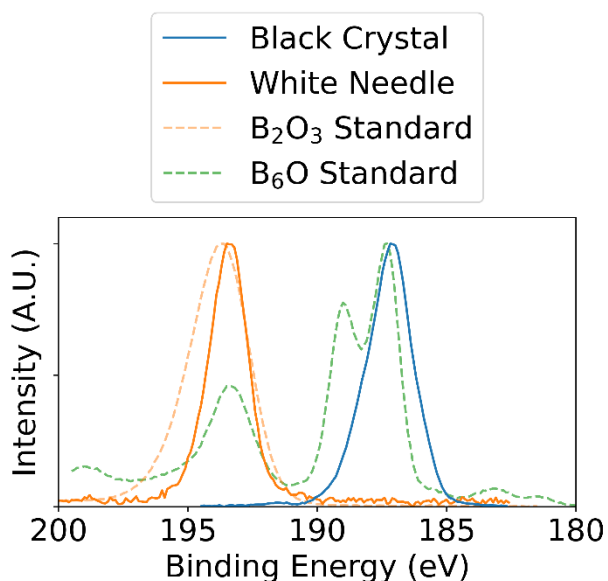


Figure 4-9. XPS data of boron derivatives compared to known standards. The experimentally grown samples are solid lines. Known standards are displayed as dashed lines. Blue is β -B, green is B_6O , and B_2O_3 is orange.

Table 4-1 shows the compounds grown at different oxygen concentrations at two different temperatures, 1300°C and 1500°C. When CuO was used as an oxygen source at both temperatures, an oxygen-to-boron ratio of at least 0.5 precipitated B_2O_3 .

Table 4-1. Compounds identified from a sample run at either 1300°C or 1500°C with varying oxygen concentrations in the flux.

CuO Oxygen Source	Compounds Identified at a Given Dwell Temperature	
Atomic O/B Ratio	1300°C	1500°C
0.17	B	B
0.25	B	B
0.33	B	B
0.43	B	B
0.5	B, B_2O_3	B, B_2O_3

There was no transition point at which the oxygen concentration in the molten metal was high enough to form B_6O yet low enough to avoid forming B_2O_3 . Therefore, the metal flux

system needs to be modified for further development. We conclude that oxygen needs to react with solid boron, which has already developed the complex icosahedral boron units, rather than react with the individual boron atoms dissolved in the flux. There are a few ways to accomplish this. The cooling rate could be significantly reduced so that oxygen in the flux has time to overcome kinetic limitations in B_6O formation while boron slowly precipitates from the molten flux. A secondary dwell time could also be implemented at a temperature low enough for some boron to precipitate, but high enough to maintain a liquid state otherwise. This would allow the relatively high concentrations of oxygen in the molten flux to react with the large boron crystals to form B_6O over a long period of time. Unfortunately, both of these methods require an unreasonably long period of time for synthesis, and growth becomes impractical.

Conclusions

A data-driven approach was taken to develop a metal flux method for B_6O synthesis. The thermodynamic stabilities of transition metals were compared to the stability of B_6O . Most transition metal oxides are too stable to expect B_6O to form. Some metals, such as Ni and Zn, form ternary complexes that could inhibit B_6O formation. However, several metals show promising thermodynamic behavior, including copper and platinum. For the experimental investigation, copper was selected for the metal flux method due to its relatively high boron and oxygen solubilities, low melting point, availability, and cost efficiency.

Gibb's energy models were generated for boron, boron oxides, copper, and copper oxide. The models agree with published boron-allotrope phase stability, validating the methodology. Across most pressures and temperatures, B_2O_3 is predicted to be more stable than B_6O . However, in an oxygen-deficient environment, B_2O_3 can be reduced by boron to form B_6O . Furthermore, the reduction of CuO by B to form B_6O is predicted to be more favorable than the reduction of

B_2O_3 , which is the traditional method to form B_6O . Therefore, a Cu-CuO-B flux is predicted to be a thermodynamically viable pathway to grow B_6O single crystals.

Crystals were precipitated from a Cu-CuO-B flux, varying the atomic ratio between boron and oxygen between 0.17 to 0.5. At low oxygen concentrations, β -B precipitated from the flux. At high oxygen concentrations, a mixture of β -B and B_2O_3 precipitated from the flux. No oxygen-boron bonds were detected by XPS, though there was some evidence of metal incorporated into the β -B crystal lattice in the XRD spectra in one sample.

There are likely kinetic limitations preventing the synthesis of B_6O from a metal flux. It is possible that B_6O cannot form directly from dissolved B in the molten flux, or that the formation of the trigonal B_2O_3 bond structure is overwhelmingly faster than the formation of a complex icosahedral matrix. Future work could test this hypothesis by working with a supersaturated Cu-CuO-B flux, where dissolved O has sufficient time to overcome the kinetic limitations of penetrating the β -B structure. Unfortunately, this method may prove to be impractically long for novel material synthesis.

Chapter 5 - Synthesis and Characterization of $C_2Al_3B_{48}$ Crystals from an Al-B-C Flux

Abstract

Boron-rich compounds are well known for their chemical inertness, extreme hardness, and ability to self-heal from radiation damage, leading to applications in nuclear batteries or as wide band gap semiconductors in extreme environments. In this study, the aluminum-boron-carbon (ABC) crystals were grown by the metal flux technique with a constant Al/B ratio and a carbon concentration between 0 – 3 wt% C, forming AlB_{12} and $C_2Al_3B_{48}$ crystals up to 7 mm in diameter. The phases present at each carbon concentration were determined by powder x-ray diffraction. The crystal structure and Al occupancy of $C_2Al_3B_{48}$ was resolved by single crystal XRD. The 1.8 eV bandgap measured in AlB_{12} is consistent with reported literature. $C_2Al_3B_{48}$ demonstrated a broad band edge between 2.4 – 2.7 eV. This study highlights the versatility of the Al-B-C system for synthesis of boron-rich semiconductors. $C_2Al_3B_{48}$ is particularly promising due to its wide bandgap relative to other ABC compounds and the wide range of carbon concentrations at which it can be grown.

Introduction

Icosahedral boron-rich compounds garnered interest due to their ability to heal from radiation damage, boron-10's high neutron capture cross-section^{14,15}, chemical inertness, high temperature stability³⁹, wide energy bandgaps^{11–13,19,54,161}, and high hardness^{16,17}. These properties make boron-rich compounds promising candidates for semiconductor applications in high radiation environments^{43,162}, such as radioisotope batteries and neutron detectors, or in mechanical applications such as body armor or diamond substitutes in cutting tools^{45,161}. These properties are the result of the unique bonding structure of boron-rich compounds. Three-

centered bonds, where two electrons are shared between three atoms in a triangular plane, result in boron atoms forming B_{12} icosahedral clusters. The icosahedra are linked together in various boron sublattices. In the α -rhombohedral sublattice, seen in materials such as B_4C^{34} , three icosahedra are linked together and stabilized using a central electron donor atom. $C_2Al_3B_{48}$ has the α -tetragonal boron sublattice^{20,21,30,33–35}, which consists of four icosahedra with a central atom between them. AlB_{12} has the β -tetragonal sublattice¹⁶¹, which is a complex combination of B_{12} icosahedra as well as B_{20} clusters forming a fused, twinned icosahedra.

Due to boron's high affinity for both aluminum and carbon, several compounds precipitate from an aluminum-boron-carbon (ABC) flux. The three primary semiconductors of interest are alpha aluminum dodecaboride (α - AlB_{12}), beta aluminum boride ($C_2Al_3B_{48}$) and a third higher carbon-content compound (C_4AlB_{24}). These are all expected to have a wide energy bandgap. AlB_{12} is reported to have a bandgap of 1.9 eV²⁹. Little literature is available on the optical and electrical properties of $C_2Al_3B_{48}$. In this study, $C_2Al_3B_{48}$ crystals were semi-transparent yellow-red, suggesting a bandgap between 2.1 – 2.5 eV, which agrees with absorption measurements. Additionally, the metallic 2D material AlB_2 may form.

As many Al-B-C compounds can form from a molten metal flux, synthesis needs to be optimized to specifically form high quality $C_2Al_3B_{48}$ for wide bandgap semiconductor applications. The metal flux method, which uses a metal solvent to dissolve high concentrations of source material, is capable of synthesizing boron-rich compounds at atmospheric pressure and moderate temperatures, 1500°C, and includes several benefits over other traditional crystal growth techniques^{58,59}. The temperature required to grow large crystals can be decreased to well below the high melting point of boron by dissolving the boron in a suitable flux. Since the boron-compounds are precipitated from a supersaturated solution, there is no thermal or

crystallographic mismatch with the unique icosahedral crystal structure that may occur with deposition techniques that require substrates, such as chemical vapor deposition (CVD) or molecular beam epitaxy (MBE)⁵⁹. Lastly, the metal flux has the additional benefit of trapping impurities in the flux instead of the precipitating crystals⁵⁸. The combination of these traits leads to crystals grown from a metal flux having low strain, minimal crystal defect densities, and low impurity concentrations^{55,58,59}.

Experimental Methods

For ABC crystal growth, Al was both a source and a solvent. 99.999% purity Al, 99% purity B, and 99% purity graphite were measured and loaded into an Al₂O₃ boat. The ratio of 14g Al / g B was kept constant throughout all. Carbon was added to each boat in variable amounts, ranging from 0 wt% - 3 wt% of the total flux. The boats were loaded into an alumina tube furnace and purged with Ar. The system was heated to 1500°C, where it was held for 12 hours to ensure homogeneity in the flux, then cooled to 1300°C at a rate of 2°C/hour before quenching. The resulting ingots were then dissolved in muriatic acid (31.45% HCl), leaving behind bulk ABC crystals. The color, size, and shape of representative crystals at each carbon concentration were documented using optical microscopy.

Bulk single-crystals were identified by Raman spectroscopy with a 532 nm laser measuring from 200 – 1400 cm⁻¹. The crystals precipitated from the Al-B-C flux were ground in a mortar and pestle, and phases were identified using powder x-ray diffraction (XRD). The samples were measured from 10° to 120° with a CuK α radiation source using a Bruker D8 Discover diffractometer. The carbon concentration in the resulting crystals was determined by energy dispersive x-ray spectroscopy (EDS) with a Bruker Quantax Compact 30 system. To refine the crystal structure and Al occupancy rates of C₂Al₃B₄₈, single-crystal XRD was

performed on a single crystal grown from a flux containing 0.43 wt% C. Single crystal X-ray data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source (Cu K α λ = 1.54184 Å). The data collection strategy was calculated using CrysAlisPro to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro¹⁶³. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structures were solved using the ShelXT structure solution program¹⁶⁴ using Intrinsic Phasing and refined by Least Squares using the ShelXL program¹⁶⁴. All atoms were refined anisotropically. Olex2 was used for the preparation of the publication materials¹⁶⁵.

Photoluminescence (PL) and absorption measurements were taken on large samples that were polished until thin, flat, and transparent using SiC sandpaper. Samples were excited with either a 325 nm He/Cd or 360 nm DPSS laser, and the samples were mounted to a sample holder cooled with a cryogen-free cryostat with optical windows, allowing measurements at temperatures between 10 K to room temperature. The majority carrier concentration was determined by hot-point probe using a Keithley 4200 parameter analyzer and soldering iron.

Results and Discussion

Three types of crystal precipitated from the Al-B-C flux: opaque black crystals (AlB₁₂), and semi-transparent yellow-red crystals (C₂Al₃B₄₈), both of which range in size from 1 – 9 mm across, as shown in **Figure 5-1**. Crystals grow from the surface of the metal flux. The exposed surface of the crystal is typically flat with a spiral pattern extending from the center face, which

is visible in **Figure 5-1a** and d. Submerged facets of the crystal typically form as triangular, hexagonal, or rectangular faces, depending on the crystal plane.

AlB_{12} crystals precipitated from fluxes with no added carbon content, as shown in **Figure 5-1b**. These crystals readily underwent conchoidal fracture, leaving curved surfaces at the fracture sites that resemble obsidian. A small amount of $\text{C}_2\text{Al}_3\text{B}_{48}$ crystal was found in samples with no added carbon, likely formed using residual carbon impurities from the source materials. In all samples with an intentional carbon content, AlB_{12} was not present. The small amount of carbon required to eliminate AlB_{12} formation demonstrates the high reactivity between boron and carbon.

$\text{C}_2\text{Al}_3\text{B}_{48}$ is abundant in samples grown from a 0.32 – 0.60 wt% C flux. These crystals ranged in color from a deep red to a light yellow or amber color, as shown in **Figure 5-1c-f**. Both the red and amber crystals were identified as $\text{C}_2\text{Al}_3\text{B}_{48}$ using Raman spectroscopy. Red crystals that are polished into plates or crushed into a powder turn amber in color, which indicates that the color is a function of thickness. In samples grown with high carbon concentrations, $\text{C}_2\text{Al}_3\text{B}_{48}$ does not form. Instead, opaque black crystals precipitate from the flux, identified as $\text{C}_4\text{AlB}_{24}$ and the crystal size is drastically reduced to less than 1 mm across.

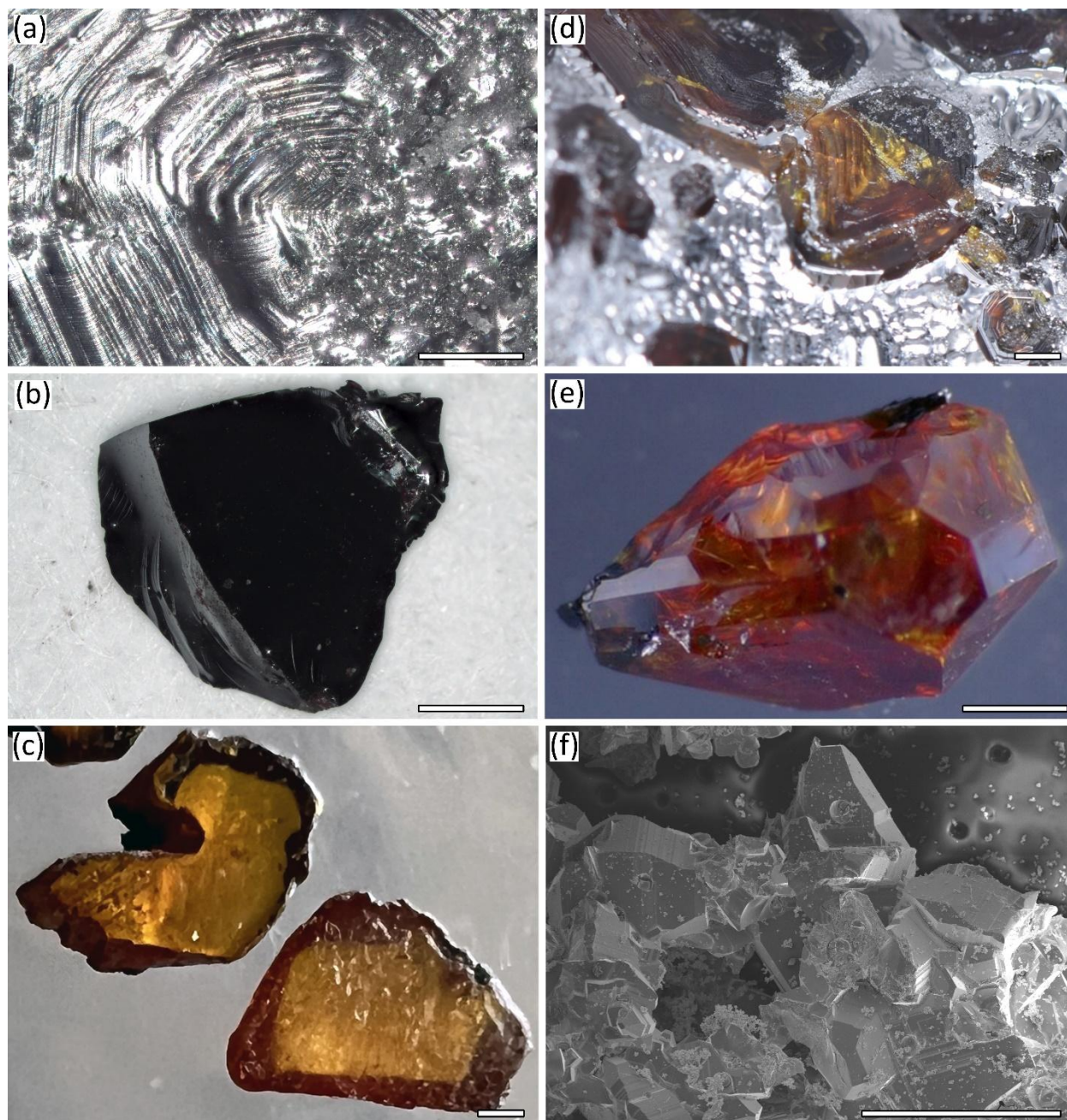


Figure 5-1. Different crystals grown from an Al-B-C flux. Scale bars are 500 μm . (a) AlB_{12} , showing the typical spiral pattern found on crystals formed on the surface of the metal flux ingot. (b) AlB_{12} after acid etching from an ingot. The curved surfaces are caused by conchoidal fracture. (c) A polished, flat $\text{C}_2\text{Al}_3\text{B}_{48}$ crystal. (d) $\text{C}_2\text{Al}_3\text{B}_{48}$ embedded in metal ingot before acid etching. (e) $\text{C}_2\text{Al}_3\text{B}_{48}$ with a deep red coloration. (f) SEM of $\text{C}_4\text{AlB}_{24}$ after acid etching from an ingot.

AlB_{12} and $\text{C}_2\text{Al}_3\text{B}_{48}$ are readily identified by Raman spectroscopy, as shown in **Figure 5-2**. AlB_{12} has a broad signature peak at 1040 cm^{-1} , a strong peak at 800 cm^{-1} , and a set of 8

peaks between 500 cm^{-1} and 700 cm^{-1} , all of which are indicative of the β -tetragonal boron sublattice. $\text{C}_2\text{Al}_3\text{B}_{48}$ has a set of three peaks between 925 cm^{-1} and 1200 cm^{-1} , which is indicative of the α -tetragonal boron sublattice. The $\text{C}_4\text{AlB}_{24}$ spectra, as shown in **Figure 5-2c**, has no Raman reference spectra in literature and was instead identified through XRD and supported by EDS. A single broad peak dominated the $1000\text{ cm}^{-1} - 1200\text{ cm}^{-1}$ region. Three weak narrow peaks appear at 478 cm^{-1} , 505 cm^{-1} , and 538 cm^{-1} respectively. A broad peak spans from 600 cm^{-1} to 875 cm^{-1} . A weak peak is present at 905 cm^{-1} .

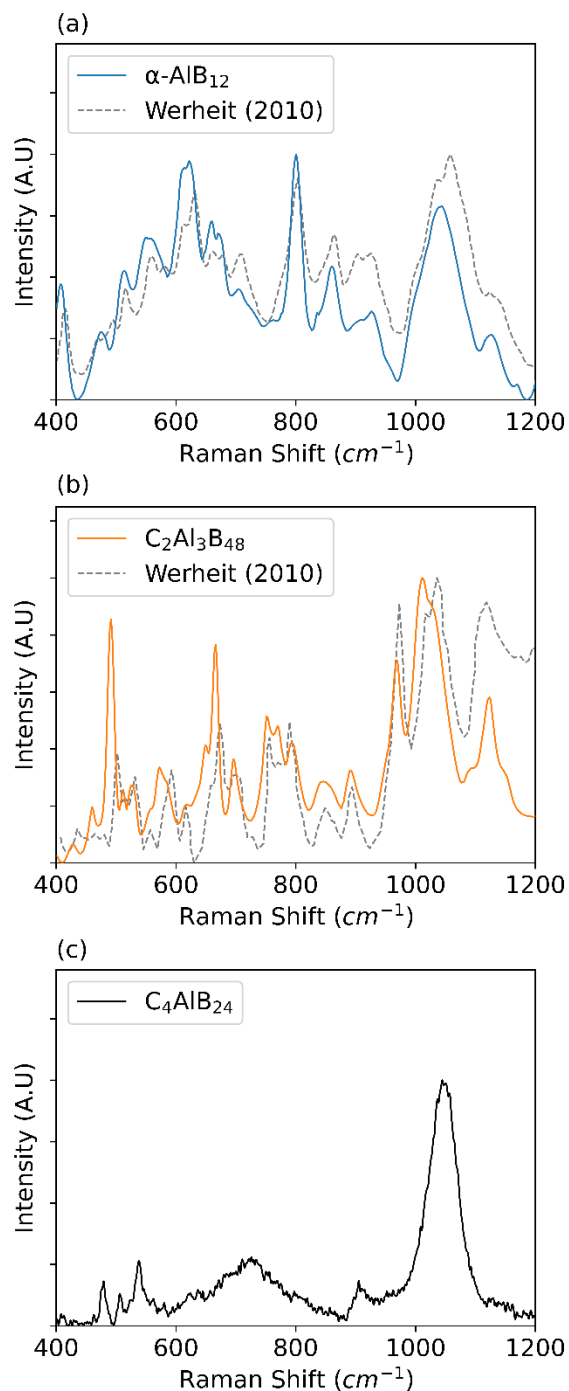


Figure 5-2. Raman spectra for (a) AlB_{12} , (b) $\text{C}_2\text{Al}_3\text{B}_{48}$, and (c) $\text{C}_4\text{AlB}_{24}$ single crystals. The colored lines are the spectra from this work, and the dashed black line is a reference spectrum from Werheit et. al.³⁴.

Samples that were precipitated from a flux containing 0 – 3 wt% C, were crushed using a mortar and pestle, and phase composition was measured using XRD, as shown in **Figure 5-3**.

Al₂O₃ is present in all samples, shown by the peaks at 25.5° and 43.4°. This is likely derived from the Al₂O₃ boats used to contain the flux during the experiment. Carbon compounds are present all samples, including the 0 wt% C flux, likely due to source material impurities or contamination issues. Crystals grown with no intentional carbon added to the flux produced predominantly opaque AlB₁₂ crystals, which has signature groups of XRD peaks between 25° - 30° and 40° - 50°, which carbon-containing samples lack. Crystals grown at carbon concentrations between 0.32 – 0.56 wt% C were semi-transparent, amber-colored C₂Al₃B₄₈. These were identified from the peaks at 14°, 20°, 22.5°, 32°, 36.5°, and 41°. Above 1.2 wt% C, no C₂Al₃B₄₈ was detected in the resulting crystals. Samples from high carbon concentrations, 0.6 wt% C – 2.9 wt% C, were primarily a type of opaque black crystal. This is closely reflected in the XRD spectra, as the C₂Al₃B₄₈ peaks were significantly reduced and new peaks appear at 21°, 34°, and 35.5°. This indicates a change in phase from predominantly C₂Al₃B₄₈ to other compounds such as C₄AlB₂₄ and C₃AlB. The sample grown at 0.6 wt% C demonstrated strong peaks from both C₄AlB₂₄ and C₂Al₃B₄₈. **Table 5-1** summarizes phases present in the samples grown from each carbon concentration. Exact phase compositions could not be estimated due to peak overlap between phases, evidence of twinning, and unknown peaks in the high wt% C samples.

Table 5-1. Table of XRD Results. Exact compositions could not be determined, but each phase could be independently detected. $C_2Al_3B_{48}$ was detected in all samples with a carbon concentration less than 1.19 wt% C. C_4AlB_{24} was detected in all samples.

wt% C	Al_2O_3	AlB_{12}	$C_2Al_3B_{48}$	C_4AlB_{24}	Other
0.0	x	x	x	x	
0.32	x		x	x	
0.43	x		x	x	
0.56	x		x	x	
0.60	x		x	x	x
1.19	x		x	x	x
1.77	x			x	x
2.37	x			x	x
2.92	x			x	x

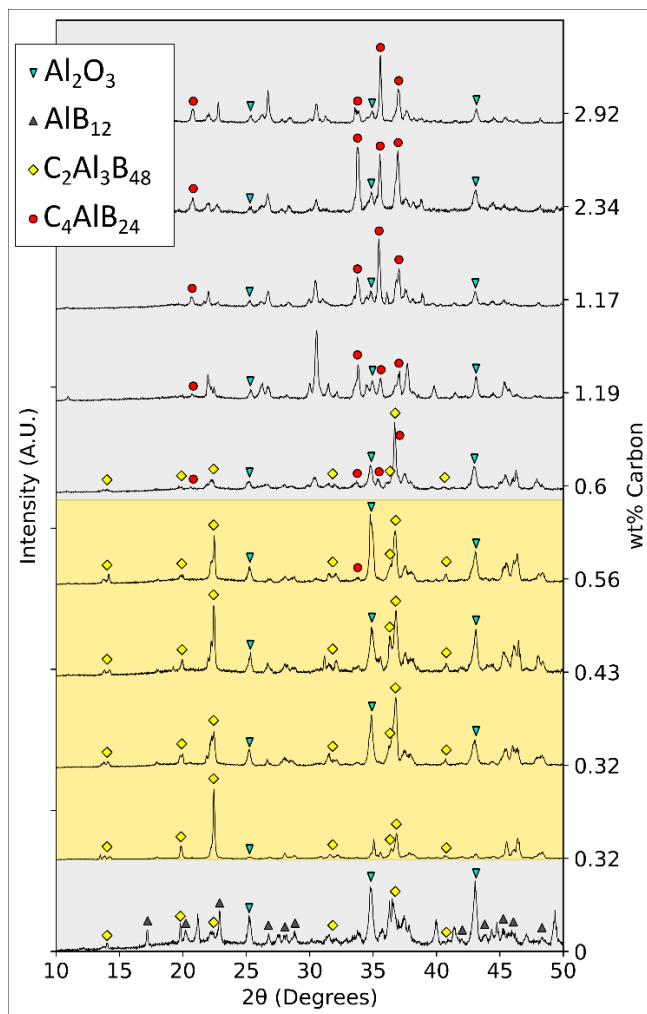


Figure 5-3. XRD of crystals grown at different carbon concentrations. Peaks for Al_2O_3 , AlB_{12} , $C_2Al_3B_{48}$, and C_4AlB_{24} are labelled. At carbon concentrations between 0.32 – 0.56 wt% C, the resulting crystals were transparent and amber or red in color. At higher carbon concentrations, the color is black, which corresponds with the presence of C_4AlB_{24} in the XRD spectra.

