

B₁₂P₂: IMPROVED EPITAXIAL GROWTH AND EVALUATION OF α
IRRADIATION ON ITS ELECTRICAL TRANSPORT PROPERTIES

by

CLINT D. FRYE

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Abstract

The wide bandgap (3.35 eV) semiconductor icosahedral boron phosphide ($B_{12}P_2$) has been reported to self-heal from radiation damage from β particles (electrons) with energies up to 400 keV by demonstrating no lattice damage using transmission electron microscopy. This property could be exploited to create radioisotope batteries–semiconductor devices that directly convert the decay energy from a radioisotope to electricity. Such devices potentially have enormous power densities and decades-long lifetimes. To date, the radiation hardness of $B_{12}P_2$ has not been characterized by electrical measurements nor have $B_{12}P_2$ radioisotope batteries been realized. Therefore, this study was undertaken to evaluate the radiation hardness of $B_{12}P_2$ after improving its epitaxial growth, developing ohmic electrical contacts, and reducing the residual impurities. Subsequently, the effects of radiation from a radioisotope on the electrical transport properties of $B_{12}P_2$ were tested.

$B_{12}P_2$ was grown epitaxially on 4H-SiC by chemical vapor deposition (CVD) over the temperature range of 1250-1450 °C using B_2H_6 and PH_3 precursor gases in a H_2 carrier gas. The epitaxial relationship between $B_{12}P_2$ and 4H-SiC was $(0001)_{B_{12}P_2}[1\bar{1}00]_{B_{12}P_2}|| (0001)_{4H-SiC}[1\bar{1}00]_{4H-SiC}$ using hexagonal indices (or $(111)_{B_{12}P_2}[1\bar{2}1]_{B_{12}P_2}|| (0001)_{4H-SiC}[1\bar{1}00]_{4H-SiC}$ using rhombohedral indices for $B_{12}P_2$). X-ray diffraction (XRD) rocking curve measurements (assessing the crystal quality) about the $B_{12}P_2$ (0003) peak were minimized at 1300 °C indicating it was the optimum growth temperature studied. By miscutting the (0001) 4H-SiC substrate 4° to the $(1\bar{1}00)$ plane, $B_{12}P_2$ rotational twinning, a type of crystal defect, was strongly suppressed to a twin density of <1% in comparison to a standard miscut to the $(11\bar{2}0)$ plane which resulted in a twin density of 30%.

Cr/Pt (500/1000 Å) and Ni/Au (1000/1000 Å) ohmic contacts to B₁₂P₂ were developed. Ni/Au contacts annealed at 500 °C for 30 s in Ar proved to be the best contact studied with a specific contact resistance of $3 \times 10^{-4} \Omega\text{-cm}^2$. Background impurities were measured by secondary ion mass spectrometry (SIMS), and Si ($\approx 1 \times 10^{19}$ - $5 \times 10^{19} \text{ cm}^{-3}$), C ($\approx 5 \times 10^{19}$ - $2 \times 10^{20} \text{ cm}^{-3}$), and O ($\approx 2 \times 10^{20} \text{ cm}^{-3}$) were the primary residual impurities when B₁₂P₂ was grown on 4H-SiC at 1250 °C. The SiC substrate caused Si and C contamination, and the TaC-coated graphite heating element was a second C source. Since Si and C are *p*-type dopants in B₁₂P₂ (confirmed by Hall Effect measurements), the 4H-SiC substrate was exchanged with AlN/sapphire, and the TaC-coated graphite susceptor was replaced with Zr metal. With the new substrate and susceptor, the Si and C concentrations were decreased to $2\text{-}3 \times 10^{18} \text{ cm}^{-3}$ and $4 \times 10^{18} \text{ cm}^{-3}$, respectively. The radiation hardness of *p*-B₁₂P₂ grown on AlN/sapphire was compared to an epi-layer of *p*-4H-SiC (a conventional radiation hard material) by temperature-dependent Hall Effect measurements. A defect band was present in B₁₂P₂ prior to irradiation, and radiation further contributed to defect band conduction and lowered the hole mobility. Evidence for self-healing of B₁₂P₂ from electrical measurements remains inconclusive. However, the steps necessary to evaluate B₁₂P₂ for device applications has been clarified, and includes further reductions in crystalline defects and residual impurities, especially carbon and oxygen.

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Approved by:

Major Professor
J.H. Edgar

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Dedication

To my mother, Donna Mae Duncan Frye.

Preface

The aim of the research contained in this dissertation was to improve the epitaxial growth of $B_{12}P_2$ so that its radiation hardness could be tested through its electrical properties.

Two chapters in this dissertation, Chapter 2 and Chapter 4, are in the form of manuscripts that have been submitted to journals. As such, the tone in those chapters is a little more formal than the other chapters. Nonetheless, the arc of the dissertation still tells a continuous story from material growth and characterization to ohmic contact development to radiation testing. A short description of the chapters in this dissertation is provided below:

Chapter 1 introduces the concept of a radioisotope battery and the material $B_{12}P_2$, a semiconductor reported to have extraordinary radiation hardness by way of a “self-healing” mechanism. A literature review of $B_{12}P_2$ and relevant $B_{12}P_2$ background information is presented to provide context for the remainder of the text. The $B_{12}P_2$ growth system is also described.

Chapter 2 discusses the growth and characterization of epitaxial $B_{12}P_2$ films on 4H-SiC by chemical vapor deposition. This chapter has been submitted to the *Journal of Crystal Growth*.

Improvements in the growth of $B_{12}P_2$ films on 4H-SiC by the suppression of rotational twins (a type of crystal defect) is described in Chapter 3. Evidence for the suppression of twins is presented, and a detailed explanation for how twins are formed and suppressed is provided.

In Chapter 4, the development and characterization of ohmic contacts to $B_{12}P_2$, which are essential to electrical characterization and device fabrication, are described. This chapter was published in the *Journal of Vacuum Science and Technology A*.

Identification and quantification of background impurities in $B_{12}P_2$ films are presented Chapter 5. Contamination sources and steps taken to reduce the background impurity

concentrations are also discussed.

Chapter 6 compares the effect of α irradiation on the electrical transport properties of a p -type B_{12}P_2 epitaxial film to a p -type 4H-SiC epi-layer by temperature-dependent Hall Effect.

Chapter 7 summarizes the results of the dissertation and outlines future that should be done to improve epitaxial growth of B_{12}P_2 and to further evaluate the “self-healing” property of the material through electrical characterization.

Chapter 1

Introduction and Background

1.1 Motivation

As microelectronics decrease in size, device performance commonly increases. However, as batteries—which are essential to powering standalone, remote electronics—decrease in size, the energy stored decreases proportionally. While increasing the energy and power density of chemical batteries has been a major thrust of materials research for many decades, the maximum theoretical energy density is limited by the chemical nature of the cells. To illustrate, the energy density of lithium ion batteries is currently on the order of 10^2 Whr/L¹ while jet fuel has an energy density in the range of 10^4 Whr/L.² Nuclear energy via radioactive decay on the other hand is far more energy dense with densities on the order of 10^7 Whr/L or higher,³ far exceeding that of chemical sources. Therefore, harnessing the immense energy stored in nuclear materials can open new opportunities in powering microelectronics or creating ultra-high power density batteries. Even more, the energy released by radioisotopes is controlled by its half-life, and the harvestable energy can be released over the course of years or even decades.

The most direct route to collecting energy from a radioisotope is through the direct conversion of the decay particle energy into electricity. The conversion is analogous to a photovoltaic cell, and in fact, the concept of alpha and betavoltaics was established in parallel with that of photovoltaics.⁴ In short, as a decay particle penetrates a semiconductor pn-junction, electron-hole pairs are generated and collected to produce an electrical current. However, unlike a photovoltaic cell which creates a single e-h pair per photon, a β (electron) or α (He^{2+} ion) particle can produce hundreds of thousands of e-h pairs per particle along the β or α trajectory (see Figure 1.1). While the release of high-energy particles provides a large energy source, the decay energy is much greater than those of chemical bonds formed between atoms that make up the material. The penetrating particle not only breaks the chemical bonds within a material but can also dislodge entire atoms from crystal lattice sites, thus creating defects and degrading the electronic properties of crystalline semiconductors. Radiation damage to the pn-junction has limited radioisotope batteries to β emitters with

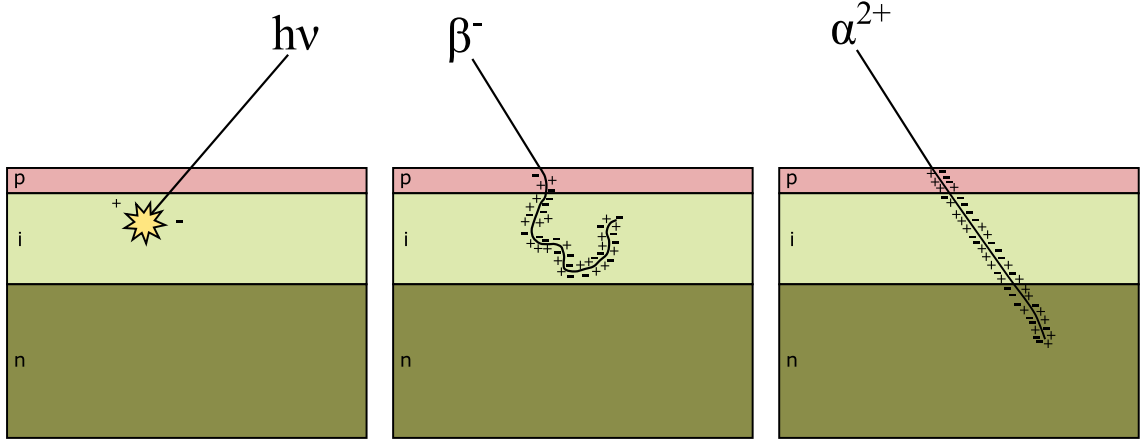


Figure 1.1: A schematic of a) a photon creating a single e-h pair, b) a β particle generating many e-h pairs along the particle track and c) an α particle producing a stream of e-h pairs along the length of the ion track in a pin semiconductor junction.

maximum energies of 300 keV or less.⁵

The icosahedral borides are a unique class of semiconductors that have been reported to be extremely resilient to radiation damage from high energy electrons (β 's) by showing no lattice damage by transmission electron microscopy (TEM).^{6,7} The compounds “self-heal” from radiation damage by spontaneous recombination of boron and boron vacancies generated in the crystal. If these materials can be fabricated into a functional device, then they could possibly be used in an alpha or betavoltaic cell and overcome lifetime limitations caused by radiation damage. However, the growth and characterization of icosahedral borides are underdeveloped, and the electronic properties and radiation tolerance of the material system need to be more robustly evaluated. The purpose of this research was to explore and improve the growth of $B_{12}P_2$ in an effort to improve its crystal and electronic properties so that it can be evaluated as a semiconductor for a radioisotope battery.

1.2 Semiconductor Radioisotope Battery

An alpha or betavoltaic battery is composed of a radioisotope (energy source) coupled to a semiconductor pn -junction (particle collector/electric current generator). β particle

radioisotope power sources, betavoltaics, were first conceived in the early 1950’s after the discovery of the electron-voltaic effect^{8,9} and developed in tandem with photovoltaics.^{4,10} While photovoltaics have seen continuous research and development, betavoltaics have only garnered sporadic interest over the decades.

The first commercially developed radioisotope battery was the Betacel.⁵ The device used ^{147}Pm as the β emitter and was composed of stacked layers of Si and $^{147}\text{Pm}_2\text{O}_3$. With an efficiency of 4%, it was able to produce up to 400 μW of power and could last for 10 years. The battery was used in pacemakers until it was supplanted by lithium batteries.

More recently, other betavoltaic devices have been developed by a variety of groups and are commercially available. Widetronix¹¹ has developed devices employing 4H-SiC and tritium (^3H) with an efficiency of 18.6%¹² but also makes batteries using ^{63}Ni . City Labs¹³ also sells a ^3H -powered battery. BetaBatt¹⁴ also uses ^3H but in conjunction with Si diodes instead of SiC. Qynergy¹⁵ also offers a betavoltaic battery using SiC with ^{85}Kr as the β emitter. Recent review articles on radioisotope batteries can be found by Olsen *et al.*⁵ and Prelas *et al.*¹⁶ To date, the selection of the radioisotope has been limited to lower energy β emitters (less than ≈ 300 keV)⁵ so that the β ’s do not damage the semiconductor which would limit the lifetime. Through its “self-healing” mechanism, B_{12}P_2 has the potential to be irradiated by much higher energy β -emitters such as ^{90}Sr and ^{90}Y which have maximum β energies of 546 keV and 2.28 MeV, respectively. Using a more energetic β -emitter could enable larger power densities and long device lifetimes.

1.3 Structure, Properties, and “Self-healing” of Icosahedral Borides

Boron is a notoriously fickle element owing to its ability to bond in a myriad of ways to both itself and to other elements. The variety of B-containing materials ranges from glasses (e.g. B_2O_3) to laminar crystals (e.g. MgB_2 and h-BN) to cluster compounds (e.g. decaborane

Table 1.1: *Basic parameters and properties of α -Boron and related icosahedral boride semiconductors.*

	Unit	α -Boron	B ₁₂ O ₂	B ₁₂ As ₂	B ₁₂ P ₂
Rhombohedral a-Constant ⁽¹⁷⁾	Å	5.06	5.14	5.32	5.25
Rhombohedral α -angle ⁽¹⁷⁾	deg.(°)	58.05	62.28	70.51	69.55
Hexagonal a-Constant ⁽¹⁷⁾	Å	4.91	5.31	6.14	5.99
Hexagonal c-Constant ⁽¹⁷⁾	Å	12.567	12.36	11.90	11.84
Density ⁽¹⁷⁾	g/cm ³	2.47	2.67	3.58	2.60
Melting Point ⁽¹⁸⁾	°C	2092	2077	-	2120
Band Gap	eV	2 ⁽¹⁹⁾	2.6 ⁽¹⁷⁾	3.47 ⁽²⁰⁾	3.35 ⁽²⁰⁾
Reported Mobility	cm ² /Vs	$\approx$ 100 ⁽²¹⁾	0.1-1 ⁽²²⁾	20-80 ^(23,24)	30-100 ^(25,26)

(B₁₂H₁₄)) to polymers (e.g. [B₃N₃H₄]_x) to the B₁₂ icosahedra-based “inverted molecular solids” (e.g. α -boron and B₁₂P₂; note: α -boron is a boron polymorph and has nothing to do with α particles) and many more. These borides span from mechanically hard to soft, from chemically inert to pyrophoric, and from electrically metallic to insulating. The propensity of B to form icosahedral clusters stems from its ability to form both 3-center in addition to typical 2-center bonds. This unusual bonding ability is responsible for the unique crystal structures and properties of the semiconducting icosahedral borides: α -Boron, B₁₂O₂, B₁₂As₂, and B₁₂P₂.

Although the B₁₂X₂ (X = P, As, O) class of semiconducting icosahedral borides has been

known for decades, the material system has only seen limited research despite indications that these materials are exceptionally radiation hard.^{6,7} A summary of the lattice parameters and select material and electrical properties of α -boron and the related icosahedral boride semiconductors is presented in Table 1.1.

The icosahedral borides are noted for their extreme hardness,^{27,28,29} thermal stability with melting points exceeding 2000 °C,¹⁸ and resistance to chemical attack. These properties lend these materials for use in harsh environments. The wide bandgaps enable high open circuit voltages and high temperature operation for potential radioisotope batteries. Further, the reasonably large hole mobilities should allow for better charge collection efficiency from such a device. The most noteworthy property of these classes of compounds is the reported ability to “self-heal” from radiation damage from β particles. The “self-healing” stems from the unusual bonding in the B₁₂ icosahedron.

1.3.1 Structure and Bonding in Icosahedral Borides

The icosahedral borides are composed of B₁₂ clusters that form icosahedral units within the crystal structure where a boron atom is positioned at each vertex of the icosahedra. The icosahedra act similarly to large atoms within the crystal lattice and are centered about the vertices of the rhombohedral unit cells, as shown in Figure 1.2. Many of the unique properties of the icosahedral borides arise directly from the icosahedral units and the unusual bonding therein.

In Figure 1.3a) and other ball and stick models throughout this text, the intra-icosahedral bonding is depicted by two-center bonds (bars) between the boron atoms; *however*, the boron atoms can also participate in unconventional three-center bonding. That is, the electron density between the boron atoms is not the greatest directly between two adjacent boron atoms but at the center of the triangle faces of the icosahedra formed by three neighboring boron atoms. Thus, the bonding within each icosahedra is more accurately—but still qualitatively—illustrated by Figure 1.3b) where color the gradient represents the

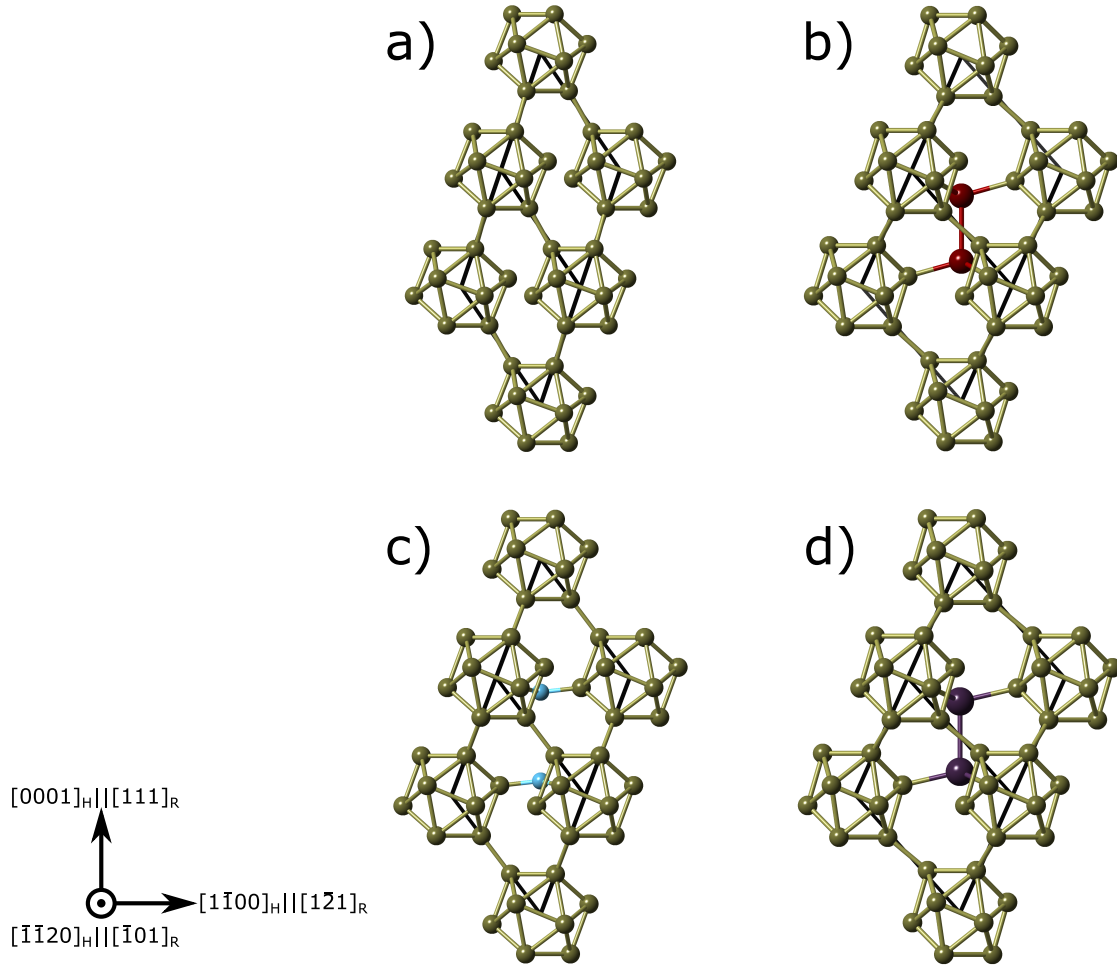


Figure 1.2: Rhombohedral unit cells and crystal structures of a) α -Boron,³⁰ b) $B_{12}P_2$,³⁰ c) $B_{12}O_2$,³¹ and d) $B_{12}As_2$ ³⁰ as viewed along the $[10\bar{1}]$ direction ($[11\bar{2}0]$ direction in hexagonal indices). The black lines denote the rhombohedral unit cell. An oblique view of the $B_{12}P_2$ rhombohedral unit cell can be found in Figure 1.7.

electron density. Further, the bonding within an icosahedron is even better understood through molecular orbital theory.³²

Thirteen bonding orbitals are present in a B_{12} icosahedron, requiring 26 electrons to satisfy each orbital.³³ Boron is a group III element and has three second shell electrons available for bonding, totaling 36 electrons in an icosahedron. For $B_{12}P_2$, $B_{12}As_2$, and $B_{12}O_2$, each of the 12 boron atoms in the icosahedra uses one of those three electrons for two-center, external bonds to either another icosahedra or to a P, As, or O atom. The remaining 24

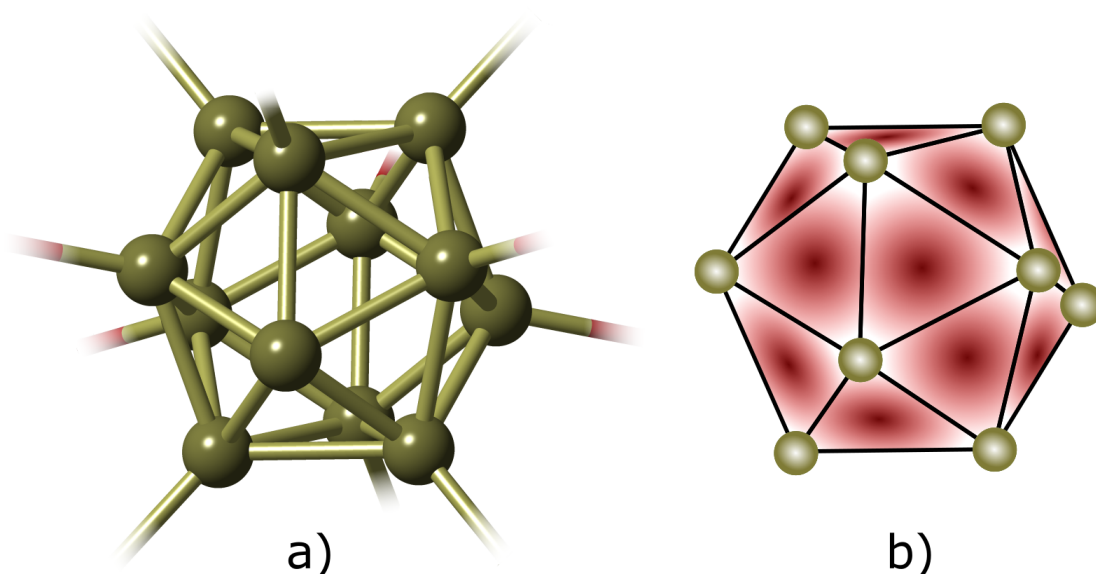


Figure 1.3: a) a typical ball and stick model of a B_{12} icosahedron. b) the intra-icosahedral bonds are actually 3-center bonds which are qualitatively depicted as a gradient on the triangular faces of the icosahedron where the darker areas indicate a higher electron density. Unlike typical 2-center bonds which are represented by the sticks (bars) in a), 3-center bonds are shared by 3 boron atoms and are located on the triangular faces. Bonds to atoms outside of the B_{12} icosahedra are however 2-center bonds.

electrons available for bonding ($3 \times 12 - 12$) are insufficient to complete the bonding orbitals and two more electrons are necessary to fill the remaining orbital. (Note: while the bonding in B_{12} clusters is best understood using molecular orbitals, the B_{12} clusters themselves do not behave similarly to molecules within a molecular crystal. The forces and bonds between atoms within a molecule are much stronger than the forces binding atoms from separate molecules together in a molecular crystal. In contrast, the internal and external icosahedral bonds in the icosahedral borides are of comparable strength, and therefore have even been referred to as “inverted molecular solids.”³⁴⁾

Group V elements, namely P and As, have five valence electrons available for bonding. Three of those second shell electrons are covalently bonded to the external two-center bonds of the B_{12} icosahedra while a fourth electron is bonded to the other group V atom in the

inter-icosahedral chain. Since both P and As have only four sp^3 hybridized orbitals to fill, the last remaining and 5th valence electron is donated to the B_{12} icosahedra. With two group V atoms per icosahedra and each donating a single electron to an icosahedra, all 13 icosahedral orbitals are fully satisfied. After the rearrangement of the electrons, the electronegative B_{12} icosahedra take on a formal charge of -2 while each group V atom accumulates a charge of +1.

O bonds differently than that of the group V elements (see Figure 1.2c)). The O atoms still donate an electron to the B_{12} icosahedra and share three two-center bonds with the icosahedra (as do both P and As atoms). However, the two O atoms do not bond with one another within the inter-icosahedral chain and the atoms become sp^2 hybridized. This leaves the O atoms with a +1 charge, and $B_{12}O_2$ remains charge neutral like $B_{12}P_2$ and $B_{12}As_2$.

The change in the bonding configuration of group V and group VI elements within the inter-icosahedral chain plays an important role when considering how these compounds can be doped, which is discussed further in Section 1.4.4.