The crystal structure of $C_2Al_3B_{48}$, as derived by single crystal XRD, is shown in **Figure 5-4**. Its composition was $C_2Al_{2.83}B_{48}$, with a residual (R_1) value of 0.0496. The crystal follows the α -tetragonal boron sublattice, where carbon atoms replace the central boron atoms. Al partially occupies four lattice positions to varying degrees. The unit cell lattice parameters are $a = 10.159 \text{ \AA}$, $b = 12.622 \text{ \AA}$, $c = 12.305 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$ in the Ibam (72) space group. Atomic coordinates and occupancy levels are reported in **Appendix Table A.4**.

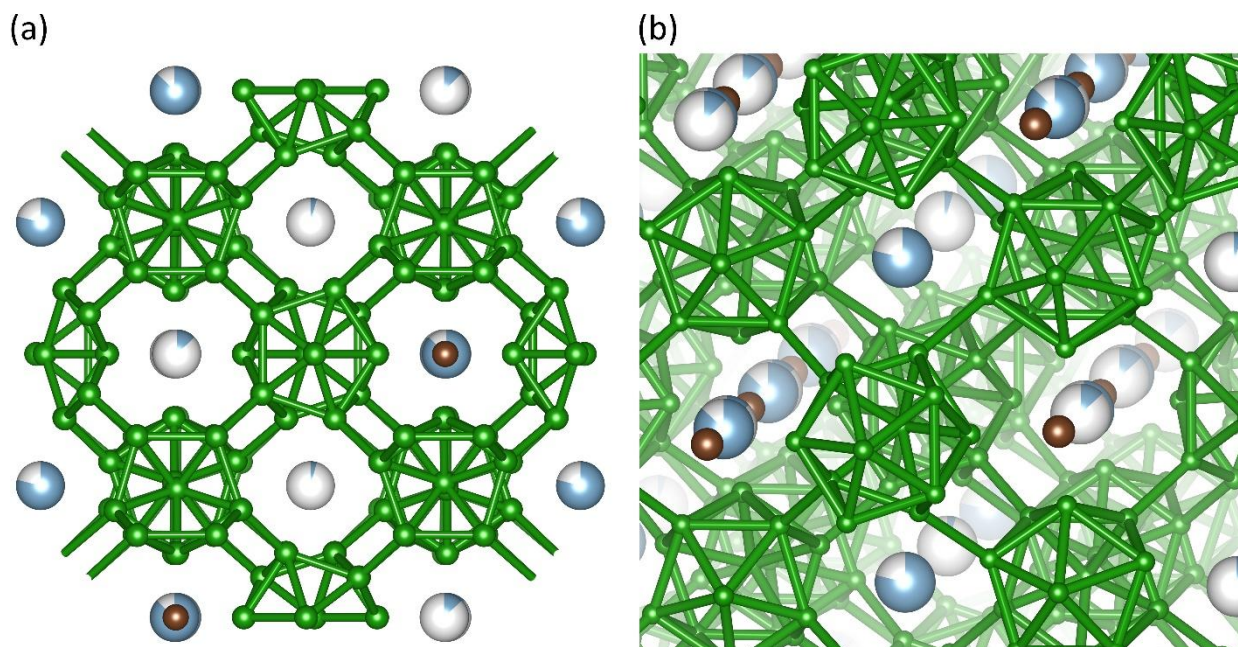


Figure 5-4. XRD derived structure of $C_2Al_3B_{48}$ (a) on the (100) plane and (b) at an orthogonal view, derived from a flux containing 0.43wt% C. It shows an α -tetragonal boron sublattice with the central boron atom replaced by a carbon atom. Interstitial aluminum atoms partially occupy the void spaces. Boron atoms are green, carbon atoms are brown, and aluminum atoms are silver. White represents the fraction of unoccupied sites.

Absorption and photoluminescence measurements were taken at different carbon concentrations to assess the band gap of AlB_{12} and $C_2Al_3B_{48}$. The absorption results, shown in **Figure 5-5**, show a soft absorption edge, so band gap estimates are not precise. **Figure 5-5a**

compares $C_2Al_3B_{48}$ crystals grown at different carbon concentrations in the flux. There is no clear trend in the absorption edge as a function of carbon concentration in the initial flux. Most samples have a band edge at ~ 2.4 eV when measured at 10 K, but values range between 2.4 to 2.7 eV. This is an expected result, based on the semi-transparent yellow coloration. **Figure 5-5b** compares AlB_{12} crystals and $C_2Al_3B_{48}$ crystals when measured at 300 K. AlB_{12} had an absorption edge at ~ 1.8 eV, which agrees with band gap estimates in literature¹⁶². This is a significant shift from $C_2Al_3B_{48}$, which is 0.5 eV higher on average. Photoluminescence was similar across all $C_2Al_3B_{48}$ samples, regardless of flux carbon concentration, with a broad peak centered at 1.9 – 2.0 eV.

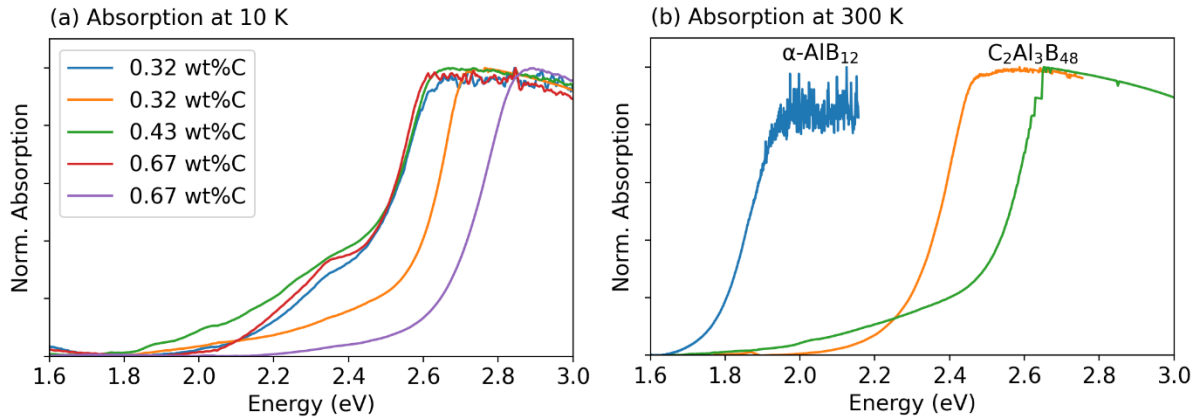


Figure 5-5. Absorption data for (a) $C_2Al_3B_{48}$ taken at 10 K from samples grown from a flux containing 0.32, 0.43, and 0.67 wt% carbon and (b) AlB_{12} compared to $C_2Al_3B_{48}$ taken at 300 K. The absorption edge for AlB_{12} is at 1.8 eV. The average absorption edge for $C_2Al_3B_{48}$ is between 2.4 and 2.5 eV.

Probes were applied to a $C_2Al_3B_{48}$ sample grown with 0.32 wt% C and a soldering iron was applied to the sample next to the positive probe, resulting in a positive current reading. This indicates that the majority carriers are electrons.

Conclusions

Boron-rich compounds were grown in an Al-B-C molten metal flux at carbon concentrations between 0 – 3 wt% C, with samples reaching 7 mm across. Samples with no intended carbon primarily formed AlB_{12} . $\text{C}_2\text{Al}_3\text{B}_{48}$ formed at carbon concentrations less than 1.2 wt% carbon. $\text{C}_3\text{Al}_3\text{B}$ formed at carbon concentrations above 0.6 wt% C. $\text{C}_4\text{AlB}_{24}$ was detected at all carbon concentrations. Based on color and changes to XRD spectra, the highest purity $\text{C}_2\text{Al}_3\text{B}_{48}$ crystals form at carbon concentrations between 0.32 – 0.56 wt% C. Single crystal XRD refined the structure and composition to $\text{C}_2\text{Al}_{2.83}\text{B}_{48}$, where Al partially occupies four distinct lattice positions. Absorption measurements on $\text{C}_2\text{Al}_3\text{B}_{48}$ showed a broad absorption edge between 2.4 – 2.7 eV, 0.5 eV higher than AlB_{12} , which had an absorption edge at 1.8 eV. The broad edge is likely due to phase mixtures and impurities in the measured sample. Hot-point probe tests indicate that the majority carriers in the $\text{C}_2\text{Al}_3\text{B}_{48}$ single crystals are electrons.

Future efforts should focus on increasing crystal size and improving phase purity. Crystal domain size from a molten metal flux can be increased in several ways, including lowering the cooling rate¹⁶⁶, optimizing dwell time⁵⁶, and optimizing flux composition¹⁶⁷. Phase purity will be more difficult to address, as XRD shows multiple phases present at all carbon concentrations. High purity $\text{C}_2\text{Al}_3\text{B}_{48}$ might be synthesized by increasing the dwell time and lowering the cooling rate at low carbon concentrations. Increasing the dwell time should improve homogeneity. Slowing crystal growth and reducing nucleation points should reduce the number of phases present in the sample. Finally, electrical characterization is of utmost importance for device consideration. Ohmic contacts need to be developed, and carrier concentrations and mobilities should be measured by Hall Effect.

Chapter 6 - Sub-bandgap Photo-gated Field Emission in SiC Nanotips

Abstract

Vacuum electronics offer significant advantages over solid-state devices in high-power, high-frequency applications, but are often bulky due to heated filament cathodes that prevent miniaturization. In this work, we fabricate a photo-gated field emission cold cathode from semi-insulating SiC. Sharp nanopillars with average tip widths of 10 nm and heights greater than 560 nm were etched into the surface to maximize the current density. This was done using a simple and easily scalable self-assembled Au nanodot array followed by SF₆ plasma etching. The field enhancement factor was determined to be as high as 205, and by using a sub-bandgap 447 nm laser, we found a turn-on field of $\sim 6.2 \text{ V}/\mu\text{m}$ and current density greater than $0.09 \text{ mA}/\text{cm}^2$ at $8.3 \text{ V}/\mu\text{m}$. By utilizing semi-insulating SiC, we minimize the dark-current through the device to increase performance in high-voltage systems.

Introduction

Vacuum electronics offer substantial benefits over solid-state devices as electron transport through vacuum is unimpeded by scattering and recombination and are used in high-power and high-frequency applications. However, typical vacuum electronic devices are large and bulky as the use of hot thermionic cathodes prevents miniaturization. To realize a miniaturized vacuum transistor, a cold cathode must be developed. While past research has focused on field emission from nano-scale tips of metal¹⁶⁸ or silicon¹⁶⁹, they rely on gate electrodes that must be placed near the field emission tips to generate the high electric fields required for electrons to tunnel into the vacuum. This design has significant limitations. First, the complex device structure leads to bulky, heavy systems or elaborate microfabrication. Second,

electrons emitted from the tips can be inadvertently collected at the gate, creating a leakage path. Third, as the gap between the tip and the gate decreases, the operating frequency becomes capacitance-limited. Photo-modulated emission from field emission tips was first reported by Schroeder in p-type silicon, but high leakage current was observed due to thermal generation of carriers from mid-gap defects present at the Si surface. While similar concepts have been proposed in p-type SiC^{170–172} or diamond^{173–175} which should have lower leakage due to the wider bandgaps, these devices require above-bandgap light to generate free electrons in the material, which in the case of diamond, requires an impractically high-energy light source.

SiC has advantages over metals or materials with narrower bandgaps such as Si. The wide bandgap of 3.0 to 3.2 eV for 6H-SiC and 4H-SiC polytypes, respectively, prevents leakage in high voltage systems, minimizing the dark-current. SiC also has high thermal stability and hardness and can therefore survive in harsh environments^{176–179}. Nitrogen is a common unintentional donor in SiC^{180,181}. Vanadium atoms are deep acceptors with trap energy level located at 0.74 eV below the conduction band minimum in 6H-SiC, and they effectively compensate the nitrogen donors to make the device semi-insulating^{182,183}, which has a typical electrical resistivity of $10^{10} - 10^{11} \Omega \text{ cm}$ ¹⁸⁴. The trapped electrons at the vanadium sites are photo-excited to the conduction band using a sub-band gap laser with a 447 nm wavelength.

The goal of high-performance field emitters is to have a large emission current and low turn-on field. Electron field emission is typically described by the Fowler-Nordheim equation in which the tunneling barrier is distorted by the large applied electric field. The electron current density, J , is expressed in **Eqn. (6-1)**^{185,186}, where k_1 and k_2 are constants $1.54 \times 10^{-6} \text{ A eV } V^{-2}$ and $6.83 \times 10^3 \text{ V eV}^{-\frac{3}{2}} \mu\text{m}^{-1}$ respectively, ϕ is the emitter work function, E is the applied electric field, and β is the field enhancement factor determined by the geometry of the emitting surface.

$$J = \frac{k_1 \beta^2 E^2}{\phi} \exp\left(-k_2 \frac{\phi^{1.5}}{\beta E}\right) \quad (6-1)$$

Figure 6-1 illustrates the design of the photo-gated field emission vacuum transistor. A photoconductive material, in this case semi-insulating SiC, absorbs light from a laser, exciting electrons into the conduction band. A large electric field is applied across the device, which allows the electron to tunnel into the vacuum.

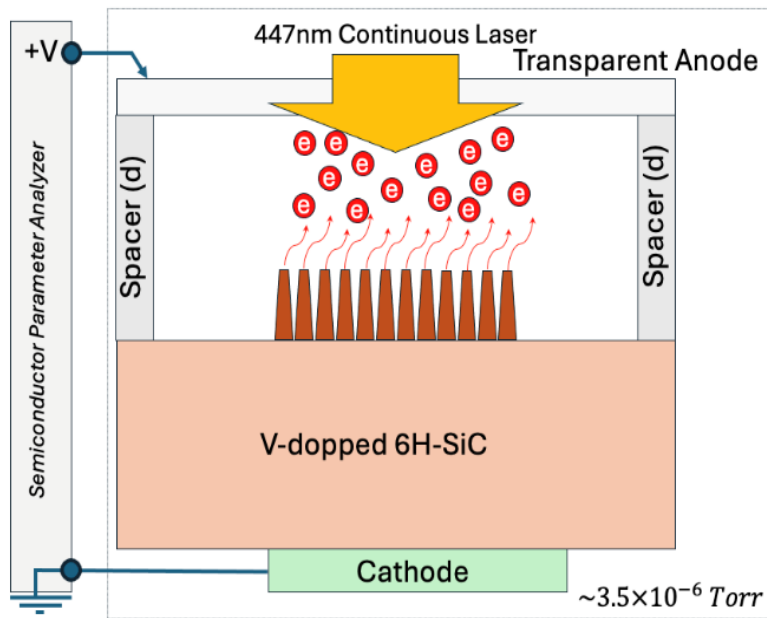


Figure 6-1. Illustration depicting a photocathode fabricated from V-doped SiC. 447nm light, λ , excites an electron into the conduction band. An electric field, E , causes the electrons to tunnel into the vacuum towards the anode.

In this work, to maximize the field enhancement factor, and thus the current density, we fabricate sharp pillars onto the cathode surface, concentrating the electric field by reducing the relative area from which electrons are emitted. The fabrication process was optimized to produce tall, sharp pillars, which was achieved using self-assembled Au nanodot arrays as plasma etch masks, providing a simple, fast, and scalable fabrication technique. We also demonstrate a SiC:V

field emitter in which electron field emission is effectively controlled by modulating its resistivity using sub-bandgap light.

Experimental Methods

Fabrication

SiC nanotips were fabricated by plasma etching in SF₆ using a self-assembled Au nano-dot etch mask. Mask and etch recipe development were done on nitrogen-doped, highly n-type 4H-SiC chips as this material is readily available and much easier to image by scanning electron microscopy (SEM) than semi-insulating SiC. The SiC chips were cleaned in an ultrasonic Micro-90 bath for 15 min, followed by a standard RCA cleaning process. On the silicon face, a 5 nm thick Au film was deposited using an electron beam physical vapor deposition system and patterned into a 3 mm diameter circle by liftoff using standard photolithography. The Au mask was then annealed at 650°C for 3 minutes under an inert Ar atmosphere using an AnnealSYS Rapid Thermal Process (RTP) system, forming Au nanodot arrays. The Au masked SiC was then etched using a Plasma-Therm Vision 320 reactive ion etching (RIE) system using SF₆ at 100 mTorr. Pillars were etched using RF powers from 100 to 250 watts for 5 to 90 minutes. The average height and tip width of the pillars etched into each N-doped sample were measured using SEM with a ThermoFisher Verios.

A photoconductive device sample was fabricated using 15 mm x 15 mm x 380 µm V-doped 6H-SiC chip. The chip was cleaned using the process described above and then a 6 mm diameter Ti/Al/Pt/Au contact was deposited on the carbon-face of the chip. The 5 nm Au film was deposited on the silicon-face of the chip and lifted-off into a 3 mm diameter circle before annealing into a self-assembled nano-dot array. An optimum etch recipe was then used to etch field emission tips. The gold mask was then removed by wet etching in Gold Etchant TFA.

Electrical testing

The 6H-SiC:V sample was soldered to a degenerately n-doped Si carrier wafer using indium spheres so that the back contact can be easily probed. A 12.7 μm thick polyimide spacer was placed over the chip around the pillars to serve as a spacer. A 10 mm diameter fused silica window coated with 125 nm of ITO was placed on the spacers over the field emission tips to act as transparent anode. The device stack was placed into a vacuum probe-station and probes were placed directly onto the window and the Si carrier. Measurements were taken at a pressure below 5×10^{-6} torr. Voltage was applied to the anode to generate an electric field at the sample surface. To conduct photo-assisted field emission measurements, a high-power laser diode (Sharp) with variable power output up to 5 W at 447 nm is fiber coupled and focused on a 2 mm diameter region of the SiC pillar area. Field emission current was measured and recorded using a semiconductor parameter analyzer through pre-amplified precise (0.3 fA) source measure unit (SMU).

Device performance was simulated to regress the field enhancement factor. For these simulations, the nitrogen concentration is $5 \times 10^{16} \text{ cm}^{-3}$, the vanadium concentration is $1 \times 10^{17} \text{ cm}^{-3}$, electron capture cross section is $7 \times 10^{-15} \text{ cm}^2$, electron low field mobility is $225 \frac{\text{cm}^2}{\text{Vs}}$, and barrier height is 3.4 eV^{187–189}. The absorption coefficient of 6H-SiC at 447 nm was measured to be 2 cm^{-1} using UV-Vis. The SiC thickness is 380 μm and the vacuum gap is 12 μm . Given the applied voltage V_a , the electric field in the vacuum (E_{vac}) is modulated by the laser intensity as described **Eqn. (6-2)**, where d_{vac} is the vacuum gap, d_{semi} is the semiconductor thickness, ρ_{semi} is the SiC resistivity with light, φ_{surf} is the surface potential, φ_m is the anode work function, φ_{semi} is the SiC work function and J is the emission current density.

$$V_a = V_{vac} + V_{semi} + V_{FB} = E_{vac}d_{vac} + J\rho_{semi}d_{semi} + \varphi_{surf} + \varphi_m - \varphi_{semi} \quad (6-2)$$

The SiC resistivity (ρ_{semi}) is inversely proportional to effective electron lifetime (τ_n) and generation rate $G(x)$, as shown in **Eqn. (6-3)**.

$$\rho_{semi} = \frac{1}{q\mu_n n_{avg}} = \frac{1}{q\mu_n \tau_n \int \frac{G(x)dx}{d_{semi}}} \quad (6-3)$$

The illuminated light intensity induces the E_{vac} change, and it exponentially modulates the emission current, as governed by Fowler-Nordheim, **Eqn. (6-1)**.

Results and Discussion

Fabrication

An array of pillar etching conditions is presented in **Figure 6-2**, where 4H-SiC samples were etched at 100 to 250 W for 5 to 90 minutes. The etch rate of the Au nanodot mask is low, and the lateral etch rates of the 4H-SiC pillars eventually completely undercuts the nanodot mask, creating a sharp tip on the end of a pillar. After the mask is removed, the plasma begins to etch the tip of the pillar, dulling the point and eventually etching the pillar into a flat plateau.

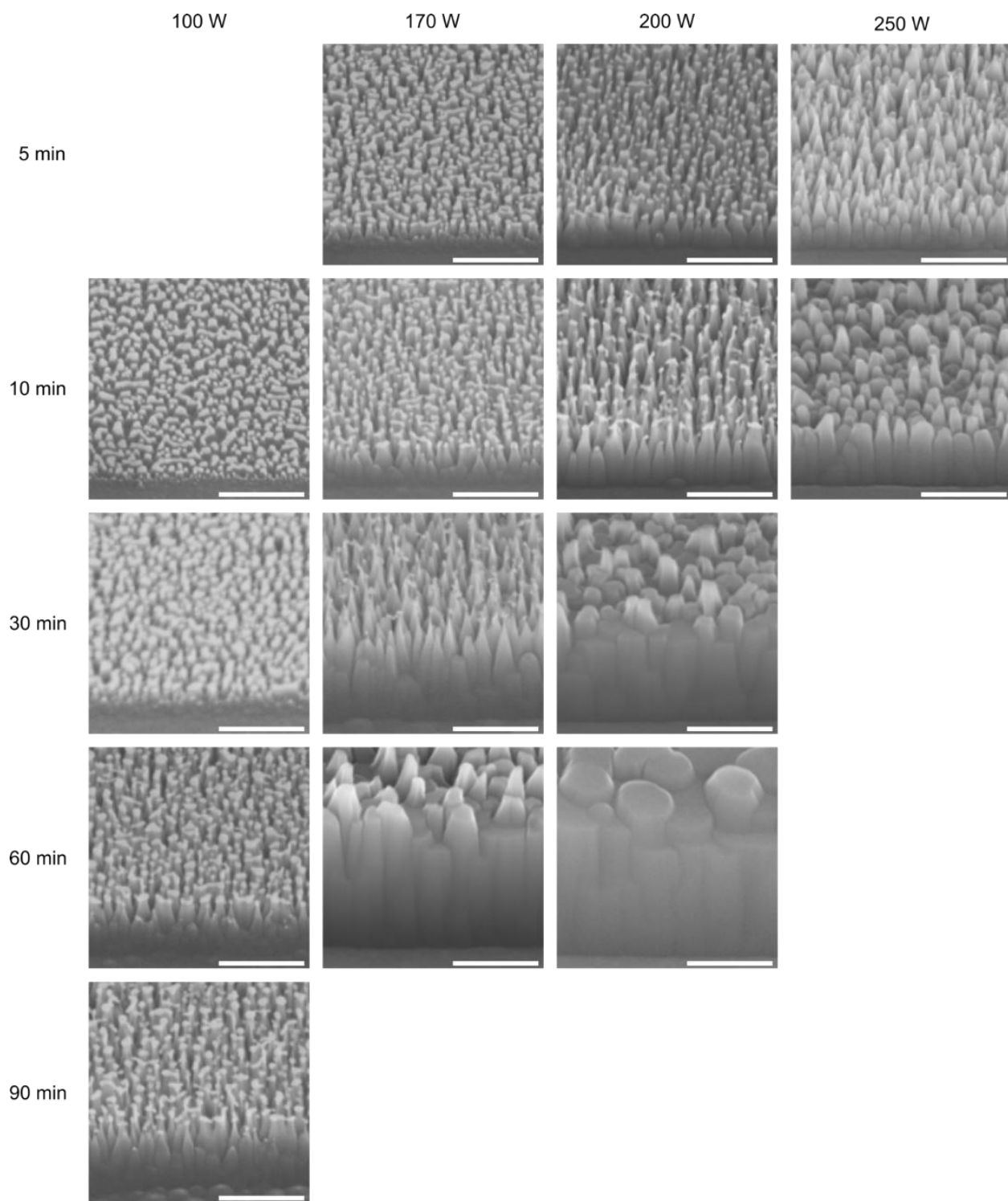


Figure 6-2. Scanning electron images of 4H-SiC pillars etched at 100-250 W RF power for 5-90 minutes in a pure SF₆ plasma. The scale bar is 500nm.

Ideal etching parameters were selected for narrow tips and tall pillars, or a high aspect ratio defined as the ratio of pillar height to tip width. These parameters were measured for every sample and are reported in **Figure 6-3**. Pillar height was measured from pillar tip to the unmasked SiC floor. The tip widths reach a minimum after a time dependent on the RF power. The smallest tip widths developed at the lowest RF powers. Therefore, the pillar aspect ratio increases with decreasing RF power. This indicates that the lateral etch rate decreases with decreasing RF power, allowing for taller pillars while maintaining sharper points before the mask is undercut. The best structures were fabricated using an RF power of 170 W for 30 minutes and produced an average tip width of 10 nm and height of 560 nm. This condition was used to fabricate the V-doped semi-insulating 6H-SiC cathode used in the device testing.

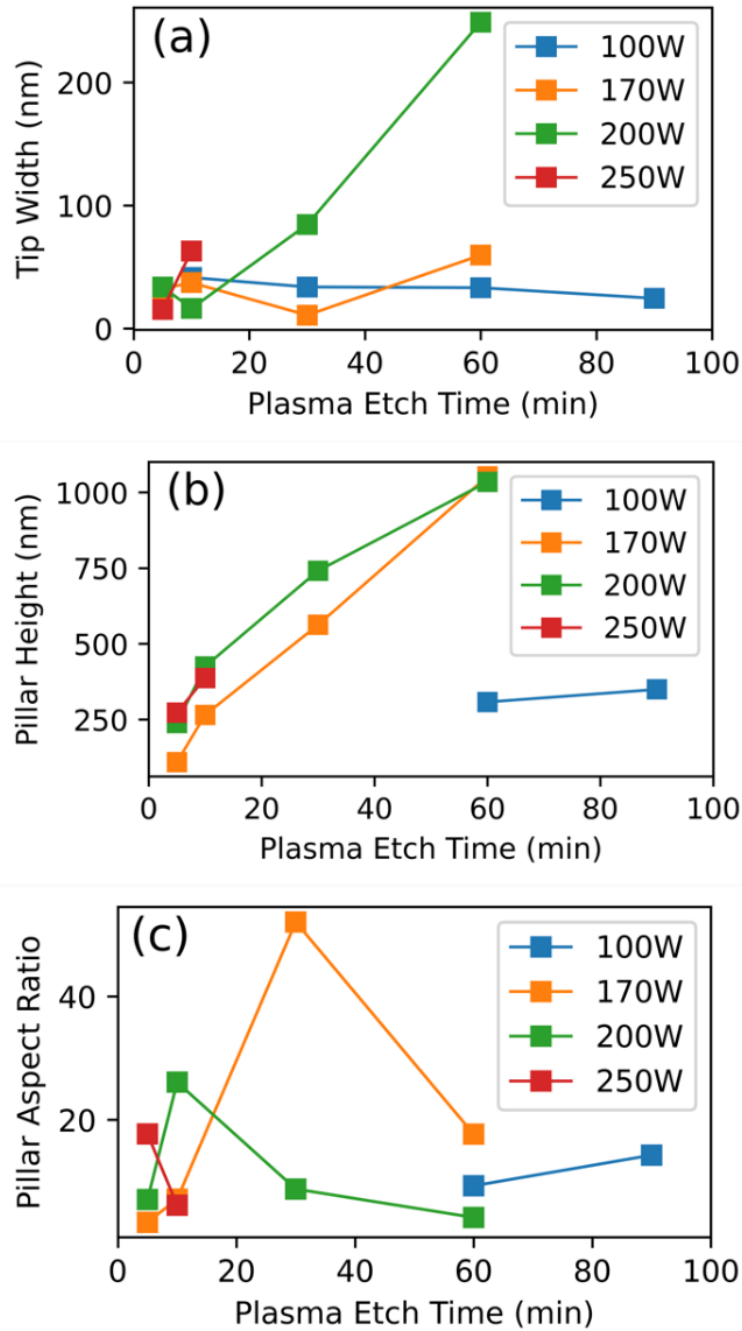


Figure 6-3. (a) Pillar tip width and (b) pillar height as a function of time at RF powers of 100-250W. (c) Aspect ratio is defined as the ratio of pillar height to tip width.

Electrical testing

The measured and simulated current densities from the optimized 6H-SiC photocathode with a thickness of 380 μm is presented in **Figure 6-4** and **Figure 6-5**, respectively. Without the

fabricated SiC pillars, the turn-on field was higher than the power supply used in this study was capable of, and no current increase was measured. The simulated current density was fit to a field enhancement factor of 205 to match the experimental current density of 0.09 mA/cm^2 at a field of $8.3 \text{ V}/\mu\text{m}$ while exciting the electrons with a laser power of 14 W/cm^2 . Error is expected in the regressed field enhancement factor due to statistical deviations in the heights and tip width of the SiC pillars, leading to some pillars emitting more strongly than others. The experimental and simulated results also indicate that the emission current density is effectively controlled by both the light power and of the applied electrical field in the vacuum. With a given anode voltage, a higher electric field in vacuum is obtained when SiC substrate resistance is reduced by a higher light power.

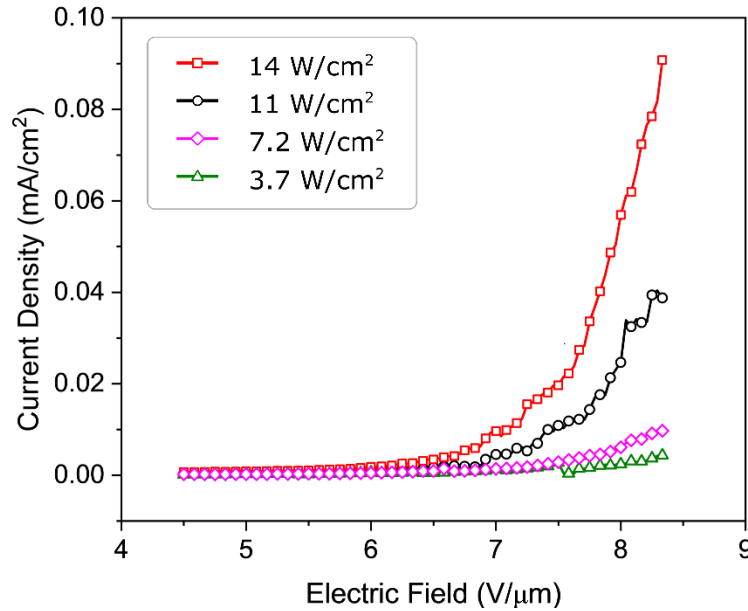


Figure 6-4. (a) Measured emission currents of 6H-SiC:V FE (380 μm) with sharp tips and vacuum gap of 12.7 μm with varied 447nm laser intensity.

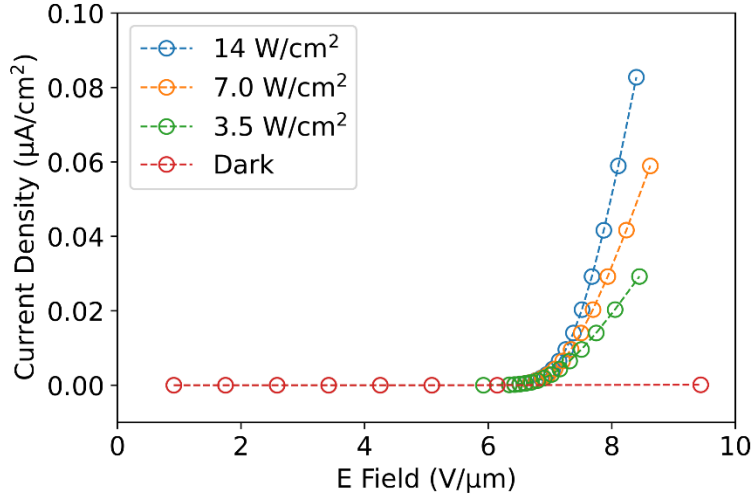


Figure 6-5. Calculated field dependent emission current with varied 447 nm laser power. E field is calculated by V_a/d_{vac} .

Conclusions

High aspect ratio SiC nanopillars were fabricated using reactive ion etching through a self-assembled Au nanodot array formed by annealing a 5 nm Au thin film. This method produced nanopillars with average tip widths as small as 10 nm and heights greater than 560 nm after etching for 30 minutes at 170 W in SF₆. The fabrication of the self-assembled Au nanodot array is both simple, scalable and could be readily transferred to other semiconductors for photocathode development.

The field enhancement factor was found to be 205 after regressing the optimized photocathode using the Fowler-Nordheim equation. This field enhancement reduces the turn-on field to $\sim 6.2 \text{ V}/\mu\text{m}$, with a current density greater than $0.09 \text{ mA}/\text{cm}^2$ at a field of $8.3 \text{ V}/\mu\text{m}$ using a 447 nm laser to incite photoconductivity. The photocathode emission depends on the laser intensity and applied voltage field. A numerical model of SiC field emitter with extrinsic absorption was built. The low current leakage and material durability make SiC photocathodes a promising device for high-power, high-frequency applications.

Chapter 7 - Formation of Tunable Diamond Micro- and Nanopillars for Field Effect Enhancement Applications

Abstract

We developed a process for the fabrication of tunable single crystal diamond micro- and nanopillars, with tip widths ranging from 40-460 nm, densities ranging from 0.5-53.5 pillars/ μm^2 , and heights greater than 4.5 μm . A self-assembled Au nanodot ensemble etch mask was formed from an annealed Au thin film. The nanodot diameter and density can be tuned using the initial film thickness. The pillars were etched from the nanodot mask using an RIE O_2 plasma, which has infinite selectivity for the diamond when applied at low RF powers (50 W). Finally, the pillars can be sharpened to ~ 40 nm tip widths by annealing in air at 650°C . These pillars can be used for applications such as field effect enhancement of diamond photocathode devices, enhancement of optical emission from N-V centers, and antireflective coatings.

Introduction

Diamond has been extensively studied for applications in high power electronics. It has proven to be an exceptional material due to its extreme hardness, ultrawide bandgap, chemical inertness, and high carrier mobility, thermal conductivity, electrical breakdown field, and radiation hardness. These properties make diamond well-suited for applications in high-power electronics, optoelectronics, and biotechnology^{71,190–193}.

Some applications can be enhanced through surface structures such as micro- and nanopillars. Diamond is a highly promising material for photocathodes due to the negative electron affinity of hydrogen-terminated diamond^{194,195} and high quantum efficiency (QE)^{64,71,196,197}. The photocathode properties are determined by the field enhancement factor (FEF), localized concentrations of the electric field through the device. The FEF can be

improved by fabricating tall, sharp micro- and nanopillars that reduce the total area from which electrons are emitted¹⁹⁸. Diamond nanostructures have also been of recent interest for applications in microplasma devices due to the robustness and chemical inertness of diamond in harsh environments^{199–201}. Confined microplasmas find many uses, such as plasma displays, tunable ultraviolet sources, confined silicon etching processes, and sensors^{199,202–204}. These structures can also enhance the optical emission efficiencies of nitrogen-vacancy (N-V) centers, nitrogen substitutional defects located next to a carbon vacancy, which behave as optical centers useful for quantum information processing and nanophotonic devices^{205–207}.

Self-assembled metal dot ensembles, formed by annealing a metal thin film, can be used as a hard mask during etching^{193,208,209}. These produce dots with dimensions significantly smaller than standard UV lithography, on the order of tens of nanometers^{205,209}. Self-assembled metal dot formations are also easily scalable, and large surface areas can be processed with no additional effort. Reactive ion etching (RIE) can be used for highly anisotropic vertical etching of submicron features, with little lateral etching, typically using O₂, H₂, Cl₂, SF₆, or CF₄^{210–212}. The diamond can also be thermally etched in an O₂ environment at temperatures above 450–500°C^{213–217}. The thermal etching process in O₂ is anisotropic, with higher etch rates on the (110) plane over other crystal planes and may be useful for lateral etching processes. In this study, thermal etching is used to convert prefabricated micro- and nanopillars into cones. By adjusting these parameters, the geometry of the resulting micro- and nanopillars can be tuned for different applications.

This study explores the tunability of diamond micro- and nanopillars by exercising control of pillar height, density, and tip width. The self-assembled metal nanodots can be used to control the initial pillar size and density, the RIE process can be used to control the pillar height,

and thermal oxidation can be used to laterally etch the pillars to reduce the tip width. This study emphasizes fabricating tall, sharp surface structures used in the field effect enhancement of diamond photocathode devices which will be tested in future studies.

Experimental Methods

300 μm thick mechanical grade single crystal diamond plates and 500 μm thick single crystal optical grade diamond plates from Audiatec were used in this study. The plates were cleaned by sonication in Micro-90 cleaning solution followed by an ethanol bath for 5 minutes each. A Plasma-Therm Vison 320 Reactive Ion Etcher (RIE) was used to further clean and remove any scratches from the surface by etching 500 nm of material from the plate. This was done at 500 W RF, 50 sccm O_2 , 60 mTorr for 10 minutes.

To create the mask, Au was deposited directly onto the cleaned (100) surface of the diamond plates using an electron beam evaporator. Au thicknesses of 7.5 nm, 10.0 nm, 12.5 nm, 15.0 nm, and 20 nm were deposited. The films were then annealed at 900°C for 3 minutes in an inert Ar atmosphere using an AnnealSYS Rapid Thermal Process (RTP) system, forming Au nanodot arrays. 900°C was chosen for the Au film annealing because higher annealing temperatures improve the size distribution and circularity of the dots^{205,208,209}, although this was not specifically optimized in this study.

The Au masked diamond was etched using the Plasma-Therm Vision 320 RIE at 50 W RF, 50 sccm O_2 , and 60 mTorr. The etch rate was determined by etching a 15 nm Au mask diamond sample for 3 hours, 8 hours, and 16 hours. All other samples were etched for 8 hours. A combination of Au mask and O_2 etchant were used due to relatively high selectivity^{209,210} and ease of application. After the pillars were fabricated, the Au mask was stripped in Gold Etchant TFA, and the pillars were sharpened via thermal annealing using the AnnealSYS system.

Thermal annealing was done in a 21% O₂ / 79% Ar atmosphere at temperatures between 500°C – 650°C in 25°C increments. This gas composition was chosen to simulate sharpening in air. Then new samples were sharpened at 650°C for 3 minutes, 5 minutes, and 8 minutes. This sample was compared to an optical grade diamond plate processed in parallel.

After each experiment, the density of the pillars, height of the pillars, and width of the pillar tips were evaluated using scanning electron microscopy (SEM) with a ThermoFisher Verios SEM. Measurements were manually taken in ImageJ to calculate the dimension standard deviations.

Results and Discussion

To achieve high selectivity with the thin Au mask on the diamond plates, a low RIE plasma power was maintained. At 50 W RF power in an O₂ plasma, the Au film etch rate was essentially null, establishing a near infinite selectivity. **Figure 7-1** shows SEM images of pillars formed after 3, 8, and 16 hours in the O₂ plasma. The physical etching process produces smooth, rounded pillars independent of diamond crystal planes, which flare outward as the diamond continues to etch.

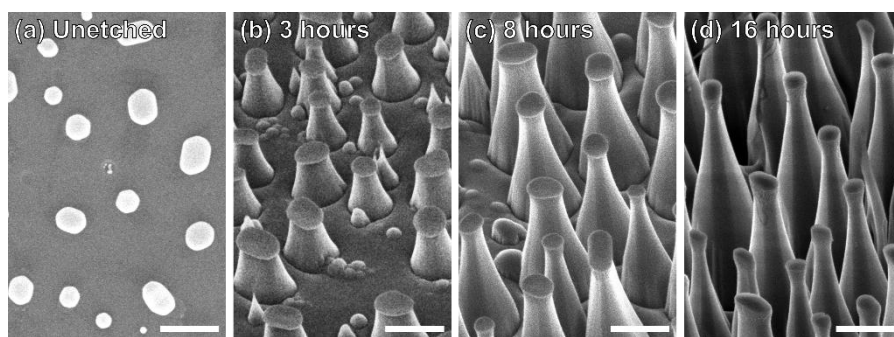


Figure 7-1. Scanning electron images of (a) Au nanodots and diamond pillars etched at 50 Watts RF power in a pure O₂ plasma for (b) 3 hours, (c) 8 hours and (d) 16 hours. The Au dots can still be seen at the tips of each pillar. The scale bars are 1 μ m.

Figure 7-2 shows the pillar height and tip width as a function of time, which was used to determine the etch rate of diamond at an RF power of 50 W in O₂. The vertical etch rate was measured to be 5 nm/minute and the lateral etch rate was 0.15 nm/minute, producing high aspect-ratio structures. The etch rate appears to be consistent across the etching process, despite the extensive etch times and tall, closely packed structures. The objective of this study was to produce tall structures in a controlled manner, so the plasma RF power was not optimized to reduce the etching time. Increasing the RF power would both shorten the time required to form the pillars, form a smooth floor free of the bumps seen in **Figure 7-1(a,b)**, and improve the verticality of the etch²¹⁰ at the expense of the selectivity of the Au mask.

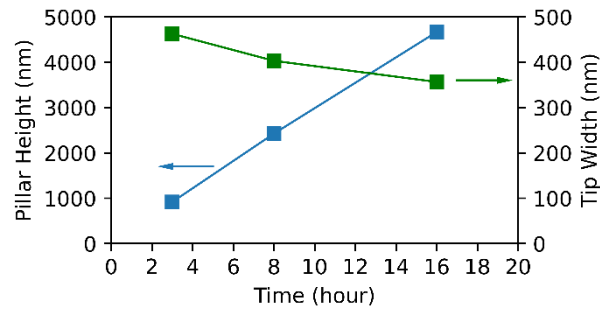


Figure 7-2. Pillar height (blue) and tip width (green) as a function of time.

The thickness of the initial Au film can be modulated to control the size and density of the diamond pillars. **Figure 7-3** shows SEM images of pillars created from annealed Au films ranging from 7.5 nm to 20 nm thick.

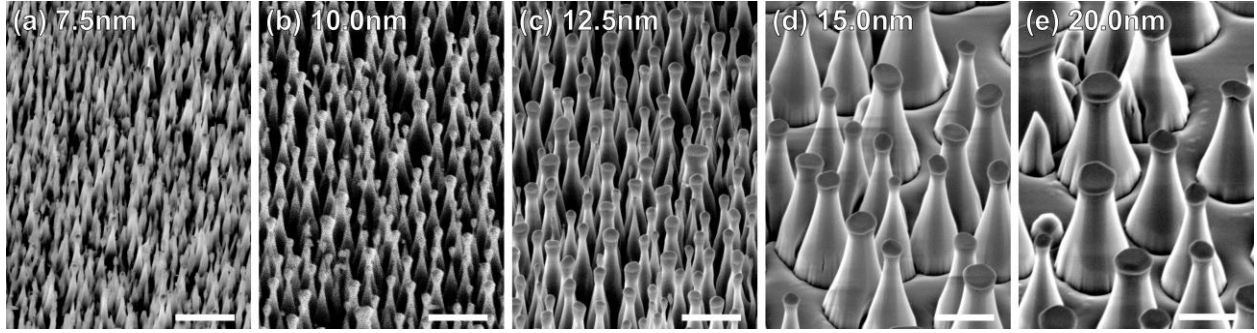


Figure 7-3. Scanning electron images of diamond pillars formed from (a) 7.5 nm, (b) 10.0 nm, (c) 12.5 nm, and (d) 15 nm, and (e) 20 nm Au masks etched at 50 Watts RF power in a pure O₂ plasma for 8 hours. The scale bars are 1μm.

The Au nanodot formation follows solid-state spinodal dewetting, which occurs when a liquid film forms droplets on a solid surface to minimize the total energy of the free and interfacial surfaces. This produces an array of dots with statistically distributed diameters and spacing, determined by the initial film thickness. The width of the diamond pillars increases with increasing film thickness, experimentally regressed to the form:

$$D = 0.00124 h^{4.67} \quad (7-1)$$

where D is the diameter and h is the initial metal film thickness in nanometers. The density of the pillars decreases quadratically with Au film thickness, following the spinodal dewetting relationship^{208,218}

$$\Lambda = \sqrt{\frac{16\pi^3\gamma}{A}} h^2 \quad (7-2)$$

where Λ is the nearest neighbor spacing, γ is the surface tension of the liquid metal film at elevated temperatures, and A is the Hamaker coefficient. For the data presented in this study, the average neighbor spacing was regressed to

$$\lambda_m = 4.46h^2 \quad (7-3)$$

where λ_m is the average neighbor spacing. However, as the Au film thickness increases beyond 15 nm, the rate of change quickly tapers off, as shown in **Figure 7-4**. Since the Au dot array is

formed via spinodal dewetting, there are significant deviations in the average tip width. The standard deviation of the pillar tip width increases with temperature, but always remains between 40%-45% of the average tip width, regardless of mask thickness, when the dot array is annealed at 900°C. Part of this large standard deviation is attributed to difficulty measuring the diameter of the Au mask particles, which are oblong rather than perfectly circular. Reducing the wettability of the metal-diamond interface should improve uniformity across the metal dot array. To address this issue, a few methods could be employed. Firstly, the annealing temperature could be increased, which would increase the energy of the metal-diamond interface. Another method would be to alter the surface energy of the metal-diamond interface directly. At this stage of the fabrication process, the diamond surface is oxygen-terminated. If the metal were annealed in a different atmosphere, such as hydrogen, the termination of diamond surface would change, potentially increasing the interfacial energy and producing more uniform metal dot distributions. This should be done in future work.

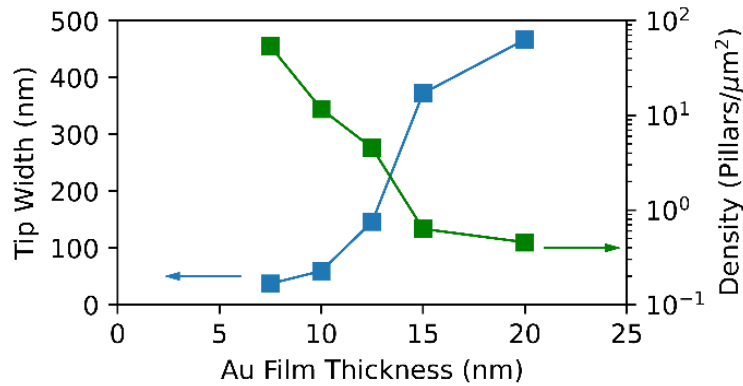


Figure 7-4. Plots showing tip width (blue) and pillar density (green) as a function of initial Au film thickness.

To maximize field effect enhancement of the pillars, they need to be sharpened to a fine point. This is achieved by heating them in an oxidizing atmosphere, as the chemical etching process drastically increases the lateral etching rate on the diamond structures, producing sharp

points. This process is self-sharpening and can be done before or after removing the Au mask on each pillar. The pillars were etched for 5 minutes in an atmosphere containing 21% O₂ to mimic annealing in air. The temperature was incrementally increased from 550°C to 675°C. At temperatures below 600°C, there was no significant change in the pillar tip widths. As shown in **Figure 7-5**, above 625°C, the etch rate increases rapidly with temperature. At 650°C after 5 minutes, the height of the pillar had decreased from 2.0 μm to 1.7 μm, indicating that they had over-etched. While the tip width of the over-etched pillars remains narrow, this process should not diminish pillar height. Therefore, controlled sharpening in 21% O₂ should be kept to between 625°C – 650°C.