1.3.2 Evidence and Mechanism of “Self-Healing”

$B_{12}P_2$ has been reported to “self-heal” from radiation damage induced by high energy electrons. Carrard *et al.*⁶ compared the radiation hardness of $B_{12}P_2$ and $B_{12}As_2$ to other borides including CaB_6 , LaB_6 , TiB_2 , and NbB_2 . By examining these compounds, a variety of different types of B bonding were tested. Samples of each of the materials were irradiated by being placed under a 200 keV electron beam inside a transmission electron microscope (TEM). The TEM could then be used to monitor defect generation and agglomeration in the materials *in situ*. According to the authors, in some cases the samples were irradiated long enough to displace every B atom in the crystal 7 times. At room temperature, defects were generated in CaB_6 , LaB_6 , and TiB_2 . No damage was observed in NbB_2 , $B_{12}P_2$, or $B_{12}As_2$. When irradiated at 91 K, damage started accumulating in NbB_2 , but again no

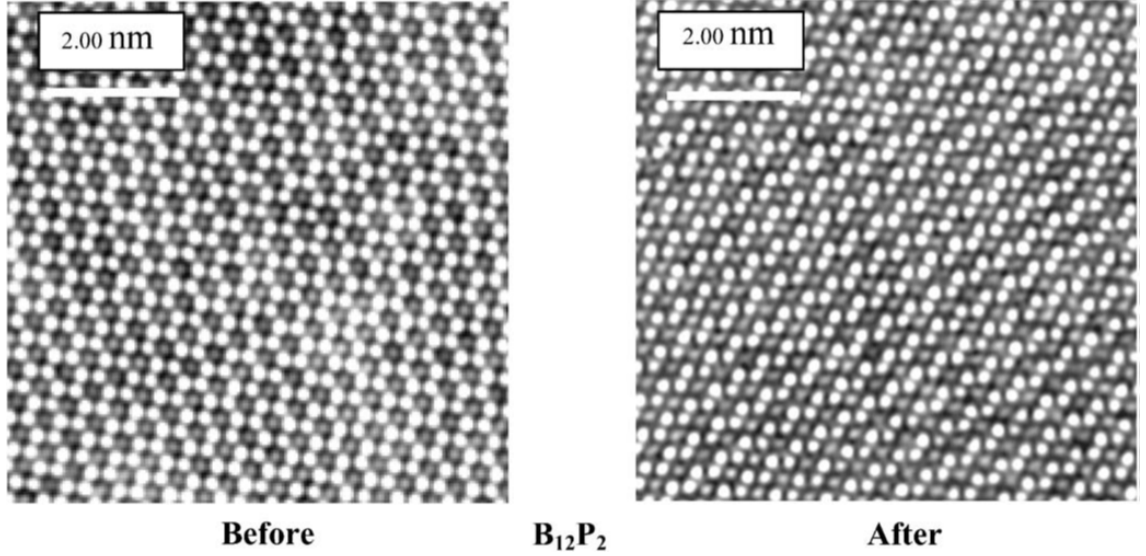


Figure 1.4: *Before and after high resolution TEM images of $B_{12}P_2$ irradiated with 400 keV electrons to a fluence of 10^{23} electrons/cm². No defect agglomeration or amorphization is observed illustrating the radiation hardness and “self-healing” of $B_{12}P_2$. The Figure is reproduced from Emin.⁷*

defects were seen in $B_{12}P_2$ or $B_{12}As_2$.

Emin also studied the radiation hardness and “self-healing” of $B_{12}P_2$.⁷ In this experiment, $B_{12}P_2$ was irradiated in a TEM by a 400 keV electron beam. After a fluence of 10^{23} electrons/cm², no damage was observed by high resolution TEM (see Figure 1.4). 400 keV is twice as energetic as the average energy of β ’s emitted from ^{90}Sr (the maximum energy is 546 keV).

Since at the electron energies and fluences used in the TEM experiments were high enough to displace all of the B atoms in the crystal, the absence of irradiation-induced damage has been ascribed to the “self-healing.” According to the hypothesized mechanism, as a B atom is displaced from a B_{12} icosahedron and forms a Frenkel pair, the icosahedron retains an electron from the displaced B atom due to its strong electron affinity. Even with a B vacancy, the icosahedron remains intact although “degraded.” The boron atom becomes a cation since the icosahedron stripped one of its electrons. Then the small boron ion can diffuse through the open crystal structure to recombine into the “degraded” icosahedron

and annihilate the Frenkel pair.

While the TEM studies show that $B_{12}P_2$ is resilient under bombardment of high-energy electrons to high fluences, the absence of defect agglomeration and material amorphization does not necessarily indicate that $B_{12}P_2$ suffers no radiation damage. Point defects and Frenkel defects within a B_{12} icosahedron cannot be detected because the B atoms within the icosahedron cannot be resolved by TEM. These types of defects may not pose a large scale structural change in the $B_{12}P_2$ lattice, but they could have an impact on the electrical properties of the material, which are much more sensitive to crystal defects. Therefore, to truly determine whether $B_{12}P_2$ is radiation hard or not, the effect of irradiation on the electrical properties should be measured.

1.4 $B_{12}P_2$ Literature Review

The following section provides an in-depth review of the $B_{12}P_2$ literature.

1.4.1 $B_{12}P_2$ Synthesis

$B_{12}P_2$ can be synthesized in one of three forms: powder, bulk crystals, or thin films. $B_{12}P_2$ powder has typically been made through the thermal decomposition of cubic BP by heating BP powder above 1000 °C under low phosphorus vapor pressures.^{20,35,36,37,38} Other methods have also been used to produce $B_{12}P_2$ powders, including flowing PH_3 over boron at 1500 °C,²⁰ direct combination of the elements at 1400 °C,³⁹ or by a self-propagating technique where $B_{12}P_2O_{23}$ or BPO_4 is reduced with magnesium metal.⁴⁰

While powders of $B_{12}P_2$ can be formed in a number of ways, large crystals are desired for device fabrication and measuring the electrical properties. Challenges synthesizing large, high-quality crystals have hampered research into its electronic characterization, materials engineering, and device fabrication. $B_{12}P_2$ is a refractory compound with a melting point exceeding 2000 °C, but it also contains P, which is highly volatile. Thus, growth from the

melt requires both extreme temperatures *and pressures* (≥ 100 atm) to maintain the proper stoichiometry at the melting point.^{20,41} Other methods to produce large crystals have been explored, such as precipitating crystals from a metal fluxes such as Pd,^{20,42} Ni,^{43,44} Al,³⁸ and Fe.³⁸

The most commonly employed method of producing large $B_{12}P_2$ crystals has been through epitaxy, usually hetero-epitaxy. Epitaxy has advantages of being able to synthesize large area crystals, at much more moderate temperatures than that required for direct melting, and typically using relatively simple equipment. While molecular beam epitaxy of $B_{12}P_2$ has been reported,^{45,46} Chemical vapor deposition (CVD) has been much more commonly used. A table of CVD-grown $B_{12}P_2$ films are summarized in Table 1.2. By far the most commonly used substrate has been Si due to its availability. Both halide and hydride precursors have been successfully used to grow $B_{12}P_2$.

Table 1.2: A summary of CVD-grown $B_{12}P_2$ growth conditions from the literature.

Boron Precursor	Phosphorus Precursor	Carrier Gas	Substrate	Deposition Temperature ($^{\circ}\text{C}$)	Reference
BBr_3	PH_3	H_2	B_{12}P_2 , Sapphire MgO, Si(111)	1250	Burmeister and Green ⁴³
B_2H_6	PH_3	H_2	Si(100), Si(110) Si(111)	700-1250	Takigawa <i>et al.</i> ⁴⁷
B_2H_6	PH_3	H_2	Si(100)	1200	Takenaka <i>et al.</i> ⁴⁸
B_2H_6	PH_3	H_2	Si(100)	1100-1250	Shohno <i>et al.</i> ⁴⁹
BBr_3	PBr_3	H_2	Si(100), Si(111) Fused Silica, W, Ni	1130	Groot <i>et al.</i> ⁵⁰
BCl_3	PCl_3	H_2/Ar	Si(100)	1190	Aselage ⁵¹
B_2H_6	PH_3	H_2	Si(100)	1100	Kumashiro <i>et al.</i> ²⁶
B_2H_6	PH_3	H_2	Si(100), Si(110) Si(111)	1050-1100	Kumashiro <i>et al.</i> ⁵²
B_2H_6	PH_3	H_2	Si(100), Si (111)	1100	Kumashiro <i>et al.</i> ²⁵
BBr_3	PBr_3	H_2	On-axis 6H-SiC (0001)	1100-1700	Peng <i>et al.</i> ⁵³

1.4.2 Electrical Properties of $B_{12}P_2$

Only a few studies by Kumashiro *et al.*^{25,54} have reported the electrical properties of $B_{12}P_2$ epitaxial films and the results are summarized in Table 1.3.

Table 1.3: *Electrical properties of $B_{12}P_2$ epitaxial films as reported in the literature.*

Resistivity ρ (Ω -cm)	Hole Concentration p (cm^{-3})	Hole Mobility μ (cm^2/Vs)	Reference
5.2×10^4 - 9.0×10^4	8.9×10^{11} - 1.2×10^{12}	100	Kumashiro <i>et al.</i> ²⁶
6.2×10^4 - 1.4×10^5	1.4×10^{12} - 9.3×10^{13}	10.8-31.7	Kumashiro <i>et al.</i> ²⁵

1.4.3 Conduction Mechanism in $B_{12}P_2$

Little information on the conduction mechanism of $B_{12}P_2$ exists in the literature. Kumashiro, *et al.*^{25,54,45} has indicated that $B_{12}P_2$ can conduct either by band or hopping conduction. Band conduction is characterized by electron transport through the conduction band (or by holes through the valence band) where electrons (or holes) are approximated as quasi-free particles. In contrast, hopping conduction is characterized by charge carriers hopping from one localized state to another either by a thermally assisted mechanism or by quantum mechanical tunneling. The two conduction mechanisms may not be mutually exclusive. Schmechel and Werheit⁵⁵ reported that boron carbide, another icosahedral boride, conducts by a superposition of hopping and band-type conduction and have shown that the band-type contribution increases at high temperatures and hopping-type conduction increases at lower temperatures and with increased disorder in the crystal.

For $B_{12}As_2$, both band and hopping conduction have been reported. Like boron carbide, $B_{12}As_2$ may conduct via a superposition of conduction types. Zhang, *et al.*⁵⁶ found that

B₁₂As₂ epitaxial films on 4H-SiC adhere to Mott's law ($\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{4}}\right)$) below room temperature, indicating hopping conduction. Zhang, *et al.*⁵⁶ was also able to extract a hole ionization energy from the $\text{Log}(p)$ versus T^{-1} from room temperature to 500 °C, suggesting that band conduction dominates at higher temperatures. Further, bulk B₁₂As₂ crystals were also found to conduct via band-type conduction from 100-400 °C.⁵⁷ Bulk crystals may be more likely to conduct via band conduction since they are expected to have fewer defects that can introduce localized states and are less disordered. Since boron carbide and B₁₂As₂ can conduct by both conduction mechanisms, B₁₂P₂ may also conduct by a superposition of the two conduction mechanisms as well.

1.4.4 Doping B₁₂P₂

Controlling the conductivity of B₁₂P₂ through the introduction of dopants is essential to developing electrical devices. However, due to the unusual and variable bonding of boron as was already discussed in Section 1.3.1, doping B₁₂P₂ is not as straightforward as that of conventional semiconductors such as Si. Only *p*-type conduction has been observed so far while *n*-type material must also be developed to form homogeneous B₁₂P₂ *pn*-junctions for devices. To date, no studies exist in which B₁₂P₂ has been intentionally doped successfully. The only experimental data on doping B₁₂P₂ is from unintentional doping via auto-doping of Si atoms from Si substrates.⁵²

Through conventional doping, one would introduce holes by replacing P with a group IV element such as Si or C. By analyzing the bonds, this method of doping may be achievable. When a *sp*³ hybridized group IV atom replaces a tetrahedrally bonded P atom, the four available valence electrons are used to satisfy the bonds to the three B₁₂ icosahedra and the bond to the other atom in the inter-icosahedral chain. Without another valence electron to donate to the molecular orbital of the B₁₂ icosahedron, the orbital is deficient a single electron and an acceptor is generated.³²

While C readily incorporates into the icosahedral borides, controlling which lattice site

the C substitutionally locates is challenging. C in $B_{12}P_2$ may behave as it does in boron carbide, a homologous icosahedral boride. In boron carbide, C atoms can displace boron atoms within a B_{12} icosahedron to form a $B_{11}C$ icosahedron, but C atoms can also form C-C, C-B, C-B-C, or C-C-B inter-icosahedral chains. The location and stoichiometry of C in boron carbide cannot be controlled, and C is deemed an unsuitable dopant for $B_{12}P_2$.

Si may be a more appropriate *p*-type dopant than C because the location of the substitution may be more easily controlled. Werheit, *et al.*^{58,59} found that Si atoms preferentially substitute into the inter-icosahedral chain to form $B_{12}(P_2)_{1-x}(Si_2)_x$ when $B_{12}P_2$ was unintentionally doped with Si concentrations as high as 10^{21} cm^{-3} . Modulation of the *p*-type doping of the similar $B_{12}As_2$ has been demonstrated by introducing SiH_4 during CVD growth,⁶⁰ and the same may be possible for *in situ* $B_{12}P_2$ doping. Although using Si to *p*-dope $B_{12}P_2$ is promising, acceptors may be passivated after crystal growth. The electrical conductivity sharply increases for Si-doped $B_{12}As_2$ after annealing at 600 °C in Ar.^{61,60}

Doping icosahedral borides *n*-type has proven difficult. Intuitively, donors could be assumed to be introduced by substituting P with a group VI atom such as O, S, or Se. As mentioned in Section 1.3.1, O bonds in a different configuration when substituted into the inter-icosahedral chain. If a pair of O atoms substitute for a pair of P atoms along a single inter-icosahedral chain, then the unit cell resembles that of $B_{12}O_2$ which remains electron exact and therefore does not introduce any donors into the crystal. If within a P-P chain only one P is replaced by an O atom, then the P atom in the chain has an unpaired electron in a non-bonding orbital which may be expected to lie at a deep state in the bandgap.³²

If S and Se behave similarly to O, then substitution of P by group VI elements may be ineffective, and other unconventional methods of doping may be necessary. However, little information exists on doping $B_{12}P_2$ with S or Se. There is limited evidence that S-S bonds may form in $B_{12}S_{2(1-x)}$ which may indicate that bonds between S and P are possible.⁶² An inter-icosahedral Se-Se chain on the other hand is expected to be too large to fit between the B_{12} icosahedra,⁶³ and Se atoms may be too big to even form a P-Se chain.

Other approaches to n -type doping $B_{12}P_2$ may be required if simple substitution of P with group VI elements is unsuccessful. While n -type conduction has not been achieved in the rhombohedral $B_{12}X_2$ type borides, interstitial n -type doping of other B_{12} icosahedra containing compounds, such as β -boron,^{64,65} $Y_xAl_yB_{14}$,^{66,67} and rare earth borides^{68,69,70} have been demonstrated. Interstitial doping in $B_{12}P_2$ may yield n -type conduction but has not yet been studied. Clearly, much more should be done to investigate $B_{12}P_2$ doping, which may be guided by simulations.⁷¹

Data and analysis of residual background impurities in the $B_{12}P_2$ films grown in this dissertation can be found in Chapter 5.

1.4.5 Devices

To make a radioisotope battery from $B_{12}P_2$, it ultimately needs to be fabricated into a functioning pn -junction. Some potential device structures are depicted in Figure 1.5. Ideally, a pin - or pn -homojunction would be created as shown in Figure 1.5 a) and b), respectively. However, since n -type $B_{12}P_2$ has not yet been demonstrated, heterojunction diodes (Figure 1.5 c) and d)) or a Schottky diode (Figure 1.5 e)) may be more achievable.

Little is reported in the literature on device structures for $B_{12}P_2$ devices. Takenaka, *et al.*⁴⁸ demonstrated Si/ $B_{12}P_2$ /Si heterostructures but reported no electrical properties other than the resistivity for $B_{12}P_2$. Takigawa, *et al.*⁴⁷ also created a n -Si/ $B_{12}P_2$ / n -Si heterostructure, reporting the current-volt characteristics. More recently, Gong, *et al.*⁷² fabricated a p - $B_{12}As_2$ / n -4H-SiC heterojunction diode with a turn-on voltage of $\approx 2V$ and an on-off ratio of 4.14×10^3 at 3 V. No $B_{12}P_2$ /SiC heterojunction diodes have been reported; however, the ability to form a heterojunction should be considered when selecting a substrate for hetero-epitaxy.

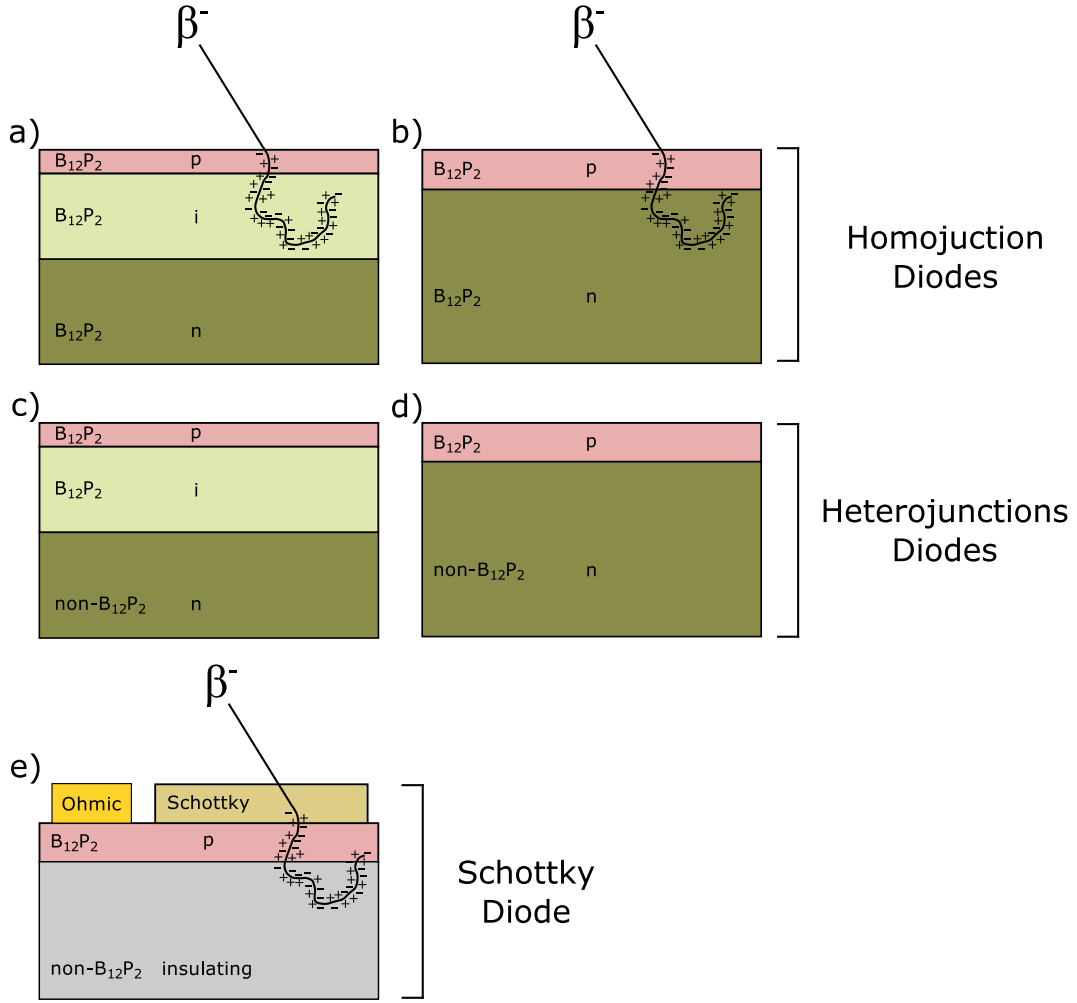


Figure 1.5: Schematics of potential semiconductor device structures for $B_{12}P_2$ betavoltaic batteries: a) pin -homojunction, b) pn -homojunction, c) pi - $B_{12}P_2$ / n -semiconductor heterojunction, d) p - $B_{12}P_2$ / n -semiconductor heterojunction and e) $B_{12}P_2$ Schottky barrier diode.

1.5 Substrate Selection

Many types of substrates have been explored for epitaxial $B_{12}P_2$ growth, including $B_{12}P_2$, Si, 6H-SiC, MgO, SiO_2 , sapphire, Ni and W; however, Si is certainly the most common substrate due to its high availability and affordability. Si is poorly suited for hetero-epitaxial growth of $B_{12}P_2$ because of its large in-plane lattice mismatch of 22%, large CTE mismatch (see Figure 1.6), low melting point, and the possibility for large amounts of unintentional auto-doping.^{26,25}

Table 1.4: *A comparison between potential substrates based on the lattice mismatch, CTE mismatch, thermal stability, ability to form a hetero-junction, and material availability.*

	Si	4H-SiC	AlN	GaN	Sapphire
Lattice Mismatch	-22.0%	-2.5%	-3.7%	-6.1%	-37.3%
CTE-induced Strain in $B_{12}P_2$	Tensile	Tensile	Compressive	Compressive/ Tensile	Compressive
Stability at Growth Temp.	Low	Moderate	Moderate	Low	Moderate
Ability to Form Hetero-junction	Yes	Yes	No	Yes	No
Availability	High	High	Moderate	Moderate	High

The majority of reports on the epitaxial growth of $B_{12}P_2$ were published before more suitable substrates such as SiC and III-nitrides became widely available. For example, bulk crystal growth of SiC has matured to the point that 150 mm wafers are now commercially available, and the crystalline quality has also immensely improved over the last 10 years since the only publication of $B_{12}P_2$ growth on SiC. Attributes and properties of possible substrates are shown in Table 1.4.

4H-SiC is an attractive substrate because of its reasonably low lattice mismatch of $\approx 2.5\%$, moderate thermal stability in hydrogen at the temperatures needed to grow $B_{12}P_2$, commercial availability, and the possibility to form a p -type $B_{12}P_2$ / n -type 4H-SiC hetero-junction diode. The hexagonal unit cell of 4H-SiC is also compatible with the rhombohedral unit cell, which can also be represented in hexagonal indices. Even more, a strategy to re-

duce rotational twinning (a type of crystal defect) has been developed by using a particular miscut to control the nucleation of icosahedral borides.^{73,74,75} However, the coefficient of thermal expansion (CTE) mismatch is large; this leaves the $B_{12}P_2$ film in tensile strain after the growth furnace has cooled to room temperature (See Figure 1.6). Because SiC is so hard and the $B_{12}P_2$ films are tensile strained, thick films will crack if grown too thick.⁵³ Since thick films are necessary for alpha or betavoltaics so that more energy from the decay particles can be collected, a strategy to grow thick films on 4H-SiC must be developed. Also, C and Si are *p*-type dopants in icosahedral borides, and auto-doping from substrates must be carefully monitored.

Growth on AlN is appealing for a couple of the same reasons as 4H-SiC: it has a moderate thermal stability and a manageable lattice mismatch. Unlike SiC, however, compressive strain is induced into the $B_{12}P_2$. While compressively strained films may form dislocations and bow the substrate, they are less likely to crack, and thicker films may be achieved, which is desirable. However, AlN has an ultrawide bandgap of 6.0 eV which makes it difficult to dope and fabricate a hetero-junction diode. Although the insulating nature of AlN prevents fabrication of a hetero-junction, electronic isolation of $B_{12}P_2$ films from the substrate make electrical characterization easier. Further, the ultrawide bandgap may allow for optical absorption measurements without a strong influence from the substrate. Even though AlN bulk wafers are available for purchase, wafers are extremely expensive and difficult to procure. AlN templates grown on sapphire on the other hand have become commoditized and are readily available. The step morphology may be more difficult to control and the defect density may be higher in AlN templates than in bulk crystals. Sapphire is also insulating and has a large optical window thereby maintaining the electrical isolation of and optical accessibility to $B_{12}P_2$ films on AlN/sapphire substrates. Sapphire has a large CTE, ensuring that the $B_{12}P_2$ film is compressively strained, which may allow thick films to be grown.

GaN, another group III-nitride, is another substrate to consider because of its ability to effectively dope it *n*-type—possibly enabling hetero-junction formation—and the rising

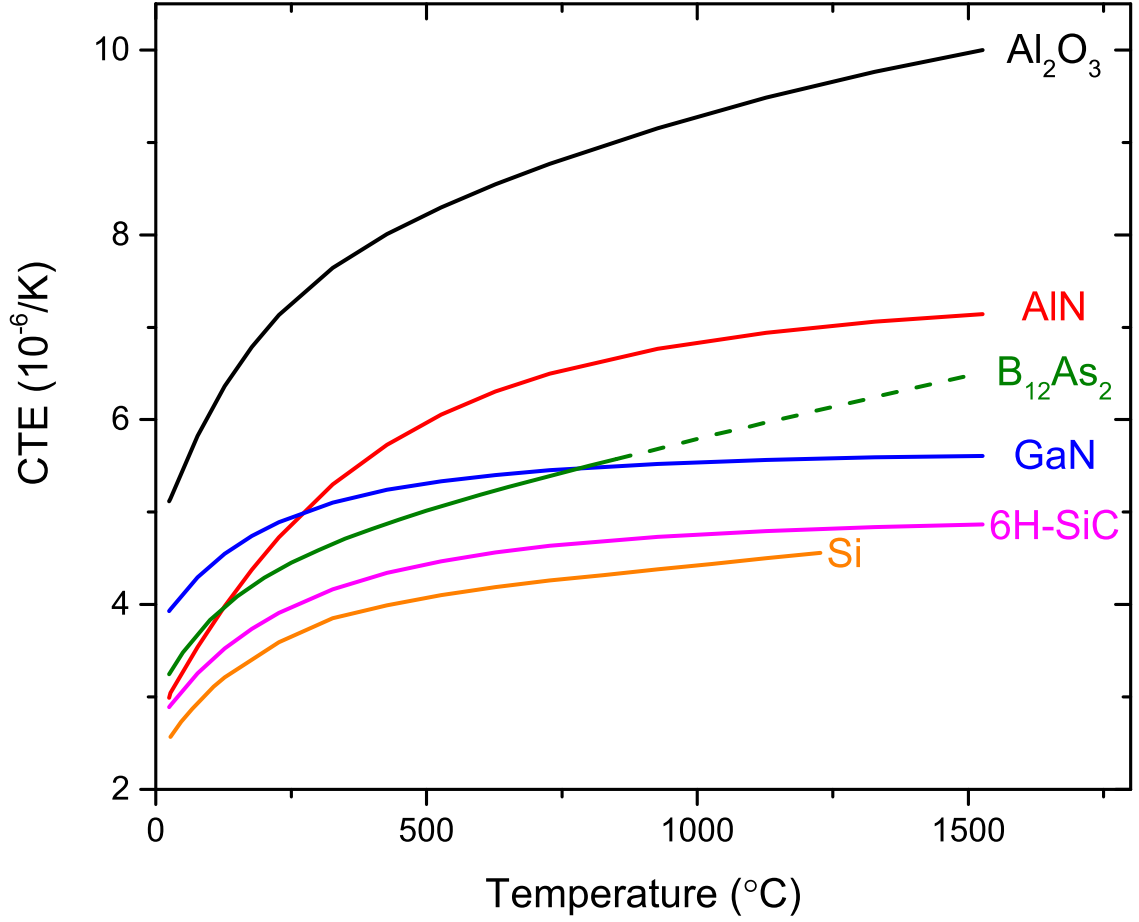


Figure 1.6: Coefficients of thermal expansion (CTE) of the a -lattice constant (or equivalent) of possible substrates. Substrates with a higher CTE than $B_{12}P_2$ will induce compressive strain in the film while substrates with a lower CTE will induce tensile strain. No CTE data is available for $B_{12}P_2$, but the CTE for $B_{12}As_2$ is expected to be very similar. The dashed line for $B_{12}As_2$ is extrapolated from data given in Whiteley, et al.⁷⁶ Data for Si is from Okada, et al.,⁷⁷ and data for Al_2O_3 , AlN, GaN, and 6H-SiC was taken from Reeber, et al.⁷⁸

availability, affordability, and quality of bulk GaN substrates. The CTE of GaN best matches that of icosahedral borides, but unlike AlN, GaN is not stable in H_2 or N_2 at the growth temperatures necessary for $B_{12}P_2$ growth. An AlGaN alloy is perhaps better since it is more thermally stable and could still be doped, but the carrier gas would need to be N_2 rather than H_2 (which was used in this work) to prevent thermal decomposition of the substrate.