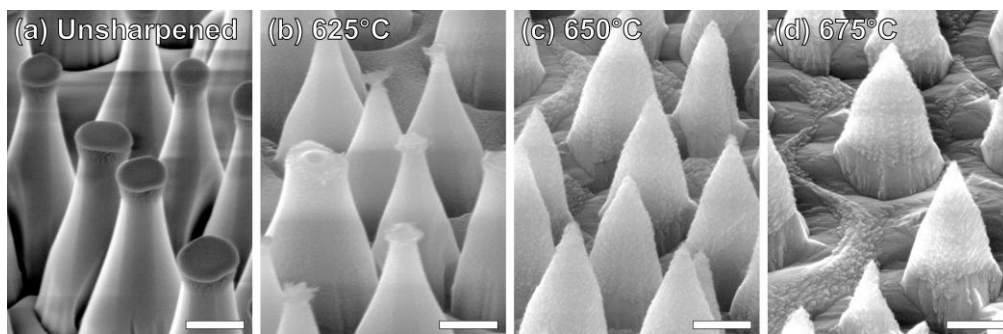


Figure 7-5. Scanning electron images of diamond pillars sharpened by oxidizing them in a 21% O₂ and 79% Ar atmosphere for 5 minutes after removal of the Au mask. The scale bars are 500 nm. (a) is unsharpened, and the others were heated to (b) 625°C, (c) 650°C, and (d) 675°C

An etching time series at 650°C was employed to refine the pillar tips, shown in **Figure 7-6**. This was performed on both mechanical and optical grade diamond, which has fewer substitutional nitrogen defects, to study how defect density in the diamond impacts the sharpening process. It is important to note that the Au mask formed larger dots on the optical grade diamond surface, an average of 410 nm rather than the 360 nm on the mechanical grade diamond. Both pieces were processed at the same time, so there should be no deviation in Au thickness or annealing temperature. This could be due to differences in the surface quality of the

diamond. It could also be attributed to natural deviation due to the statistical processing of this fabrication method. In either instance, the impact of the diamond quality on the Au dot formation was not further explored.

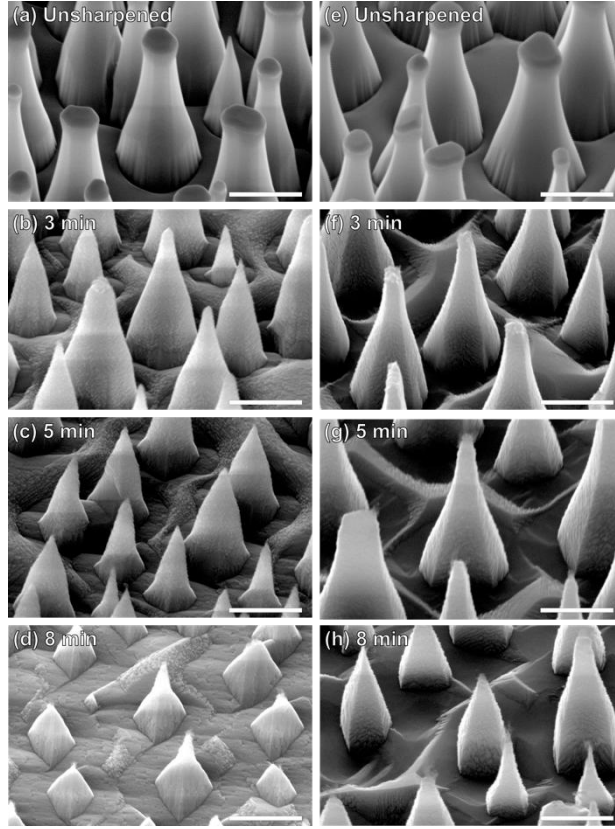


Figure 7-6. Comparison between mechanical (left) and optical (right) grade diamond pillars sharpened at 650°C for (b,f) 3 minutes, (c,g) 5 minutes, and (d,h) 8 minutes. Scale bars are 1 μm .

On both mechanical and optical grade diamond, sharpening in a 21% O_2 atmosphere results in an initial rapid sharpening stage where the bulk of the pillar tip is removed. Eventually, the impact of further sharpening decays as the bottle neck formed by the plasma stage is etched away, eventually eliminating the pillar entirely. The tip width of the pillars formed by a 15 nm Au mask is limited to 40 nm, as shown in **Figure 7-7**. Better control might be achieved if the temperature is lowered, slowing the etching process. However, this comes at the sacrifice of fabrication speed.

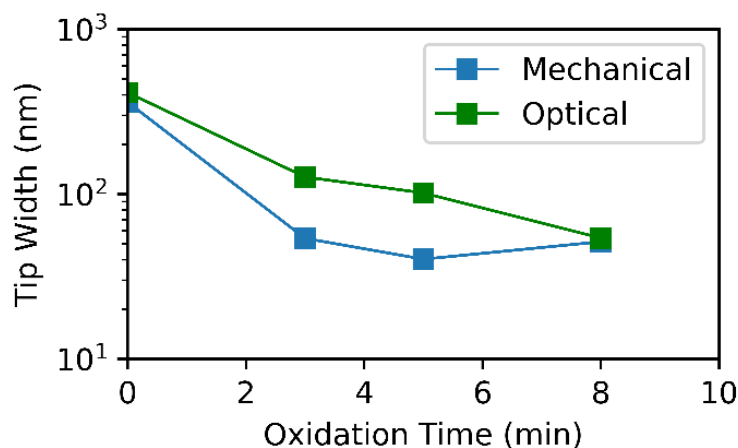


Figure 7-7. Tip width as a function of oxidation time for diamond pillars etched from a 15 nm Au mask dot array. The gas composition was 21% O₂ in Ar.

Anisotropic etching was present on both the mechanical and optical grade diamond plates, where pillars form faces with sides oriented to the (110) crystal planes, as shown in **Figure 7-8**, which agrees with other thermal oxidation studies^{216,219}. The pit surrounding the pillars etches outward into a square where the faces are oriented to the (100) plane, rotated 45° relative to the pillars. This can be explained with anisotropic etching rates. For convex surfaces, the faster etching plane will emerge²²⁰. In this case, the (110) plane on the side of the now rectangular pillar. For concave surfaces, the slower etching facet emerges. In this case, the (100) plane on the now rectangular pits surrounding the pillars. The crystal facets are more prominent on the optical grade diamond, and distinguishable at lower etch times, likely due to the reduced defect density in the diamond, which significantly impacts anisotropic etching behavior²¹³⁻²¹⁵.

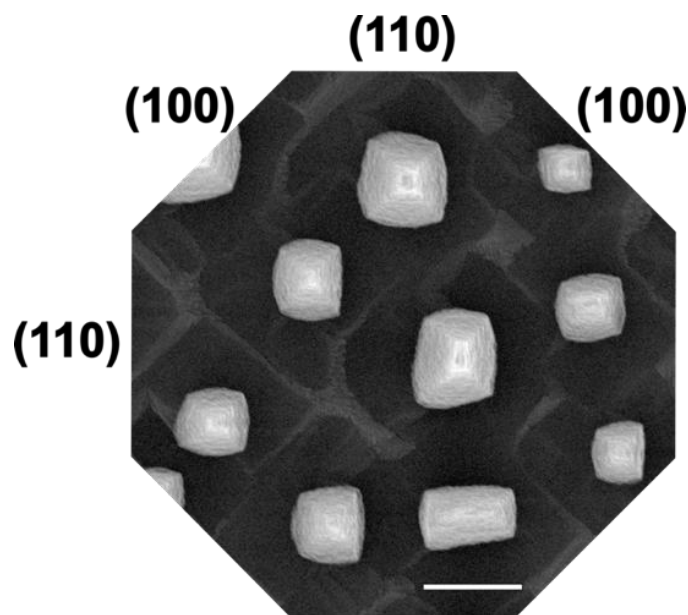


Figure 7-8. Top-down view of the optical grade diamond pillars sharpened at 650°C in 21% O₂ for 8 minutes. Scale bar is 1 μm. The pillars clearly turned into rectangular pyramids with faces in the (110) plane.

On a single crystal diamond surface, the Au cap is not necessary for pillar sharpening because the apex, a (100) plane, etches slower than the sides of the pillars, which have exposed faster etching (110) planes. If this technique was applied to polycrystalline diamond films, self-sharpening should still occur so long as the crystallites are significantly smaller than the size of the pillars. In this case, the nanocrystalline structure should etch pseudo-isotropically. Sharpening would occur by reducing the pillar diameter, eventually pinching off a sharpened tip. Isotropic etching has been used to sharpen silicon nanocones in the past^{221,222}. If the polycrystalline grains are on the same scale as the pillars, then the anisotropic oxidation risks uneven etching, which could lead to dull tips or uneven, malformed pillars. These three scenarios are displayed in **Figure 7-9**.

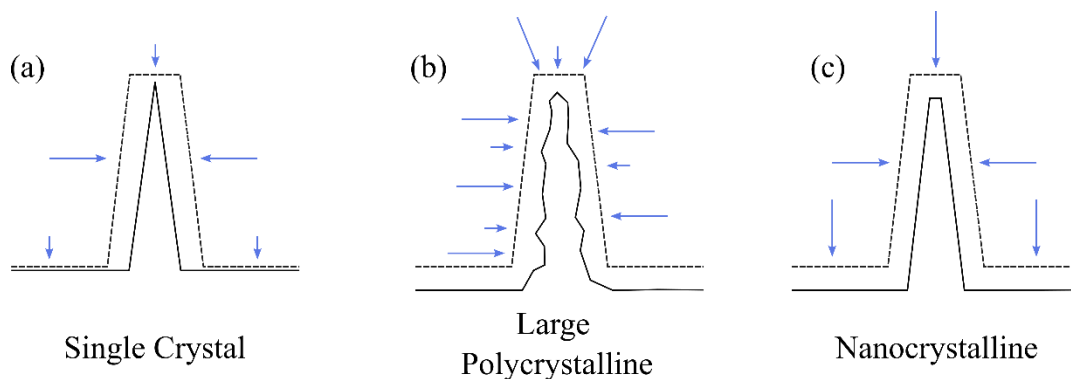


Figure 7-9. Diagram showing the expected etching behavior of (a) single crystal diamond, (b) polycrystalline diamond with large grains relative to pillar size, and (c) polycrystalline diamond with small grains relative to pillar size. The blue arrows show relative etch direction and magnitude. The dashed gray lines indicate pillar shape before etching and the solid black line is the expected pillar shape after etching.

Conclusions

This study demonstrated pillars etched into the surface of diamond substrates with tunable parameters such as pillar density, height, and tip width using a thermally dewetted Au thin film mask and various oxygen treatments. The thickness of the Au thin film was modulated to vary the density of the pillar ensemble between 0.5-53.5 pillars/ μm^2 . The height can be accurately controlled with a low RF power O_2 plasma. Finally, the pillar tips can be sharpened down to ~ 40 nm points through thermal oxidation in air. In future studies, these structures will be tuned to test field effect enhancement of diamond photocathode devices by producing tall, well-spaced pillars that taper down to minimized tip widths.

Further optimization can be done to improve device fabrication goals. Increasing the RIE RF power can drastically shorten the pillar etching process, which is by far the longest step in this fabrication technique. It will also produce smoother walls with improved verticality. This is at the expense of the selectivity of the Au mask, and since the thickness of the Au mask cannot be increased without changing the final pillar geometry, the RIE power should be optimized to achieve a specific pillar height. The uniformity of the nanodots can also be problematic, as the

spinodal dewetting tends to produce oblong dots, and asymmetry reduces the ability to sharpen the pillars to a fine point. The uniformity of the metal dot array can be improved in two ways: increasing the temperature of the metal film annealing step or reducing the wettability of the metal on diamond. The wettability can be tuned by either changing the masking metal, or by annealing in an atmosphere that maintains a different diamond surface termination, such as a H_2 atmosphere.

Chapter 8 - Plasma-free Hydrogenation of Oxygen-Terminated Polycrystalline Diamond as Determined by Circular Transmission Line Measurements (CTLTM)

Abstract

We developed a process to fully hydrogen-terminate diamond by annealing in forming gas. The surface was characterized using circular transmission line measurements (CTLTM) to evaluate the onset and degree of hydrogen termination. No hydrogenation occurred at temperatures at or below 500°C. Hydrogenation occurs after annealing for 5 minutes at temperatures between 600°C-1000°C, with complete hydrogenation achieved at 1000°C, which showed the same sheet resistance as diamond terminated in a hydrogen plasma. Annealing at temperatures lower than 1000°C resulted in only partial hydrogenation but can be compensated by increasing the anneal time. At temperatures exceeding 1100°C, the sheet resistance suddenly and drastically increases, indicating instability of a hydrogen-terminated diamond surface at elevated temperatures under forming gas. The activation energy was determined to be 1.20 eV. SEM inspection showed that annealing in hydrogen produced significantly reduced surface roughness compared to diamond surfaces hydrogenated in an H₂ plasma.

Introduction

Vacuum electronic devices (VEDs) have superior electron transport for high-frequency, high-power devices due to the high critical field and absence of electron scattering in the vacuum. This leads to applications in wireless communication, electron microscopy, radar, x-ray sources, remote sensing and imaging, cancer treatment, and energy conversion^{61–63}. There is a need for further development of photocathodes that can be used as an electron emitter in these

VEDs. Current semiconductor photocathodes have high quantum efficiency, the ability to emit electrons in response to excitation by photons, but suffer from sensitivity to trace concentrations of impurities, resulting in low device operating lifetimes and strict vacuum packaging requirements^{62,64}. Nitrogen-doped diamond has proven to have exceptional properties that make it a promising material for photocathodes, including such as an high quantum efficiency, high thermal conductivity, high breakdown voltage, high radiation hardness, and exceptional chemical inertness, making it an excellent candidate for applications where environmental robustness is necessary^{64,71,191,192,223,224}. Oxygen and hydrogen are the two most common surface terminations on diamond and have distinct properties. Oxygen-terminated diamond is electrically insulative and has a positive electron affinity (PEA), while hydrogen-terminated diamond exhibits p-type electrical conductivity as well as a negative electron affinity (NEA), which makes it ideal for use in photocathodes²²³ and preserving surface optical centers used in quantum information processing and nanophotonics^{206,207}.

The conductivity in H-terminated diamond is induced by a 2-dimension hole gas (2DHG), which is formed by the interaction between the dipole on the carbon-hydrogen (C-H) bond and adsorbates from the atmosphere, as explained by the surface transfer doping model⁷⁷. A hole layer forms on the diamond surface and an electron layer forms at the first monolayer of adsorbates. Adsorbates with low conduction band minimums produce denser hole gasses⁷⁷⁻⁷⁹. The conductivity induced by the 2DHG is useful in high-power field effect transistors (FETs)^{75,225}. In these devices, hydrogen termination of the diamond surface has been used to successfully bypass doping requirements to make high quality FETs⁸²⁻⁸⁴. The high carrier mobility in diamond reduces device switching times, minimizing switching losses and maximizing operating frequency²²⁶. Incomplete H-termination or replacement of the hydrogen

by oxygen results in breakages in the 2DHG layer, increasing sheet resistance and degrading device performance. Therefore, it is essential that fabrication processes produce diamond surfaces with complete hydrogen coverage.

Hydrogen-terminated diamond is typically prepared by plasma treatment in pure hydrogen, which requires specialized equipment and can cause unintended etching^{80,227} or degradation of engineered surface structures such as field emission enhancement tips. This study explored the reaction kinetics of hydrogenation of diamond by annealing in forming gas consisting of 4% H₂ in Ar. Forming gas was used as a commercially available, nonflammable, low cost, accessible alternative to pure hydrogen plasmas, requiring less specialized equipment and allowing for simple scale-up for industrial processes. Characterization was performed by circular transmission line measurements (CTLM) using annealed molybdenum contacts to measure the sheet resistance, which is proportional to the concentration of hydrogen-termination coverage on the diamond surface. Our experiments show that oxygen-terminated polycrystalline diamond can be completely hydrogenated by annealing in forming gas for 5 minutes at 1000°C, reaching nearly the same level of conductivity as a sample treated in a hydrogen plasma for 10 minutes. It was found that the reaction process has an activation energy of 1.20 eV. However, higher temperatures reduced the measured sheet resistance, indicating a potential limit to the operating temperature of diamond photocathodes that should be further explored.

Methods

8 μm thick, high purity polycrystalline diamond grown on silicon wafer purchased from SP3 Technologies was used for this study. The wafer was cleaned by using piranha solution for 15 minutes, followed by sonication in Micro-90 cleaning solution for 10 minutes. A Nordson AP-300 vacuum plasma treatment system was used to further clean the surface with a 300 W O₂

plasma for 3 minutes. Standard lithography was used to pattern a CTLM array, shown in **Figure 8-1**, which was designed after the CTLM pattern by Jacobs et. al²²⁸. The gap spacings of the nine CTLM circles, or the thickness of the exposed polycrystalline diamond ring, are 4, 8, 12, 16, 20, 24, 32, 40, and 48 μm respectively. The CTLM contact was 100 nm molybdenum deposited using a KJ Lesker PRO Line™ PVD 75™ THIN FILM DEPOSITION SYSTEM. Afterwards, the contacts were annealed in pure Ar at 600°C for 20 minutes in an AnnealSYS Rapid Thermal Process (RTP) system to minimize contact resistance²²⁹. The wafer was cleaved into pieces 3-5 mm across to create individual samples that could be independently terminated.

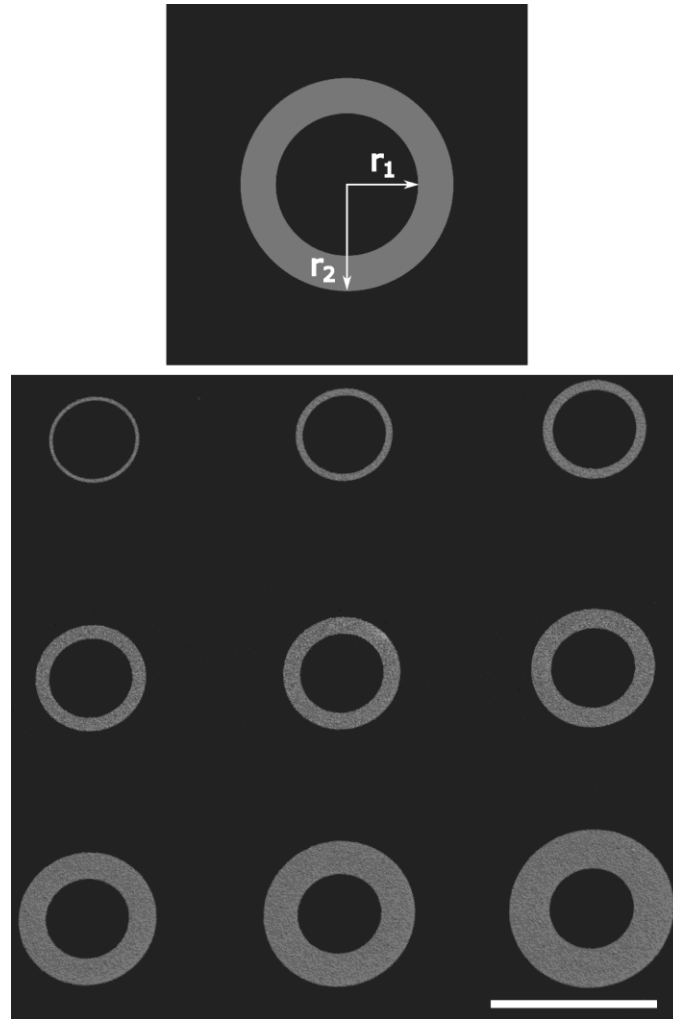


Figure 8-1. CTLM pattern on a polycrystalline diamond surface. The dark area is Mo, the light rings are exposed polycrystalline diamond. The scale bar is 200 μm .

Every sample was initially full oxygen-terminated in a Nordson plasma system using a 300 W pure oxygen downstream secondary plasma for 10 minutes prior to further surface treatment. One sample was set aside as an oxygen-terminated sample standard. As a control, a fully hydrogen-terminated diamond sample standard was terminated using a 750 W pure H₂ plasma (~800°C) at 120 Torr for 10 minutes in a Seki series 6000 microwave plasma CVD.

To test the impact of temperature on hydrogen termination, eight samples were individually placed on a silicon carrier wafer, a vacuum was pulled to less than $1 * 10^4$ torr, backfilled with forming gas (4% H₂ in Ar), then annealed for 5 minutes at temperatures ranging from 500°C – 1100°C in 100°C increments using the AnnealSYS. The bulk of this study was done using forming gas since it is non-flammable and simple to work with. However, another sample was annealed in pure H₂ at 600°C for 5 minutes for comparison to forming gas. To test the impact of time on hydrogen termination, samples were annealed at 600°C in forming gas for times ranging between 5-60 min. The anneals were at atmospheric pressure with a total gas flow rate of 2000 sccm.

To measure the sheet resistance on each sample, a voltage bias ranging from -5 to 5 V was applied across the exposed polycrystalline diamond ring and the current was measured using a Keithley 4200 parameter analyzer. Each ring was measured in series for every sample. The total resistance across the gap increases with gap spacing, which is calculated from the slope of the resulting I-V curve, deconvoluting the sheet resistance from the contact resistance. For an ohmic contact, the I-V curve is a simple line. However, some samples showed Schottky contact behavior, with non-linear behavior at low voltages. At higher voltages, electrons overcome the

Schottky energy barrier, resulting in a linear trend. For these samples, resistance was calculated using only the linear portions of the I-V curve at higher voltages.

The surface quality of the diamond and Mo films was monitored using scanning electron microscopy (SEM) with a ThermoFisher Verios scanning electron microscope. Surface damage was compared between an untreated sample, a sample treated in a hydrogen plasma, samples annealed in hydrogen at 600°C and 1000°C for 5 minutes each, and a sample annealed at 600°C for 60 minutes.

To account for error due to changes in the environment (e.g. humidity, temperature, etc.) or measurement error from the probe station, the order at which the samples were annealed was randomized. Furthermore, the samples were each annealed individually and measured directly after the surface treatment.

Results and Discussion

The total resistance measured across the exposed diamond ring increases with gap spacing, indicated by the decreasing slope on the resulting I-V curve shown in **Figure 8-2a**. Correction factors²²⁸, listed in **Table 8-1**, were applied to the corresponding total resistance measurements.

Table 8-1. Correction values for the nine different gap spacings used in CTLM calculations.

Gap Spacing [μm]	Correction Factor
4	0.962
8	0.928
12	0.896
16	0.868
20	0.841
24	0.817
32	0.773
40	0.735
48	0.701

The resistance measurements of samples annealed at 600°C for 5 minutes with respect to gap spacing are shown in **Figure 8-2b**. The sheet resistance, R_{sh} , was calculated from the slope using Eqn. (8-1), where r_1 is the internal radius of the exposed polycrystalline diamond ring.

$$R_{sh} = 2\pi r_1 * (Slope) \quad (8-1)$$

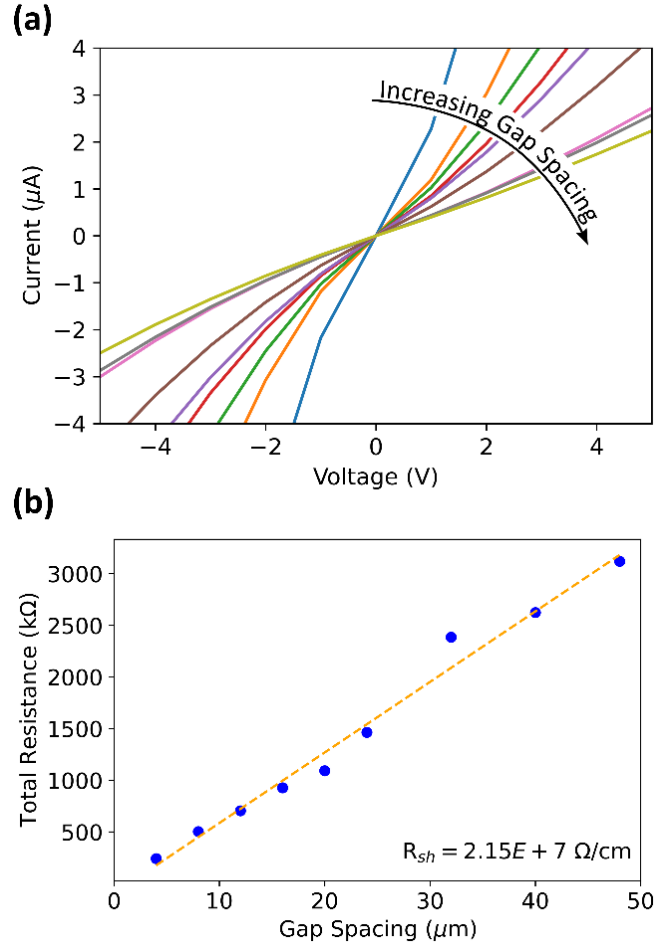


Figure 8-2. (a) I-V curves for each gap spacing annealed at 600°C for 5 minutes. (b) Total resistance as a function of gap spacing with a dashed line of best fit for sample annealed at 600°C for 5 minutes.

This process was repeated for the remaining samples. The oxygen-terminated sample standard showed a sheet resistance of $9.34 * 10^{11} \Omega/sq$. The hydrogen-terminated sample showed a sheet resistance of only $1.32 * 10^5 \Omega/sq$ — a nearly 7 order magnitude decrease — showing a drastic improvement on the surface conductivity due to the increased hydrogen

coverage. As the annealing temperature in forming gas increased, the sheet resistance of the sample decreased exponentially, as shown in **Figure 8-3**.