1.6 Rotational Twins

One potential caveat of using 4H-SiC or a III-nitride as a substrate is the ability for the (0001) face of icosahedral boride compounds such as $B_{12}P_2$ to orient in two rotational variations (rotated by 60° relative to one another) on the (0001) SiC or III-nitride surface. These orientations arise because $B_{12}P_2$ does not have the same symmetry as 4H-SiC or the III-nitrides.

The crystal structure of $B_{12}P_2$ belongs to the $R\bar{3}M$ space group and can be represented by both rhombohedral and by hexagonal coordinates. While rhombohedral coordinates reflect the true symmetry of the crystal, hexagonal indices are often easier to visualize and are convenient to use when relating a $B_{12}P_2$ crystal to a crystal in the hexagonal system such as during hetero-epitaxy of $B_{12}P_2$ on 4H-SiC or AlN. For example, the crystallographic relationship between $B_{12}P_2$ and 4H-SiC is intuitively understood using hexagonal indices: $(0001)_{B_{12}P_2} [1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$. When using a combination of rhombohedral indices for $B_{12}P_2$ and hexagonal indices for 4H-SiC, the same epitaxial relationship is more difficult to interpret: $(111)_{B_{12}P_2} [1\bar{2}1]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$.

The rhombohedral and the hexagonal unit cell for $B_{12}P_2$ are depicted using black lines in Figure 1.7. The two unit cells are crystallographically aligned to one another to show the relationship between the two representations. The rhombohedral structure in Figure 1.7 shows B atoms outside of the unit cell to illustrate how B_{12} icosahedra are located at the vertices of the rhombohedral unit cell and can be thought of as “super atoms” within the crystal structure.

Crystals like 4H-SiC and AlN in the hexagonal system have 6-fold symmetry about the [0001] direction. Therefore, there are six planes in the $\{1\bar{1}00\}$ family of planes: $(1\bar{1}00)$, $(\bar{1}100)$, $(10\bar{1}0)$, $(\bar{1}010)$, $(01\bar{1}0)$, and $(0\bar{1}10)$. All six of these planes are equivalent and identical. Rhombohedral crystals like $B_{12}P_2$ have 3-fold symmetry about the $[0001]_H || [111]_R$ direction. Therefore, when using hexagonal indices for $B_{12}P_2$, there are three planes in the $\{1\bar{1}00\}$ family rather than six: $(1\bar{1}00)$, $(01\bar{1}0)$, and $(\bar{1}010)$. The $\{1\bar{1}00\}$ family then consists

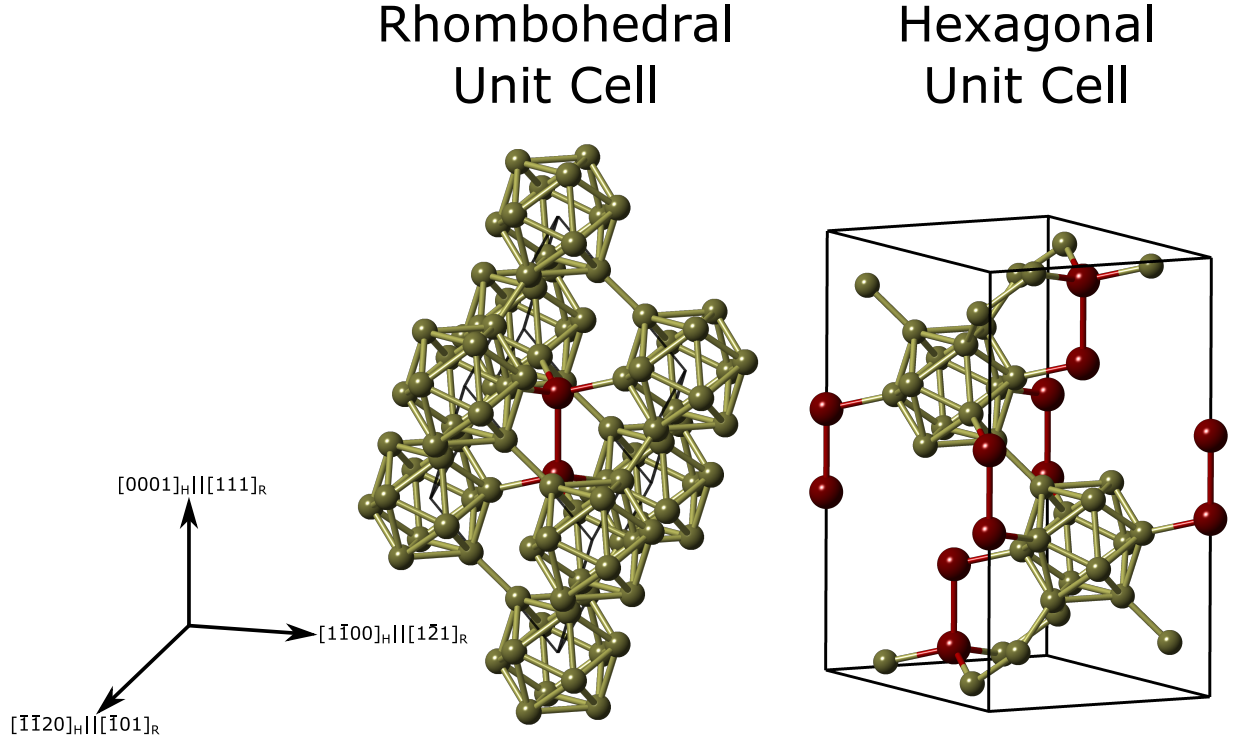


Figure 1.7: The $B_{12}P_2$ unit cells depicted in a) the rhombohedral system and b) the hexagonal system. Boron icosahedra are centered on the vertices of the rhombohedral unit cell. Boron atoms are the smaller green spheres, phosphorus atoms are the larger red spheres.

of $(\bar{1}100)$, $(0\bar{1}10)$, and $(10\bar{1}0)$.

Because $B_{12}P_2$ only 3-fold symmetry, (0001) $B_{12}P_2$ can orient in two ways on (0001) 4H-SiC. To illustrate, $B_{12}P_2$ can orient to 4H-SiC with an epitaxial relationship of $(0001)_{B_{12}P_2} [1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$. In this case the $[1\bar{1}00]$ direction of $B_{12}P_2$ is parallel with the $[1\bar{1}00]$ direction of 4H-SiC. However, the $[1\bar{1}00]$ direction and the $[\bar{1}100]$ direction of 4H-SiC are equivalent such that $B_{12}P_2$ could just as easily orient to the 4H-SiC with a relationship of $(0001)_{B_{12}P_2} [1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC} [\bar{1}100]_{4H-SiC}$. In this epitaxial relationship, the $B_{12}P_2$ crystal is rotated by 180° from $(0001)_{B_{12}P_2} [1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$. These two $B_{12}P_2$ orientations are called rotational twins because the two orientations are rotated 180° (or equivalently 60° or 300°) from one another.

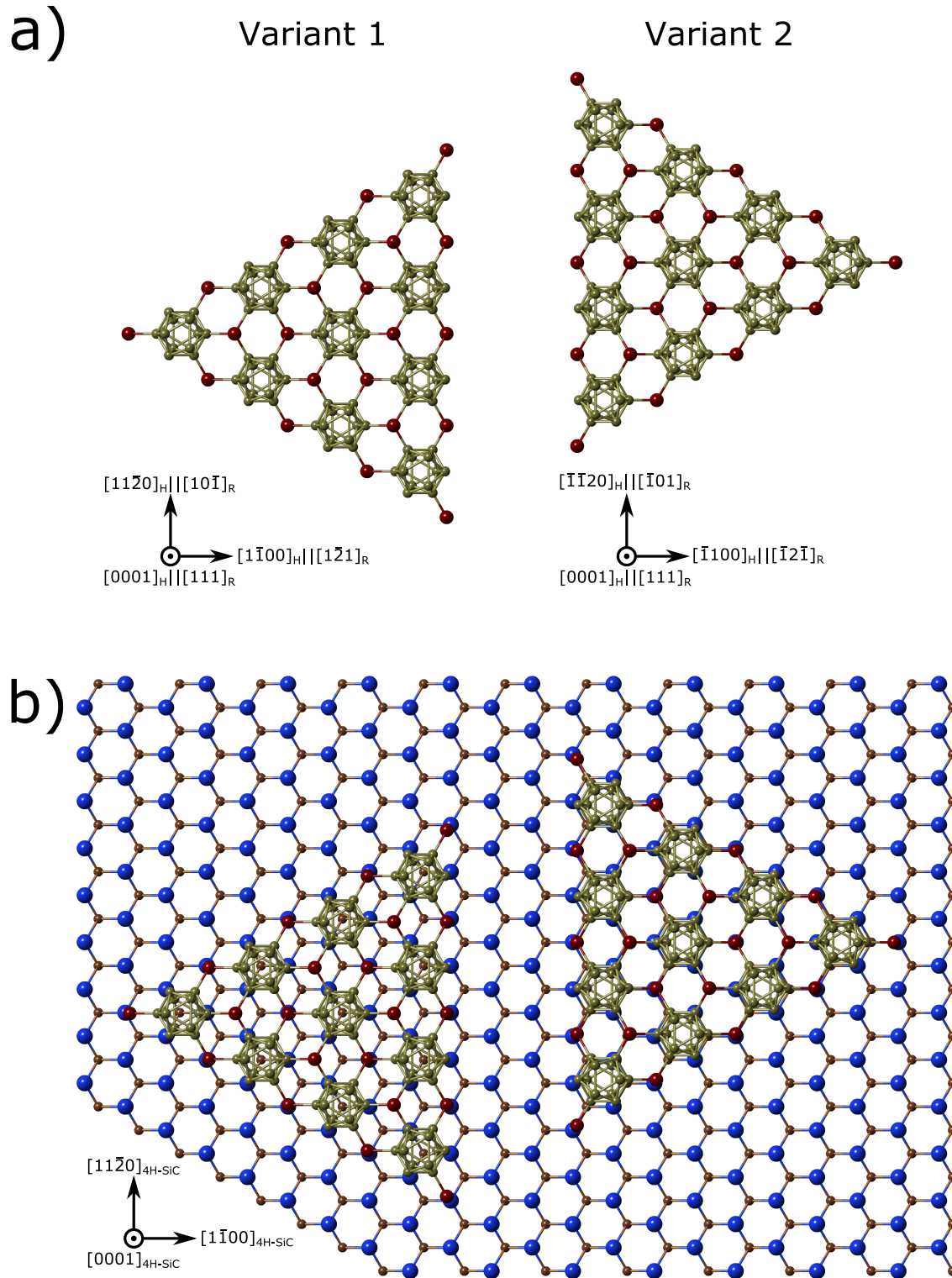


Figure 1.8: (0001) face view of a) rotational variants (twins) of $B_{12}P_2$. b) $B_{12}P_2$ twins bonded to a 4H-SiC bilayer demonstrating the epitaxial relationship between $B_{12}P_2$ twins to 4H-SiC.

Figure 1.8a) depicts a “top view” of the two rotational variants of (0001) $B_{12}P_2$ with a point of view along the $[000\bar{1}]$ direction, where rotation between the two orientations can be easily seen. To help illustrate the relationship of the $B_{12}P_2$ crystal to the 4H-SiC substrate, the rotational variants have been placed on a 4H-SiC bi-layer in Figure 1.8b), where the crystal lattices are drawn to scale. A few things need to be noted here. One is that hexagonal symmetry is not present in a single SiC bi-layer. The hexagonal symmetry in SiC arises from how the bi-layers stack along the $[0001]$ direction. Other bi-layers in 4H-SiC (layers beneath the surface) are rotated by 180° relative to the one shown in Figure 1.8b). For clarity, only a single bi-layer is shown in the figure. The other thing to note is that translational variants of $B_{12}P_2$ on 4H-SiC are ignored here. Chen *et al.*⁷⁹ provides a nice treatment of this topic and on twinning of $B_{12}As_2$ on 6H-SiC. In that study, boundaries between translational variants were observed to quickly terminate during growth epitaxial growth of $B_{12}As_2$ on 6H-SiC, effectively eliminating all translational variants except one.

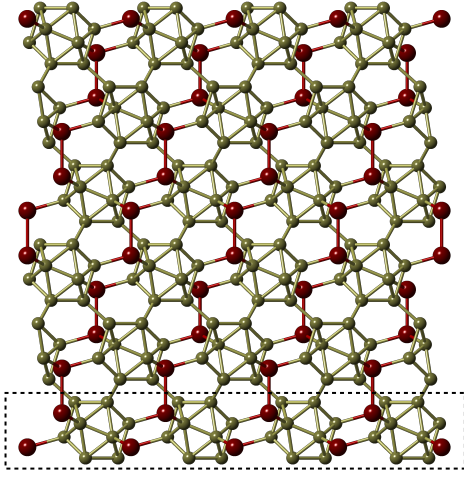
Another, “cross-sectional” view of the two $B_{12}P_2$ twin orientations is depicted in Figure 1.9 a) where the point of view is along the $[\bar{1}\bar{1}20]$ direction. A plausible bonding arrangement between the bottom icosahedral layer of each $B_{12}P_2$ twin (the outlined portion of Figure 1.9 a)) and the 4H-SiC bilayer.

The propensity of rotational twinning is well documented in the epitaxy of icosahedral borides on SiC.^{79,24,80,81,82} While neither rotational variant is preferred over the other, when two twin domains meet, the interface becomes a 2D defect that may act as a charge carrier scattering center or trap. Therefore, the suppression or elimination of twin domains is essential for the fabrication of electronic devices. Fortunately, suppression of rotational twinning of epitaxial layers of $B_{12}As_2$ was demonstrated on vicinal 4H-SiC substrates tilted 7° towards the $(1\bar{1}00)$ ^{73,74}. Furthermore, twin suppression has also been demonstrated for (111)-oriented BP films on 4H-SiC substrates tilted 4° towards the $(1\bar{1}00)$.⁷⁵ Chapter 3 further discusses $B_{12}P_2$ twins on 4H-SiC including how they form and how they can be suppressed by growing $B_{12}P_2$ on vicinal (0001) 4H-SiC substrates tilted toward the $(1\bar{1}00)$

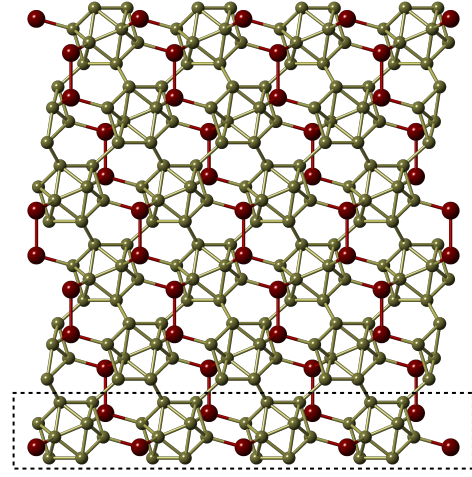
a)

Variant 1

Variant 2

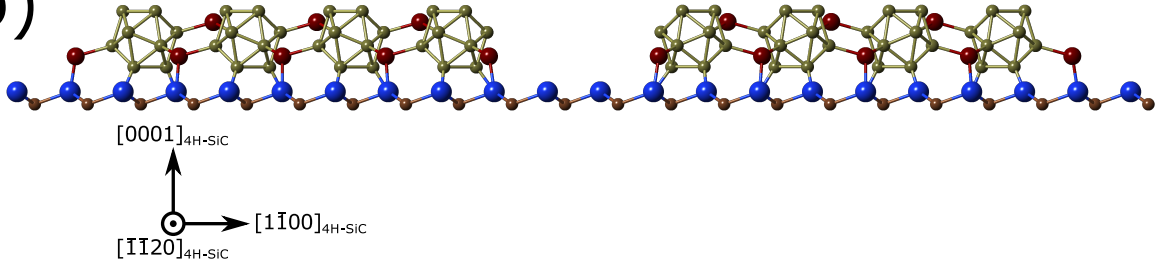


$$\begin{array}{c}
 [0001]_H || [111]_R \\
 \uparrow \\
 \odot \rightarrow [1\bar{1}00]_H || [1\bar{2}1]_R \\
 [\bar{1}\bar{1}20]_H || [\bar{1}01]_R
 \end{array}$$



$$\begin{array}{c}
 [0001]_H || [111]_R \\
 \uparrow \\
 \odot \rightarrow [\bar{1}100]_H || [\bar{1}2\bar{1}]_R \\
 [11\bar{2}0]_H || [10\bar{1}]_R
 \end{array}$$

b)



$$\begin{array}{c}
 [0001]_{4H-SiC} \\
 \uparrow \\
 \odot \rightarrow [1\bar{1}00]_{4H-SiC} \\
 [\bar{1}\bar{1}20]_{4H-SiC}
 \end{array}$$

Figure 1.9: $(\bar{1}\bar{1}20)$ face view of a) rotational variants (twins) of $B_{12}P_2$, b) $B_{12}P_2$ twins bonded to a $4H-SiC$ bilayer demonstrating the epitaxial relationship between $B_{12}P_2$ twins to $4H-SiC$. The icosahedron layers in b) are the same as those outlined with dashed rectangles in a).

plane.

1.7 Chemical Vapor Deposition System

1.7.1 Growth Chamber

In this work, $B_{12}P_2$ was grown in a cold-walled, inductively heated chemical vapor deposition (CVD) reactor. A photo of the reactor is shown in Figure 1.10, and a cartoon cross-section of the reactor is presented in Figure 1.11. Two concentric quartz tubes form the walls of the reactor and water flows counter current (from right to left in Figure 1.11) to the gas flow. A conductive, rectangularly tubular susceptor is placed inside thermal insulation which is in turn fitted into a third quartz tube. This tube serves as a “dump” tube and catches parasitic deposition on the reactor walls and can be easily removed and cleaned between depositions. Next, the substrate is loaded into the susceptor. The susceptor, thermal insulation, and dump tube are then inserted into the water jacket from the downstream side until the susceptor is $\approx 2\text{-}3$ mm from the gas distributor tube. A thermocouple sheathed with alumina is inserted about 2 cm into the susceptor from the downstream side. The thermocouple is calibrated by melting a chip of Si on a dummy SiC substrate. The susceptor is heated via a radio-frequency (RF) induction coil placed around the outside of the tubes. Precursor and carrier gases are introduced into the susceptor through the gas distributor tube.

The interior of the susceptor is tapered to help mitigate precursor gas depletion in the boundary layer as the gases pass over the substrate. The susceptor was initially made from graphite coated with a TaC-coating, a common material for III-nitride and SiC epitaxy. However, due to concerns that the susceptor was a source for C impurity, susceptors made from other materials such as Zr metal were tested.

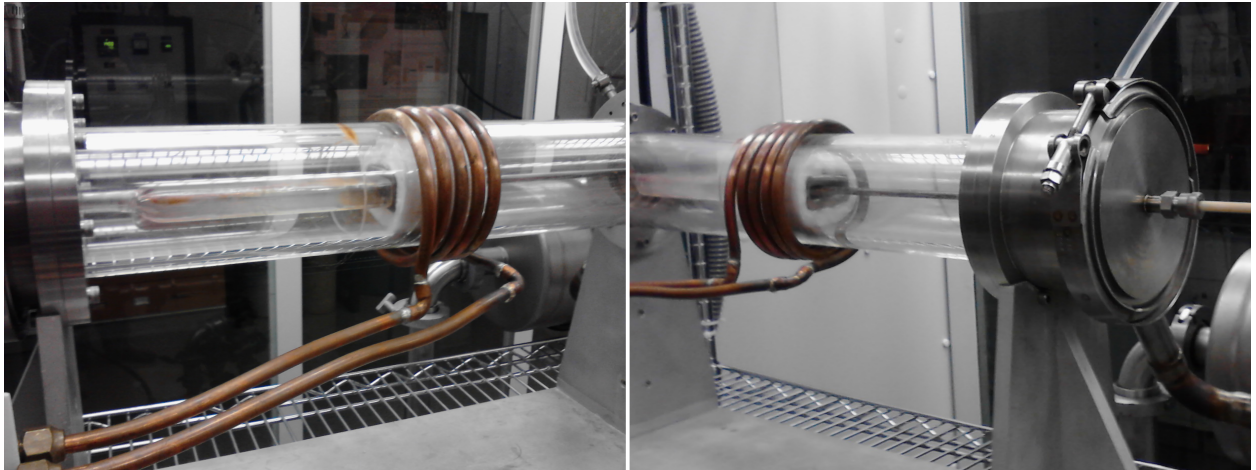


Figure 1.10: A photograph of the upstream end of the growth chamber is shown on the left. The gas distributor tube is seen directing the gas flow to the opening of the susceptor. The downstream end of the growth chamber is shown on the right. The high temperature thermocouple can be seen entering the growth chamber and inserted into the susceptor.

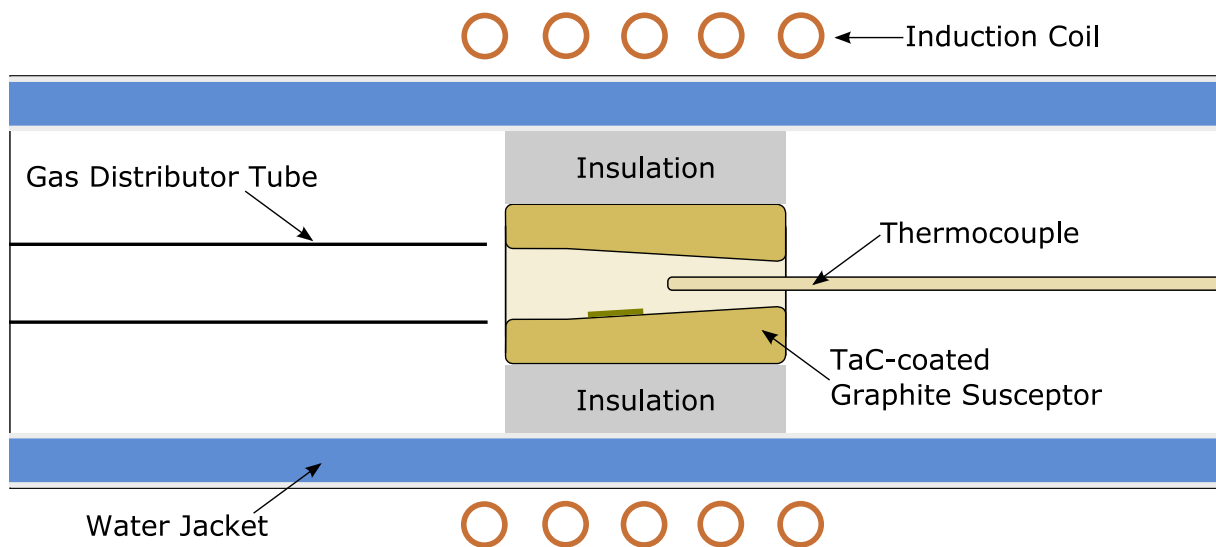


Figure 1.11: A cross-sectional cartoon of the growth chamber. The insulation was made from either alumina or zirconia. The gas flow is from left to right, but the water flows right to left.

1.7.2 System Setup

A schematic of the gas lines of the CVD system is depicted in Figure 1.12. Low purity H_2 carrier gas passes through a palladium membrane H_2 purifier before mixing with the precursor gases and entering the growth chamber. From the purifier, the gas lines are split. One line runs to the growth chamber while the other line allows the gas to bypass the growth chamber. At all times during operation, H_2 flows through both lines, and the flow is controlled by mass flow controllers (MFC's). A N_2 line is also connected the H_2 line to not only purge the hydrogen purifier during start-up and shut-down but to also vent the growth chamber before opening the chamber to air.

Pure phosphine (PH_3) can be diverted between two separate MFC's, which are calibrated for either large (up to 150 sccm) or small (up to 10 sccm) mass flows. From the MFC's, the precursor line is routed to a three-way valve that directs the gas to flow either to the growth chamber or to the bypass. Similarly, diborane (B_2H_6 diluted to 1% in H_2) passes through a (100 sccm) MFC before being diverted either to the growth chamber or the bypass via a three-way valve. A pressure sensor measures the pressure differential between the line routed to the growth chamber and the bypass and modulates the flow via a valve to maintain equal pressure in each line to prevent back flow of any gases.

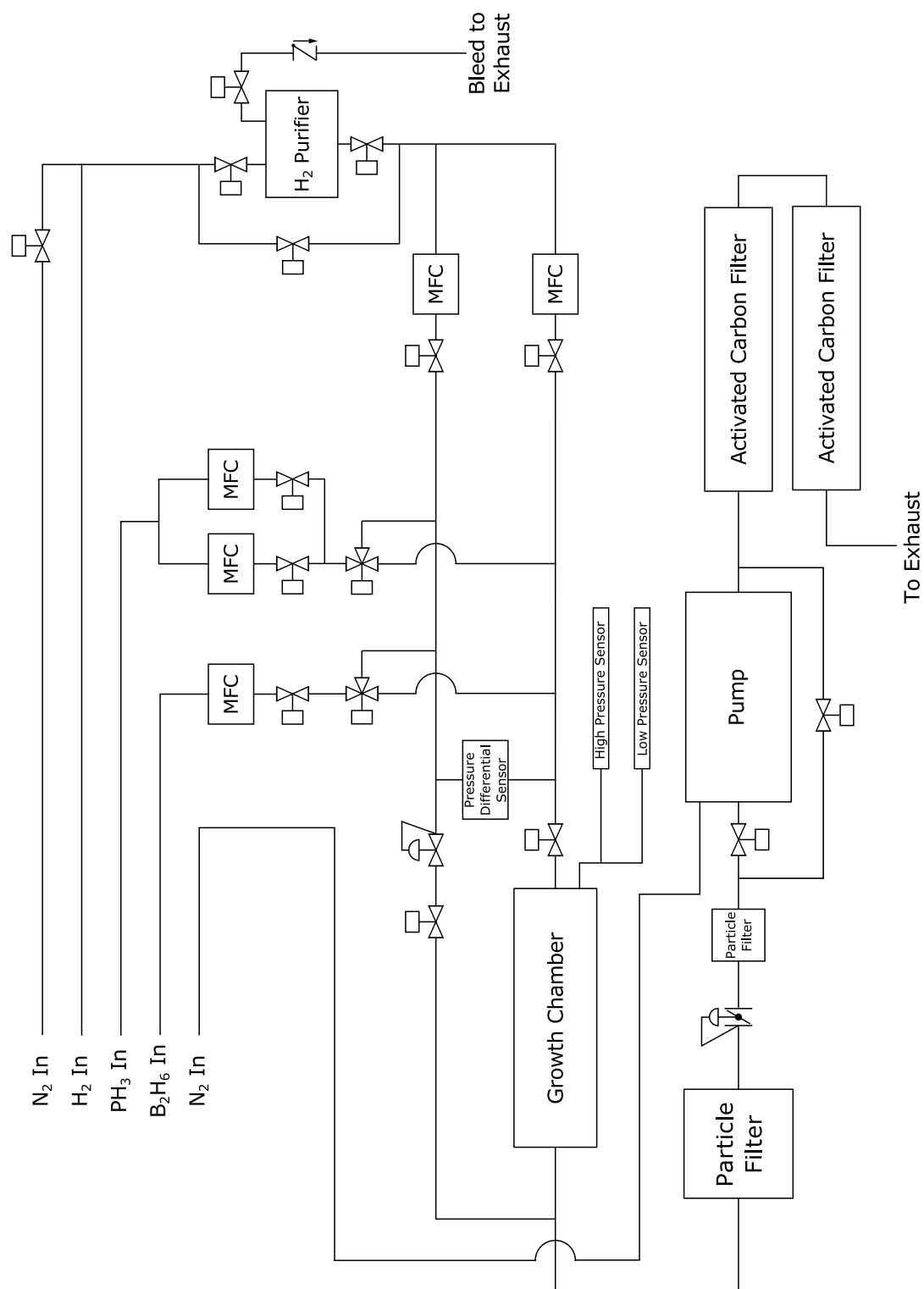


Figure 1.12: A schematic of the gas and vacuum lines of the CVD growth system used in this work.