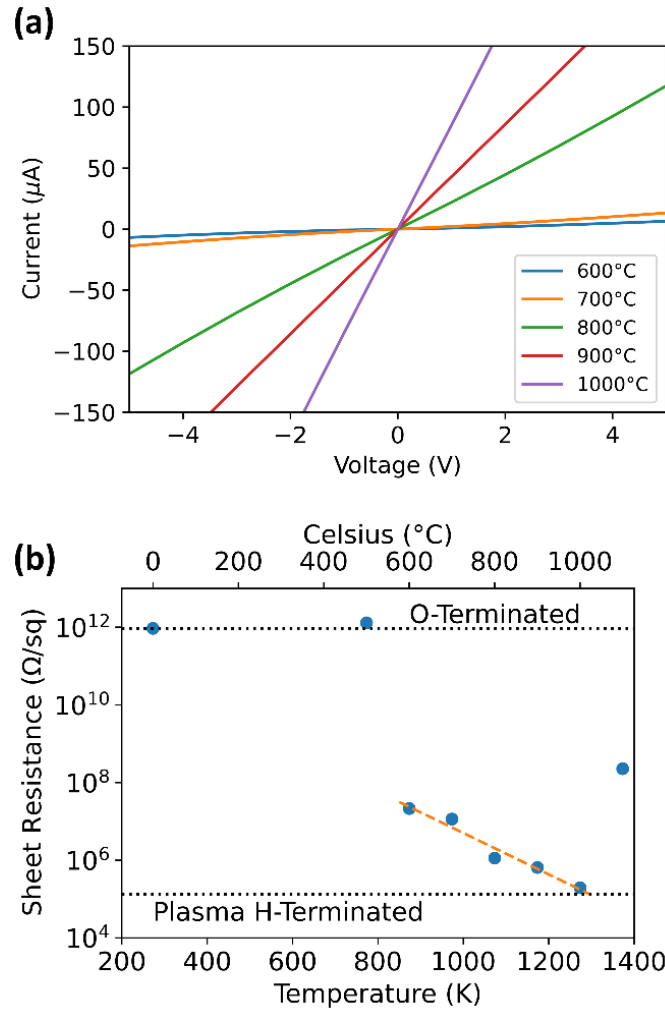


Figure 8-3. (a) I-V curve of annealing in forming gas polycrystalline diamond at different temperatures measured across the 16 μm gap spacing. (b) Sheet resistance as a function of temperature. The dotted lines mark the sheet resistance of the plasma treated (top) oxygen- and (bottom) hydrogen-terminated samples.

The sample annealed at 500°C did not show a significant difference from the oxygen-terminated sample standard, indicating that the reaction is only favorable at temperatures above 500 °C. Between 600°C and 1000°C, the normalized sheet resistance follows the exponential trend in Eqn. (8-2),

$$\left(\frac{R_{sh} - R_{sh,H}}{R_{sh,O} - R_{sh,H}} \right) = 1.13e^{-0.012T} \quad (8-2)$$

where T is temperature in kelvin. The sample annealed at 1100°C in forming gas had a sheet resistance of $2.27 \times 10^8 \Omega/\text{sq}$, an order of magnitude higher than even the sample annealed at only 600°C. This annealing condition was independently repeated twice more to ensure repeatability, and the elevated sheet resistance was consistent. The suggested hypothesis is that the rate of hydrogen dissociation from the surface begins to overtake the rate of adsorption, causing to a fraction of the surface to maintain carbon-termination. Exploring this increase in sheet resistance was saved for future work, as the goal of this study is to minimize the sheet resistance of polycrystalline diamond annealed in forming gas, which occurs at 1000°C.

The activation energy of hydrogen-termination was determined by converting the sheet resistance into a reaction rate and applying the Arrhenius equation. To determine the reaction rate, it is assumed that surface conductivity is directly proportional to the coverage of hydrogen on the surface. Since the hydrogen coverage of the oxygen- and hydrogen-terminated samples are known, the reaction rate can be determined using Eqn. (8-3),

$$r = \frac{R_{sh,O} - R_{sh}}{t(R_{sh,O} - R_{sh,H})} \quad (8-3)$$

where r is the average reaction rate in fractional coverage per minute, t is the time (5 minutes for this experiment), R_{sh} is the sheet resistance from the measured sample, $R_{sh,O}$ is the sheet resistance from the oxygen-terminated standard, and $R_{sh,H}$ is the sheet resistance from the hydrogen-terminated sample standard.

Hydrogen-termination of diamond is assumed to follow a first order reaction limited by the desorption of oxygen from the surface²³⁰. Therefore, the reaction rate constant is calculated by dividing the rate by the average surface concentration of oxygen throughout the five-minute reaction. It was then paired with the Arrhenius equation to produce Eqn. (8-4).

$$k = \left(\frac{2}{t}\right) \left(\frac{R_{sh,O} - R_{sh}}{R_{sh} - R_{sh,H}}\right) = Ae^{-\frac{E_a}{RT}} \quad (8-4)$$

This relationship was used to calculate the activation energy of 1.20 eV, as shown in

Figure 8-4. Previous studies produced activation energies of 1.95 – 2.86 eV for desorption of oxygen from diamond into a vacuum^{231,232}. This large decrease in activation energy indicates that hydrogen is active in the desorption process of oxygen from the diamond surface, creating a lower energy reaction pathway than the desorption of oxygen in a vacuum. In an H₂-containing atmosphere, it is likely that the oxygen is desorbed as H₂O, which has a reported activation energy between 1.1 – 1.7 eV depending on the surface plane according to Tran and Righi (2022)²³³, which is consistent with this work. However, it is likely that the activation energy predicted in this work is low, as the assumption of a linear relationship between sheet resistance and hole density neglects hole-hole interactions that limit hole mobility in a dense 2DHG²³⁴.

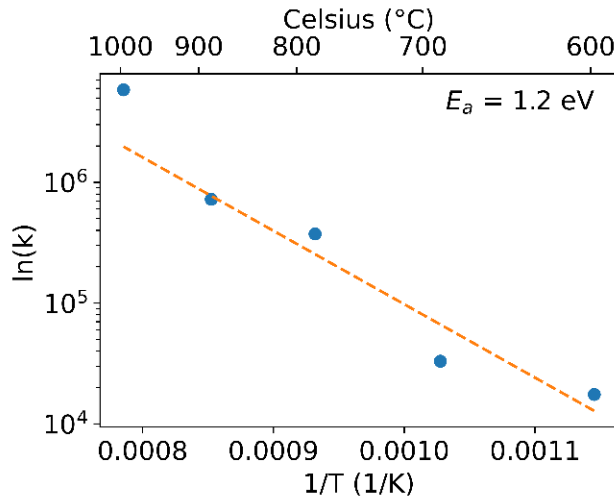


Figure 8-4. Arrhenius plot relating reaction coefficient k and inverse temperature for polycrystalline diamond annealed in forming gas.

An annealing time series was tested at 600°C to determine if diamond can be fully hydrogen-terminated at moderate temperatures. To find the reaction time constant, the normalized sheet resistance is set to follow the exponential formula in Eqn. (8-5),

$$\left(\frac{R_{sh} - R_{sh,H}}{R_{sh,O} - R_{sh,H}} \right) = Ae^{-\tau t} \quad (8-5)$$

where A is the pre-exponential factor and τ is the time constant. The time constant was found to be 0.040 min^{-1} , as shown in **Figure 8-5**. After an hour of annealing in forming gas, the sheet resistance was reduced to $2.28 \times 10^6 \text{ } \Omega/\text{sq}$, and order of magnitude higher than the fully hydrogen-terminated sample standard.

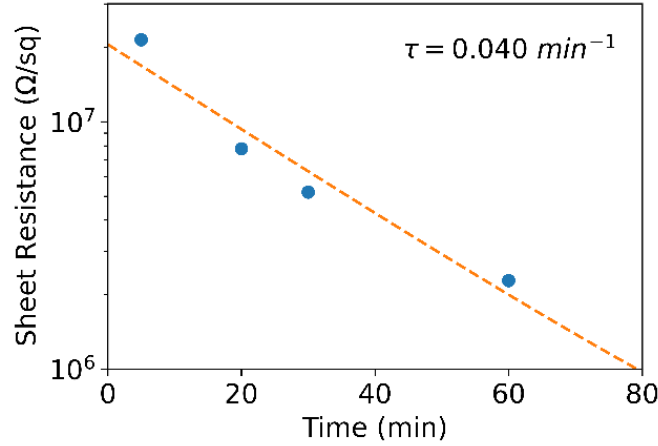


Figure 8-5. Plot of sheet resistance vs time for a polycrystalline diamond sample annealed in forming gas for 5-60 minutes at 600°C.

Assuming no equilibrium is reached before the sample is fully hydrogen-terminated at this temperature, it would take 2.5 hours to produce similar results to the sample annealed at 1000°C. Therefore, it is recommended to anneal samples at temperatures as close to 1000°C as possible to ensure complete hydrogen termination of the diamond surface to reduce the required annealing time.

To test the reversibility of the hydrogen termination, the sample annealed at 600°C for 5 minutes, whose resistance lowered by 7 orders of magnitude, was treated with a 300 W O_2 for 5 minutes. **Figure 8-6** demonstrates that the hydrogen termination is fully reversible, as the sheet resistance of the oxygenated sample was close to the original sheet resistance.

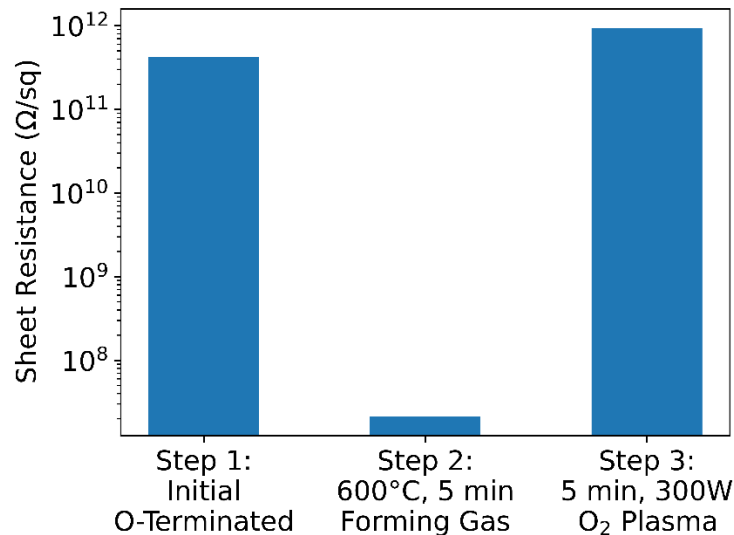


Figure 8-6. Reversibility of hydrogen termination. The initially oxygen-terminated sample was treated with forming gas at 600°C for 5 minutes before being treated with a 300 W oxygen plasma for 5 minutes. The sheet resistance was measured at each step.

Figure 8-7 shows SEM images of samples that were untreated, hydrogen-plasma treated, and annealed in forming gas at 600°C, 1000°C, and 1100°C. The untreated sample shows a typical polycrystalline diamond surface: randomly oriented crystallites with well defined, sharp edges and clear grain boundaries. The Mo film is mostly unblemished, but there is a small degree of delamination at the boundary of the film, likely due to the lithography lift-off process. The hydrogen plasma treatment resulted in significant deterioration of the diamond surface. Pits were etched into the previously smooth facets and the grain boundaries were attacked. The etching of the diamond grain boundaries is most significant, as shallow trenches highlight the individual grains post-plasma treatment. This makes sense, as the grain boundaries consist of sp^2 bonding structure which behave as high energy sites relative to the stable sp^3 bonding found in bulk diamond, making the grain boundaries prime locations for chemical reactions with the high energy hydrogen plasma. Nevertheless, the bulk diamond crystallites reacted with the hydrogen plasma, albeit to a lesser degree. The sharp corners of the untreated crystallites dulled into

rounded edges, and divots can be found across the crystal faces. Hydrogenation via annealing in forming gas produced significantly smoother surface topology. Across all temperatures, the diamond surface remains unchanged. The grain boundaries remain intact, and the corners of the diamond crystallites remain well-defined and sharp. There was some deterioration of the Mo film at high temperatures. At 1000°C, the Mo film became rough and dimpled. This was further exaggerated at 1100°C.

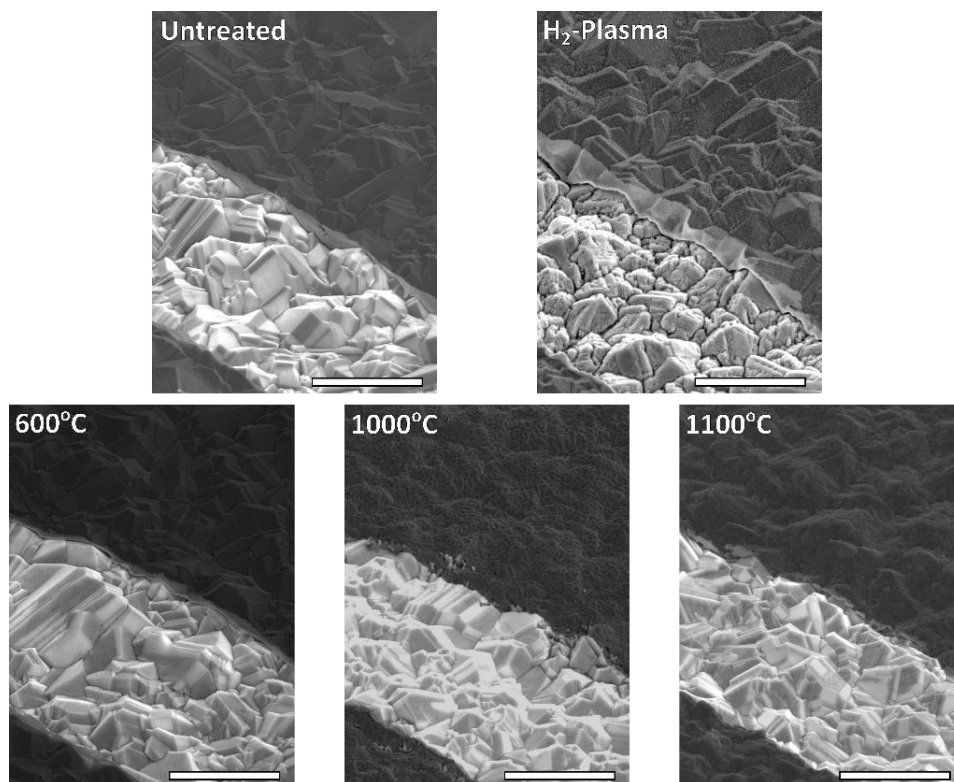


Figure 8-7. Scanning electron microscopy of diamond surfaces before and after various treatments. The bright regions are the bare diamond surfaces. The dark regions are the Mo films. The top bottom samples were annealed in 4% H₂ forming gas for 5 minutes each. The scale bars are 4 μ m.

SEM images taken of the sample annealed at 600°C for 60 minutes showed similar results, confirming the stability of diamond in forming gas. Therefore, diamond devices sensitive to deterioration in a plasma environment can be successfully terminated by annealing in forming gas at moderate temperatures.

Conclusions

This study demonstrated the hydrogenation of oxygen-terminated polycrystalline diamond surfaces by annealing in forming gas and coverage was measured using circular transmission line measurements to calculate the sheet resistance. After annealing for 5 minutes at temperatures below 600°C, the sheet resistance of the diamond film remains unchanged. Hydrogen adsorption onto the diamond surface occurs at temperatures at or between 600°C – 1000°C. After annealing for 5 minutes in forming gas at 1000°C, the sheet resistance indicates near complete hydrogenation of the diamond surface. At 1100°C, the sheet resistance drastically increases, indicating that the rate of desorption of hydrogen is significant at higher temperatures. The activation energy of the hydrogenation process was determined to be 1.20 eV. SEM inspection showed that annealing in forming gas significantly reduces surface deterioration compared to hydrogen plasma treatments.

Future studies should emphasize exploring the reaction mechanism of the interaction between hydrogen and oxygen bonded to the diamond surface. The activation energy is significantly lower than that of oxygen desorption from diamond in a vacuum, indicating that hydrogen plays an active role in oxygen removal. At higher temperatures, the hydrogen seems to desorb from the diamond surface, presumably leaving behind a carbon-terminated surface, causing the diamond to maintain a high sheet resistance. This hydrogen desorption process should also be explored, as it could be a limiting factor to the environmental conditions that diamond photocathodes can operate in. Overall, annealing in forming gas proved to be a successful method of hydrogen-terminating polycrystalline diamond, providing a safe and accessible alternative to plasma treatments for diamond photocathode processing.

Chapter 9 - Conclusions and Recommendations

Summary

Boron-Rich Compound Synthesis

Density functional theory (DFT) was used to study the thermodynamic stability of bulk crystals from the B-O system. B₆O demonstrates great potential for nuclear batteries due to the ‘self-healing’ from radiation damage, provided by the low activation energy for B and O diffusion through the B₆O lattice, on the order of a few meV. It was also found that the formation of B₆O is thermodynamically favorable, including at atmospheric pressure. Copper was selected as a solvent for B₆O growth from a metal flux due to the reasonably high boron solubility and ability to precipitate icosahedral boron from a Cu flux. Unfortunately, growth experiments demonstrated the precipitation of B₂O₃ and β -B from a Cu flux, leading to the conclusion that the metal flux technique does not alleviate the kinetic limitations of B₆O formation. Therefore, this project pivoted to the growth of Al-B-C (ABC) compounds, primarily C₂Al₃B₄₈, which readily grows from a molten metal flux. An initial optimization study, varying the carbon composition in a constant Al-B mixture, showed that multiple boron-rich compounds precipitate from an Al-B-C flux. C₂Al₃B₄₈ forms at carbon concentrations less than 1.2 wt% C, but the highest purity C₂Al₃B₄₈ crystals form at carbon concentrations between 0.32 – 0.56 wt% C, based on color changes and XRD spectra. Initial absorption measurements indicate a bandgap between 2.4 – 2.7 eV, with a broad absorption edge due to the phase impurities.

Photocathode Development

A Au film was annealed into a self-assembled Au nanodot array and used to etch nanopillars into the surface of semi-insulating 6H-SiC as a proof-of-concept for photocathode fabrication. The nanopillars developed from this technique lead to a field enhancement factor of

205, and the SiC photocathodes had a turn-on field of $\sim 6.2 \text{ V}/\mu\text{m}$, with a current density greater than $0.09 \text{ mA}/\text{cm}^2$ at an electric field of $8.3 \text{ V}/\mu\text{m}$. This process was transferred to a Type Ib diamond substrate, and the pillars were optimized for field emission by varying the initial Au thickness and by following pillar formation with a thermal oxidation step to sharpen the pillars. This leads to tunable pillar density, height, and tip width. The pillar density can be controlled between $0.5 - 53.5 \text{ pillars}/\mu\text{m}^2$ depending on the Au film thickness and the pillar tips can be sharpened down to $\sim 40 \text{ nm}$ during thermal annealing.

To obtain a negative electron affinity (NEA) without etching surface features, diamond was hydrogen terminated by annealing in forming gas, and the sheet resistance was measured using circular transmission line measurements (CTLM). After annealing for 5 minutes at temperatures below 600°C , the sheet resistance of the diamond film remains unchanged. Hydrogen adsorption onto the diamond surface occurs at temperatures at or between $600^\circ\text{C} - 1000^\circ\text{C}$. After annealing for 5 minutes in forming gas at 1000°C , the sheet resistance indicates near complete hydrogenation of the diamond surface. At 1100°C , the sheet resistance drastically increases relative to the sample annealed at 1000°C , indicating that the rate of desorption of hydrogen is significant at higher temperatures. The activation energy of hydrogen adsorption was determined to be 1.20 eV when annealing in forming gas, and SEM inspection showed a significant decrease in surface quality when compared to samples terminated in a hydrogen plasma.

Future Work

Boron-Rich Compound Synthesis

Due to the kinetic limitations of B_6O synthesis, I recommend focusing on other boron-rich compounds for use in nuclear batteries. Future efforts on boron-rich ABC compounds

should focus on increasing crystal size and improving phase purity. Crystal domain size from a molten metal flux can be increased in several ways, including lowering the cooling rate¹⁶⁶, optimizing dwell time⁵⁶, and optimizing flux composition¹⁶⁷. Phase purity will be more difficult to address, as XRD shows multiple phases present at all carbon concentrations. High purity $C_2Al_3B_{48}$ might be synthesized by increasing the dwell time and lowering the cooling rate at low carbon concentrations. Increasing the dwell time should improve homogeneity. Slowing crystal growth and reducing nucleation points should reduce the number of phases present in the sample.

Significant characterization work needs to be done on the ABC boron-rich compounds, particularly $C_2Al_3B_{48}$. Naturally, fabrication techniques should be developed to prepare $C_2Al_3B_{48}$ for characterization, including proficient polishing techniques to reduce crystals down to thin platelets without shattering the crystal, etching techniques to produce large smooth surfaces, and the development of ohmic contacts for electrical measurements. With better sample preparation techniques, the bandgap can be further characterized using more precise absorption spectra. After ohmic contacts are developed, Hall effect measurements can determine the carrier concentrations and mobilities, which are essential for device design. The structural integrity of the $C_2Al_3B_{48}$ crystals should also be investigated to determine the density of voids or metal inclusions in the large single crystals. Finally, β irradiation experiments should be performed to determine the viability of this material as a semiconductor for nuclear batteries.

Photocathode Development

Significant improvements should be made to single-crystal diamond photocathode fabrication processes before moving to device testing. The statistically distributed self-assembled nanodot array used to fabricate pillars are non-uniform, and the standard distribution of the nanodot size should be reduced in order to minimize the final tip size after thermal sharpening in

oxygen. Furthermore, surface treatments, such as hydrogen termination, should be applied to the diamond before Au deposition or during annealing in order to decrease wettability between the nanodots and diamond surface, which would improve both size uniformity and the circularity of the elliptical nanodots, allowing for more precise control of the final tip widths. Further optimization can be done to reduce the fabrication time for the photocathodes. Increasing the RIE RF power can drastically shorten the pillar etching process, which is by far the longest step in this fabrication technique. It will also produce smoother walls with improved verticality. This is at the expense of the selectivity of the Au mask, and since the thickness of the Au mask cannot be increased without changing the final pillar geometry, the RIE power should be optimized to achieve a specific pillar height. The operating temperature range for diamond photocathodes is also limited by the desorption of hydrogen from the diamond surface, which was shown by the increase in sheet resistance when terminating diamond at 1100°C. Future studies should also include device tests at high operating temperatures to define the potential applications for diamond photocathodes.