Two pressure gauges are attached to the upstream end of the growth chamber. One, a thermocouple sensor, measures vacuum levels down to the millitorr range and is used during pump-down before and after deposition. The other pressure gauge, a capacitance monometer measuring in the range from atmospheric pressure to ≈ 10 torr, is used for feedback control of the operating pressure.

The exhaust from the growth chamber and the bypass is routed through a particle filter to remove dust formed by the decomposition of the precursor gases. The gases then pass through a butterfly valve that is used in conjunction with a controller and the capacitance monometer to maintain a constant operating pressure in the growth chamber. The gas line then passes through another particle filter and then splits to either run through the dry pump or to a line that bypasses the pump. In addition to the process gases, a N_2 purge line is routed to the dry pump to dilute the H_2 gas before the eventual mixing with air. The exhaust of the pump then passes through two cylinders packed with activated carbon to remove any residual precursor gases before being vented to the fume hood exhaust.

Since both B_2H_6 and PH_3 are extremely toxic, a 4-point hydride toxic gas monitor was installed to monitor both gases. One probe was used to monitor the area near the opening of the reaction chamber during loading and unloading. Another monitor was placed to draw process gas from between the two activated carbon filters to test when the upstream cylinder was spent and needed to be replaced. A third probe was placed near the MFC's, and the last probe drew air from outside the fume hood to prompt personnel evacuation in the circumstance of a severe gas leak.

1.7.3 Standard System Operation

After the substrates, susceptor, and dump tube are loaded into the growth chamber and the system is sealed, the system is pumped down (slowly as to not dislodge the substrates in the susceptor) for at least 30 min until a base pressure of ≈ 50 mTorr is achieved. The chamber is backfilled with H_2 to a pressure of 600 Torr and then the chamber is again

pumped down to base pressure. Three vacuum and backfill cycles are carried out before the system is stabilized to 100 Torr under H_2 flow. The induction heater is then turned on and the susceptor is heated. SiC substrates were H_2 etched in situ at 1650 °C for 20 min before lowering the substrate temperature to the growth temperature. AlN substrates were etched at 1250 °C for 20 min prior to deposition.

PH_3 is first introduced into the system at the desired flowrate through the growth chamber and allowed to stabilize. Next, the B_2H_6 is adjusted to the desired flowrate through the bypass line and allowed to stabilize for 2 min. The deposition is then initiated by switching the B_2H_6 three-way valve to the direct the flow to the growth chamber. After the desired growth time is complete, the deposition is terminated by switching the B_2H_6 line to flow back through the bypass, allowing the PH_3 to flow through the chamber for 2 min, switching the PH_3 flow to the bypass line, waiting 2 min, cooling the chamber to <1000 °C at a rate of ≈ 100 per min, and then turning the power of the induction heater to zero as the susceptor cools to room temperature under H_2 flow. The growth chamber is evacuated and backfilled for three cycles with H_2 to purge any remaining B_2H_6 and PH_3 . Then the chamber is vented with N_2 before opening the chamber to air and removing the samples. Additional details concerning B_{12}P_2 growth will be discussed in Chapter 2.

Chapter 2

Hydride CVD Hetero-epitaxy of B_{12}P_2 on 4H-SiC

As submitted to *Journal of Crystal Growth* (2016) by C.D. Frye, C.K. Saw, Balabalaji Padavala, R.J. Nikolić, and J.H. Edgar.

2.1 Abstract

Icosahedral boron phosphide ($B_{12}P_2$) is a wide bandgap semiconductor (3.35 eV) that has been reported to “self-heal” from high-energy electron bombardment, making it attractive for potential use in radioisotope batteries, radiation detection, or in electronics in high radiation environments. This study focused on improving $B_{12}P_2$ hetero-epitaxial films by growing on 4H-SiC substrates over the temperature range of 1250-1450 °C using B_2H_6 and PH_3 precursors in a H_2 carrier gas. XRD scans and Laue transmission photographs revealed that the epitaxial relationship was $(0001)\langle 11\bar{2}0 \rangle_{B_{12}P_2} \parallel (0001)\langle 11\bar{2}0 \rangle_{4H-SiC}$. The film morphology and crystallinity were investigated as a function of growth temperature and growth time. At 1250 °C, films tended to form rough, polycrystalline layers, but at 1300 and 1350 °C, films were continuous and comparatively smooth ($R_{RMS} \leq 7$ nm). At 1400 or 1450 °C, the films grew in islands that coalesced as the films became thicker. Using XRD rocking curves to evaluate the crystal quality, 1300 °C was the optimum growth temperature tested. At 1300 °C, the rocking curve FWHM decreased with increasing film thickness from 1494 arcsec for a 1.1 μm thick film to 954 arcsec for a 2.7 μm thick film, suggesting a reduction in defects with thickness.

2.2 Introduction

Two boron phosphide compound semiconductors exist: cubic, zincblende BP and rhombohedral $B_{12}P_2$, which is often referred to as boron subphosphide or icosahedral boron phosphide. Icosahedral boron phosphide derives its name from the B_{12} icosahedra centered on each of the vertices of the rhombohedral unit cell and features interlinking phosphorus-phosphorus chains along the body diagonal in the $[111]$ direction ($[0001]$ direction of the hexagonal unit cell). Note: hexagonal indices will be used throughout this report unless otherwise noted to maintain consistent indices between the epitaxial film and substrate.

$B_{12}P_2$ has garnered interest from its wide bandgap of 3.35 eV,²⁰ chemical inertness,

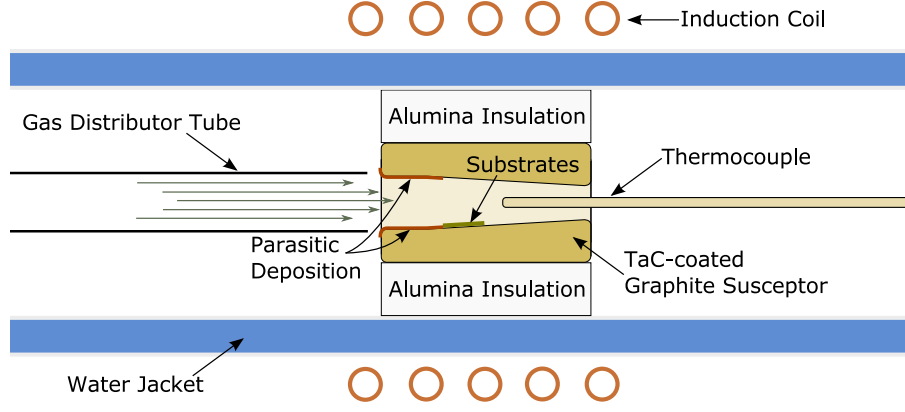


Figure 2.1: A schematic of the CVD reactor used in this study.

and reported ability to withstand intense bombardment from high-energy electrons without agglomerating defects or becoming amorphous.^{6,83,7} These properties make $B_{12}P_2$ attractive as a material in radiation detection, electronics located in high radiation environments, or in radioisotope batteries. Unfortunately, $B_{12}P_2$ crystal growth is still in its early stages, and material quality has limited the detailed characterization of radiation induced effects on its electronic properties and prevented the fabrication of $B_{12}P_2$ diodes. Thus, thick, high quality $B_{12}P_2$ with long charge carrier transport lengths and the ability to control doping levels through improved crystal growth is essential to evaluating its potential as an electronic material.

Native $B_{12}P_2$ substrates are not commercially available, thus a variety of non-native substrates have been previously employed for the growth of $B_{12}P_2$ thin films, including Si,^{43,47,49,50,51,52} sapphire,⁴³ MgO,⁴³ SiO_2 ,^{43,50} Ni,⁵⁰ W,⁵⁰ and most recently 6H-SiC.⁵³ Although silicon has been the most prominent substrate for VPE-grown $B_{12}P_2$ reported in the literature, the symmetry mismatch of the (100) and (110) faces, lattice mismatch (22.0%) for the (111) face, and thermal instability of silicon at high growth temperatures (melting point = 1414 °C) make it poorly suited as a substrate for the epitaxial growth of $B_{12}P_2$.

Several promising crystalline substrates have become available in the years since the majority of the reports of $B_{12}P_2$ epitaxial growth were published. For instance, GaN and AlN templates on sapphire as well as bulk substrates of GaN and AlN are just now becoming

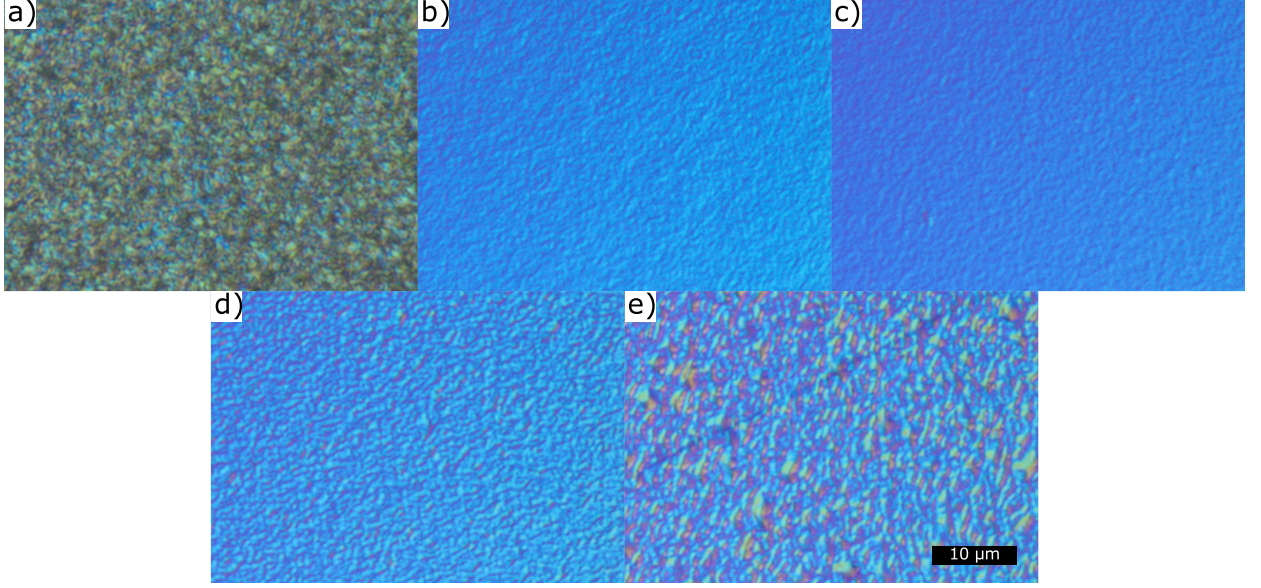


Figure 2.2: Nomarski interference optical micrographs of $B_{12}P_2$ films grown on 4H-SiC tilted 4° towards the $(1\bar{1}00)$ at a) 1250°C , b) 1300°C , c) 1350°C , d) 1400°C , and e) 1450°C . The scale bar is the same for all images and is $10\ \mu\text{m}$. At 1250°C , the film is rough and polycrystalline. The films become smooth when the growth temperature is increased to 1300 - 1350°C but become rougher as the temperature is further increased. R_{RMS} roughness measurements for these films can be found in Table 3.1.

commercially available. Most recently, Lu, *et al.*⁵³ reported on the growth of $B_{12}P_2$ on 6H-SiC using BBr_3 and PBr_3 in H_2 —the only report to date of $B_{12}P_2$ grown on SiC.⁵³ However, the maturity, quality and availability of bulk SiC substrates has greatly improved in the ten years since that study.

SiC is an appealing substrate for numerous reasons. First, unlike Si, SiC has a hexagonal lattice which is compatible with the rhombohedral unit cell of $B_{12}P_2$, which can also be represented as a hexagonal system. Furthermore, the $3.073\ \text{\AA}$ a -lattice constant of SiC is approximately half that of the $B_{12}P_2$ a -lattice constant of $5.99\ \text{\AA}$,¹⁷ giving an effective lattice mismatch of $\sim 2.5\%$. The inertness and thermal stability of SiC allows for growth temperatures exceeding the melting point of Si, extending the growth window in which $B_{12}P_2$ can be deposited. Additionally, an n -type SiC/ p -type $B_{12}P_2$ heterojunction diode could be fabricated using an n -type SiC substrate, similar to the work of Gong, *et al.*⁷² for

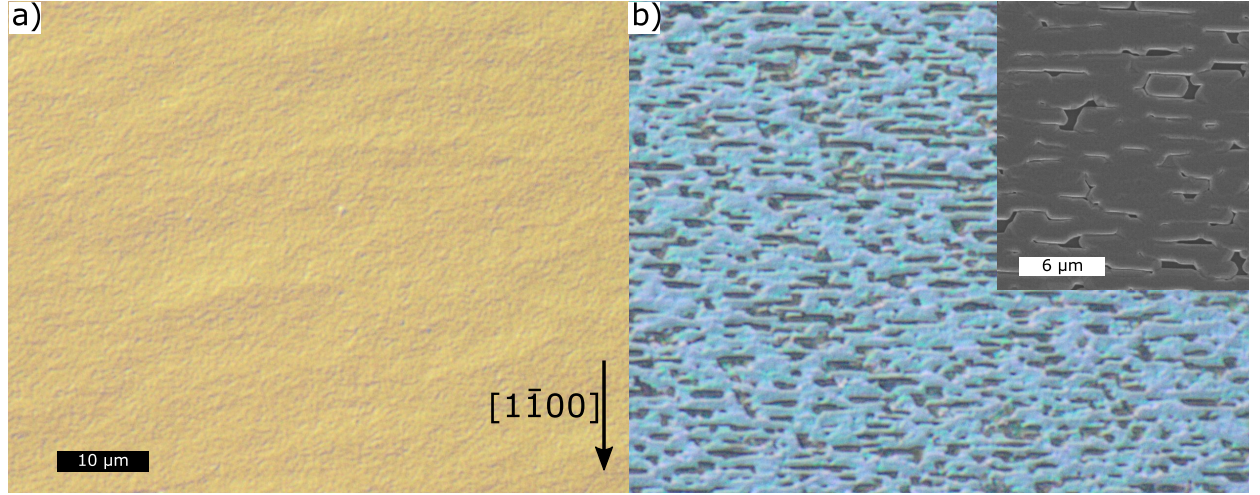


Figure 2.3: *Nomarski interference micrographs of $B_{12}P_2$ films grown at a) 1300 °C and b) 1400 °C for 15 min (black scale bar = 10 μm and is the same for both optical images). Inset shows an SEM micrograph of the $B_{12}P_2$ film in b) (white scale bar = 6 μm). At 1400 °C, the $B_{12}P_2$ film grows in elongated islands while growth at 1300 °C is continuous.*

$B_{12}As_2$ on SiC. Moreover, carefully choosing the miscut direction of 4H-SiC can reduce the density of twin domains in hetero-epitaxially grown films.^{75,73,80}

Here, $B_{12}P_2$ is grown over the temperature range of 1250-1450 °C on 4H-SiC miscut 4° to the $(1\bar{1}00)$ to coarsely optimize the growth temperature. Although there are several reports on BP growth on SiC,^{75,84,85,86} this is only the second report of $B_{12}P_2$ growth on SiC and is the first using hydride precursors to grow it on this type of substrate. Further, it is the first to report $B_{12}P_2$ XRD rocking curve data. By optimizing the growth temperature, this study hopes to lay the ground work for improved $B_{12}P_2$ films that will enable the evaluation of the electrical properties in conjunction with the radiation hardness of $B_{12}P_2$.

2.3 Experimental Methods

$B_{12}P_2$ films were grown on 4H-SiC substrates in a home-built, horizontal, cold-walled CVD system (Figure 2.1). Details on the setup can be found elsewhere.⁸⁷ The precursors were B_2H_6 and PH_3 diluted in a H_2 carrier gas purified by a palladium membrane purifier. The

4H-SiC substrates were $10 \times 10 \text{ mm}^2$ and $350 \text{ }\mu\text{m}$ thick. The substrates rested inside a tubular TaC-coated graphite susceptor, which was enclosed in alumina insulation, and heated inductively via a RF coil. The precursor and carrier gases passed through a quartz distributor tube and over the heated substrates. The temperature was measured using an alumina-sheathed thermocouple centered in the susceptor downstream of the substrates. The thermocouple was calibrated by melting a $300\text{-}500 \text{ }\mu\text{m}$ thick piece of Si in the same position of a substrate in the susceptor.

Prior to loading into the reactor, the substrates were sequentially sonicated in tetrachloroethylene, isopropyl alcohol, and methanol for 5 min each to remove particulates and any organic residue. Once the substrates (two $10 \times 10 \text{ mm}^2$ substrates) and susceptor were loaded, the reactor was evacuated to $<75 \text{ mTorr}$ and backfilled with H_2 three times to remove air from the system before maintaining the carrier gas flow rate at 3.5 slm of H_2 at 100 Torr. The substrates were heated to $1650 \text{ }^\circ\text{C}$ for 20 min to etch the surface in preparation for epitaxy, which removes any impurities or surface oxide.^{88,89} Then, the substrates were cooled to the growth temperature. Next, a PH_3 flow rate of 6 sccm was introduced into the reactor and flowed over the substrates for 2 min. The deposition was initiated by introducing 80 sccm of 1% B_2H_6 in H_2 . The reaction was terminated by switching off the B_2H_6 flow and allowing PH_3 to flow for 2 min as any remaining B_2H_6 was reacted or flushed out of the system, turning off the PH_3 flow and waiting for 2 more min to flush out the PH_3 , and then cooling the substrates from the growth temperature under H_2 flow. B_{12}P_2 was assumed to not desorb P during cooling.

B_{12}P_2 was grown on 4H-SiC substrates miscut 4° toward the $(1\bar{1}00)$ plane over the temperature range of $1250\text{-}1450 \text{ }^\circ\text{C}$ in increments of $50 \text{ }^\circ\text{C}$ to coarsely optimize the growth temperature under these flow rates and this operating pressure. This particular miscut of 4H-SiC was chosen because a miscut to the $(1\bar{1}00)$ suppressed rotational twinning in films of the similar icosahedral B_{12}As_2 ^{73,80} and BP.⁷⁵

The surface and growth morphology were imaged by both Normarski interference optical

microscopy and scanning electron microscopy (SEM). The roughness was measured with an optical profilometer using phase-shift interferometry. To measure the film growth rates, films were diced in half in the direction of the gas flow during growth, and the cross-section was measured by SEM. X-ray diffraction scans were taken to determine the out-of-plane epitaxial relationship, while Laue photographs were used to determine the in-plane epitaxial relationship. Rocking curves were taken about the (0003) B_{12}P_2 peak to evaluate the crystal quality of the films.

2.4 Results and Discussion

2.4.1 Surface Morphology

As a first-order gauge of the quality and roughness of the films and to evaluate the growth mode, the surface topology was analyzed using Nomarski interference contrast optical microscopy (Figure 2.2) and optical profilometry. For 30 min growths, the surface morphology of the films varied from continuous and smooth to rough (Figure 2.2); the surface roughness was minimized at 1350 °C (Table 3.1). At 1250 °C, the surface morphology was so rough that an accurate measurement by optical interferometry was not possible. While the 1250 °C film appeared polycrystalline in the center and on the upstream edge of the substrate, the downstream edges of the substrate exhibited a thinner film that was much smoother. The rough polycrystalline region likely started growing on top of the smoother morphology during growth since the rough area was thicker than the smoother area and consistently decreased in area when the deposition time was reduced to 15 min from 30 min. The smooth region of the 1250 °C-grown sample strongly resembled the surface of the 1300 °C sample, which was comparatively smooth ($R_{\text{RMS}} = 7 \text{ nm}$) and uniform over the entire substrate. However, small, isolated hexagonal crystals ~ 3 to $5 \mu\text{m}$ in diameter were interspersed in a few areas of the 1300 °C sample. At shorter deposition times, the films have fewer of these isolated crystals, and at sufficiently short times, none form at all. At longer growth times,

Table 2.1: R_{RMS} roughness (nm) as measured by optical interferometry, FWHM (arcsec) of the (0003) plane of $B_{12}P_2$ films grown for 30 min, and growth rate ($\mu\text{m/hr}$) of $B_{12}P_2$.

	Growth Temperature ($^{\circ}\text{C}$)				
	1250	1300	1350	1400	1450
R_{RMS} Roughness (nm)	>100	7	3	10	19
FWHM (arcsec)	2196	1080	1224	1728	2664
Growth Rate ($\mu\text{m/hr}$)	5.3	4.2	4.3	3.1	3.5

the concentration of the crystals increases. At 1350 $^{\circ}\text{C}$, the film was the smoothest of any of the samples with an R_{RMS} value of 3 nm and remained largely uniform over the substrate. At 1400 $^{\circ}\text{C}$ the film was rougher. At the edge of some samples, hexagonal $B_{12}P_2$ islands merged together to form a continuous film. At 1450 $^{\circ}\text{C}$, the film was rougher yet, and other crystal orientations nucleated in regions of the film. The non-orientated nuclei on the film may have originated from homogeneous nucleation in the gas phase above the substrate. That is, crystalline particles might form in the gas phase and land on the growing surface and thus form a non-oriented crystal orientation. Like growth at 1400 $^{\circ}\text{C}$, islands formed at the sample edges but were even more pronounced.

Depositions for shorter times at 1400 and 1450 $^{\circ}\text{C}$ more clearly exhibited island growth and did not form continuous films over large areas of the substrates. Typically, the islands' shapes were hexagons elongated perpendicular to the direction of miscut (see Figure 2.3 b)). The bare 4H-SiC surface after surface preparation consisted of series of stepped hillocks that were parallel to one another but perpendicular to the miscut direction. The $B_{12}P_2$ films thus nucleated and grew out from the step edges of the hillocks of the substrate. In contrast, films grown at 1300 $^{\circ}\text{C}$ remained continuous for the same deposition time (Figure 2.3 a)).

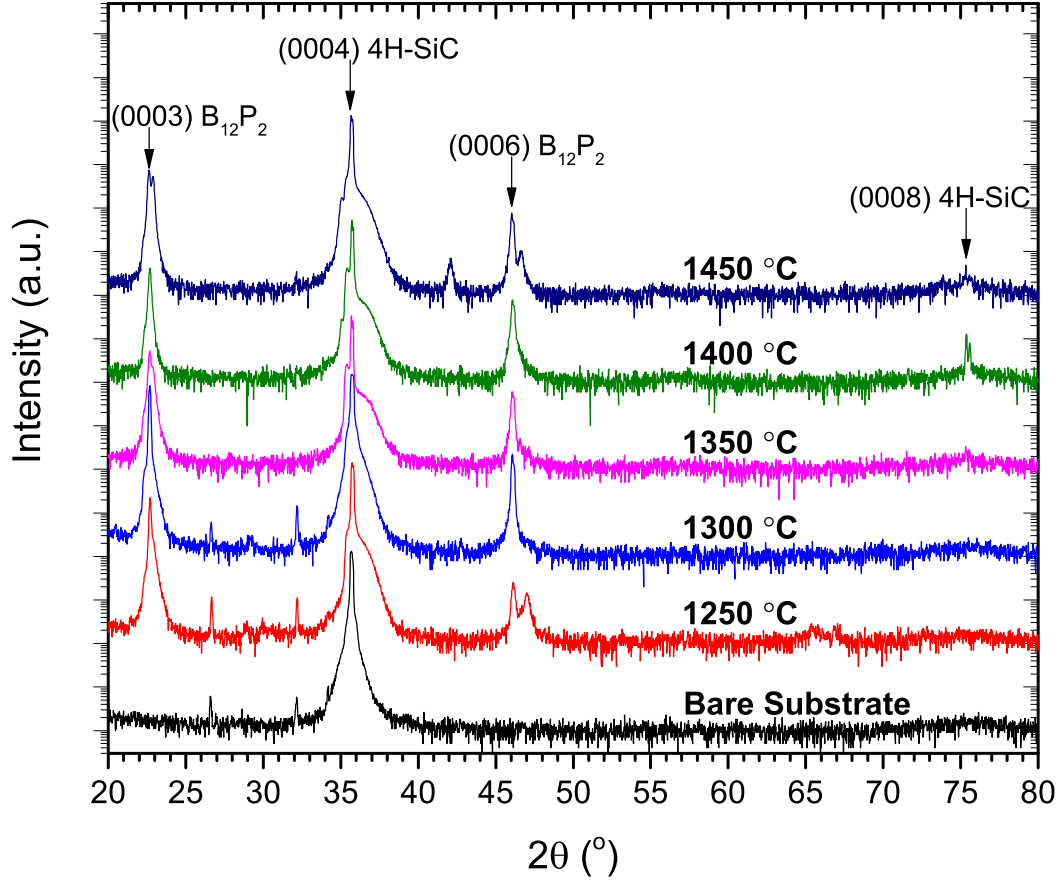


Figure 2.4: XRD scans of 4H-SiC substrate and $B_{12}P_2$ films grown on 4H-SiC. The y-axis is a logarithmic scale. Films grown at 1250 and 1450 °C have $(02\bar{2}4)$ doublet peaks at 46.4° , indicating that they are partially polycrystalline while the other films are single crystalline as they only have (0003) and (0006) peaks. Peaks at $\approx 26.5^\circ$ and 32° originate from the 4H-SiC substrate.

2.4.2 Growth Rate

The growth rate of $B_{12}P_2$, measured over the temperature range of 1250-1450 °C, varied from about 3 to 5 $\mu\text{m/hr}$ (Table 3.1). The maximum growth rate was 5.3 $\mu\text{m/hr}$ at 1250 °C. The enhanced growth rate at this temperature could be a result of higher growth rates of crystal faces that are not (0001) (the growth rate of the smoother area was smaller and comparable to growth at 1300 °C). Error could also be introduced when measuring the growth rate since the top surface is not flat. As the temperature was increased to 1300 and 1350 °C, the growth rate decreased to around 4.2 $\mu\text{m/hr}$. The growth rate decreased further

at higher temperatures (1400 °C and 1450 °C) probably due to precursor depletion before reaching the substrates ($B_{12}P_2$ also deposits on the susceptor walls (see Figure 2.1)). The films also became thinner along the direction of gas flow due to precursor depletion as the gas passed over the substrate. The reported growth rates were determined by measuring the film thickness 5 mm downstream of the leading edge of the substrate.

2.4.3 The Epitaxial Relationship as Determined by X-ray Diffraction

The out-of-plane crystallographic relationship between the $B_{12}P_2$ films and the 4H-SiC substrate were determined from XRD scans (Figure 3.2). For all growth temperatures, three main peaks were observed: (0003) $B_{12}P_2$ at $\approx 22.5^\circ$, (0004) 4H-SiC at $\approx 35.7^\circ$, and (0006) $B_{12}P_2$ at $\approx 45.9^\circ$, confirming that the preferred out-of-plane epitaxial relationship was $(0001)_{B_{12}P_2} \parallel (0001)_{4H-SiC}$. A shoulder on the right side of the (0004) SiC peak appeared after a $B_{12}P_2$ film was grown. No $B_{12}P_2$ peaks are predicted to be located at this shoulder. The shoulder is likely a result of strain and distortions in the SiC lattice near the $B_{12}P_2$ interface. $B_{12}P_2$ is a hard material and the epilayers were tensile strained caused by both the lattice constant mismatch and the coefficient of thermal expansion mismatch.⁷⁶ The strain is so large that the $B_{12}P_2$ films frequently cracked if they were about 2 μm thick or thicker. Cracks have even been found in the underlying SiC substrate. Domains of cracked areas may cause some peak splitting or broadening. Secondary phases as a result of process gases reacting with the SiC could also potentially play a role.

At the upper and lower temperature bounds (1250 and 1450 °C, respectively), several extra peaks are clearly present, indicating that the films are partially polycrystalline, consistent with the morphological observations. Since both of these films have a $(02\bar{2}4)$ doublet peak located next to the (0006) peak, the $(01\bar{1}2)$ peak may also be present though it is not obvious because the d-spacings of the (0003) and $(01\bar{1}2)$ planes are similar (3.95 and 3.91 Å, respectively), and the peaks overlap. The origin of the $(01\bar{1}2)$ orientation could possibly

be a result of strain causing a $(0001)\|(01\bar{1}2)$ twin plane to form.⁹⁰

The samples grown from 1300-1400 °C generally have cleaner spectra. The films grown at 1350 and 1400 °C may have a $(02\bar{2}1)$ peak to the left of the (0004) 4H-SiC peak or a shoulder on the (0006) peak caused by a weak adjacent $(02\bar{2}4)$ peak, but the (0001) orientation still dominates. At 1300 °C, the film is a single texture. It also has both the sharpest (0003) and (0006) peaks and the most intense (0003) peak relative to the (0004) 4H-SiC peak, suggesting that films grown at this temperature are higher quality than the others.

To confirm that the $B_{12}P_2$ films are epitaxial to the 4H-SiC, transmission Laue photographs normal to the (0001) plane were taken (not shown) and revealed that the epitaxial relationship between $B_{12}P_2$ and 4H-SiC is $(0001)\langle 11\bar{2}0 \rangle_{B_{12}P_2} \|(0001)\langle 11\bar{2}0 \rangle_{4H-SiC}$. This is the same orientation as $B_{12}As_2$ on 4H-SiC.⁸⁰

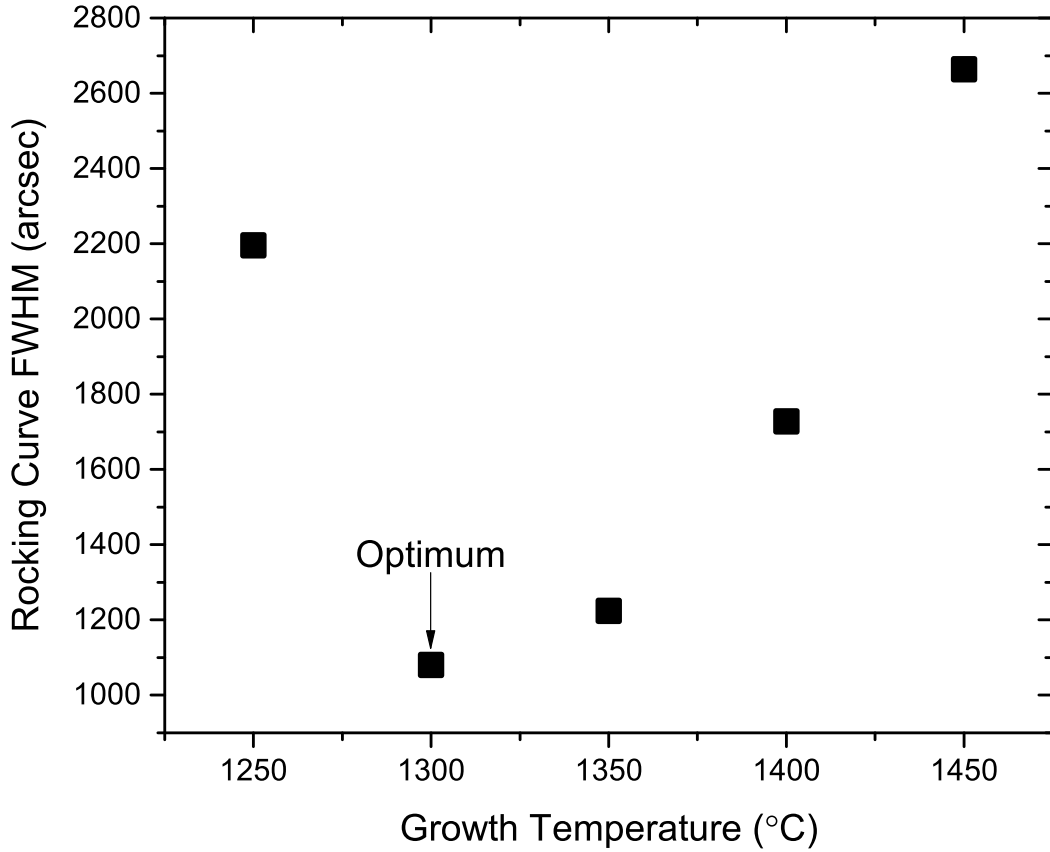


Figure 2.5: Plot of the X-ray rocking curve FWHM's of $B_{12}P_2$ films grown for 30 min in the temperature range of 1250-1450 °C. The optimum growth temperature is 1300 °C.

2.4.4 Effect of Growth Temperature and Film Thickness On Rocking Curve

While the surface morphology and XRD spectra hint that growth at 1300 °C may produce the highest crystal quality, X-ray rocking curves were taken to quantitatively evaluate the optimum growth temperature. Figure 2.5 depicts the full width at half maximum (FWHM) of the rocking curves of the (0003) $B_{12}P_2$ peak as a function of the growth temperature. At 1250 °C, the film has a FWHM of ≈ 2200 arcsec which drops sharply to 1080 arcsec at 1300 °C. The polycrystalline overgrowth is likely responsible for the increased FWHM value in the film grown at 1250 °C. The FWHM value increases monotonically above 1300 °C, reaching nearly 2700 arcsec at 1450 °C. Since the minimum value was achieved at 1300 °C, this was the optimum growth temperature for the growth conditions we tested.

The influence of the film thickness on the film quality of $B_{12}P_2$ grown at 1300 °C was also evaluated by measuring the X-ray rocking curve about the (0003) $B_{12}P_2$ peak. As seen in Figure 2.6, the FWHM decreased as the film thickness increased. This trend is also seen in other hetero-epitaxial material systems such as GaN on sapphire^{91,92} and 3C-SiC on Si⁹³ and was most likely due to relaxation of the lattice and annihilation of defects as the films grew thicker.⁷⁹

To the authors' knowledge, no rocking curve data has been reported in the literature for $B_{12}P_2$ prior to this publication, and therefore, direct comparisons to past studies is not possible. While the intrinsic (theoretical minimum) FWHM is unique to every material, a comparison to $B_{12}As_2$ may be the most appropriate since its crystal structure is a direct analog to $B_{12}P_2$. Both Zhang⁵⁶ and Nagarajan *et al.*²⁴ have reported rocking curve values of the (0003) $B_{12}As_2$ peak on films grown on SiC. Zhang measured FWHM values ranging from 730-812 arcsec over the temperature range of 1200-1350 °C while Nagarajan *et al.* reported values of 758-1223 arcsec in the range of 1300-1450 °C. The lower FWHM values for $B_{12}As_2$ may be due to fewer dislocations in those films as a result of the smaller lattice mismatch between $B_{12}As_2$ and SiC ($\sim 0.1\%$) versus that of $B_{12}P_2$ and SiC ($\sim 2.5\%$).

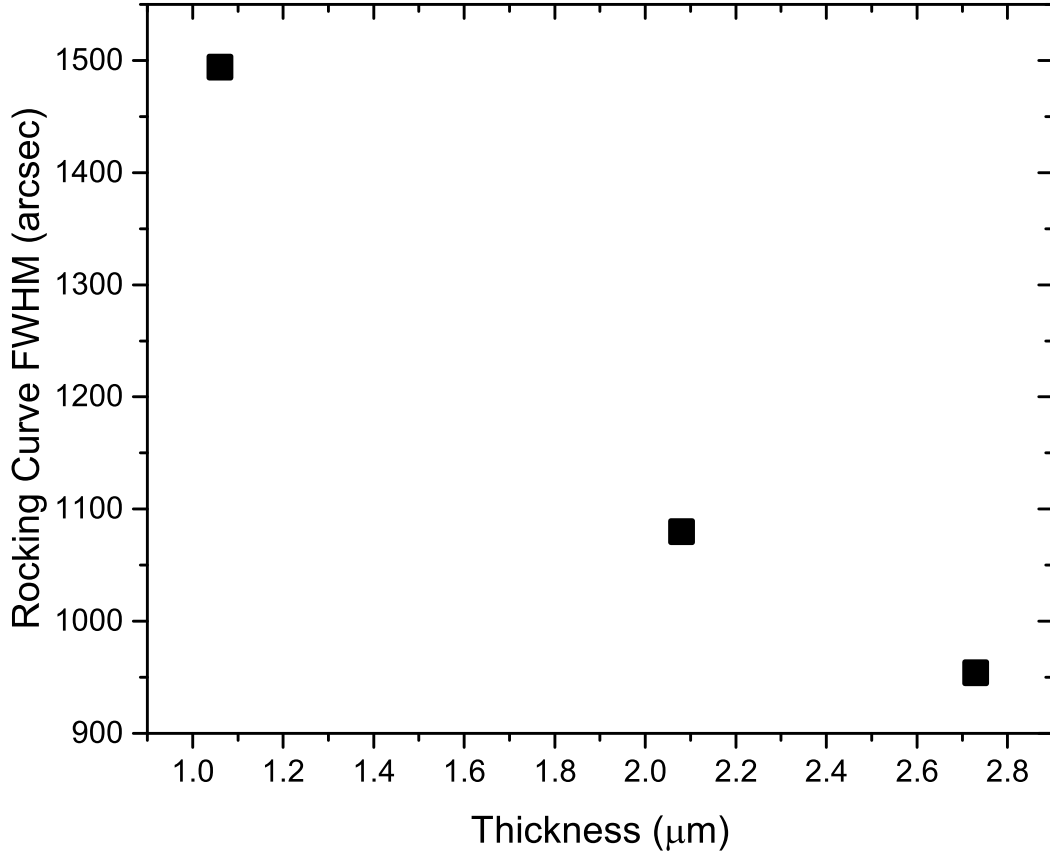


Figure 2.6: *Plot of the X-ray rocking curve FWHM's of $B_{12}P_2$ films grown at 1300 °C for various thicknesses. The crystal quality of the film improves as the thickness increasing, likely due to defect annihilation during continued growth.*

2.4.5 Influence of Growth Temperature on Nucleation and Growth Mode

Since the films were grown on vicinal surfaces, ideally the $B_{12}P_2$ should nucleate at a step edge and continue to grow in a step-flow growth mode. However, differences in surface energy due to the dissimilarity of the epitaxial and substrate materials may drive the growth into an island-type growth regime. The formation of islands elongated in the same direction as the vicinal step edges for growth at 1400 °C (see Figure 2.3b)) suggests that the film nucleated on step edges but then grew in a 3D island growth mode. Further evidence that the films are nucleating on vicinal steps is supported by the suppression of rotational twinning on

films grown at 1300 °C on 4H-SiC substrates specifically miscut towards the $(1\bar{1}00)$, which will be reported in a follow up publication.

Above 1350 °C, the films are thought to nucleate as islands which subsequently coalesce into a continuous film. The strong island-type growth caused increased mosaicity in the films and therefore wider rocking curves at the high growth temperatures. Island growth may have been further promoted by an increase in the adatom mobility at higher temperatures. Large adatom diffusion lengths may allow surface atoms to preferentially diffuse to and locate on lower surface energy $B_{12}P_2$ islands over the higher surface energy $B_{12}P_2/4H-SiC$ interface, thus minimizing strain in the film.

At 1300 °C or lower, the films were continuous after 15 min of growth (Figure 2.3 a)). At 1250 °C, the films are smooth and continuous down to growth times of 90 seconds. The decreased diffusion lengths at lower growth temperatures may have promoted a 2D growth mechanism by forcing adatoms to attach locally near step edges. Ideally, the diffusion length would be matched to the terrace width of the stepped substrate. While the surface of films grown at 1250 °C for short deposition times were smooth, at longer growth times, i.e. >15 min, the films were dominated by rough polycrystalline growth seen in Figure 2.2 which prevented growth of quality $B_{12}P_2$ films. This change in growth mode may be attributed limited adatom diffusion lengths at this low growth temperature. Changes in the precursor flow rates may influence or reduce the formation of the polycrystalline overlayer at 1250 °C.

2.5 Conclusions and Future Work

$B_{12}P_2$ was successfully grown on Si-face (0001) 4H-SiC substrates miscut 4° toward the $(1\bar{1}00)$ from 1250-1450 °C. The optimum growth temperature was 1300 °C as evidenced by XRD rocking curves even though the smoothest film was grown at 1350 °C. At a growth temperature of 1300 °C, the epitaxial relationship is $(0001)\langle 11\bar{2}0 \rangle_{B_{12}P_2} \parallel (0001)\langle 11\bar{2}0 \rangle_{4H-SiC}$. The decrease in the rocking curve FWHM as the film thickness increased suggests that

defects are annihilating as the films grow thicker.

Hetero-epitaxy of $B_{12}P_2$ on 4H-SiC can be further improved by modifying the growth conditions to more finely control the growth mode, and further work to optimize the surface structure before epitaxy should be pursued. Ideally, since the films are grown on vicinal surfaces, the adatom diffusion length should be adjusted to match the terrace width to ensure a step flow growth mode. This could be done by fine tuning the growth temperature and adjusting the III/V ratio to control the B and P adatom concentrations which can influence the adatom mean free path and the surface energy. As with many other hetero-epitaxial systems, a buffer layer may improve the crystal quality. To help prevent supersaturation or gas phase nucleation, the B_2H_6 flow rate could be reduced. Further work should also include characterization of the effect of the crystal quality and twinning on the electrical properties of $B_{12}P_2$ films grown on 4H-SiC.

More research could also be done to better understand the stoichiometry of $B_{12}P_2$. Some researchers have reported that $B_{12}P_2$ can accommodate substitutional defects of B atoms located on P sites and that the composition can vary according to $B_{12}(P_{2-x}B_x)$ where x is allowed to be $0 \leq x \leq 1$.¹⁷ It may be possible to measure the compositions of the films indirectly using the volume of the unit cell¹⁷ which can be calculated based on measured lattice constants via XRD. The composition could be different nearer to the substrate than near the film surface, and composition measurements as a function of film thickness could also be done in the future.

Chapter 3

Suppression of Rotational Twins in Epitaxial B_{12}P_2 on 4H-SiC

3.1 Introduction

As discussed in Chapters 1 and 2, 4H-SiC has advantages as a substrate for hetero-epitaxial growth of $B_{12}P_2$. These include 1) a relatively low lattice constant mismatch of about 2.5% when the a -lattice constant of $B_{12}P_2$ (5.99 Å) is compared to length $2 \times a$ of 4H-SiC (2×3.073 Å = 6.146 Å) and 2) a higher thermal stability of 4H-SiC over that of Si which decreases auto-doping and increases the temperature window in which $B_{12}P_2$ can be deposited. However, one drawback of using 4H-SiC as a substrate is that it has true hexagonal symmetry while $B_{12}P_2$ only truly has rhombohedral symmetry, which—as will be briefly reviewed below—can result in twin defects. More explanation of $B_{12}P_2$ twins and why they form on the (0001) face of hexagonal crystals is described in section 1.6.

In Chapter 2, only ($hkil$) Bravais-Miller hexagonal crystal coordinates were used and $B_{12}P_2$ was treated as a hexagonal crystal since rhombohedral crystal systems can also be represented using hexagonal coordinates. Figure 1.7 from Chapter 1 depicts the unit cell of $B_{12}P_2$ using both the rhombohedral and hexagonal system. The hexagonal coordinate system is convenient as it can be applied to both the substrate and the epitaxial layer, and it in many ways clarifies the epitaxial relationship. For example, when using hexagonal indices, the epitaxial relationship between $B_{12}P_2$ and 4H-SiC is written as $(0001)_{B_{12}P_2} [1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$. Here, the crystallographic alignment is intuitively understood. In contrast, when using rhombohedral indices for $B_{12}P_2$ and hexagonal indices for 4H-SiC, the epitaxial relationship is written as $(111)_{B_{12}P_2} [1\bar{2}1]_{B_{12}P_2} || (0001)_{4H-SiC} [1\bar{1}00]_{4H-SiC}$, and the crystallographic alignment is less obvious.

While using the hexagonal ($hkil$) system is convenient for $B_{12}P_2$, it is imperative to keep in mind that the hexagonal indices for the 4H-SiC and $B_{12}P_2$ are not one-to-one interchangeable. $B_{12}P_2$ still only has 3-fold rotational symmetry about the (0001) axis. Therefore, $[1\bar{1}00]$ and $[\bar{1}100]$ are *not* equivalent directions in $B_{12}P_2$ like they are in true hexagonal crystals. Likewise, $(1\bar{1}00)$ and $(\bar{1}100)$ are also *not* equivalent crystal planes in

$B_{12}P_2$.

Due to the 3-fold rotational symmetry of $B_{12}P_2$ and the 6-fold rotational symmetry of 4H-SiC, $B_{12}P_2$ can adopt two different orientations on the (0001) face of 4H-SiC during epitaxy: $(0001)_{B_{12}P_2}[1\bar{1}00]_{B_{12}P_2} || (0001)_{4H-SiC}[1\bar{1}00]_{4H-SiC}$ or $(0001)_{B_{12}P_2}[\bar{1}100]_{B_{12}P_2} || (0001)_{4H-SiC}[1\bar{1}00]_{4H-SiC}$. These two rotational variants are called twin orientations. Neither is inherently advantageous over the other; however, when the two rotational variants meet, they form twin boundaries. These 2-dimensional defects that can act as charge carrier scattering centers and/or introduce defect energy levels in the band gap. To make device quality material, twin boundaries must be avoided; this can only be done by ensuring that only a single orientation forms and grows during epitaxy.

Twin formation of another icosahedral boride, $B_{12}As_2$, grown on on-axis hexagonal SiC substrates is well-documented in the literature.^{79,24,80,81,82} Zhang, *et al.*^{73,80} and Padavala *et al.*⁷⁵ found that twins could be suppressed during epitaxy of $B_{12}As_2$ and BP when 4H-SiC is miscut 4-7° toward $(1\bar{1}00)$. Whether twins form or not when growing an icosahedral boride on 4H-SiC with a standard miscut to $(11\bar{2}0)$ has not yet been reported.

In this chapter, $B_{12}P_2$ was grown on (0001) 4H-SiC substrates miscut 4° to the $(1\bar{1}00)$ and on substrates miscut 4° to the $(11\bar{2}0)$ under the optimized conditions discussed in Chapter 2. An idealized etch model as postulated by Zhang *et al.*^{80,94} is presented in detail to explain how the step morphology of the substrates evolves during an *in-situ* etch and to describe how $B_{12}P_2$ twins nucleate on the substrate surfaces. By selecting the miscut to be toward the $(1\bar{1}00)$, the surface morphology can be engineered to suppress rotational twin formation during epitaxy. The data shows that $B_{12}P_2$ grown on 4H-SiC substrates miscut to the $(11\bar{2}0)$ has a twin density of 70% twin orientation I and 30% twin orientation II and that $B_{12}P_2$ grown on substrates miscut to the $(1\bar{1}00)$ have a twin density of less than 1% twin orientation II.

3.2 Experimental Methods

B_{12}P_2 films were deposited on 4H-SiC substrates miscut to both the a -plane and the m -plane at 1300 °C for 30 min as described in Chapter 2 and had a nominal thickness of 2 μm . These two miscuts were chosen because substrates miscut to the $(11\bar{2}0)$ are the industry standard substrates for doing 4H-SiC homoepitaxy while substrates miscut 7° to the $(1\bar{1}00)$ suppress twinning in B_{12}As_2 epitaxy. On-axis (0001) substrates were neglected from this study because twinning of epitaxial borides on these substrates is well documented. The surface morphology of the films were imaged and characterized by scanning electron microscopy (SEM) while the root mean squared roughness (R_{RMS}) was measured by white light interferometry. XRD 2θ - ω scans were taken on both films to confirm that the out-of-plane epitaxial relationship was $(0001)_{\text{B}_{12}\text{P}_2} || (0001)_{4\text{H-SiC}}$. The film quality was assessed by XRD rocking curves. To determine the in-plane epitaxial relationship and reveal the orientation of the films as well as the amount of twinning, transmission Laue photographs were taken, and the diffracted spots were indexed. For the Laue photographs, a white spectrum X-ray beam was generated from a Mo source, and the X-ray beam was collimated to a diameter of 0.7 mm. The photographs were recorded in a 16-bit format so that spot intensities could be measured. In addition to the Laue photographs, XRD pole figures were taken to further characterize the amount of twinning in the samples.

To evaluate the substrate surface morphology just before B_{12}P_2 epitaxy, substrates of each miscut type were prepared in the same procedure used during epitaxy. That is, they were loaded into the growth chamber, etched at 1600 °C, and cooled to 1300 °C. Then PH_3 was flowed over the substrates as is done immediately before epitaxy, but instead of introducing B_2H_6 to initiate growth, the PH_3 flow was terminated and the substrates were cooled to room temperature and removed from the chamber. The surfaces of each miscut type after the surface preparation were imaged by atomic force microscopy (AFM) to characterize the surface step morphology.

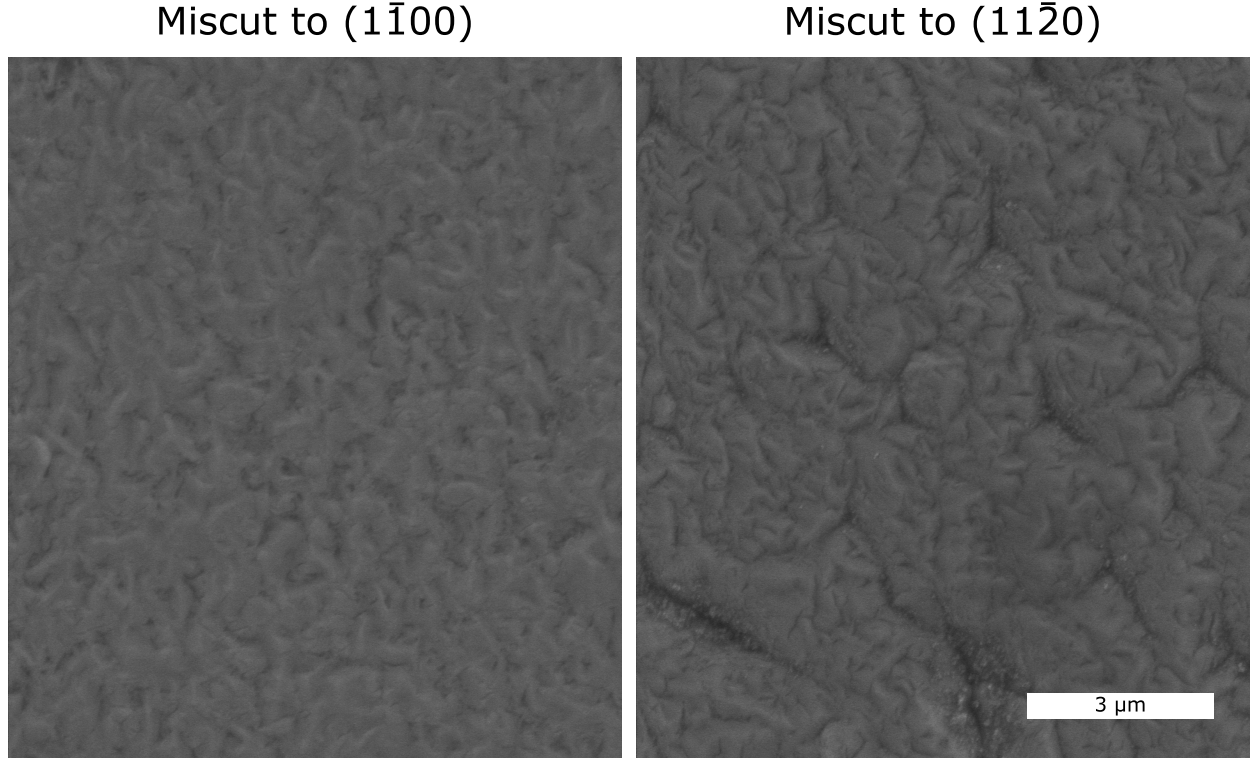


Figure 3.1: SEM micrographs of $B_{12}P_2$ films grown on 4H-SiC miscut 4° to the $(1\bar{1}00)$ (left photo) and 4H-SiC miscut 4° to the $(11\bar{2}0)$ (right photo). The scale bar is $3\ \mu\text{m}$ and is the same for both photos.

3.3 Results

3.3.1 Surface Morphology of $B_{12}P_2$ Films

SEM micrographs of the two films reveal that both films are composed of sub-micron, faceted grains (Figure 3.1). The R_{RMS} of the film grown on the $(1\bar{1}00)$ miscut (measured by white light interferometry) is much smaller than the film on the $(11\bar{2}0)$ miscut substrate (Table 3.1). As mentioned in Chapter 2, small secondary nuclei are scattered around the films, possibly from homogeneous nucleation in the gas phase.