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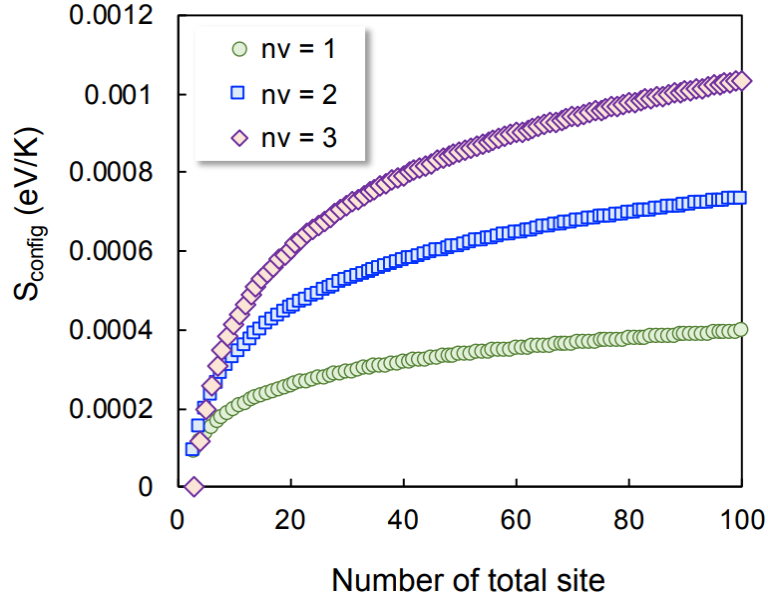
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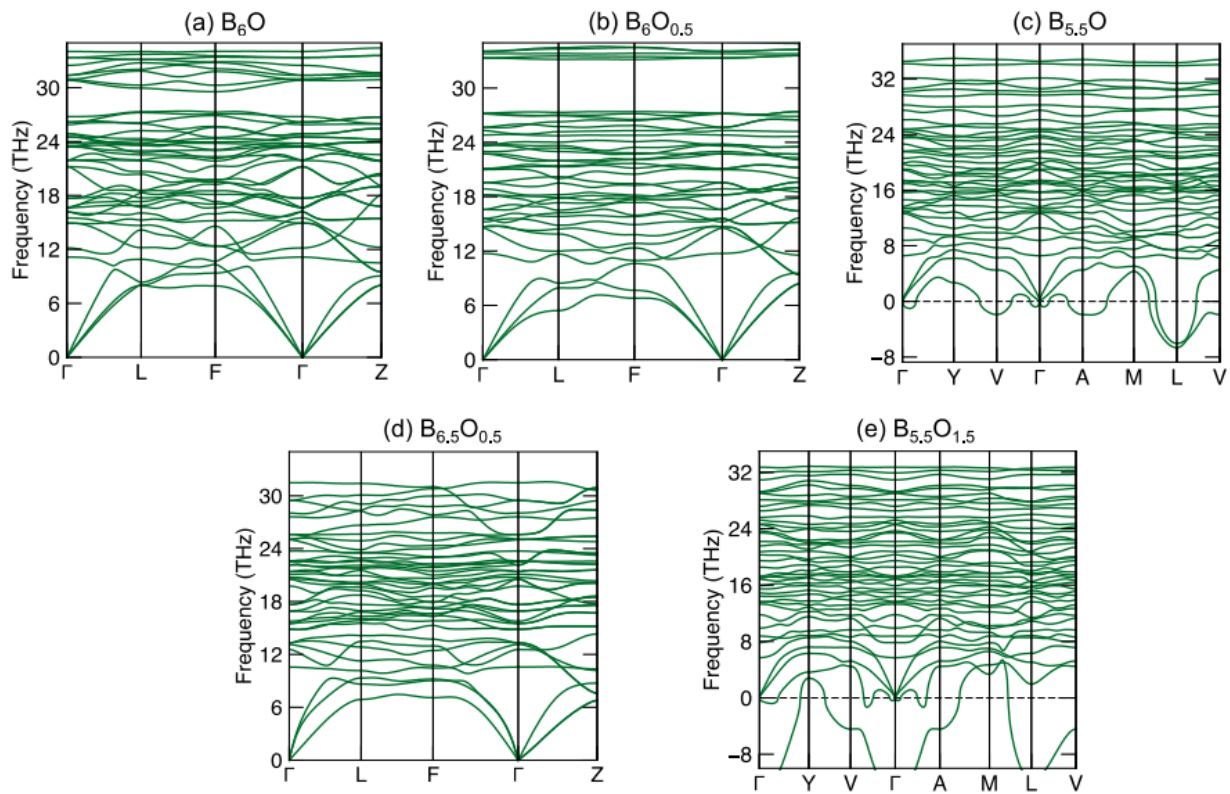
Appendix A - Supplemental Materials

B₆O DFT Study

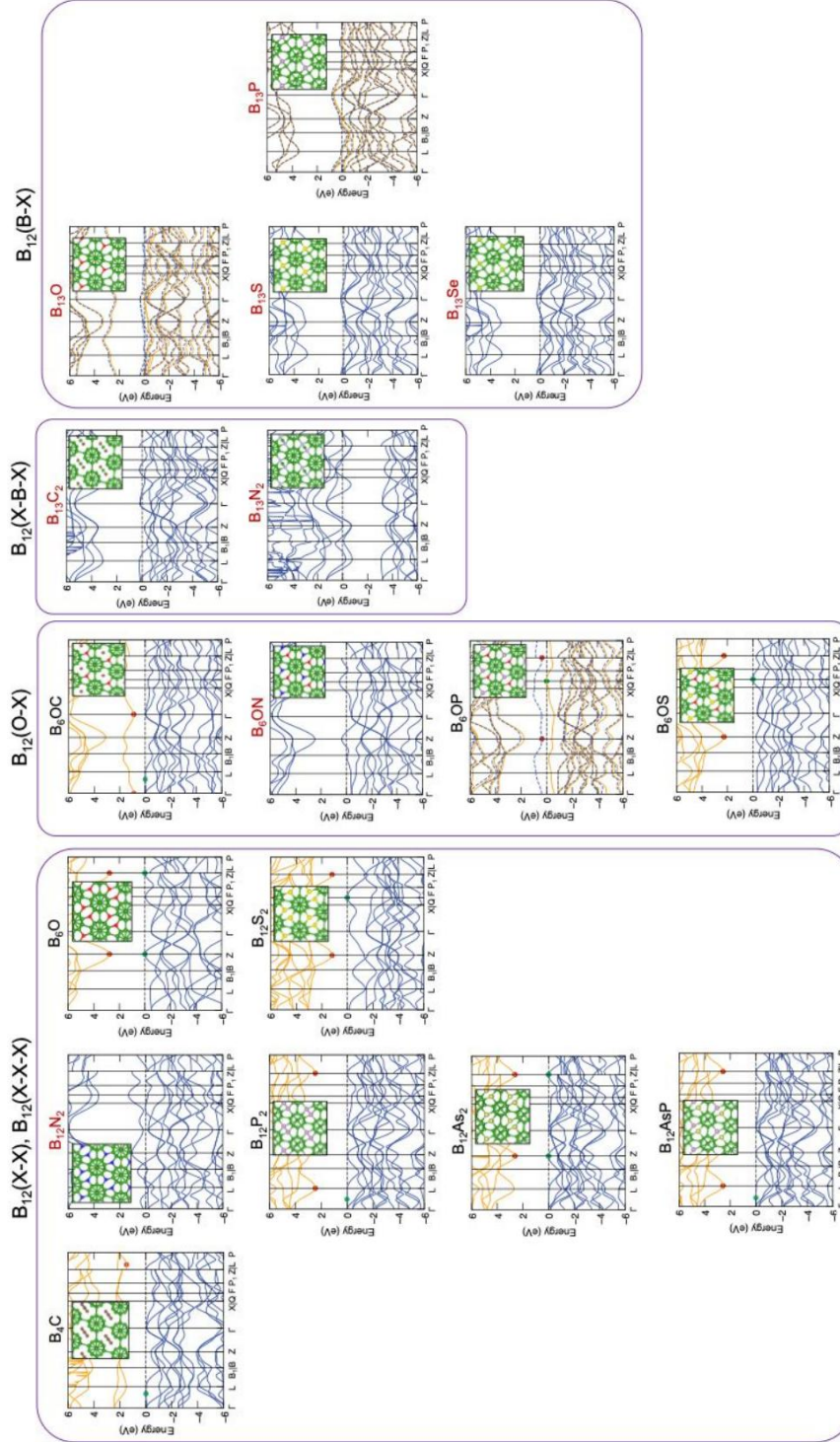


Appendix Figure A.1. Estimation of configurational entropies (S_{config}) as a function of defect concentration. Green circle: $n_v = 1$, blue square: $n_v = 2$, and purple diamond: $n_v = 3$.

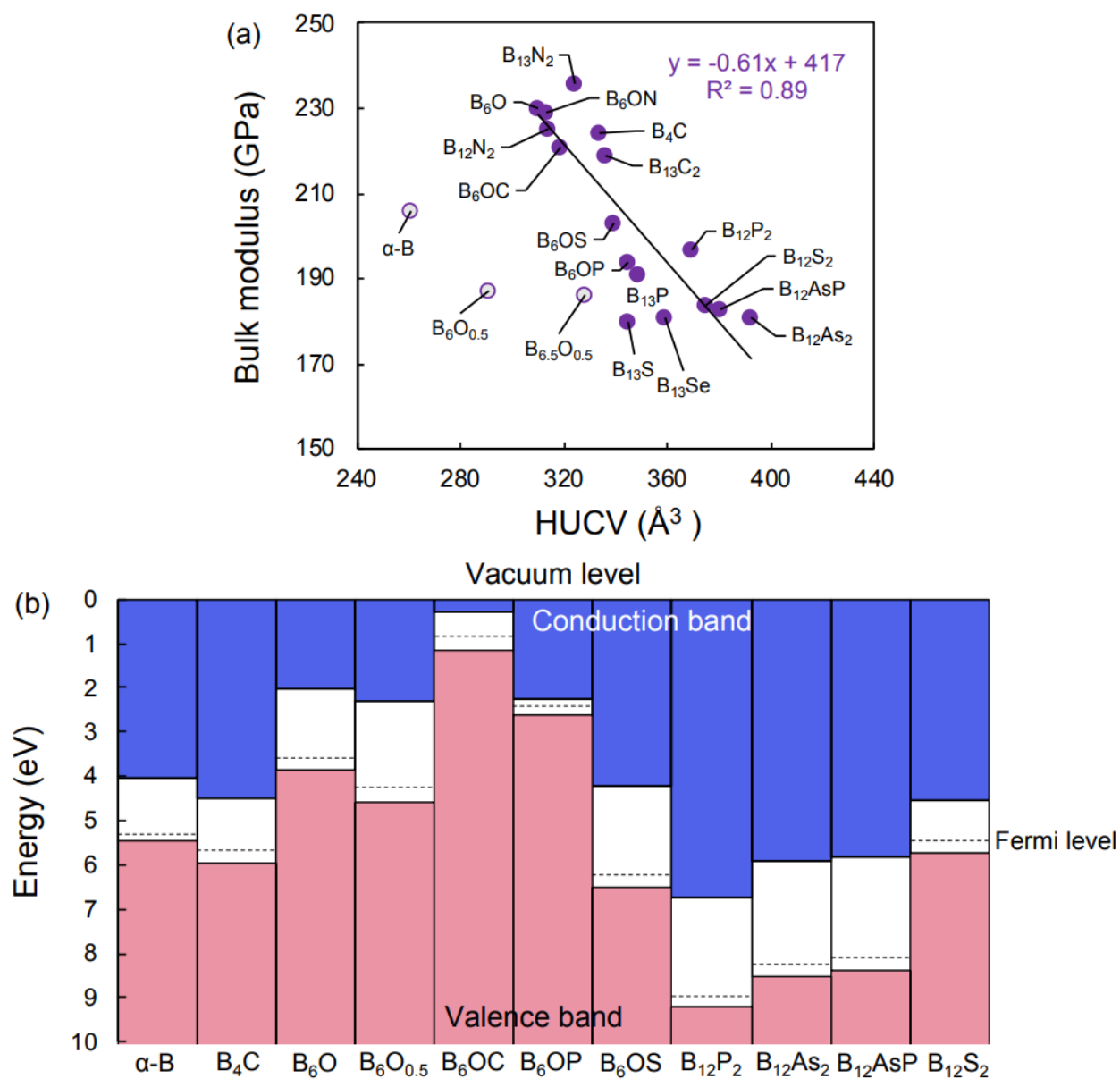
The variations of S_{config} with the total available site (N) and the number of defect site (n_v) config based on Eqn. (3-5). Overall, S_{config} increases with both N and n_v , resulting in larger impact on the config free energies. Particularly, S_{config} is more sensitive to defect concentrations. This is also because local defect breaks the lattice symmetry and leads to higher N values.



Appendix Figure A.2. Phonon dispersions of (a) B_6O , (b) $B_6O_{0.5}$, (c) $B_{5.5}O$, (d) $B_{6.5}O_{0.5}$, and (e) $B_{5.5}O_{1.5}$ at 0 GPa. The plots were automatically generated using the sumo python package.



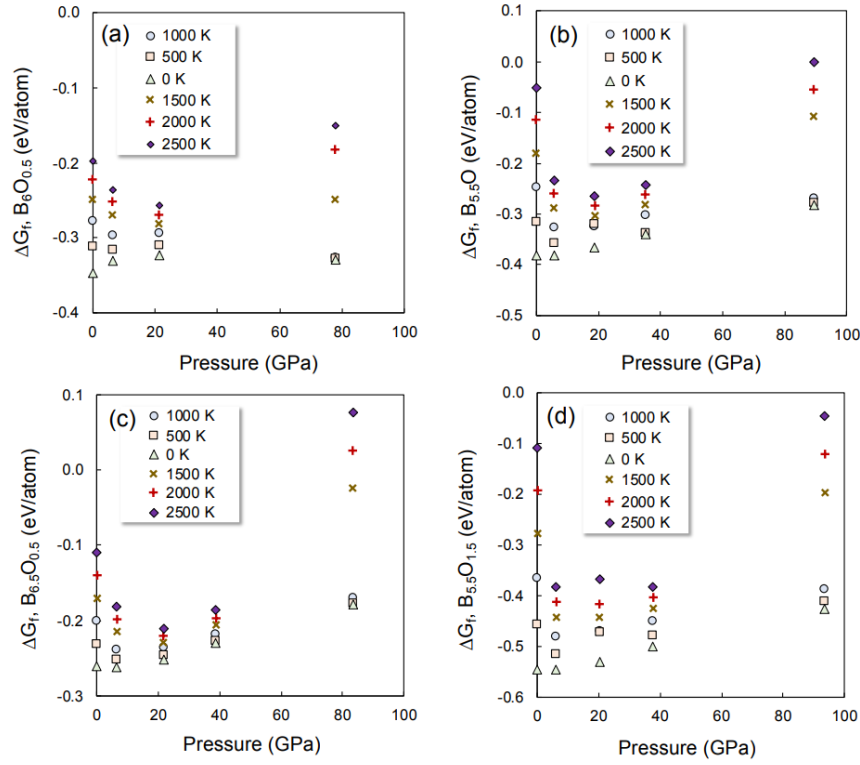
Appendix Figure A.3. Band structures of α -boron compounds based on the atomic types and compositions at the interstitial sites. Here, the compounds are groups as: $B_{12}(X-X)$ or $B_{12}(X-X-X)$; $B_{12}(O-X)$; $B_{12}(X-B-X)$; and $B_{12}(B-X)$, where $X = C, N, P, S, As, Se$. The optimized structures are shown as inset figures. The plots are arranged according to the position of the element in the periodic table. The band structures were plotted automatically using the sumo python package.



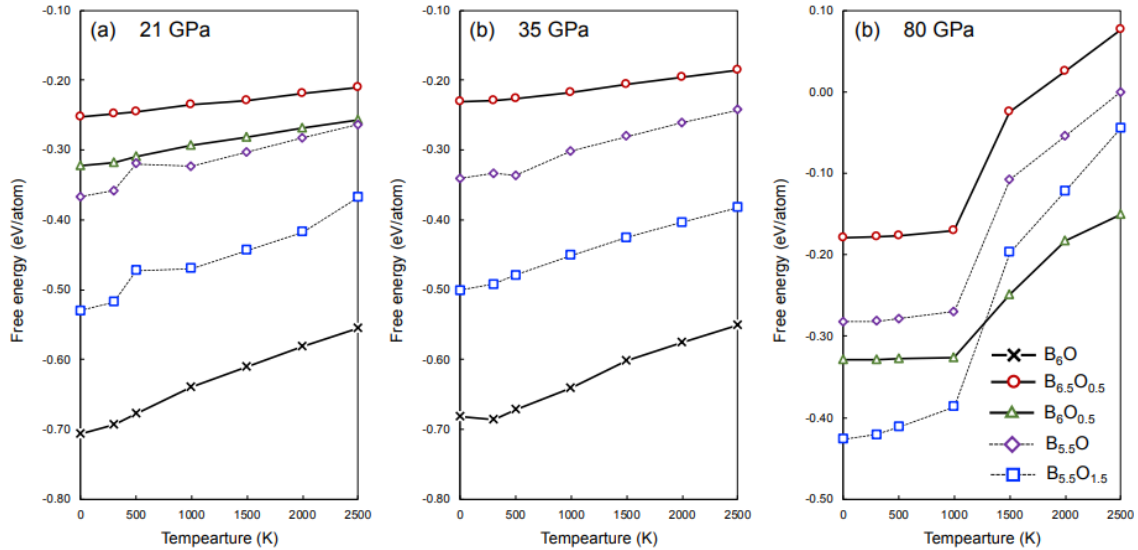
Appendix Figure A.4. (a) Plot of bulk moduli as a function of HUCV. $\alpha\text{-B}$, $\text{B}_6\text{O}_{0.5}$, and $\text{B}_{6.5}\text{O}_{0.5}$ are outliers (in lighter colors) and were not included in the linear regression. (b) Energy band diagrams with Fermi levels (dashed lines), valence bands (red), and conduction bands (blue) of the semiconducting materials shown in **Appendix Figure A.3**.

Appendix Table A.1. Hexagonal lattice parameters, HUCV, bulk moduli (GPa) and bandgaps of the compounds in **Appendix Figure A.3**.

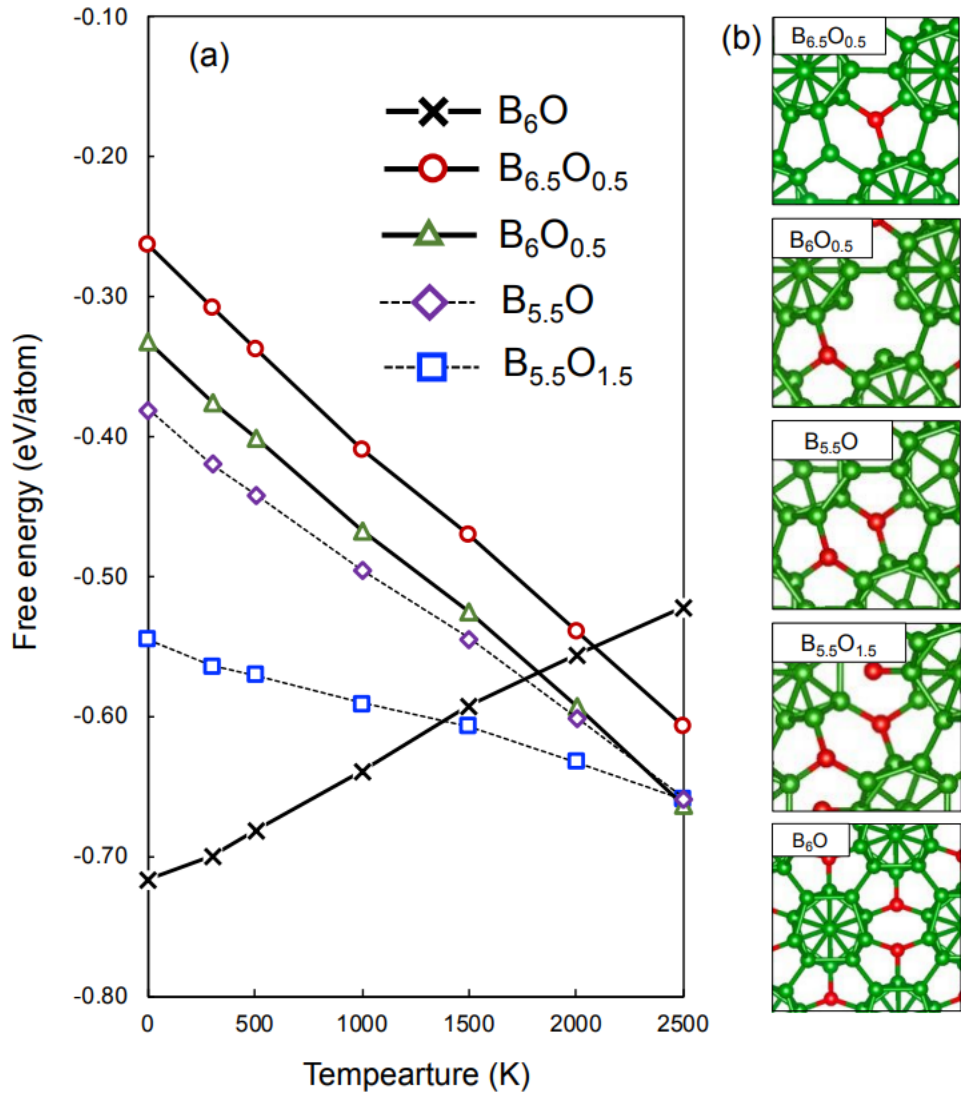
Compounds	a (Å)	c (Å)	HUCV (Å³)	Bulk modulus (Gpa)	Bandgap (eV)
B ₄ C	5.64	12.12	334	224	1.5 (indirect)
B ₁₂ N ₂	5.44	12.22	314	225	metallic
B ₁₂ P ₂	5.99	11.85	369	197	2.47 (indirect)
B ₁₂ As ₂	6.16	11.92	392	181	2.63 (direct)
B ₁₂ AsP	6.08	11.90	380	183	2.58 (indirect)
B ₁₂ S ₂	5.92	12.34	375	184	1.20 (indirect)
B ₆ OC	5.47	12.28	319	221	0.89 (indirect)
B ₆ ON	5.41	12.29	313	229	metallic
B ₆ OP	5.71	12.25	345	194	0.37 (indirect)
B ₆ OS	5.63	12.35	339	203	2.28 (indirect)
B ₁₃ C ₂	5.66	12.12	336	219	metallic
B ₁₃ N ₂	5.49	12.44	324	236	metallic
B ₁₃ P	5.82	11.92	349	191	metallic
B ₁₃ S	5.80	11.93	345	180	metallic
B ₁₃ Se	5.90	11.90	359	181	metallic



Appendix Figure A.5. Defect formation energies (ΔG_f in eV/atom) of (a) $B_6O_{0.5}$, (b) $B_{5.5}O$, (c) $B_{6.5}O_{0.5}$, and (d) $B_{5.5}O_{1.5}$, plotted as a function of pressure (GPa) for selected temperatures (i.e., 0, 500, 1000, 1500, 2000, and 2500 K).



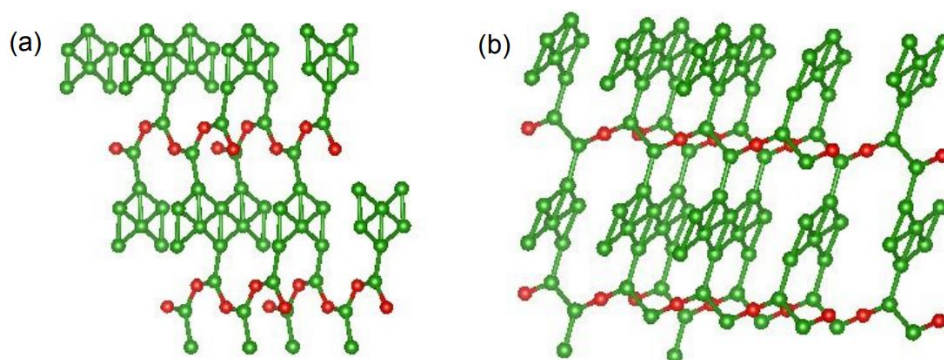
Appendix Figure A.6. Free energies (ΔG_f in eV/atom) of defect formations of B_6O , $B_6O_{0.5}$, $B_{5.5}O$, $B_{6.5}O_{0.5}$, and $B_{5.5}O_{1.5}$, plotted as a function of temperature (0-2500K) at 6 GPa. Cross: perfect B_6O ; square: $B_{5.5}O_{1.5}$; diamond: $B_{5.5}O$; triangle: $B_6O_{0.5}$; circle: $B_{6.5}O_{0.5}$. Thin dashed lines indicate that these structures are not dynamically stable.



Appendix Figure A.7. (a) Free energies (ΔG_f in eV/atom) of defect formations of B_6O , $B_6O_{0.5}$, $B_{5.5}O$, $B_{6.5}O_{0.5}$, and $B_{5.5}O_{1.5}$, plotted as a function of temperature (0-2500K) at 6 GPa. Cross: perfect B_6O ; square: $B_{5.5}O_{1.5}$; diamond: $B_{5.5}O$; triangle: $B_6O_{0.5}$; circle: $B_{6.5}O_{0.5}$. Thin dashed lines indicate that these structures are not dynamically stable. (b) Visualization of the defect structure.

Appendix Table A.2. Lattice constants and energies (eV/atom) of α -B, B_2O_3 , and B_6O .

Crystals	Lattice System	Lattice Constants
α -B	Rhombohedral	$a = b = 4.90 \text{ \AA}$, $c = 12.55 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
B_2O_3	Hexagonal	$a = b = 4.40 \text{ \AA}$, $c = 8.82 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
B_6O	Rhombohedral	$a = b = 5.39 \text{ \AA}$, $c = 12.32 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$



Appendix Figure A.8. Optimized structures of (a) B_6O_2 ; (b) B_6O by successively removing O atoms from the B_2O_3 lattice.

Appendix Table A.3. Lattice vibration frequencies at the gamma point for the equilibrated compounds.