Table 3.1: R_{RMS} roughness (nm) as measured by optical interferometry, XRD rocking curve FWHM (arcsec), and % twin orientation I as measured by Laue spot intensity for $B_{12}P_2$ films grown on 4H-SiC miscut 4° to the $(1\bar{1}00)$ and 4H-SiC miscut 4° to the $(11\bar{2}0)$.

	Substrate Miscut	
	4° to $(1\bar{1}00)$ (Custom)	4° to $(11\bar{2}0)$ (Standard)
R_{RMS} Roughness (nm)	7	16
FWHM (arcsec)	1080	1050
% Twin Orientation I	>99%	30%

3.3.2 Out-of-plane X-ray Diffraction

XRD spectra of $B_{12}P_2$ films grown on each substrate miscut as well as a substrate without a $B_{12}P_2$ film are shown in Figure 3.2. From the XRD spectra, $B_{12}P_2$ on both substrates have an out-of-plane epitaxial relationship of $(0001)_{B_{12}P_2} || (0001)_{4H-SiC}$. As mentioned in Chapter 2, there may be a small shoulder on the (0003) $B_{12}P_2$ peak and on the 4H-SiC (0004) peak. Rocking curves were also taken about the (0003) $B_{12}P_2$ peak on both films with FWHM values of 1080 arcsec and 1050 arcsec for films grown on the $(1\bar{1}00)$ miscut and $(11\bar{2}0)$ miscut substrates, respectively. Rocking curve measurements are a direct measure of the mosaicity of the films, i.e. in this case, small misalignments of the (0003) plane from different crystal domains throughout the film. Similar values for the FWHM should be expected for films grown under the same conditions regardless of the amount of twinning present, as the twins are parallel with respect to the (0001) plane and should have little influence on the mosaicity.

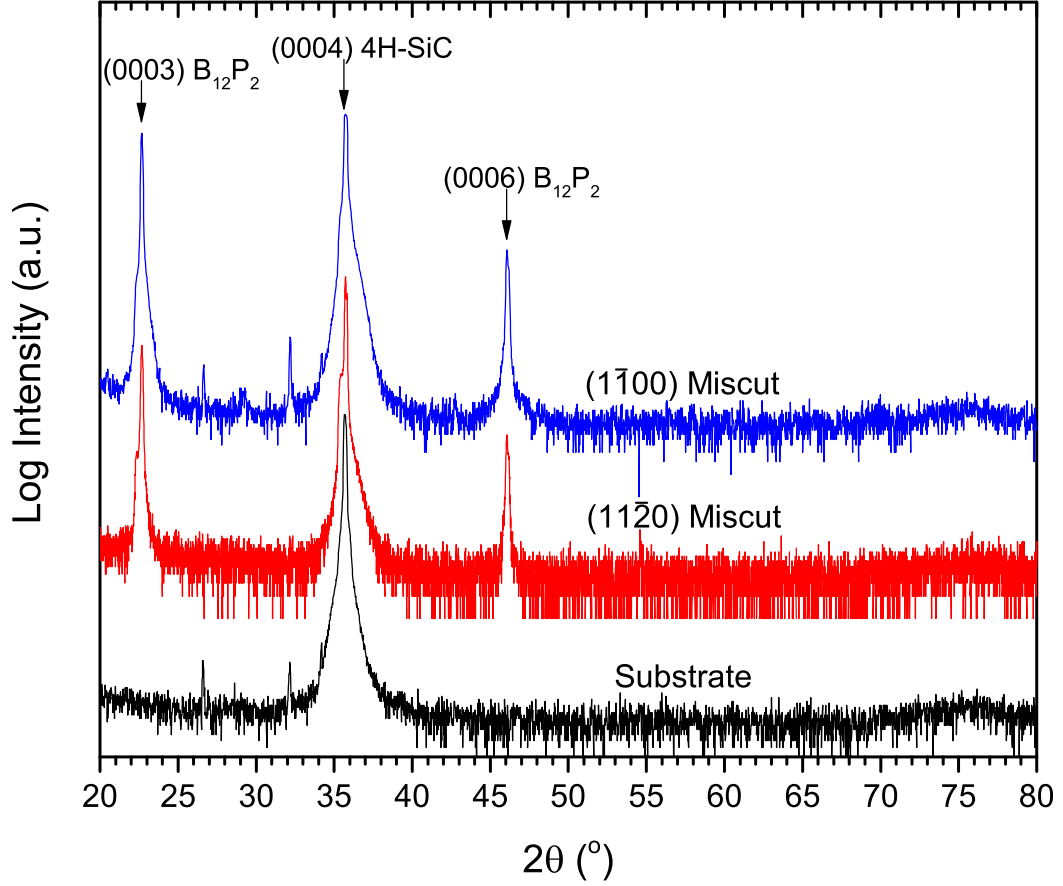


Figure 3.2: The XRD 2θ spectra of a bare 4H-SiC substrate and $B_{12}P_2$ films grown on 4H-SiC miscut in towards the $(1\bar{1}00)$ and $(1\bar{1}20)$. The out-of-plane epitaxial relationship of $B_{12}P_2$ to 4H-SiC is $(0001)_{B_{12}P_2} || (0001)_{4H-SiC}$ as is indicated by the $\{000l\}$ family of planes for both $B_{12}P_2$ and 4H-SiC.

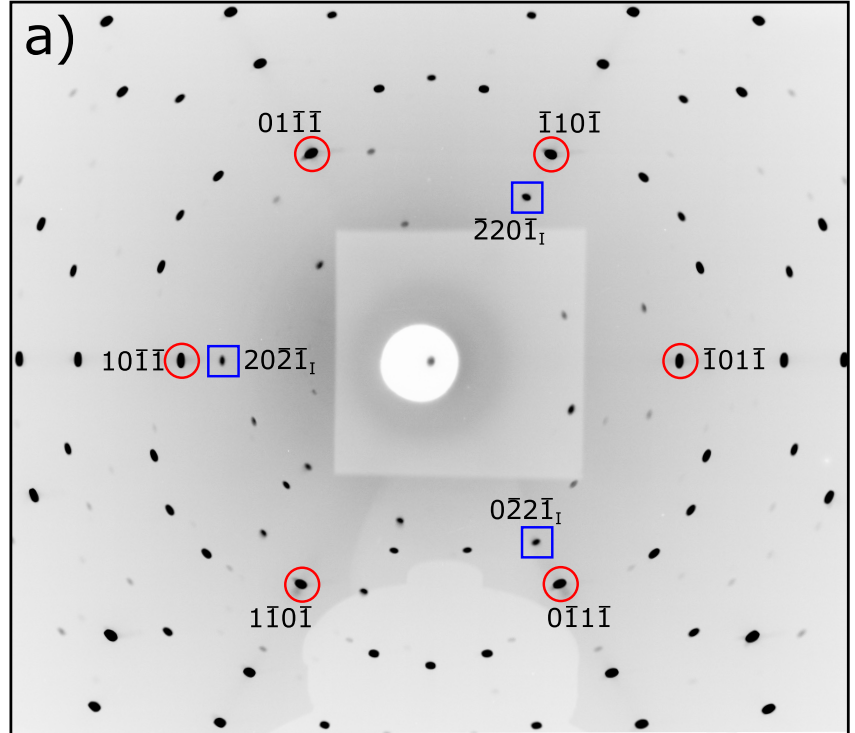
3.3.3 In-plane X-ray Diffraction

Laue photographs were taken to both reveal the in-plane epitaxial relationship and characterize the presence and amount of rotational twinning in the films. Figure 3.3 shows the diffraction patterns generated from a broad spectrum Mo X-ray beam incident normal to the (0001) of the substrate and film. $B_{12}P_2$ films grown on the $(1\bar{1}00)$ miscut substrate and $(1\bar{1}20)$ miscut substrates are depicted in Figure 3.3 a) and b), respectively. All of the diffraction spots in Laue photos have been indexed, but to improve clarity, only select spots have been labeled here. In each photograph, the 4H-SiC $\{10\bar{1}\bar{1}\}$ spots are circled, and

squares are placed around the $B_{12}P_2$ $\{20\bar{2}1\}$ spots. To distinguish between the two rotational variants of $B_{12}P_2$, a subscript of “I” or “II” was included on the $B_{12}P_2$ spot labels to represent spots from each respective twin orientation. The alignment of the $B_{12}P_2$ $\{20\bar{2}1\}$ spots along a straight line from the center beam spot to the 4H-SiC $\{10\bar{1}1\}$ spots confirms that the in-plane epitaxial relationship is $(0001)\{1\bar{1}00\}_{B_{12}P_2} \parallel (0001)\{1\bar{1}00\}_{4H-SiC}$. There were no extraneous spots in the photos, which would indicate that another $B_{12}P_2$ orientation is present. If another orientation were present, for example from a possible overlapping $(01\bar{1}2)$ peak over the (0003) in Figure 3.2, it was too minor to be detected above the background noise level in these measurements.

The most notable difference in the diffraction patterns between the two vicinal substrates is the presence of only $\{20\bar{2}1\}_I$ spots in the $B_{12}P_2$ film on the $(1\bar{1}00)$ miscut substrate and the appearance of both $\{20\bar{2}1\}_I$ and $\{20\bar{2}1\}_{II}$ spots in the film on the $(11\bar{2}0)$ miscut substrate. Thus, suppression of rotational twinning on $(1\bar{1}00)$ miscut substrates is clearly demonstrated. Since the X-ray beam for the Laue photographs was 700 μm in diameter, the beam was assumed to be far larger than any twin domain and that a statistically significant amount of each twin was present in the beam line. Although two twin orientations are present in the $(11\bar{2}0)$ miscut sample, one twin orientation is more prevalent than the other, as indicated by the difference in intensity between the two sets of spots on the $(11\bar{2}0)$ miscut sample. To quantify the amount of each variant in the films, the intensity of the $(20\bar{2}1)_I$ and $(20\bar{2}1)_{II}$ spots were integrated. The ratio of $(20\bar{2}1)_I:(20\bar{2}1)_{II}$ was $\approx 7:3$ or about 70% $(20\bar{2}1)_I$. Upon closer inspection to the $(1\bar{1}00)$ tilted sample, no $\{20\bar{2}1\}$ spots above the noise from air scattering could be observed on the Laue photograph, even at an exposure time of four hours. However, the pole figure contained a very faint signal from a second twin orientation (Figure 3.4). In the pole figure, the three strong $\{01\bar{1}2\}$ satellite peaks originate from twin orientation I. The three weak satellite peaks are from twin orientation II. The second twin orientation may be due to the small secondary nuclei located on the surface. On the other hand, the X-ray beam of the 4 circle diffractometer used for the pole figure is much

Miscut to $(1\bar{1}00)$
(custom)



Miscut to $(11\bar{2}0)$
(standard)

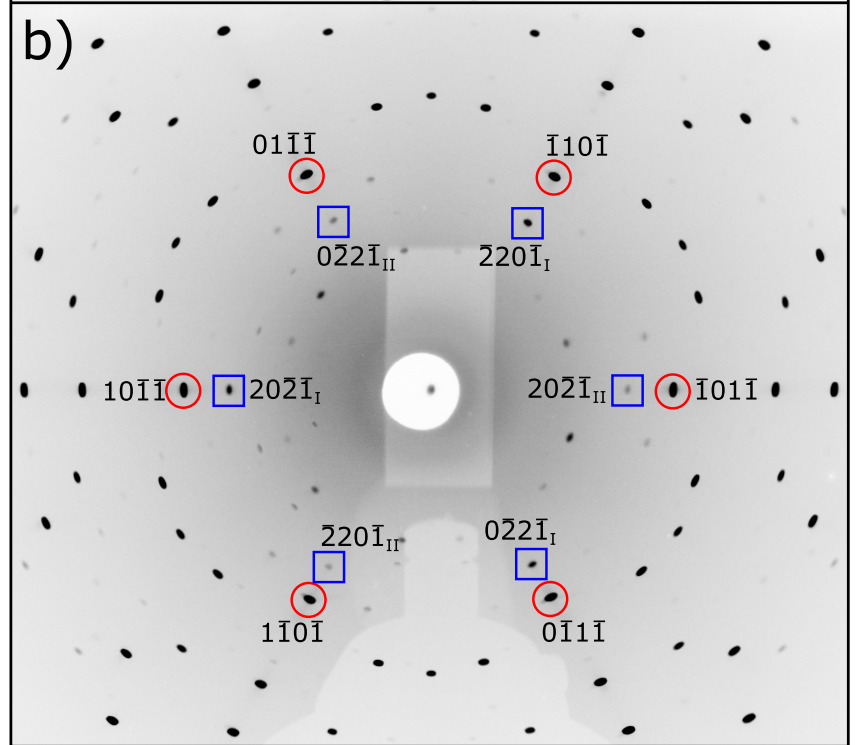


Figure 3.3: Laue photographs taken of $B_{12}P_2$ grown at 1300°C on $4H\text{-SiC}$ miscut a) 4° toward the $(1\bar{1}00)$ and b) 4° toward the $(11\bar{2}0)$. The X-ray beam is incident normal to the (0001) face of the film and substrate. Red circles enclose $4H\text{-SiC}$ spots while blue squares surround the $B_{12}P_2$ spots. Subscripts “I” and “II” denote the two twin orientations.

larger than the Laue beam, and the technique is more sensitive to the surface structure than the Laue photography. Therefore, a small amount of the second variant could be present throughout the film. Nonetheless, by integrating the intensities of the $01\bar{1}2$ satellite peaks of each variant in the pole figures, the film grown on the $(1\bar{1}00)$ miscut SiC is >99% variant I. As in the Laue photograph for the $(11\bar{2}0)$ miscut sample, both twin orientations are clearly present in the pole figure.

3.4 Discussion

3.4.1 Mechanism of Rotational Twin Suppression

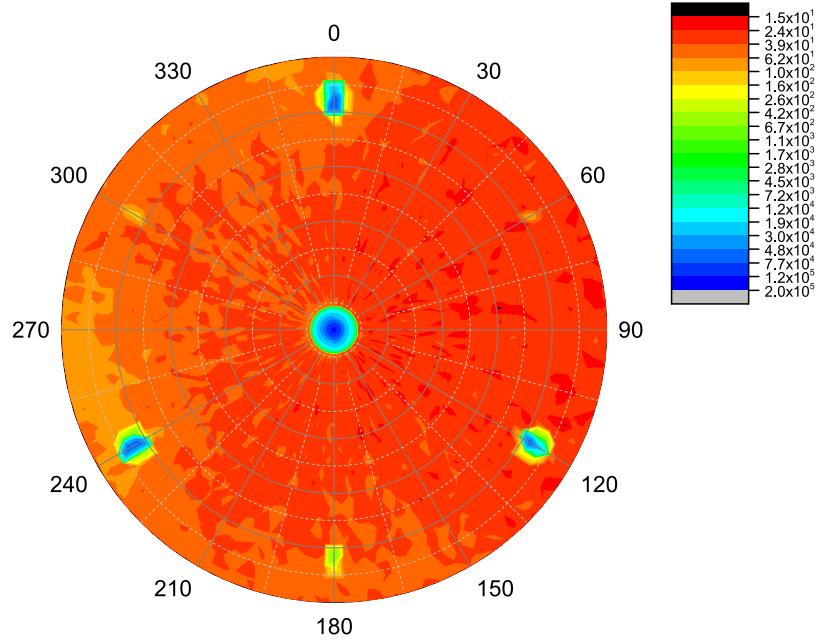
A “reverse” step-flow model will be described and can explain how different types of step edges form on either type of miscut 4H-SiC during the *in situ* H_2 etch. The shape and orientation of these steps influence the nucleation sites of the two rotational variants of $B_{12}P_2$.

In this model, carbon atoms are presumed to etch to produce methane (CH_4), and silicon atoms are etched into silane (SiH_4) molecules. In the etch processes described below, the term “dangling bonds” is used, but the dangling bonds are assumed to actually be terminated by H atoms as the atoms are etched into the reaction products. In this chapter, “dangling bonds” simply refers to C and Si bonds that are not bound to the substrate.

Etching of 4H-SiC miscut 4° to the $(1\bar{1}00)$

Figure 3.5 depicts two cross-sectional views of a vicinal (0001) 4H-SiC substrate miscut 4° to the $(1\bar{1}00)$ as viewed along the $[11\bar{2}0]$ direction. In the upper cross-section, the steps are equally spaced apart in an ideal unetched surface. In each unit cell length along the $[0001]$, four step risers exist. Within each unit cell height, there are two types of step edges, each with terminating atoms in different bonding configurations. In one type (labeled with green arrows in Figure 3.5), the terminating C atoms have a single dangling bond and are bound to

Miscut to $(1\bar{1}00)$
(custom)



Miscut to $(11\bar{2}0)$
(standard)

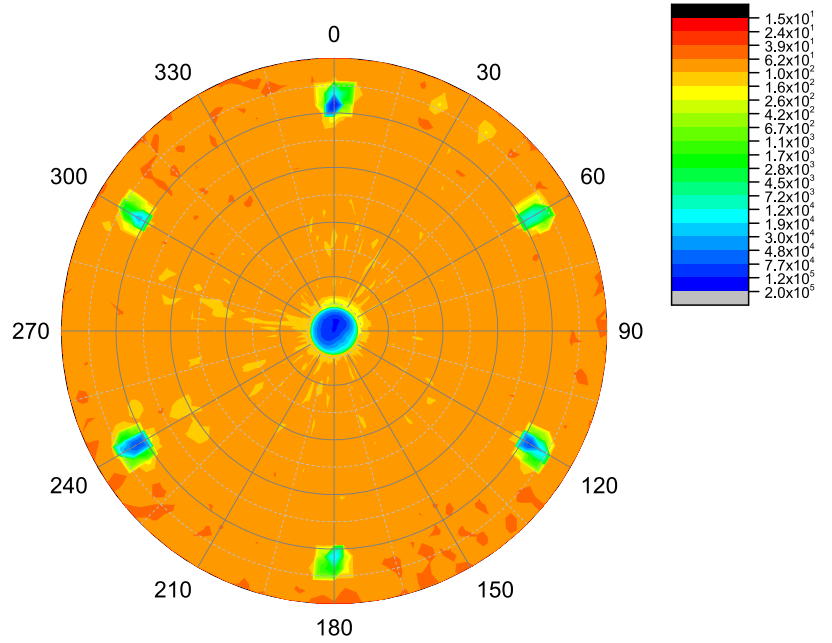


Figure 3.4: XRD pole figures for $B_{12}P_2$ films grown on $4H$ -SiC miscut 4° to the $(1\bar{1}00)$ and $4H$ -SiC miscut 4° to the $(11\bar{2}0)$. The center peak is the (0003) $B_{12}P_2$ peak while the satellite peaks are $\{01\bar{1}\bar{2}\}$ peaks. The satellite peaks at $0, 120,$ and 240° originate from twin orientation I while the satellite peaks at $60, 180,$ and 300° originate from twin orientation II.

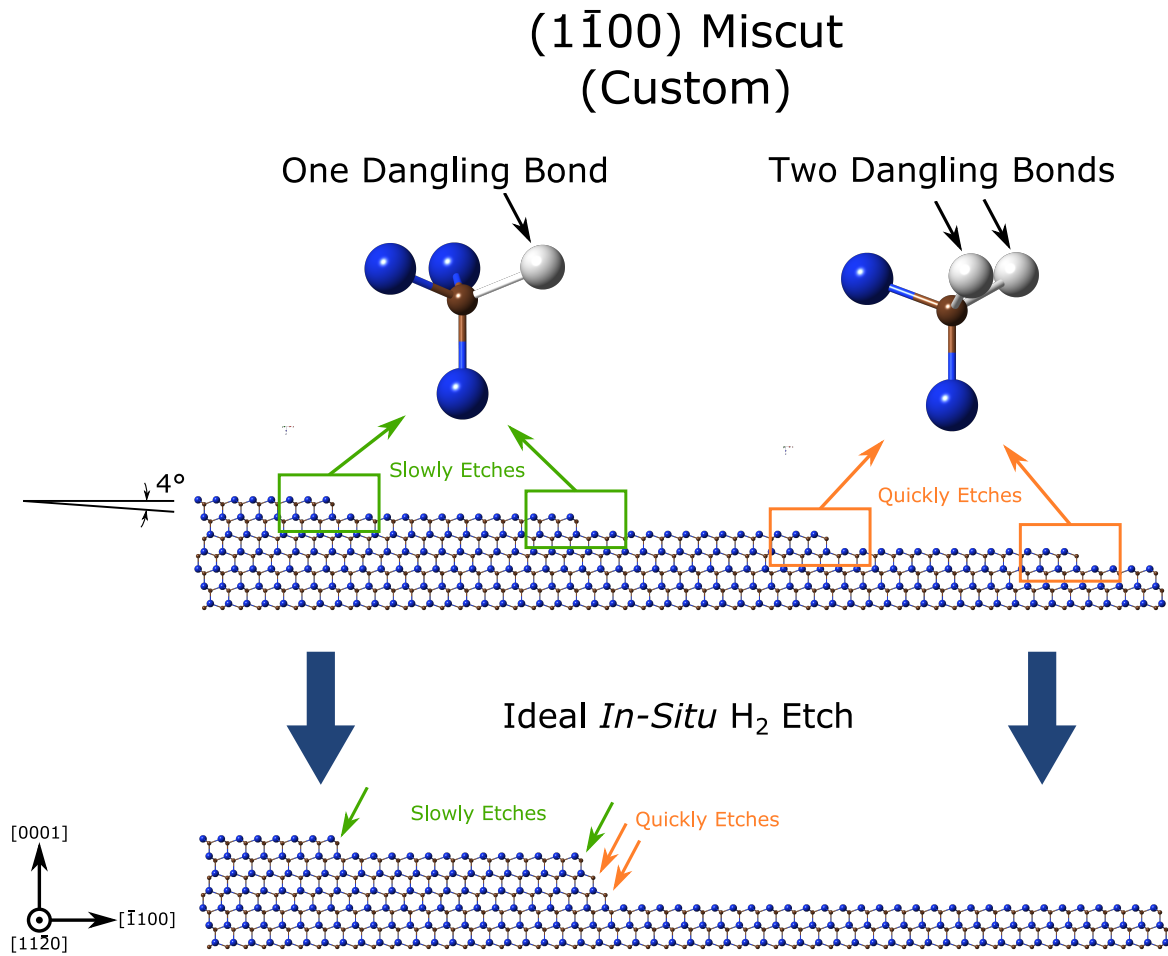


Figure 3.5: On the top is a cross-sectional view of an ideal vicinal (0001) 4H-SiC substrate miscut 4° to the (1 $\bar{1}$ 00); the surface steps are equally spaced apart. The larger blue atoms are Si while the smaller brown atoms are C. A perspective view of the terminating C atoms of the two step types are shown above the upper cross-sectional view where dangling bonds are represented by bonds to fictitious white atoms. After an ideal in-situ etch, the quickly etching orange-labeled steps bunch together under a slowly etching green-labeled step as depicted in the lower cross-sectional view.

the rest of the substrates by three bonds. In the second type (labeled with orange arrows), the terminating C bonds have two dangling bonds and are only bound to the surface by two bonds. A close-up perspective view of the terminating C atoms and their respective bonding configurations are shown above the upper cross-sectional view with dangling bonds shown as bonds to fictitious white atoms (the white atoms only exist in the figure to clearly demonstrate the location of the dangling bonds). Since the C atoms in the second (orange) type step are bound less strongly to the substrate because they only have two bonds to the substrate, one would expect that these C atoms would more readily etch during the in-situ H_2 etch than the C atoms in the other type step which are bound by an extra bond. During an ideal surface etch, both types of steps should etch back (towards the left as depicted in Figure 3.5). Because C atoms with two dangling bond can be etched more readily, these steps etch faster than the other type. As the orange steps catch up to the nearest green step, the steps bunch together and the step etch rate becomes limited by the green step edge etch rate. The difference in etch rate of the two step types is exaggerated in Figure 3.5, showing that the green steps do not etch while the orange steps do. Regardless of the actual etch rates, as long as the orange steps etch more quickly, the final result will be the step structure depicted in the lower cross-sectional view of Figure 3.5.

The four step risers shown in Figure 3.5 compose a unit cell height and therefore repeat along the surface of the substrates. A larger cross-sectional view of the ideally etched steps are shown in the upper portion of Figure 3.6. A one-to-one scale schematic of the (0001) face of the SiC is depicted in the lower portion of Figure 3.5 and illustrates how the step edges would appear on the surface. Dotted green and orange lines lead from the step edges in the cross-sectional view to the top view to help guide the eye between the two perspectives. Note: in the top view, *all of the step edges are parallel*.

(1 $\bar{1}$ 00) Miscut (Custom)

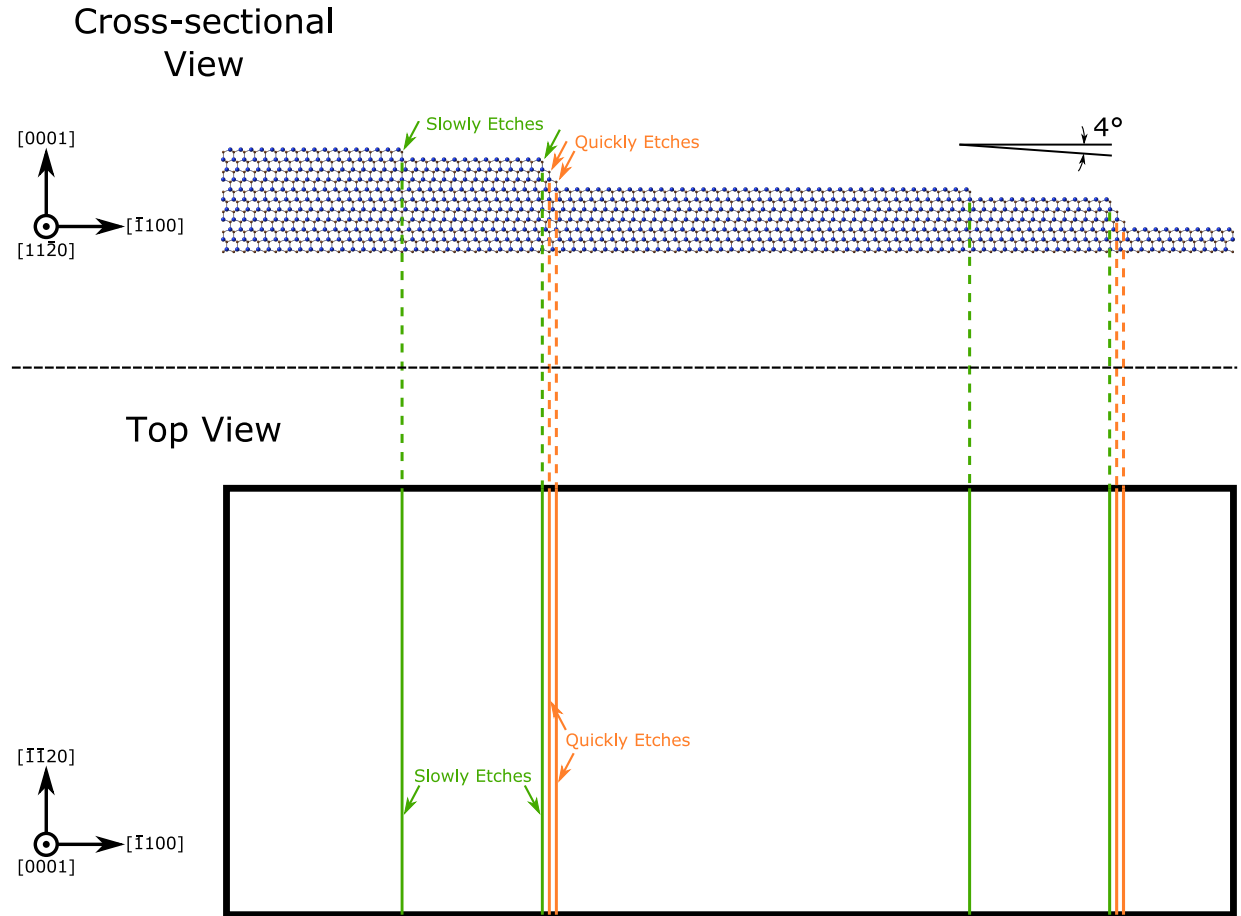


Figure 3.6: A zoomed-out, cross-sectional view of the ideally etched surface steps of a 4H-SiC substrate miscut 4° to the (1 $\bar{1}$ 00) is depicted. On the bottom, a schematic of the ideally etched steps are shown as a top view. Solid green and orange lines represent each type of step edge on the SiC surface while broken green and orange lines from the cross-sectional view to the top view exist to lead the eye between the two views.

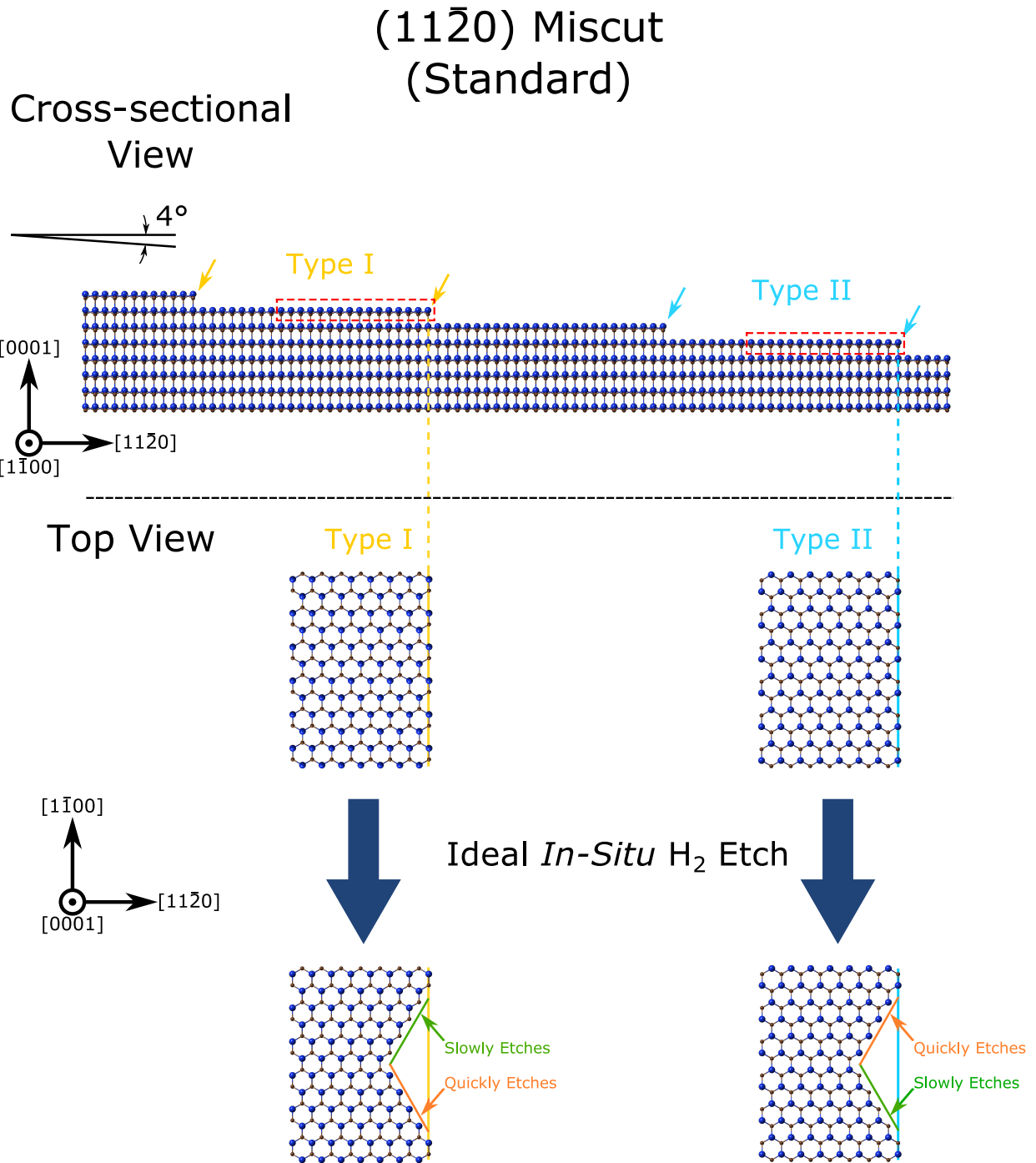


Figure 3.7: On the top is a cross-sectional view of an ideal vicinal (0001) 4H-SiC substrate miscut 4° to the (11 $\bar{2}$ 0) where the surface steps are equally spaced apart. The two step types are marked with yellow and blue arrows. Below the cross-sectional view is a top view of a SiC bilayer from each of the two step types. A solid yellow line represents a step edge of type I while a solid blue represents a step edge of type II. Dotted yellow and blue lines exist to lead the eye between the cross-sectional and top views. After the ideal in situ etch, the two types of bilayers (and step edges) form angled step edges as depicted in the lowest part of the figure. For each step type, a slowly etching green-labeled step and a quickly etching orange-labeled step are generated. A detailed etched process for each bilayer are depicted in Figures 3.8 and 3.9 for steps type I and II, respectively.

Etching 4H-SiC 4° to the $(11\bar{2}0)$

The same method of step etching that was applied to substrates miscut to the $(1\bar{1}00)$ can be applied to the substrates that are miscut to the $(11\bar{2}0)$. As was done in section 3.4.1, the starting point is a cross-sectional view of a 4H-SiC substrate ideally miscut 4° so that all step risers are equally spaced apart. A cross-sectional view of the steps as viewed along the $[\bar{1}100]$ is shown in Figure 3.7. Unlike in Figure 3.5 where the atomic bonding configuration is evident when viewed along the $[11\bar{2}0]$, the steps here are essentially indistinguishable from this viewpoint. Nonetheless, as with the other miscut, there are still two types of step edges with different bonding configurations, denoted here as step type I (marked with yellow arrows) and step type II (marked with blue arrows). To better visualize the terminating bonds on the two types of step edges, a bilayer from each step type (enclosed by red dashed rectangles) are depicted below the cross-sectional view and are viewed along the $(000\bar{1})$ in a top view. It is important to keep in mind in the top view of these bilayers that all of the Si atoms have dangling bonds pointing out of the page while the C atoms are bonded to Si atoms beneath them with bonds pointed directly into the page. At a glance, the two step types in the top view appear to be similar, but they are rotated 180° about the $[0001]$ from one another, or equivalently, *they are rotated by 60°* . Following the same method for ideally etching the step edges as was done in section 3.4.1, i.e. atoms with only one dangling do not etch while atoms with two dangling bonds do etch, the step edges etch into the morphology depicted in the lower half of Figure 3.5. To better illustrate how these step morphologies are produced from this method of etching, a detailed step-by-step description is provided next.

First, etching of step type I is considered, and the process is depicted in Figure 3.8 in a series of nine frames. In the first frame, the step is unetched and the yellow line denotes the ideal step edge as denoted with yellow arrows in Figure 3.7. Along this edge, the Si atoms have dangling bonds pointed directed out of the page as mentioned previously but also have another dangling bond. The two bonds by which the Si atoms are attached to

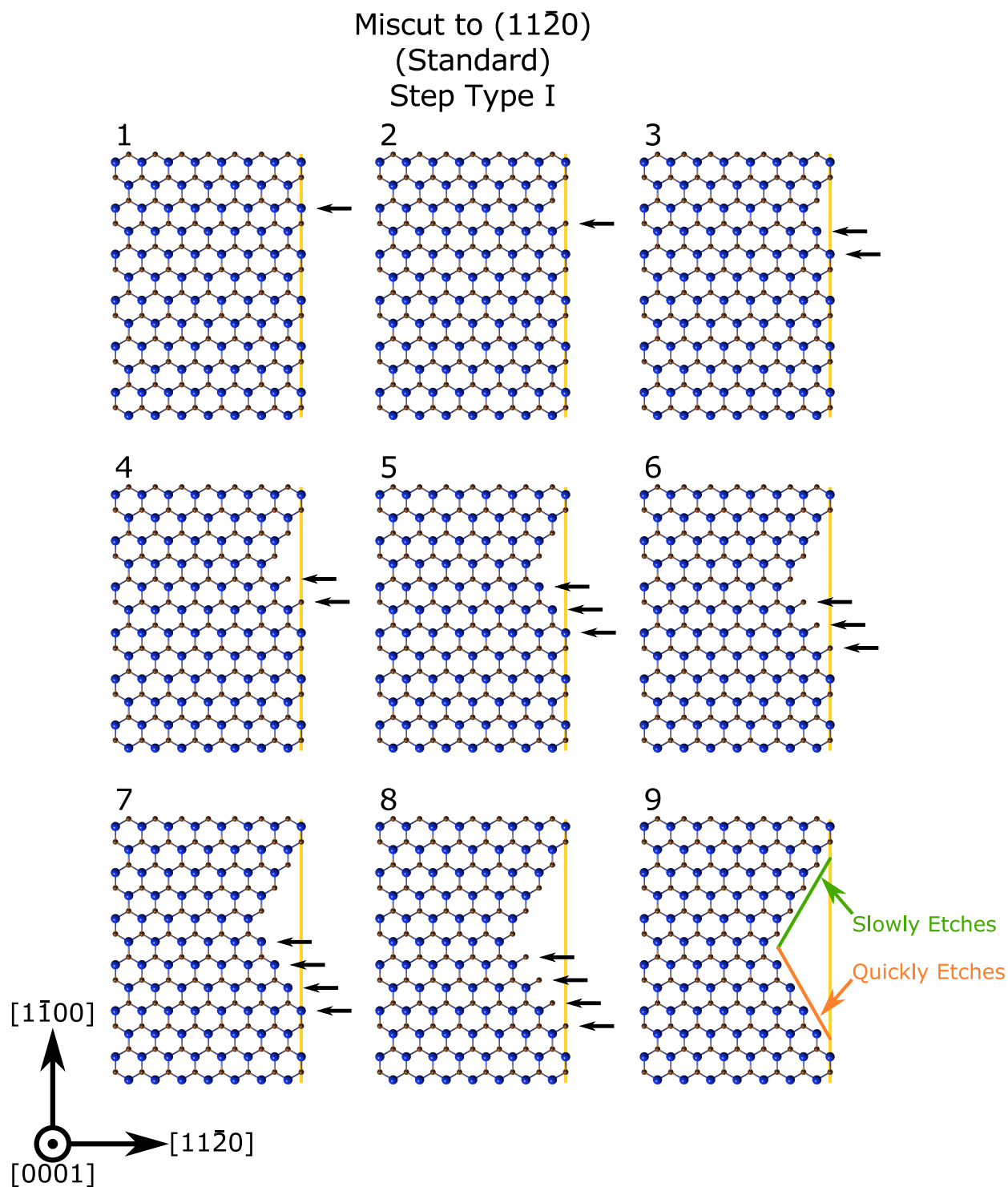


Figure 3.8: A detailed, step-by-step ideal etch process is depicted for a bilayer of step type I. An ideally, unetched bilayer is shown in frame 1 where the yellow line indicates the step edge. In each frame, a black arrow points to an atom located at the step edge that has two dangling bonds. The marked atoms are removed (etched) in the following frame. Frame 9 depicts the same bilayer configuration in Figure 3.7.

the substrate can be directly viewed from the top view and the dangling bonds are absent. To simplify the etch procedure, only one terminal Si atom (denoted by a black arrow) is considered for the first etch step. Since this Si atom has two dangling bonds, it is removed in frame 2. In frame 2, the newly removed Si atom has exposed two C atoms that are now part of the step edge. One C atom has one dangling bond while the other C atom (denoted by a black arrow) has two dangling bonds (this atom has one visible real bond while the other real bond is pointing into the page). The C atom with two dangling bonds is removed in frame 3, and the C atom with one dangling bond remains unetched. In frame 3, black arrows denote two Si atoms with two dangling bonds, and these atoms are thus etched and removed in frame 4. Now, two C atoms with two dangling bonds are exposed in frame 4 and are removed in the next frame. In each frame, the atoms denoted with black arrows have two dangling bonds and are removed in the following frame. After nine etch steps, the straight, original step edge transformed into two co-planar step edges rotated from one another by 60° . Furthermore, these two co-planar step edges have two different bonding configurations. Even more, the step edge on the upper half of frame 9 is crystallographically identical to the slowly etching green step edges found on the substrates miscut 4° to the $(1\bar{1}00)$ while the step edge on the lower half of frame 9 is crystallographically identical to the quickly etching orange step edges on the $(1\bar{1}00)$ miscut substrates. The newly formed step edges are pairs of $\{1\bar{1}00\}$ edges.

When considering the etching of step type II, the etch procedure can be followed as was done for step type I and is similarly depicted in Figure 3.9. Now, the step edge shown in frame 1 is the ideal type II unetched step edge and is marked with a blue line to indicate that it is the same step edge as those shown with blue arrows in Figure 3.7. As before, the atom marked with a black arrow has two dangling bonds and is removed in each subsequent frame. Just like in the type I steps, two co-planar steps edges rotated by 60° have formed by the ninth frame. In contrast to step type I, the slowly etching green steps are now located on the bottom half of frame 9 while the quickly etching orange steps are on the upper half.

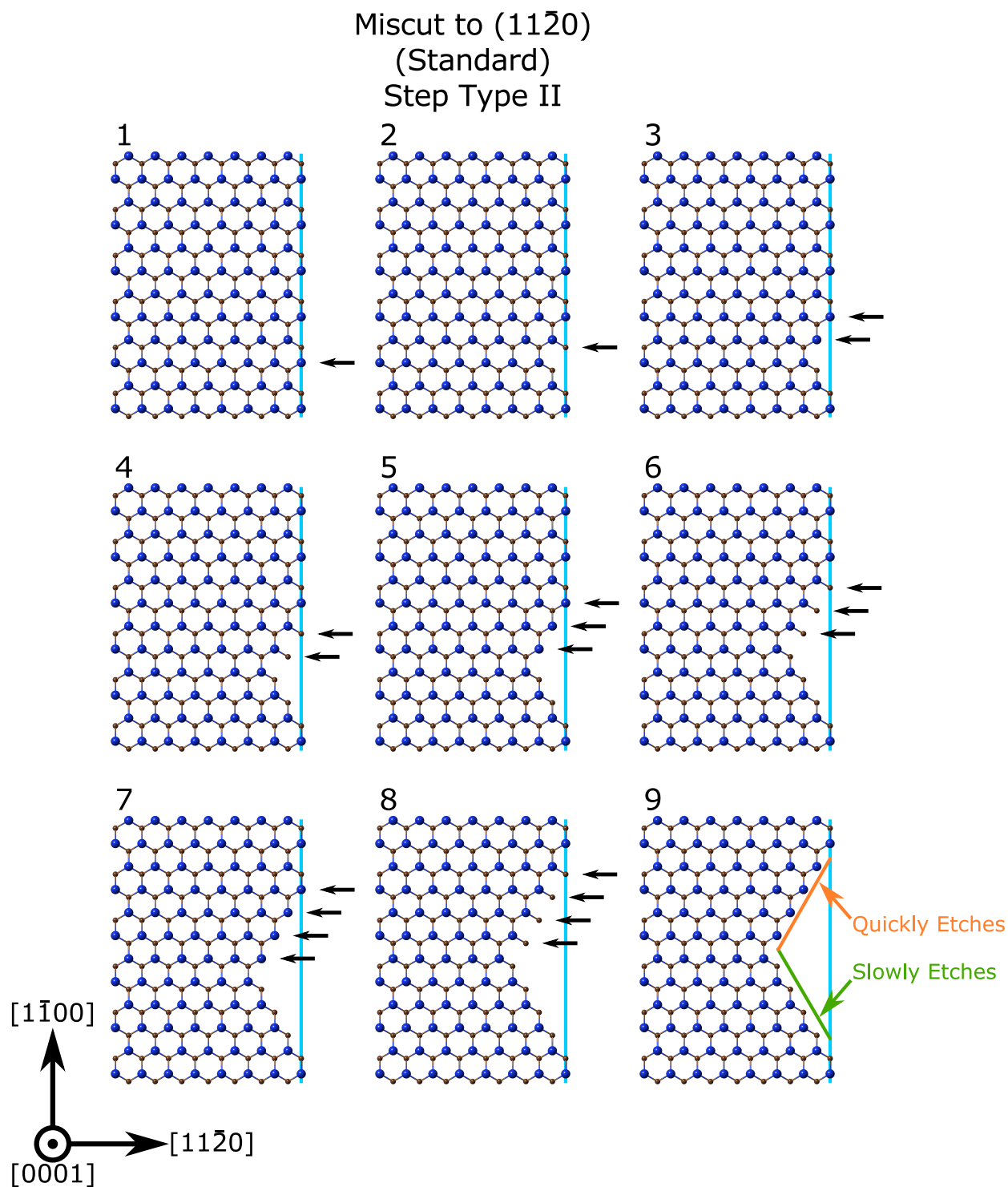


Figure 3.9: A detailed, step by step ideal etch process is depicted for a bilayer of step type II. An ideally, unetched bilayer is shown in frame 1 where the blue line indicates the step edge. In each frame, a black arrow points to an atom located at the step edge that has two dangling bonds. The marked atoms are removed (etched) in the following frame. Frame 9 depicts the same bilayer configuration in Figure 3.7.

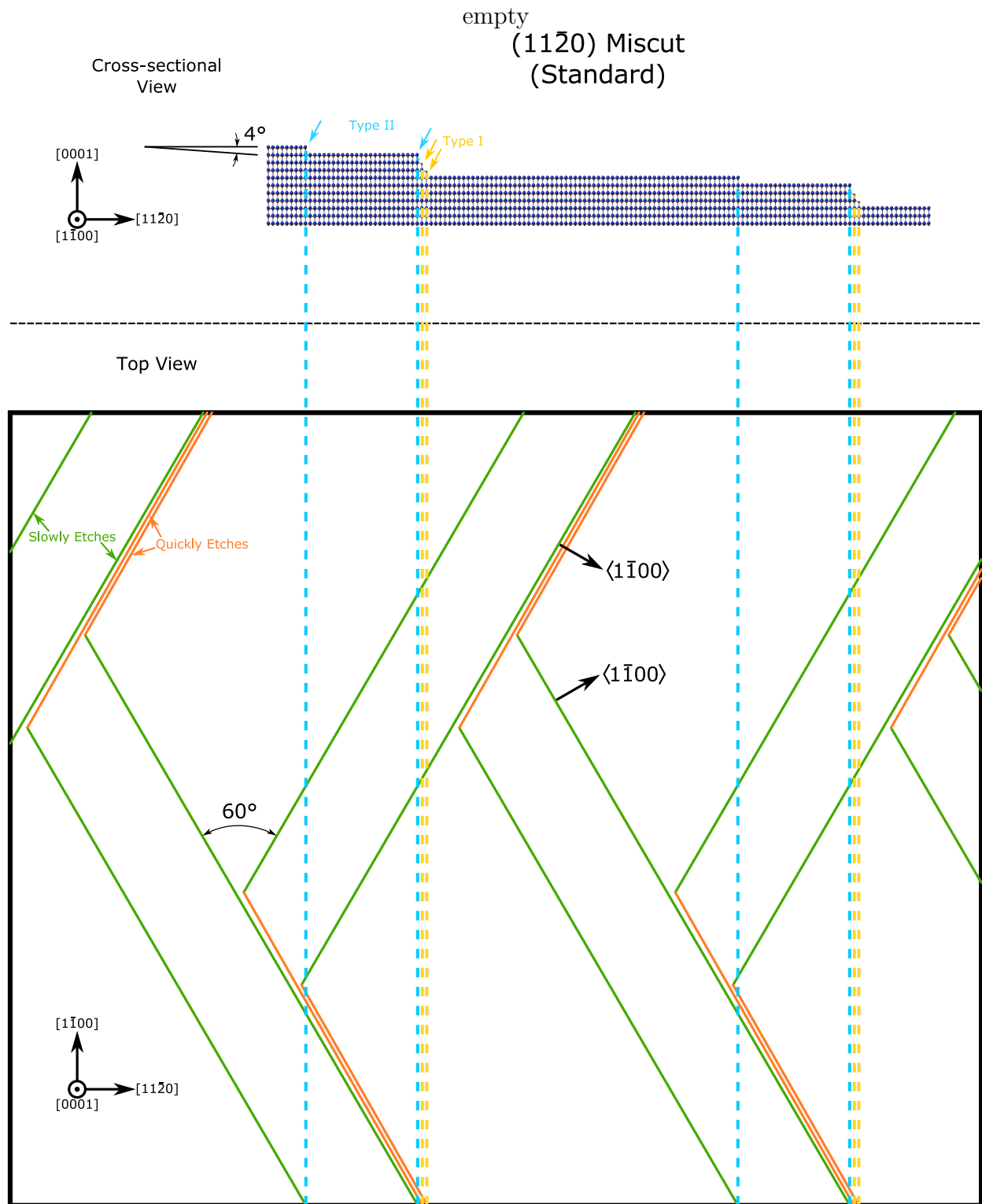


Figure 3.10: A zoomed-out, cross-sectional view of the ideally etched surface steps of a 4H-SiC substrate miscut 4° to the (11 $\bar{2}$ 0) is depicted. Yellow and blue arrows mark type I and type II steps, respectively. On the bottom, a schematic of the ideally etched steps are shown as a top view. The face of the cross-sectional view is equivalent to the bottom edge (black line) of the top view. To guide the eye, dotted yellow and blue lines lead from the visible step edges in the cross-sectional view to the equivalent position on the top view. After ideally etching, both step types transform into coplanar slowly etching green steps and quickly etching orange steps that are rotated by 60° . The green and orange step edges are parallel to {11 $\bar{1}$ 00} planes.

If the ideal etch process for both step types are continued, the etch will create the cross-sectional structure shown in the upper portion of Figure 3.10. As was done for the $(1\bar{1}00)$ miscut substrate in Figure 3.6, a surface can be constructed from how the two step types etch and the surface structure is illustrated in Figure 3.10. The cross-sectional face is represented as the bottom edge of the top view in the lower portion of the figure. Dotted yellow and blue lines denoting step types I and II, respectively, have been drawn from the cross-sectional view to the bottom edge of the top view to help guide the eye. The resulting surface morphology after etching is much more complicated than that found for the $(1\bar{1}00)$ miscut substrates; however, the surface is still composed of familiar step patterns that are comprised of pairs of slowly etching green steps and pairs of quickly etching orange steps that have bunched together underneath a slowly etching green step. Two pairs of green and orange steps are present with one pair parallel to one $(1\bar{1}00)$ and the other pair parallel to an $(1\bar{1}00)$ that is rotated by 60° . Pairs of green steps transform into orange steps and eventually back into green steps again, in a continuous zig-zag pattern across the surface of the substrate. The 60° rotation of these step edges plays an important role in the nucleation of twin orientations of $B_{12}P_2$.

3.4.2 $B_{12}P_2$ Nucleation on 4H-SiC Steps

Zhang, *et al.*^{73,74} found that for $B_{12}As_2$ growth on 4H-SiC miscut 7° to the $(1\bar{1}00)$, the $B_{12}As_2$ crystal likely nucleates on the slowly etching unbunched, isolated green-labeled step riser and grows laterally outward. Here, $B_{12}P_2$ is presumed to ideally nucleate at the same location and in the same way due to its structural similarity to $B_{12}As_2$. A plausible heterostructure of $B_{12}P_2$ nucleation on such a solitary green step edge of a 4H-SiC substrate miscut 4° to the $(1\bar{1}00)$ is shown in Figure 3.11. Only one twin orientation can nucleate on a particular step edge and the epitaxial relationship is locally fixed where $(0001)[1\bar{1}00]_{B_{12}P_2} \parallel (0001)[1\bar{1}00]_{4H-SiC}$, or unambiguously using rhombohedral coordinates: $(111)[1\bar{2}1]_{B_{12}P_2} \parallel (0001)[1\bar{1}00]_{4H-SiC}$.

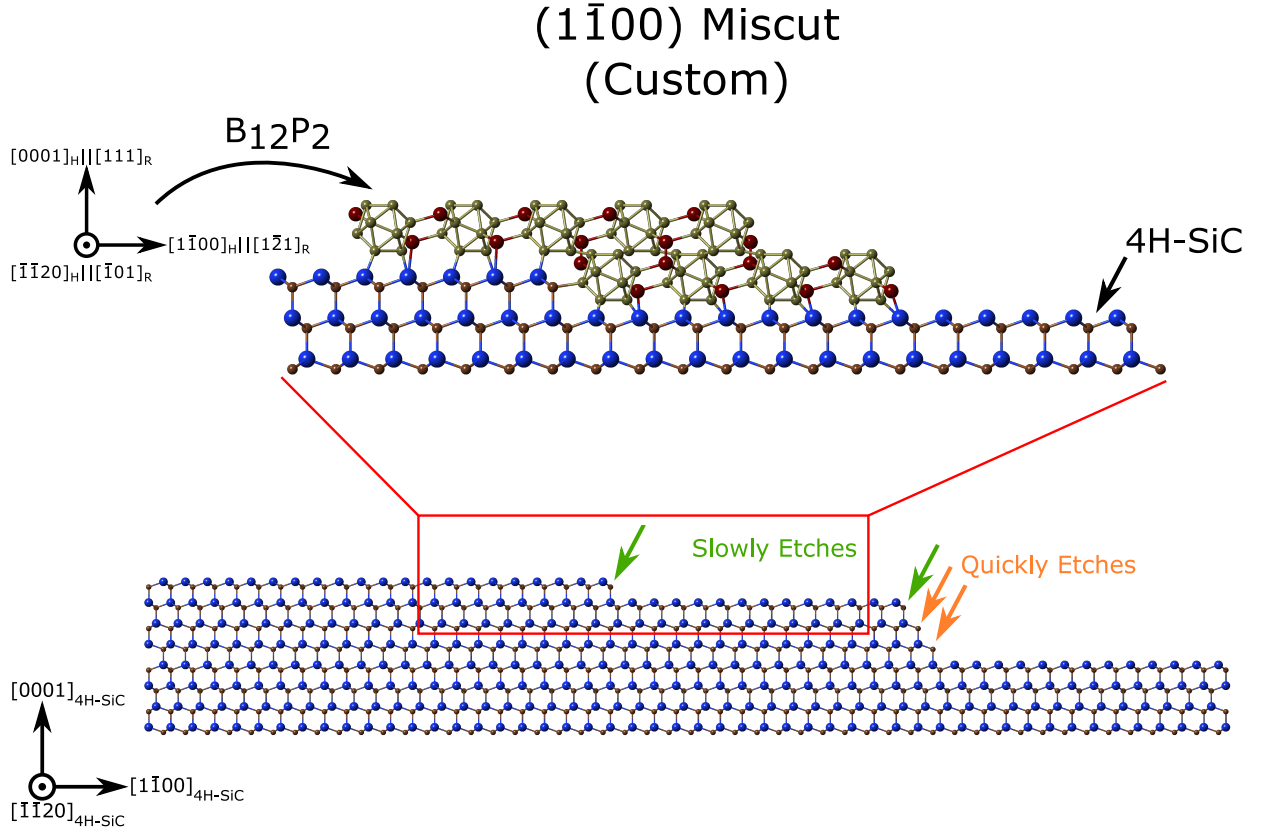


Figure 3.11: A cross-section view of an ideal $B_{12}P_2$ nucleation site is depicted. $B_{12}P_2$ is expected to nucleate at a solitary slowly etching green step edge. A plausible epitaxial bonding arrangement is shown on the step edge.