Compound	Frequencies (THz)
α -B	0.48, 0.48, 0.77, 14.31, 14.92, 15.48, 15.48, 16.68, 16.68, 17.59, 17.59, 17.91, 17.91, 20.80, 20.93, 21.44, 21.44, 21.51, 23.25, 23.25, 23.73, 23.74, 23.74, 23.79, 23.98, 24.14, 24.14, 24.41, 26.23, 26.23, 27.82, 27.96, 33.55, 33.55, 35.15
B_6O	0.43, 0.43, 0.67, 11.14, 12.18, 14.92, 14.92, 15.46, 16.08, 16.08, 16.73, 16.73, 16.74, 17.70, 17.70, 21.14, 21.14, 21.90, 21.99, 21.99, 23.40, 23.51, 23.52, 23.52, 23.81, 24.52, 24.52, 24.87, 24.87, 25.90, 26.17, 26.17, 26.77, 30.81, 30.94, 30.94, 31.38, 31.38, 32.48, 33.36, 33.36, 34.03
$B_6O_{0.5}$	0.45, 0.45, 0.70, 11.74, 14.49, 14.66, 14.66, 15.27, 15.55, 15.55, 16.63, 16.63, 18.22, 18.22, 18.86, 19.55, 19.55, 21.00, 21.12, 21.12, 22.74, 22.74, 22.99, 23.61, 23.78, 23.78, 24.81, 25.31, 25.67, 25.67, 27.15, 27.15, 27.21, 33.33, 33.33, 33.80, 34.05, 34.05, 35.08
$B_{5.5}O$	-6.32, -6.32, -0.35, -0.35, 0.72, 10.56, 12.55, 13.11, 13.30, 13.30, 14.85, 14.85, 15.52, 15.52, 15.79, 16.92, 16.92, 17.67, 17.67, 19.74, 20.48, 20.48, 20.73, 21.09, 21.43, 21.43, 22.21, 22.21, 22.52, 22.59, 22.59, 23.73, 25.03, 25.03, 25.05, 25.62, 25.62, 27.61, 28.05, 29.46, 29.46, 31.48
$B_{6.5}O_{0.5}$	-6.32, -6.32, -0.35, -0.35, 0.72, 10.56, 12.55, 13.11, 13.30, 13.30, 14.85, 14.85, 15.52, 15.52, 15.79, 16.92, 16.92, 17.67, 17.67, 19.74, 20.48, 20.48, 20.73, 21.09, 21.43, 21.43, 22.21, 22.21, 22.52, 22.59, 22.59, 22.73, 25.03, 25.03, 25.05, 25.62, 25.62, 27.61, 28.05, 29.46, 29.46, 31.48
$B_{5.5}O_{1.5}$	-14.17, 0.09, 0.54, 0.58, 5.70, 7.86, 8.76, 9.91, 11.80, 13.28, 13.58, 13.66, 14.42, 14.85, 15.48, 15.92, 16.87, 16.90, 17.20, 17.31, 18.54, 19.46, 20.31, 20.75, 21.57, 22.19, 23.39, 23.69, 24.57, 24.66, 25.23, 25.60, 26.53, 27.18, 28.10, 29.02, 29.13, 29.26, 30.93, 31.92, 32.73, 36.43

Note: The negative frequencies indicate that the compound is dynamically unstable

C₂Al₃B₄₈ Atomic Coordinates

Appendix Table A.4. Atomic coordinates of C₂Al₃B₄₈ as determined by XRD from a sample grown in an Al-B-C flux with a carbon concentration of 0.32 wt%.

#	Atom	x	y	z	Occupancy
1	Al	0.500	-0.500	0.750	0.789
2	Al	0.656	-0.752	1.000	0.870
3	Al	0.611	-0.753	1.000	0.130
4	Al	0.500	-1.000	0.750	0.044
5	C	0.368	-0.750	1.000	1.000
6	B	0.327	-0.544	0.879	1.000
7	B	0.418	-0.507	1.000	1.000
8	B	0.315	-0.624	1.000	1.000
9	B	0.169	-0.588	0.925	1.000
10	B	0.083	-0.492	1.000	1.000
11	B	0.188	-0.377	1.000	1.000
12	B	0.332	-0.410	0.924	1.000
13	B	0.173	-0.455	0.878	1.000
14	B	0.435	-0.753	0.878	1.000
15	B	0.332	-0.752	0.756	1.000
16	B	0.420	-0.639	0.797	1.000
17	B	0.580	-0.679	0.844	1.000
18	B	0.580	-0.826	0.843	1.000
19	B	0.422	-0.871	0.795	1.000

Appendix B - Code for DFT Analysis

Cu-B-O Phase Analysis

```
import matplotlib.pyplot as plt
import numpy as np
import pandas as pd
import sympy as sym
import scipy.optimize as sc
import warnings
warnings.filterwarnings("ignore")
##### Data Collection from Excel Sheets #####

Direct = r"C:\Users\dylan99\Documents\Data Access\Molecular Modelling\DFT.xlsx"
AlphaR_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=7,
skiprows=range(0, 1), usecols='A:F'))
BetaR_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=8,
skiprows=range(0, 11), usecols='A:F'))
Gamma_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=8,
skiprows=range(0, 22), usecols='A:F'))
B2O3_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=7, skiprows=range(0,
55), usecols='A:F'))
B6O_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=5, skiprows=range(0,
65), usecols='A:F'))
B8O_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=5, skiprows=range(0,
73), usecols='A:F'))
B36O5_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=5,
skiprows=range(0, 81), usecols='A:F'))
B84O11_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=5,
skiprows=range(0, 89), usecols='A:F'))
B4C_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=5, skiprows=range(0,
97), usecols='A:F'))
O2_DFT = 0.09652 # (eV/molecule)
CO2_DFT = 0.315 # (eV/molecule)
CuO_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=7, skiprows=range(0,
105), usecols='A:F'))
Cu_DFT = np.array(pd.read_excel(Direct, sheet_name="Phase stability", nrows=7, skiprows=range(0,
115), usecols='A:F'))

#Import Vibrational Energy Phonopy
Direct = r"C:\Users\dylan99\Documents\Data Access\Molecular Modelling\Phonopy Entropy Data
Collection.xlsx"
```

```

AR_Sv = np.array(pd.read_excel(Direct, sheet_name="B12_mp-160", nrows=200, header=None,
usecols='A:F'))
AR_Sv = np.array( [AR_Sv[2:183, 1:6].transpose().flatten(), np.array([AR_Sv[2:183, 0]]*5).flatten(),
np.array([AR_Sv[0, 1:6]]*181).transpose().flatten() ] , float).transpose()
BR_Sv = np.array(pd.read_excel(Direct, sheet_name="B106_mp-161", nrows=200, header=None,
usecols='A:G'))
BR_Sv = np.array([BR_Sv[2:183, 1:7].transpose().flatten(), np.array([BR_Sv[2:183, 0]]*6).flatten(),
np.array([BR_Sv[0, 1:7]]*181).transpose().flatten() ] , float).transpose()
G_Sv = np.array(pd.read_excel(Direct, sheet_name="B28_mp-1193675", nrows=200, header=None,
usecols='A:B'))
G_Sv = np.array([G_Sv[2:183, 1].transpose().flatten(), np.array([G_Sv[2:183, 0]]).flatten(),
np.array([G_Sv[0, 1]]*181).transpose().flatten() ] , float).transpose()
B2O3_Sv = np.array(pd.read_excel(Direct, sheet_name="B2O3_mp-306", nrows=200, header=None,
usecols='A:F'))
B2O3_Sv = np.array([B2O3_Sv[2:183, 1:6].transpose().flatten(), np.array([B2O3_Sv[2:183,
0]]*5).flatten(), np.array([B2O3_Sv[0, 1:6]]*181).transpose().flatten() ] , float).transpose()
B6O_Sv = np.array(pd.read_excel(Direct, sheet_name="B6O_mp-1346", nrows=200, header=None,
usecols='A:F'))
B6O_Sv = np.array([B6O_Sv[2:183, 1:6].transpose().flatten(), np.array([B6O_Sv[2:183, 0]]*5).flatten(),
np.array([B6O_Sv[0, 1:6]]*181).transpose().flatten() ] , float).transpose()
B8O_Sv = np.array(pd.read_excel(Direct, sheet_name="B8O_mp-530033", nrows=200, header=None,
usecols='A:F'))
B8O_Sv = np.array([B8O_Sv[2:183, 1:6].transpose().flatten(), np.array([B8O_Sv[2:183, 0]]*5).flatten(),
np.array([B8O_Sv[0, 1:6]]*181).transpose().flatten() ] , float).transpose()
B36O5_Sv = np.array(pd.read_excel(Direct, sheet_name="B36O5_mp-32715", nrows=200,
header=None, usecols='A:F'))
B36O5_Sv = np.array([B36O5_Sv[2:183, 1:6].transpose().flatten(), np.array([B36O5_Sv[2:183,
0]]*5).flatten(), np.array([B36O5_Sv[0, 1:6]]*181).transpose().flatten() ] , float).transpose()
B84O11_Sv = np.array(pd.read_excel(Direct, sheet_name="B84O11_mp-758800", nrows=200,
header=None, usecols='A:F'))
B84O11_Sv = np.array([B84O11_Sv[2:183, 1].transpose().flatten(), np.array([B84O11_Sv[2:183,
0]]).flatten(), np.array([B84O11_Sv[0, 1]]*181).transpose().flatten() ] , float).transpose()
B4C_Sv = np.array(pd.read_excel(Direct, sheet_name="B4C_mp-696746", nrows=200, header=None,
usecols='A:F'))
B4C_Sv = np.array([B4C_Sv[2:183, 1].transpose().flatten(), np.array([B4C_Sv[2:183, 0]]).flatten(),
np.array([B4C_Sv[0, 1]]*181).transpose().flatten() ] , float).transpose()
CuO_Sv = np.array(pd.read_excel(Direct, sheet_name="CuO", nrows=200, header=None, usecols='A:F'))
CuO_Sv = np.array([CuO_Sv[2:183, 1].transpose().flatten(), np.array([CuO_Sv[2:183, 0]]).flatten(),
np.array([CuO_Sv[0, 1]]*181).transpose().flatten() ] , float).transpose()
Cu_Sv = np.array(pd.read_excel(Direct, sheet_name="Cu", nrows=200, header=None, usecols='A:F'))
Cu_Sv = np.array([Cu_Sv[2:183, 1].transpose().flatten(), np.array([Cu_Sv[2:183, 0]]).flatten(),
np.array([Cu_Sv[0, 1]]*181).transpose().flatten() ] , float).transpose()

```

```
O2_Sv = np.array(pd.read_excel(Direct, sheet_name="Ideal Gas", nrows=22, skiprows=2, header=None,
usecols='A:B'))
CO2_Sv = np.array(pd.read_excel(Direct, sheet_name="Ideal Gas", nrows=22, skiprows=2,
header=None, usecols='D:E'))
```

```
##### Input Parameters #####
```

```
#Phase Diagram Settings
HighPres = int(50)
HighTemp = int(1800)
#Pressure Range
ResP = int(100)
PresRange = np.linspace(0, HighPres, ResP+1)
#Temperature Range
ResT = int(50)
TempRange = np.linspace(0, HighTemp, ResT+1)
Vres = ResP+1
```

```
EntropyTemp = 1773 #float(input('At What Temperature Should The Entropy Be Considered? (K) '))
Pressures = 0.001 #float(input('What Pressure do you want to test? (GPa) '))
```

```
#Number of Atoms in each lattice
```

```
AR_atom = 12
BR_atom = 106
G_atom = 28
B2O3_atom = 15
B6O_atom = 14
B8O_atom = 54
B36O5_atom = 82
B84O11_atom = 95
O2_atom = 2
CO2_atom = 3
B4C_atom = 15
CuO_atom = 8
Cu_atom = 4
```

```
##### Enthalpy Calculations #####
```

```
#Define Volume Range for EOS
```

```
AR_Vspan = np.linspace(AlphaR_DFT[0, 0], AlphaR_DFT[-1, 0], Vres)
BR_Vspan = np.linspace(BetaR_DFT[0, 0], BetaR_DFT[-1, 0], Vres)
G_Vspan = np.linspace(Gamma_DFT[0, 0], Gamma_DFT[-1, 0], Vres)
B2O3_Vspan = np.linspace(B2O3_DFT[0, 0], B2O3_DFT[-1, 0], Vres)
B6O_Vspan = np.linspace(B6O_DFT[0, 0], B6O_DFT[-1, 0], Vres)
```

```

B8O_Vspan = np.linspace(B8O_DFT[0, 0], B8O_DFT[-1, 0], Vres)
B36O5_Vspan = np.linspace(B36O5_DFT[0, 0], B36O5_DFT[-1, 0], Vres)
B84O11_Vspan = np.linspace(B84O11_DFT[0, 0], B84O11_DFT[-1, 0], Vres)
B4C_Vspan = np.linspace(B4C_DFT[0, 0], B4C_DFT[-1, 0], Vres)
CuO_Vspan = np.linspace(CuO_DFT[0, 0], CuO_DFT[-1, 0], Vres)
Cu_Vspan = np.linspace(Cu_DFT[0, 0], Cu_DFT[-1, 0], Vres)

#Symbolic Variables
V = sym.Symbol('V')
#Define E(V) EOS (eV)
def E(V, a, b, c, d):
    return a + b/np.power(V,2/3) + c/np.power(V,4/3) + d/np.power(V,2)
#First Derivative: Pressure (eV/cubic angstrom)
def P(V, b, c, d):
    return (2/3)*b/np.power(V,5/3) + (4/3)*c/np.power(V,7/3) + 2*d/np.power(V,3)

#Calculate E(V) Equations (eV)
AR_EVcoeff, covariance = sc.curve_fit(E, AlphaR_DFT[:,0], AlphaR_DFT[:,1])
AR_EV = E(AR_Vspan, AR_EVcoeff[0], AR_EVcoeff[1], AR_EVcoeff[2], AR_EVcoeff[3])
BR_EVcoeff, covariance = sc.curve_fit(E, BetaR_DFT[:, 0], BetaR_DFT[:, 1])
BR_EV = E(BR_Vspan, BR_EVcoeff[0], BR_EVcoeff[1], BR_EVcoeff[2], BR_EVcoeff[3])
G_EVcoeff, covariance = sc.curve_fit(E, Gamma_DFT[:, 0], Gamma_DFT[:, 1])
G_EV = E(G_Vspan, G_EVcoeff[0], G_EVcoeff[1], G_EVcoeff[2], G_EVcoeff[3])
B2O3_EVcoeff, covariance = sc.curve_fit(E, B2O3_DFT[:,0], B2O3_DFT[:,1])
B2O3_EV = E(B2O3_Vspan, B2O3_EVcoeff[0], B2O3_EVcoeff[1], B2O3_EVcoeff[2],
B2O3_EVcoeff[3])
B6O_EVcoeff, covariance = sc.curve_fit(E, B6O_DFT[:,0], B6O_DFT[:,1])
B6O_EV = E(B6O_Vspan, B6O_EVcoeff[0], B6O_EVcoeff[1], B6O_EVcoeff[2], B6O_EVcoeff[3])
B8O_EVcoeff, covariance = sc.curve_fit(E, B8O_DFT[:,0], B8O_DFT[:,1])
B8O_EV = E(B8O_Vspan, B8O_EVcoeff[0], B8O_EVcoeff[1], B8O_EVcoeff[2], B8O_EVcoeff[3])
B36O5_EVcoeff, covariance = sc.curve_fit(E, B36O5_DFT[:,0], B36O5_DFT[:,1])
B36O5_EV = E(B36O5_Vspan, B36O5_EVcoeff[0], B36O5_EVcoeff[1], B36O5_EVcoeff[2],
B36O5_EVcoeff[3])
B84O11_EVcoeff, covariance = sc.curve_fit(E, B84O11_DFT[:,0], B84O11_DFT[:,1])
B84O11_EV = E(B84O11_Vspan, B84O11_EVcoeff[0], B84O11_EVcoeff[1], B84O11_EVcoeff[2],
B84O11_EVcoeff[3])
B4C_EVcoeff, covariance = sc.curve_fit(E, B4C_DFT[:,0], B4C_DFT[:,1])
B4C_EV = E(B4C_Vspan, B4C_EVcoeff[0], B4C_EVcoeff[1], B4C_EVcoeff[2], B4C_EVcoeff[3])
CuO_EVcoeff, covariance = sc.curve_fit(E, CuO_DFT[:,0], CuO_DFT[:,1])
CuO_EV = E(CuO_Vspan, CuO_EVcoeff[0], CuO_EVcoeff[1], CuO_EVcoeff[2], CuO_EVcoeff[3])
Cu_EVcoeff, covariance = sc.curve_fit(E, Cu_DFT[:,0], Cu_DFT[:,1])
Cu_EV = E(Cu_Vspan, Cu_EVcoeff[0], Cu_EVcoeff[1], Cu_EVcoeff[2], Cu_EVcoeff[3])

#Calculate P(V) (eV/cubic angstrom)

```

```

AR_PV = P(AR_Vspan, AR_EVCoeff[1], AR_EVCoeff[2], AR_EVCoeff[3])
BR_PV = P(BR_Vspan, BR_EVCoeff[1], BR_EVCoeff[2], BR_EVCoeff[3])
G_PV = P(G_Vspan, G_EVCoeff[1], G_EVCoeff[2], G_EVCoeff[3])
##### Special B2O3 Pressure EOS Fit #####
B2O3_PVCoeff, covariance = sc.curve_fit(P, B2O3_DFT[:,0], B2O3_DFT[:,4])
B2O3_PV = P(B2O3_Vspan, B2O3_PVCoeff[0], B2O3_PVCoeff[1], B2O3_PVCoeff[2])
#####
B6O_PV = P(B6O_Vspan, B6O_EVCoeff[1], B6O_EVCoeff[2], B6O_EVCoeff[3])
B8O_PV = P(B8O_Vspan, B8O_EVCoeff[1], B8O_EVCoeff[2], B8O_EVCoeff[3])
B36O5_PV = P(B36O5_Vspan, B36O5_EVCoeff[1], B36O5_EVCoeff[2], B36O5_EVCoeff[3])
B84O11_PV = P(B84O11_Vspan, B84O11_EVCoeff[1], B84O11_EVCoeff[2], B84O11_EVCoeff[3])
B4C_PV = P(B4C_Vspan, B4C_EVCoeff[1], B4C_EVCoeff[2], B4C_EVCoeff[3])
CuO_PV = P(CuO_Vspan, CuO_EVCoeff[1], CuO_EVCoeff[2], CuO_EVCoeff[3])
Cu_PV = P(Cu_Vspan, Cu_EVCoeff[1], Cu_EVCoeff[2], Cu_EVCoeff[3])

#Data Storage and Enthalpy Calculation (eV/atom)
AR_Data = [AR_EV, AR_Vspan, AR_PV*160.2176621, (AR_EV+AR_Vspan*AR_PV)/(AR_atom)]
BR_Data = [BR_EV, BR_Vspan, BR_PV*160.2176621, (BR_EV+BR_Vspan*BR_PV)/(BR_atom)]
G_Data = [G_EV, G_Vspan, G_PV*160.2176621, (G_EV+ G_Vspan* G_PV)/(G_atom)]
B2O3_Data = [B2O3_EV, B2O3_Vspan, B2O3_PV*160.2176621,
(B2O3_EV+B2O3_Vspan*B2O3_PV)/(B2O3_atom)]
B6O_Data = [B6O_EV, B6O_Vspan, B6O_PV*160.2176621,
(B6O_EV+B6O_Vspan*B6O_PV)/(B6O_atom)]
B8O_Data = [B8O_EV, B8O_Vspan, B8O_PV*160.2176621,
(B8O_EV+B8O_Vspan*B8O_PV)/(B8O_atom)]
B36O5_Data = [B36O5_EV, B36O5_Vspan, B36O5_PV*160.2176621,
(B36O5_EV+B36O5_Vspan*B36O5_PV)/(B36O5_atom)]
B84O11_Data = [B84O11_EV, B84O11_Vspan, B84O11_PV*160.2176621,
(B84O11_EV+B84O11_Vspan*B84O11_PV)/(B84O11_atom)]
B4C_Data = [B4C_EV, B4C_Vspan, B4C_PV*160.2176621,
(B4C_EV+B4C_Vspan*B4C_PV)/(B4C_atom)]
CuO_Data = [CuO_EV, CuO_Vspan, CuO_PV*160.2176621,
(CuO_EV+CuO_Vspan*CuO_PV)/(CuO_atom)]
Cu_Data = [Cu_EV, Cu_Vspan, Cu_PV*160.2176621, (Cu_EV+Cu_Vspan*Cu_PV)/(Cu_atom)]

#Generate E(P) Equation (eV/atom (func of GPa))
EqDegree = 3
AR_EP = np.poly1d(np.polyfit(AR_Data[2], AR_Data[3], EqDegree), variable='P')
BR_EP = np.poly1d(np.polyfit(BR_Data[2], BR_Data[3], EqDegree), variable='P')
G_EP = np.poly1d(np.polyfit(G_Data[2], G_Data[3], EqDegree), variable='P')
B2O3_EP = np.poly1d(np.polyfit(B2O3_Data[2], B2O3_Data[3], EqDegree), variable='P')
B6O_EP = np.poly1d(np.polyfit(B6O_Data[2], B6O_Data[3], EqDegree), variable='P')
B8O_EP = np.poly1d(np.polyfit(B8O_Data[2], B8O_Data[3], EqDegree), variable='P')
B36O5_EP = np.poly1d(np.polyfit(B36O5_Data[2], B36O5_Data[3], EqDegree), variable='P')

```

```

B84O11_EP = np.poly1d(np.polyfit(B84O11_Data[2], B84O11_Data[3], EqDegree), variable='P')
B4C_EP = np.poly1d(np.polyfit(B4C_Data[2], B4C_Data[3], EqDegree), variable='P')
CuO_EP = np.poly1d(np.polyfit(CuO_Data[2], CuO_Data[3], EqDegree), variable='P')
Cu_EP = np.poly1d(np.polyfit(Cu_Data[2], Cu_Data[3], EqDegree), variable='P')

# Special Ideal Gas Equations (eV/atom)
def O2_EP(P):
    return O2_DFT/O2_atom + 0*P
def CO2_EP(P):
    return CO2_DFT/CO2_atom + 0*P

##### Vibrational Entropy Calcs #####
P = sym.Symbol('P')
T = sym.Symbol('T')
#Define Entropy Equation (J/K/mol)
def SV(PT, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v):
    P,T = PT
    return (b+c*P+d*P**2)*T + (e+f*P+g*P**2)*T**2 + (h+i*P+j*P**2)*T**3 +
(k+l*P+m*P**2)*T**4 + (n+o*P+p*P**2)*T**5 + (q+r*P+s*P**2)*T**6 + (t+u*P+v*P**2)*T**7

#Calculate Coefficients (J/K/mol), need to convert in Gibb Equation
AlphaR_SVCoeff, covariance = sc.curve_fit(SV, (AR_Sv[:,2],AR_Sv[:,1]), AR_Sv[:,0])
BetaR_SVCoeff, covariance = sc.curve_fit(SV, (BR_Sv[:,2],BR_Sv[:,1]), BR_Sv[:,0])
B2O3_SVCoeff, covariance = sc.curve_fit(SV, (B2O3_Sv[:,2],B2O3_Sv[:,1]), B2O3_Sv[:,0])
B6O_SVCoeff, covariance = sc.curve_fit(SV, (B6O_Sv[:,2],B6O_Sv[:,1]), B6O_Sv[:,0])
B8O_SVCoeff, covariance = sc.curve_fit(SV, (B8O_Sv[:,2],B8O_Sv[:,1]), B8O_Sv[:,0])
B36O5_SVCoeff, covariance = sc.curve_fit(SV, (B36O5_Sv[:,2],B36O5_Sv[:,1]), B36O5_Sv[:,0])

# Special Ideal Gas vibrational entropy (J/K/mol)
O2_SVCoeff = np.polyfit(O2_Sv[:, 0], O2_Sv[:, 1], 10)
O2_SV = np.poly1d(O2_SVCoeff, variable='T')
CO2_SVCoeff = np.polyfit(CO2_Sv[:, 0], CO2_Sv[:, 1], 10)
CO2_SV = np.poly1d(CO2_SVCoeff, variable='T')

### Temporary Calculation for only 0 pressure entropy ###
Gamma_SVCoeff = np.polyfit(G_Sv[:, 1], G_Sv[:, 0], 10)
G_SV = np.poly1d(Gamma_SVCoeff, variable='T')
B84O11_SVCoeff = np.polyfit(B84O11_Sv[:, 1], B84O11_Sv[:, 0], 10)
B84O11_SV = np.poly1d(B84O11_SVCoeff, variable='T')
B4C_SVCoeff = np.polyfit(B4C_Sv[:, 1], B4C_Sv[:, 0], 10)
B4C_SV = np.poly1d(B4C_SVCoeff, variable='T')
CuO_SVCoeff = np.polyfit(CuO_Sv[:, 1], CuO_Sv[:, 0], 10)
CuO_SV = np.poly1d(CuO_SVCoeff, variable='T')
Cu_SVCoeff = np.polyfit(Cu_Sv[:, 1], Cu_Sv[:, 0], 10)

```

```
Cu_SV = np.poly1d(Cu_SVCoeff, variable='T')
```

```
##### Gibbs Energy Calculations #####
```

```
#Gibbs Energy as a function of Pressure (eV/atom (GPa))
```

```
def AR_Gibb(P, T):
```

```
    return AR_EP(P) - T*SV((P,T), *AlphaR_SVCoeff)/(AR_atom)/1000/96.484934
```

```
def BR_Gibb(P, T):
```

```
    return BR_EP(P) - T*SV((P,T), *BetaR_SVCoeff)/(BR_atom)/1000/96.484934
```

```
def G_Gibb(P, T):
```

```
    return G_EP(P) - T*G_SV(T)/(G_atom)/1000/96.484934
```

```
def B2O3_Gibb(P, T):
```

```
    return B2O3_EP(P) - T*SV((P,T), *B2O3_SVCoeff)/(B2O3_atom)/1000/96.484934
```

```
def B6O_Gibb(P, T):
```

```
    return B6O_EP(P) - T*SV((P,T), *B6O_SVCoeff)/(B6O_atom)/1000/96.484934
```

```
def B8O_Gibb(P, T):
```

```
    return B8O_EP(P) - T*SV((P,T), *B8O_SVCoeff)/(B8O_atom)/1000/96.484934
```

```
def B36O5_Gibb(P, T):
```

```
    return B36O5_EP(P) - T*SV((P,T), *B36O5_SVCoeff)/(B36O5_atom)/1000/96.484934
```

```
def B84O11_Gibb(P, T):
```

```
    return B84O11_EP(P) - T*B84O11_SV(T)/(B84O11_atom)/1000/96.484934
```

```
def B4C_Gibb(P, T):
```

```
    return B4C_EP(P) - T*B4C_SV(T)/(B4C_atom)/1000/96.484934
```

```
def O2_Gibb(P,T):
```

```
    return O2_EP(P) - T*O2_SV(T)/(O2_atom)/1000/96.484934
```

```
def CO2_Gibb(P,T):
```

```
    return CO2_EP(P) - T*CO2_SV(T)/(CO2_atom)/1000/96.484934
```

```
def CuO_Gibb(P, T):
```

```
    return CuO_EP(P) - T*Cuo_SV(T)/(CuO_atom)/1000/96.484934
```

```
def Cu_Gibb(P, T):
```

```
    return Cu_EP(P) - T*Cuo_SV(T)/(Cu_atom)/1000/96.484934
```

```
##### Reaction Energy Equations #####
```

```
#eV/atom
```

```
# B6O Formations
```

```
def Reaction1(P,T): #B2O3 + 16 B(alpha) -> 3 B6O (Direct oxidation)
```

```
    return (3*B6O_Gibb(P,T)*7 - 1*B2O3_Gibb(P,T)*5 - 16*AR_Gibb(P, T)*1)/21
```

```
def Reaction2(P,T): #B2O3 + 16 B(Beta) -> 3 B6O (Direct oxidation)
```

```
    return (3*B6O_Gibb(P,T)*7 - 1*B2O3_Gibb(P,T)*5 - 16*BR_Gibb(P, T)*1)/21
```

```
def Reaction3(P,T): #1/2 O2 + 6 B(Beta) -> B6O
```

```
    return (1*B6O_Gibb(P,T)*7 - 0.5*O2_Gibb(P,T)*2 - 6*BR_Gibb(P, T)*1)/7
```

```
def Reaction4(P,T): #3 B2O3 -> B6O + 4 O2 (decomposition)
```

```
    return (1*B6O_Gibb(P,T)*7 + 4*O2_Gibb(P,T)*2 - 3*B2O3_Gibb(P,T)*5)/15
```

```

def Reaction7(P,T):
    return (1*B6O_Gibb(P,T)*7 + 1*CO2_Gibb(P,T)*3 - 1*B4C_Gibb(P, T)*5 -
1*B2O3_Gibb(P,T)*5)/10
def Reaction8(P,T):
    return (2*B6O_Gibb(P,T)*7 + 3*CO2_Gibb(P,T)*3 - 3*B4C_Gibb(P, T)*5 - 4*O2_Gibb(P,T)*2)/23

# B2O3 Formations
def Reaction5(P,T): #1.5 O2 + 2 B(Alpha) -> B2O3
    return (1*B2O3_Gibb(P,T)*5 - 1.5*O2_Gibb(P,T)*2 - 2*AR_Gibb(P, T)*1)/5
def Reaction6(P,T): #1.5 O2 + 2 B(Beta) -> B2O3
    return (1*B2O3_Gibb(P,T)*5 - 1.5*O2_Gibb(P,T)*2 - 2*BR_Gibb(P, T)*1)/5

# Direct Oxidation Reactions from Alpha Boron
def Oxi1(P,T):
    return (B6O_Gibb(P,T)*7 - 1*O2_Gibb(P,T) - 6*AR_Gibb(P, T))/7
def Oxi2(P,T):
    return (B8O_Gibb(P,T)*9 - 1*O2_Gibb(P,T) - 8*AR_Gibb(P, T))/9
def Oxi3(P,T):
    return (B36O5_Gibb(P,T)*41 - 5*O2_Gibb(P,T) - 36*AR_Gibb(P, T))/41
def Oxi4(P,T):
    return (B84O11_Gibb(P,T)*95 - 11*O2_Gibb(P,T) - 84*AR_Gibb(P, T))/95
def Oxi5(P,T):
    return (B2O3_Gibb(P,T)*5 - 3*O2_Gibb(P,T) - 2*AR_Gibb(P, T))/5

# CuO Oxidation Reactions from Alpha Boron
def Cu1(P,T):
    return (B6O_Gibb(P,T)*7 + 1*Cu_Gibb(P,T) - 1*CuO_Gibb(P,T)*2 - 6*AR_Gibb(P,T))/8
def Cu2(P,T):
    return (B8O_Gibb(P,T)*8 + 1*Cu_Gibb(P,T) - 1*CuO_Gibb(P,T)*2 - 8*AR_Gibb(P,T))/10
def Cu3(P,T):
    return (B36O5_Gibb(P,T)*41 + 5*Cu_Gibb(P,T) - 5*CuO_Gibb(P,T)*2 - 36*AR_Gibb(P,T))/46
def Cu4(P,T):
    return (B84O11_Gibb(P,T)*95 + 11*Cu_Gibb(P,T) - 11*CuO_Gibb(P,T)*2 - 84*AR_Gibb(P,T))/106
def Cu5(P,T):
    return (1*B2O3_Gibb(P,T)*5 + 3*Cu_Gibb(P,T)*1 - 3*CuO_Gibb(P,T)*2 - 2*AR_Gibb(P,T)*1)/8

##### Phases #####
### Formation Groups ###
# Oxygen Deficient Environment #
def ODefic1(P,T): # Cu + B6O
    return ( 1*Cu_Gibb(P, T)*1 + 1*B6O_Gibb(P, T)*7 )/8
def ODefic2(P,T): # 3Cu + 16B + B2O3
    return ( 3*Cu_Gibb(P, T)*1 + 16*AR_Gibb(P, T)*1 + 1*B2O3_Gibb(P, T)*5 )/24
def ODefic3(P,T): # CuO + 6B

```

```

return ( 1*CuO_Gibb(P, T)*2 + 6*AR_Gibb(P, T)*1 )/8*0

# Oxygen Rich Environment #
def ORich1(P,T): # Cu + 8CuO + B6O
    return ( 1*Cu_Gibb(P, T)*1 + 8*CuO_Gibb(P, T)*2 + 1*B6O_Gibb(P, T)*7 )/24
def ORich2(P,T): # 3Cu + B2O3
    return ( 3*Cu_Gibb(P, T)*1 + 1*B2O3_Gibb(P, T)*5 )/8
def ORich3(P,T): # 3CuO + 2B
    return ( 3*CuO_Gibb(P, T)*2 + 2*AR_Gibb(P, T)*1 )/8

##### Plot Results #####
### Plot Constants ###
fontsize = 20
Aspect = (6,4)
res = 500
plt.rc('font', size=fontsize)
plt.rcParams["figure.dpi"]=res

Temp1 = 0
Temp2 = 1773
Press1 = 0.00010132

# Gibbs Plots (At Set Temp) # 1
fig, (ax1, ax2) = plt.subplots(2, 1)
plt.subplots_adjust(left=0.1, bottom=0.1, right=2.0, top=2.3, wspace=0.3, hspace=0.5)
ax2.set_xlabel('Pressure (GPa)')
ax2.set_ylabel('ΔE (eV/atom)', y=1.125)
ax1.plot(PresRange, AR_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), label='α-B')
ax1.plot(PresRange, BR_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), label='β-B')
ax1.plot(PresRange, G_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), label='$\gamma$-B')
ax1.text(0, 0.05, '(a) {A} K'.format(A=Temp1), va="bottom")
ax1.set_xlim([0, 25])
ax1.set_ylim([-0.05, 0.05])
ax2.plot(PresRange, AR_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), label='α-B')
ax2.plot(PresRange, BR_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), label='β-B')
ax2.plot(PresRange, G_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), label='$\gamma$-B')
ax2.text(0, 0.05, '(b) {B} K'.format(B=Temp2), va="bottom")
ax2.set_xlim([0, 25])
ax2.set_ylim([-0.05, 0.05])
ax2.legend(loc = 'right', bbox_to_anchor=(1.25, 1.125))
plt.show()

# Gibbs Plots for Suboxides # 2
fig, (ax1, ax2) = plt.subplots(2, 1)

```

```

plt.subplots_adjust(left=0.1, bottom=0.1, right=2.0, top=2.3, wspace=0.3, hspace=0.5)
ax2.set_xlabel('Pressure (GPa)')
ax2.set_ylabel('ΔE (eV/atom)', y=1.125)
ax1.plot(PresRange, B2O3_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), label='$B_2O_3$')
ax1.plot(PresRange, B6O_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), label='$B_6O$')
ax1.plot(PresRange, B8O_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), linestyle='dashed',
label='$B_8O$')
ax1.plot(PresRange, B36O5_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1), linestyle='dashed',
label='$B_{36}O_5$')
ax1.plot(PresRange, B84O11_Gibb(PresRange, Temp1)-AR_Gibb(PresRange, Temp1),
linestyle='dashed', label='$B_{84}O_{11}$')
ax1.text(0, -0.17, '(a) {A} K'.format(A=Temp1))
ax1.set_xlim([0, 40])
ax1.set_ylim([-0.8, -0.2])
ax2.plot(PresRange, B2O3_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), label='$B_2O_3$')
ax2.plot(PresRange, B6O_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), label='$B_6O$')
ax2.plot(PresRange, B8O_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), linestyle='dashed',
label='$B_8O$')
ax2.plot(PresRange, B36O5_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2), linestyle='dashed',
label='$B_{36}O_5$')
ax2.plot(PresRange, B84O11_Gibb(PresRange, Temp2)-AR_Gibb(PresRange, Temp2),
linestyle='dashed', label='$B_{84}O_{11}$')
ax2.text(0, -0.17, '(b) {B} K'.format(B=Temp2))
ax2.set_xlim([0, 40])
ax2.set_ylim([-0.8, -0.2])
ax2.legend(loc = 'right', bbox_to_anchor=(1.3, 1.25))
plt.show()

```

Compare B6O and B203 formation # 3

```

plt.rc('font', size=16)
fig, (ax1, ax2) = plt.subplots(1, 2)
plt.subplots_adjust(left=0.1, bottom=0.1, right=2, top=1, wspace=0.2, hspace=0.55)
ax2.plot(PresRange, Cu5(PresRange,Temp2), label='$3CuO$ + 2B ⇌ $B_2O_3$ + 3Cu')
ax2.plot(PresRange, Cu1(PresRange,Temp2), label='$CuO$ + 6B ⇌ $B_6O$ + Cu')
ax2.plot(PresRange, Reaction1(PresRange,Temp2), label='$B_2O_3$ + 16B ⇌ 3$B_6O$')
ax2.text(0, 0.05, '(b) {A} K'.format(A=Temp2))
ax2.set_xlim([0, 50]), ax2.set_ylim([-1, 0])
ax2.set_xlabel('Pressure (GPa)')
ax1.plot(TempRange, Cu5(Press1,TempRange), label='$3CuO$ + 2B($\alpha$) -> $B_2O_3$ + 3Cu')
ax1.plot(TempRange, Cu1(Press1,TempRange), label='$CuO$ + 6B($\alpha$) -> $B_6O$ + Cu')
ax1.plot(TempRange, Reaction1(Press1,TempRange), label='$B_2O_3$ + 16B($\alpha$) -> 3$B_6O$')
ax1.set_xlabel('Temperature (K)')
ax1.set_ylabel('Energy (eV/atom)')
ax1.set_xlim([0, 1800]), ax1.set_ylim([-1, 0]), ax2.set_yticklabels([])

```

```

ax1.text(0, 0.05, '(a) {:.2E} GPa'.format(Press1).replace('E-0', 'E-'))
ax2.legend(loc = 'center', bbox_to_anchor=(-0.1, -0.5))
plt.show()

##### Environmental Plots #####
# Energy of Formation Groups - Oxygen Deficient # 4
plt.rc('font', size=16)
fig, (ax1, ax2) = plt.subplots(1, 2)
plt.subplots_adjust(left=0.1, bottom=0.1, right=2.0, top=1, wspace=0.1, hspace=0.2)
xlim = [0, 50]
ylim = [-8, -5]
ax1.plot(PresRange, ODefic1(PresRange, Temp2), label = '$B_6O + Cu$')
ax1.plot(PresRange, ODefic2(PresRange, Temp2), label = '$B_2O_3 + 16B + 3Cu$')
ax1.set_xlim(xlim), ax1.set_xlabel('Pressure (GPa)')
ax1.set_ylim(ylim), ax1.set_ylabel('Formation Energy (eV/atom)')
ax1.text(np.mean(xlim), ODefic1(np.mean(xlim), Temp2)+0.1, 'B$_6$O, Cu', ha='center', va='top',
rotation=28)
ax1.text(np.mean(xlim), ODefic2(np.mean(xlim), Temp2)-0.4, 'B$_2$O$_3$, 16B, 3Cu', ha='center',
va='bottom', rotation=30)
ax1.text(xlim[1], ylim[1]+np.ptp(ylim)/10, 'Oxygen-Deficient Environment', va='bottom', ha='center')
xlim = [0, 1800]
ax2.plot(TempRange, ODefic1(Press1, TempRange), label = '$B_6O + Cu$')
ax2.plot(TempRange, ODefic2(Press1, TempRange), label = '$B_2O_3 + 16B + 3Cu$')
ax2.set_xlim(xlim), ax2.set_xlabel('Temperature (K)')
ax2.set_ylim(ylim), ax2.set_yticklabels([])
ax2.text(np.mean(xlim), ODefic1(Press1, TempRange.mean()), 'B$_6$O, Cu', va='top', ha='center',
rotation=-11)
ax2.text(np.mean(xlim), ODefic2(Press1, TempRange.mean())-0.1, 'B$_2$O$_3$, 16B, 3Cu',
va='bottom', ha='center', rotation=-13)
plt.show()

# Energy of Formation Groups - Oxygen Rich # 5
plt.rc('font', size=16)
fig, (ax1, ax2) = plt.subplots(1, 2)
plt.subplots_adjust(left=0.1, bottom=0.1, right=2.0, top=1, wspace=0.1, hspace=0.2)
xlim = [0, 50]
ylim = [-7, -4]
ax1.plot(PresRange, ORich1(PresRange, Temp2), label = '$B_6O + 8CuO$ + Cu$')
ax1.plot(PresRange, ORich2(PresRange, Temp2), label = '$B_2O_3 + 3Cu$')
ax1.set_xlim(xlim), ax1.set_xlabel('Pressure (GPa)')
ax1.set_ylim(ylim), ax1.set_ylabel('Formation Energy (eV/atom)')
ax1.text(np.mean(xlim)-5, ORich1(np.mean(xlim)-5, Temp2)-0.4, 'B$_6$O, 8CuO, Cu', ha='center',
va='bottom', rotation=36)

```

```

ax1.text(np.mean(xlim), ORich2(np.mean(xlim), Temp2)+0.2, 'B$_2$O$_3$, 3Cu', ha='center', va='top',
rotation=38)
ax1.text(xlim[1], ylim[1]+np.ptp(ylim)/10, 'Oxygen-Rich Environment', va='bottom', ha='center')
xlim = [0, 1800]
ax2.plot(TempRange, ORich1(Press1, TempRange), label = '$B_6O + 8CuO$ + Cu')
ax2.plot(TempRange, ORich2(Press1, TempRange), label = '$B_2O_3 + 3Cu$')
ax2.set_xlim(xlim), ax2.set_xlabel('Temperature (K)')
ax2.set_ylim(ylim), ax2.set_yticklabels([])
ax2.text(np.mean(xlim), ORich1(Press1, TempRange.mean())-0.2, 'B$_6$O, 8CuO, Cu', ha='center',
va='bottom', rotation=-16)
ax2.text(np.mean(xlim), ORich2(Press1, TempRange.mean()), 'B$_2$O$_3$, 3Cu', ha='center', va='top',
rotation=-14)
plt.show()

```

Appendix C - Code for Material Characterization

Raman Spectroscopy Single Peak Analysis

```
import matplotlib.pyplot as plt
import numpy as np
import scipy.optimize as sc
import pandas as pd
from tkinter.filedialog import askopenfilename
from BaselineRemoval import BaselineRemoval

##### Define Functions #####
##### Lorentzian Equation #####
def Lorentz(X, I, FWHM, Shift, Base):
    return I*((0.25*FWHM**2)/(np.square(X-Shift)+0.25*FWHM**2)) + Base

##### Gui Data Selection #####
##### Ask for Data File #####
def import_data(): ### Allow import of .dpt, excel, or text files
    FileName = askopenfilename(filetypes=[("DPT files", "*.dpt"), ("Text files", "*.txt"), ("Excel files",
    "*.xlsx *.xls")])
    return np.loadtxt(FileName).transpose()
data = import_data()

##### Initialize Data #####
X = data[0]
Y = data[1]
Yraw = Y

##### Analysis #####
##### Normalization #####
# Baseline Removal # Double Pass #
Y = BaselineRemoval(Y).ZhangFit(lambda_=500)
Y = BaselineRemoval(Y).ZhangFit()

# Normalize Data #
Y = (Y-min(Y))/(max(Y)-min(Y))

##### Peak Analysis #####
Initial = np.array([max(Y)*0.99, 10, X[np.where(Y == max(Y))[0][0]], min(Y)])
Param , Covariance = sc.curve_fit(Lorentz, X, Y,
                                bounds= # I    FWHM    Shift    Base
                                [(min(Y), 0, min(X), -1*np.Inf),
```

```

        (max(Y)*2, 100, max(X), np.Inf],
        p0=Initial)

##### Tabulate Fit Parameters #####
Param = pd.DataFrame({
    'Intensity': [Param[0]],
    'FWHM': [Param[1]],
    'Peak Shift': [Param[2]],
    'Baseline': [Param[3]] })

#### Generate Lorentzian Curve for Plotting ####
X_Range = np.arange(min(X), max(X)+0.1, 0.1)
Y_Lorentz = Lorentz(X_Range, Param['Intensity'][0], Param['FWHM'][0], Param['Peak Shift'][0],
Param['Baseline'][0])

##### Figures #####
##### Plot Settings #####
plt.rc('font', size=14)
plt.figure(figsize=(8, 6))
plt.rcParams["figure.dpi"] = 500
XWidth = 60

##### Set-Up Subplot Dimensions #####
fig, (ax1, ax2) = plt.subplots(2)
plt.subplots_adjust(left=0.1, bottom=0.1, right=1.0, top=2.0, wspace=0.1, hspace=0.3)

##### Plot Raw Data #####
ax1.plot(X, Yraw, label='Raw Data')
# ax1.plot(X_Range, Y_Lorentz, label='Lorentzian Fit', color='orange')
ax1.set_xlim(min(X), max(X))
ax1.set_ylim([min(Yraw).round(0), 1.1*max(Yraw).round(0)])
ax1.legend()

##### Plot Narrow Peak Range #####
ax2.scatter(X, Y, label='Normalized Data', s=10)
ax2.plot(X_Range, Y_Lorentz, label='Lorentzian Fit', color='orange')
ax2.set_xlim([(Param['Peak Shift'][0]-XWidth*3/4).round(0), (Param['Peak
Shift'][0]+XWidth/4).round(0)])
ax2.set_ylim([min(Y).round(0), 1.1*Param['Intensity'][0]])

##### Plot Labels #####
ax1.set_title('Raman Analysis')
ax2.set_xlabel('Raman Shift ( $\text{cm}^{-1}$ )')
ax2.set_ylabel('Intensity (A.U)')

```

```
ax2.legend()
```

```
##### Parameter List #####
```

```
ax2.table(cellText=Param.values.round(2), colLabels=Param.columns, cellLoc='center', bbox=[0, -0.5, 1, 0.2])
```

CTLM Analysis

```
import matplotlib.pyplot as plt
```

```
import numpy as np
```

```
import pandas as pd
```

```
##### Measurement Parameters #####
```

```
r1 = 50 #um
```

```
d = [4, 8, 12, 16, 20, 24, 32, 40, 48] #um
```

```
CF = [0.96, 0.93, 0.90, 0.87, 0.84, 0.82, 0.77, 0.73, 0.701]
```

```
Sample = "600C Pyro 5min"
```

```
FirstRing = 1
```

```
LastRing = 9
```

```
##### Data Import #####
```

```
### Resistance Regression ###
```

```
## Set Total Resistance Collection VArable ##
```

```
R_tot = [0] * 9
```

```
for i in np.linspace(FirstRing, LastRing, LastRing):
```

```
## Set Directory from Flashdrive ##
```

```
Location = r"C:/Users/dinch/Documents/Data Access/LW 24_10 Hydrogen Termination/"
```

```
Directory = Location+Sample+"/"+str(int(i))+".xls"
```

```
## Import Data ##
```

```
Voltage = pd.read_excel(Directory, usecols="D")
```

```
Current = pd.read_excel(Directory, usecols="C")
```

```
## Line Fit ##
```

```
R_tot[int(i-1)], intercept = np.polyfit(Current["AI"], Voltage["AV"], 1)
```

```
## IV Curve Plot ##
```

```
# plt.gca().add_patch(patches.FancyArrowPatch((0,3), (4,0), connectionstyle="arc3,rad=-0.3",  
arrowstyle='->', mutation_scale=20, color='white', linewidth=10)).set_zorder(10)
```

```
# plt.gca().add_patch(patches.FancyArrowPatch((0,3), (4,0), connectionstyle="arc3,rad=-0.3",  
arrowstyle='->', mutation_scale=20)).set_zorder(11)
```

```
plt.plot(Voltage, Current*1E6, label="Gap:"+str(d[int(i)-1])+"$μm")
```

```
# plt.legend(loc='lower right', fontsize=10)
```

```
plt.ylim([-4, 4])
```

```

plt.xlim([-5, 5])
plt.ylabel("Current ( $\mu$ A)"), plt.xlabel("Voltage (V)")
plt.rc('font', size=11.5)
plt.rcParams["figure.dpi"]=1000
plt.show()

## Correction Factor ##
R_tot = np.array(R_tot[(FirstRing-1):(LastRing)])/np.array(CF[(FirstRing-1):(LastRing)])
## Report Data ##
print(), print("Total Resistances:"), print(np.round(R_tot[(FirstRing-1):(LastRing)],0))
##### Regression of Characteristics #####

## Regress Slope ##
last = int(input("How many data points do you want to regress? "))
Slope, Intercept = np.polyfit(d[(FirstRing-1):FirstRing+last-1], R_tot[0:last], 1)

## Calculate Electrical Parameters ##
Rs = 2*np.pi*(r1)*Slope
Rc = np.pi*(r1)*Intercept
Lt = abs((1/Intercept)/2*1000)
rho = Rs*(Lt/10000)**2
Params = pd.DataFrame({
    'Sheet Resistance (ohm/cm)': [Rs],
    'Contact Resistance (ohm/cm)': [Rc],
    'Transfer Length (um)': [Lt],
    'Specific Contact Resistance (ohm cm^2)': [rho]})
print(Params.transpose().round(2)), print()

##### Plots #####
plt.plot(d[(FirstRing-1):(LastRing)], np.array(R_tot)*0.001, 'bo')
plt.plot(np.array(d[(FirstRing-1):FirstRing+last-1]), ((np.array(d[FirstRing-1:FirstRing+last-1]))*Slope +
Intercept)*0.001, '--', color='orange')
plt.ylabel("Total Resistance (k $\Omega$ )")
plt.xlabel("Gap Spacing ( $\mu$ m)"), plt.xlim([0, 50])
# plt.title(Sample)
plt.text(49, (min(R_tot)*0.001), r"R$_{\{sh\}}$ = {A:.2E}$ $ $\Omega$ /cm".format(A=Rs).replace("E+0", "
E+"), horizontalalignment="right")
plt.rc('font', size=14)
plt.rcParams["figure.dpi"]=1000
plt.show()

```