For substrates miscut to the (11 $\bar{2}$ 0), two competing nucleation sites form on the stepped surfaces (isolated green step edges), which are a result of how the two step types etched. A zoomed-out view of the surface schematic from Figure 3.10 is depicted on the left in Figure 3.12, illustrating the zig-zag step structure. These nucleation sites are rotated by 60° which is the same degree of rotation between the two $B_{12}P_2$ rotational variants. Since $B_{12}P_2$ can nucleate on either of the two step edges, an $B_{12}P_2$ nucleus on one step edge will be rotated by 60° relative to an $B_{12}P_2$ nucleates on the competing step edge. Therefore, $B_{12}P_2$ films grown on 4H-SiC substrates miscut to the (11 $\bar{2}$ 0) will be twinned as was determined in section 3.3.3. A schematic of the nucleation of the two twin orientations is illustrated on the left in Figure 3.12. Triangles were added to the $B_{12}P_2$ structures to help clarify the rotation

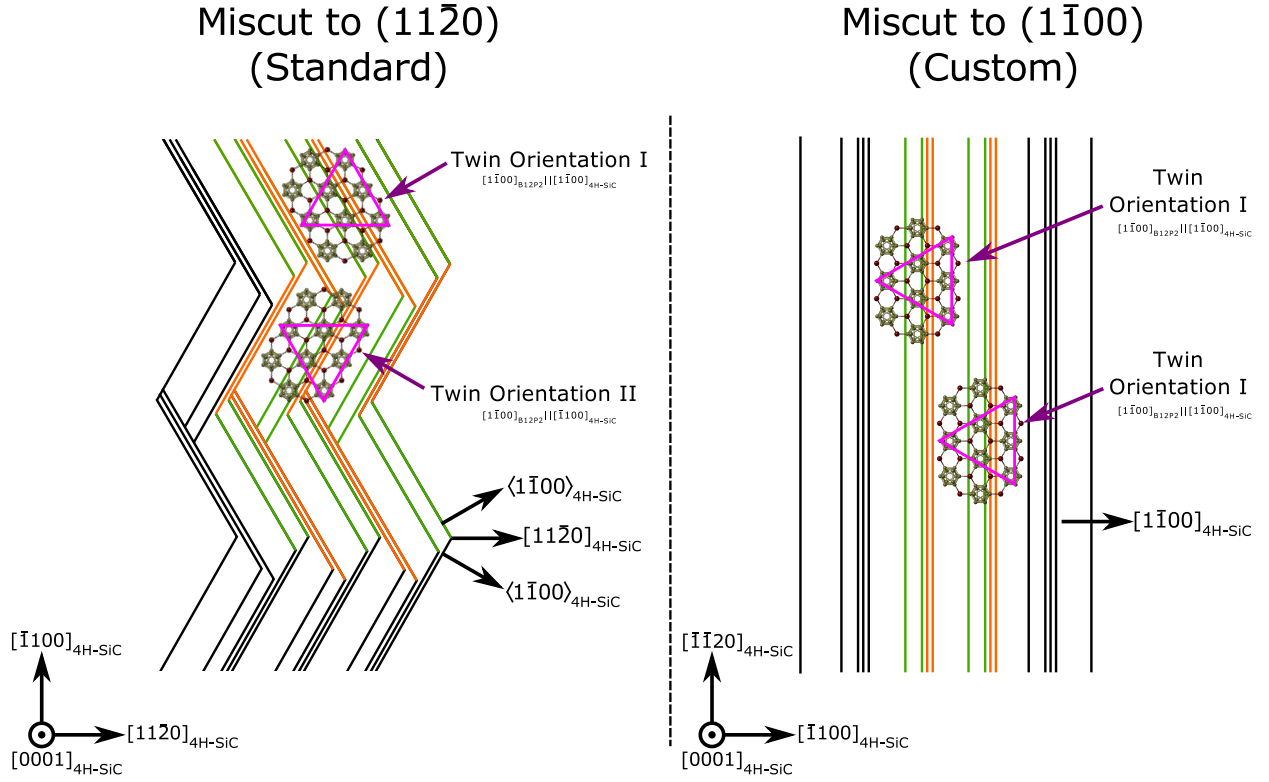


Figure 3.12: Zoomed-out, top view schematic of the ideally etched (0001) 4H-SiC surfaces for substrates miscut 4° to the $(11\bar{2}0)$ (left) and to the $(1\bar{1}00)$ (right). The $(11\bar{2}0)$ miscut substrates have zig-zagged surface steps while the surface steps on $(1\bar{1}00)$ miscut substrates are parallel. Cartoon $B_{12}P_2$ nuclei are placed on nucleation sites (solitary green steps). Triangles are added to the $B_{12}P_2$ structures to help aid in the rotational orientation of the nuclei. On $(11\bar{2}0)$ miscut substrates, $B_{12}P_2$ nucleates in two rotational variants—twin orientation I and twin orientation II—because the step edges are rotated by 60° , the same amount of rotation between $B_{12}P_2$ rotational variants. In contrast, on $(1\bar{1}00)$ miscut substrates, only one twin orientation nucleates because all of the step edges are parallel.

of the crystal structure.

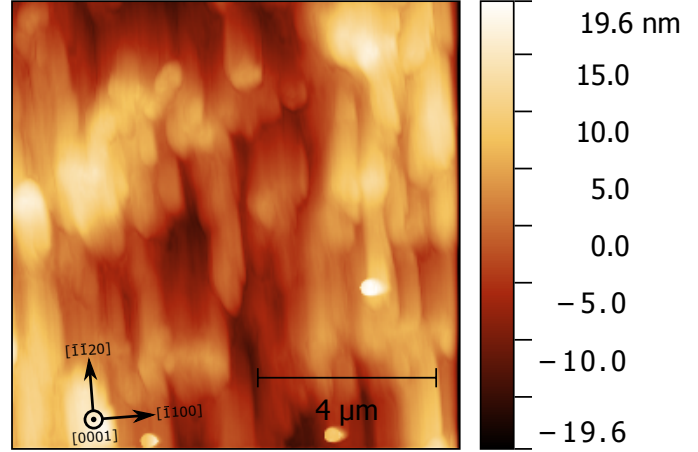
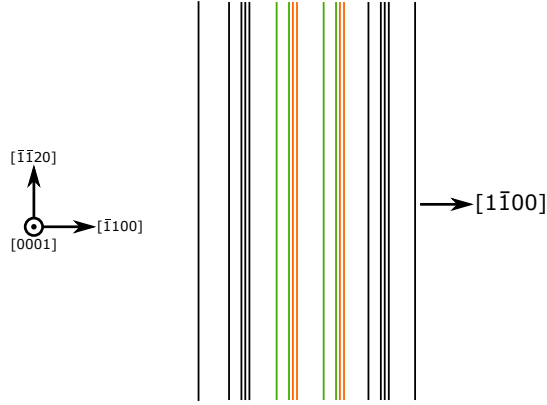
A zoomed-out view of the surface steps on substrates miscut to the $(1\bar{1}00)$ is illustrated on the right side of Figure 3.12. Unlike in $(11\bar{2}0)$ miscut substrates, all of the steps and thus all of the nucleation sites are parallel to one another, and therefore, the crystallographic directions of all $B_{12}P_2$ nuclei must all also be parallel. Regardless of which step edge $B_{12}P_2$ nucleates, only one twin orientation forms and the film will be untwinned.

3.4.3 Evidence for Hypothesized Step Morphologies

The ideal etch mechanism outlined above makes several assumptions: the starting surface is perfectly stepped, the surface only etches at step edges, and perfect control over the step etch rate is achieved. To evaluate whether the ideally etched surface is representative of the actual etched surfaces used during growth of the $B_{12}P_2$ films in this study, substrates of each miscut type were prepared in the same way as those used to grow the $B_{12}P_2$ films. Then, the substrates were imaged by AFM. The substrates were etched at 1600 °C for 15 min in H_2 and then cooled to 1300 °C where 6 sccm of PH_3 was flowed for 2 min before the substrates were cooled back down to room temperature under H_2 flow. AFM images were taken of the surface morphology of the etched substrates and are shown in Figure 3.13 alongside the schematics for the ideally etched steps. While the surfaces are not the perfectly etched steps depicted in the schematic, there is definitely a qualitative resemblance between the actual and ideally etched surfaces. The striations on the $(1\bar{1}00)$ miscut substrate are all largely parallel as predicted by the etch model, and the surface of the $(11\bar{2}0)$ miscut substrate has zig-zag-like structures with step edges that are rotated by about 30° in each direction from the $[11\bar{2}0]$ as the etch model predicts.

For both of the etched substrates, the surface is more hillocky than it is a smoothly descending series of atomic steps. The deviation from the ideal etch model results from less-than-optimal etch and surface preparation conditions. For hillocks to form, etching must take place at locations other than the step edges. The surface etching at 1600 °C is likely a

Miscut to $(1\bar{1}00)$
(Custom)



Miscut to $(11\bar{2}0)$
(Standard)

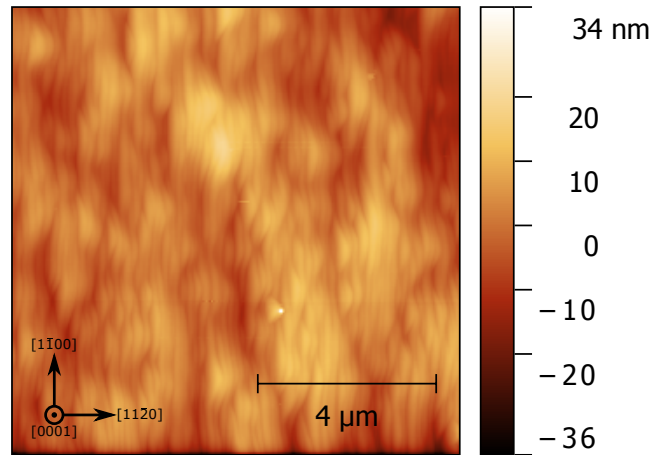
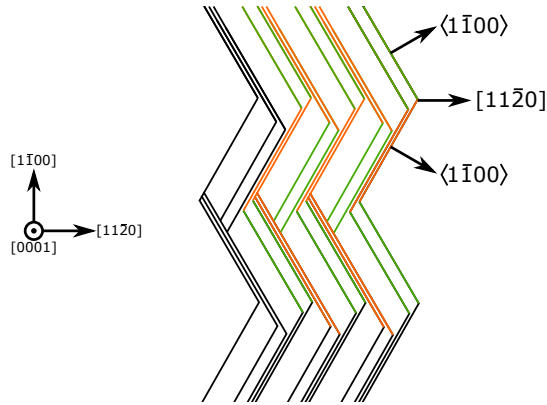


Figure 3.13: *Cartoon depictions of the ideally etched surface morphology of 4H-SiC substrates miscut 4° to the $(1\bar{1}00)$ and to the $(11\bar{2}0)$ are located on the left. AFM images of the surface of each substrate type etched under the conditions used in this study are shown on the right.*

too high of a temperature, and the etch is too aggressive. At such extreme temperatures, surface atoms away from the step edges may etch or even thermally dissociate away from the substrate. Etching under less aggressive conditions should promote etching more similar to the idealized etch model that was outlined in this text. Although the surfaces are hillocked, the substrate is still macroscopically stepped in the direction of the miscut. In the case of the substrate miscut to the $(1\bar{1}00)$, even if opposing twin orientations nucleate on the $(1\bar{1}00)$ side of the hillock and the opposing $(\bar{1}100)$ side of the hillock, the twin that has nucleated on the $(1\bar{1}00)$ side should still dominate. The twin orientation that has nucleated on the $(1\bar{1}00)$ side of the hillock can grow laterally out and away from the substrate due to substrate crystal's tilt. When the twin orientation that has nucleated on the $(\bar{1}100)$ side of the hillock grows laterally out, it will terminate as it grows towards and effectively into the substrate. Twins nucleating on each side of a hillock may be the source of the slight detection of a second twin orientation in the pole figure of the $(1\bar{1}00)$ miscut film.

For $B_{12}P_2$ growth on the ideally etched $(11\bar{2}0)$ miscut substrate, there should be an equal amount of each twin orientation; however, the film is about 70% twin orientation I. The cause for the increased amount of that twin orientation is unknown, but some possible explanations could be that the substrate is not miscut perfectly towards the $(11\bar{2}0)$ or that stacking faults or inclusions of other SiC polytypes influence twin nucleation.

3.5 Conclusions and Future Work

$B_{12}P_2$ films were grown on 4H-SiC substrates miscut 4° to the $(1\bar{1}00)$ and 4H-SiC substrates miscut 4° to the $(11\bar{2}0)$. The films were characterized by XRD $2\theta - \omega$ scans to confirm the out-of-plane epitaxial relationship, XRD rocking curves to evaluate the crystal quality, Laue photography to determine the in-plane epitaxial relationship and characterize the amount of rotational twinning, and XRD pole figures to further measure the degree of rotational twinning. The epitaxial relationship for $B_{12}P_2$ grown on both

types of substrate miscut was $(0001)\langle 1\bar{1}00\rangle_{\text{B}_{12}\text{P}_2} \parallel (0001)\langle 1\bar{1}00\rangle_{4\text{H-SiC}}$ and more specifically $(0001)[1\bar{1}00]_{\text{B}_{12}\text{P}_2} \parallel (0001)[1\bar{1}00]_{4\text{H-SiC}}$ for films grown on 4H-SiC substrates miscut to the $(1\bar{1}00)$ (neglecting the small amount of the twin orientation II). Films grown on $(1\bar{1}00)$ miscut substrate were >99% twin orientation I while films grown on $(11\bar{2}0)$ miscut substrates had a twin density of 70% twin orientation I and 30% twin orientation II. An idealized etch model was described to explain the suppression of twin formation on substrates miscut to the $(1\bar{1}00)$ by explaining how step edges form on 4H-SiC after performing an in-situ etch and then how B_{12}P_2 nucleates on those step edges. The etch model was then verified by imaging the etched 4H-SiC surface by AFM. Since rotational twinning was suppressed on 4H-SiC miscut towards the $(1\bar{1}00)$, this miscut proves to be a superior substrate for hetero-epitaxial growth of B_{12}P_2 .

In future work, a better etch recipe should be developed to prevent the formation of hillocks and to create a stepped surface that more closely resembles the ideally etched surface from the model. An atomically smooth and abrupt interface between B_{12}P_2 and SiC is desired for $p/\text{B}_{12}\text{P}_2$ - n -SiC heterojunction diodes. Measurements of the carrier mobility on twinned and untwinned samples could demonstrate the influence of twin planes on the transport of charge carriers in the epitaxial films. The modification and engineering of the step structure of other types of hexagonal substrates such as AlN or GaN could also potentially be used to control the nucleation and suppression of rotational twins in 3-fold symmetry crystals such as B_{12}P_2 or even in other materials such as cubic (111) compounds.

Chapter 4

Sintered Cr/Pt and Ni/Au Ohmic Contacts to B₁₂P₂

As published in *Journal of Vacuum Science and Technology A* (2015) by C.D. Frye, S.O. Kucheyev, J.H. Edgar, L.F. Voss, A.M. Conway, Q. Shao, and R.J. Nikolić.

4.1 Abstract

Icosahedral boron phosphide ($B_{12}P_2$) is a wide-bandgap semiconductor possessing interesting properties such as high hardness, chemical inertness, and the reported ability to self-heal from irradiation by high energy electrons. Here, we developed Cr/Pt and Ni/Au ohmic contacts to epitaxially-grown $B_{12}P_2$ for materials characterization and electronic device development. Cr/Pt contacts became ohmic after annealing at 700 °C for 30 s with a specific contact resistance of $2 \times 10^{-4} \Omega\text{cm}^2$, as measured by the linear transfer length method. Ni/Au contacts were ohmic prior to any annealing, and their minimum specific contact resistance was $\sim 1\text{--}4 \times 10^{-4} \Omega\text{cm}^2$ after annealing over the temperature range of 500–800 °C. Rutherford backscattering spectrometry revealed a strong reaction and intermixing between Cr/Pt and $B_{12}P_2$ at 700 °C and a reaction layer between Ni and $B_{12}P_2$ thinner than ~ 25 nm at 500 °C.

4.2 Introduction

Boron and phosphorus form two distinct semiconductor compounds, cubic zincblende BP and rhombohedral $B_{12}P_2$, which in addition to having different stoichiometries also have different crystal structures and electronic properties. $B_{12}P_2$, often called icosahedral boron phosphide, is a wide-bandgap semiconductor ($E_g = 3.35$ eV²⁰) composed of boron icosahedra with interlinking phosphorus-phosphorus chains. It possesses many properties such as high hardness and chemical inertness that make it desirable as a semiconductor that can withstand extreme environments. Moreover, $B_{12}P_2$ can reportedly self-heal from intense beta-irradiation.^{7,6} This unusual property makes $B_{12}P_2$ very attractive for a number of technologies, including radiation detection, electronics in harsh radiation environments, and radioisotope batteries—devices that directly convert nuclear energy into electricity.

Recent advancements in the improved hetero-epitaxial growth of a similar rhombohedral boride, $B_{12}As_2$, have been achieved on SiC, including suppression of double-position

twinning^{74,80} and control of p -type doping⁶⁰ (note: n -type conductivity in neither $B_{12}P_2$ nor $B_{12}As_2$ has been reported yet). Hetero-junction pn -diodes of p - $B_{12}As_2/n$ -SiC have also been demonstrated.⁷² However, before $B_{12}P_2$ diodes can be fabricated and characterized, a process for creating low resistance ohmic contacts to p -type $B_{12}P_2$ must be developed.

For many wide-bandgap materials, forming a low resistance ohmic contact is challenging. For instance, p -type GaN contacts typically have specific contact resistances on the order of 10^{-4} – 10^{-6} Ωcm^2 .⁹⁵ Ino *et al.*⁹⁶ recently published a study on the electrical characteristics of various metal contacts to n -type ($n \sim 10^{19}$ cm^{-3}) cubic boron phosphide (BP), reporting specific contact resistances of 10^{-2} – 10^{-5} Ωcm^2 . Wang *et al.*⁶¹ developed Cr/Pt ohmic contacts with a specific contact resistance of 3×10^{-4} Ωcm^2 to $B_{12}As_2$ by annealing at 700 °C. However, there is little data in the literature on metal contacts to $B_{12}P_2$. Use of sintered Al has been mentioned in multiple publications by Kumashiro *et al.*,^{97,26} and while Si has been used to form a hetero-junction diode with $B_{12}P_2$,⁴⁷ the current-voltage characteristics display a nearly ohmic relationship.

While studies on ohmic contacts to BP and $B_{12}As_2$ have been reported, this is the first study on the characterization of ohmic contacts to $B_{12}P_2$, which will enable further material characterization and development of functional $B_{12}P_2$ electronic devices. Here, Cr/Pt and Ni/Au ohmic metal- $B_{12}P_2$ contacts have been developed. Since Cr/Pt forms ohmic contacts to $B_{12}As_2$,⁶¹ the same metal scheme was tested to determine if the process could be extended to $B_{12}P_2$. Additionally, Cr forms conductive borides⁹⁸ and phosphides⁹⁹ of varying composition that are stable to high temperatures.^{100,101} Pt also alloys with both B and P, even forming eutectics below 600 °C.^{102,103} Ni/Au, a well-established ohmic contact to p -type GaN,⁹⁵ was chosen as an alternate metal scheme. Like Cr, Ni forms various stoichiometries of electrically conductive Ni-B alloys¹⁰⁴ and nickel phosphides.¹⁰⁵ Further, Ni readily reacts with and/or dissolves both BP and $B_{12}P_2$,^{106,107,108,109} aiding in the sintering process. However, the nickel phosphides and borides have melting points at temperatures above 800 °C, which may lead to stability at higher temperatures than Cr/Pt. In addition,

Ni has a large work function which may reduce the barrier height. A top Au layer was used to provide a conductive oxide barrier for probing.

4.3 Experimental Methods and Processing

$B_{12}P_2$ was grown epitaxially on on-axis (0001) 6H-SiC substrates via the thermal decomposition of B_2H_6 and PH_3 in H_2 at 1300 °C and a pressure of 100 torr. Si-face, c -plane SiC was chosen due to its relatively low lattice mismatch of 2.54% and high thermal stability compared to Si. A detailed report on the epitaxial growth of $B_{12}P_2$ on SiC will be provided in a future publication. To prevent current flow through the substrate during electrical measurements, vanadium-doped, semi-insulating SiC was used. The $B_{12}P_2$ films were nominally 2 μm thick as measured by cross-sectional SEM. The hole concentration was $8 \times 10^{18} \text{ cm}^{-3}$ as determined from Hall Effect measurements using the Van der Pauw method and Ni/Au ohmic contacts fabricated as described below.

Annealing epitaxial $B_{12}As_2$ above 600 °C drastically reduces its sheet resistance.^{60,61} This effect has also been observed in $B_{12}P_2$ films grown in our group, which may influence the electrical properties of the metal-semiconductor interface independently of any sintering effects. To decouple the effects of annealing-induced changes in the sheet resistance from the sintering of metal contacts, the $B_{12}P_2$ films were annealed in Ar at 800 °C for 30 s before any metal contacts were deposited.

Cr/Pt (500Å/1000Å) and Ni/Au (1000Å/1000Å) were evaluated as ohmic contacts to $B_{12}P_2$. The sheet resistance and specific contact resistance were measured by the linear transfer length method (TLM). The TLM patterns nominally consisted of $100 \times 100 \mu m^2$ metal pads separated by spacings of 5, 10, 25, 40, 50, and 75 μm (see the inset of Figure 4.1). The metal contacts were formed via photolithography and electron-beam evaporation. The $B_{12}P_2$ films were cleaned in an O_2 plasma, dipped in BOE (buffered oxide etch) for 10 s, quickly rinsed in deionized water, and blown dry with N_2 immediately prior to loading

into the electron-beam evaporator.

After the metal was patterned, the samples were annealed in Ar in a rapid thermal annealing furnace. The films were annealed for 30 s at sequentially higher temperatures in 100 °C increments. Current-voltage (I - V) measurements were taken after each anneal on three adjacent sets of TLM patterns. The purpose of these measurements was to determine the minimum anneal temperature needed to form ohmic contacts for a given metal scheme and to test the effect of anneal temperature on the specific contact resistance. After ohmic conduction was achieved, the contact resistance was extracted from the current-voltage plots in the range of -1 V to +1 V with standard techniques.¹¹⁰

Because Rutherford backscattering spectrometry (RBS) is a nondestructive technique that provides depth-resolved information on individual elements independently of one another, it was employed to study the interface between the metals and $B_{12}P_2$ and to delineate the diffusion of metals into $B_{12}P_2$ and/or the diffusion of B or P into the metal. Since RBS may induce changes in the electrical properties of the film or contacts, separate samples were used for RBS analysis. Measurements were repeated on the same samples before and after annealing. They were done with a 2 MeV $^4\text{He}^+$ ion beam incident normal to the sample surface and a detector located at 164° from the incident beam direction.

4.4 Results and Discussion

The conduction mechanism between a metal and a semiconductor can be predicted by comparing the thermal energy, kT , with the characteristic energy, E_{00} , which is a strong function of the carrier concentration.¹¹¹ For $B_{12}P_2$ with a hole concentration of $8 \times 10^{18} \text{ cm}^{-3}$, $E_{00} \approx kT$. In this case, the conduction mechanism is in the thermionic field emission regime prior to sintering.

Despite the high background doping level in the $B_{12}P_2$ films, the carrier concentration is not large enough to facilitate pure field emission. Thus, the barrier height must be lowered

Table 4.1: *The work function, optimum anneal temperature (for 30 s anneals), and the corresponding specific contact resistance for the metals studied here.*

	Cr/Pt 500Å/1000Å	Ni/Au 1000Å/1000Å
Work Function ¹¹²	4.5/5.65 eV	5.15/5.1 eV
Anneal Temperature	700 °C	500 °C
Specific Contact Resistance	$2 \times 10^{-4} \Omega\text{cm}^2$	$3 \times 10^{-4} \Omega\text{cm}^2$

by choosing a high work function metal or the contacts must react with and/or effectively dope the surface of the B_{12}P_2 film to induce ohmic conduction. With this information in mind, Cr/Pt and Ni/Au are evaluated. The results are summarized in Table 4.1.

4.4.1 Cr/Pt Contacts

Cr/Pt contacts were annealed at 400, 500, 600, and 700 °C for 30 s at each temperature. After annealing at 700 °C, conduction became ohmic. The progression of the I - V characteristics can be seen in Figure 4.1. The I - V curve changes only slightly after the 400 and 500 °C anneals but becomes progressively linear after the 600 and 700 °C anneals. At 700 °C, the Cr/Pt contacts visibly react with the B_{12}P_2 film, apparently even wetting it (Figure 4.2(b)). Cr does not form a eutectic with B, P, or Pt below 1300 °C^{100,101,113} and by itself is unlikely to cause wetting of the contact to the semiconductor. However, Pt readily forms phosphides that have melting points below 700 °C and as low as 590 °C.¹⁰³ The temperature of these phase changes corresponds well to the changes in electrical properties and surface morphology observed here.

Figure 4.3 shows the RBS spectra collected before any heat treatment of the contacts and after annealing at 700 °C for 30 s. Prior to annealing, Cr and Pt form discrete peaks,

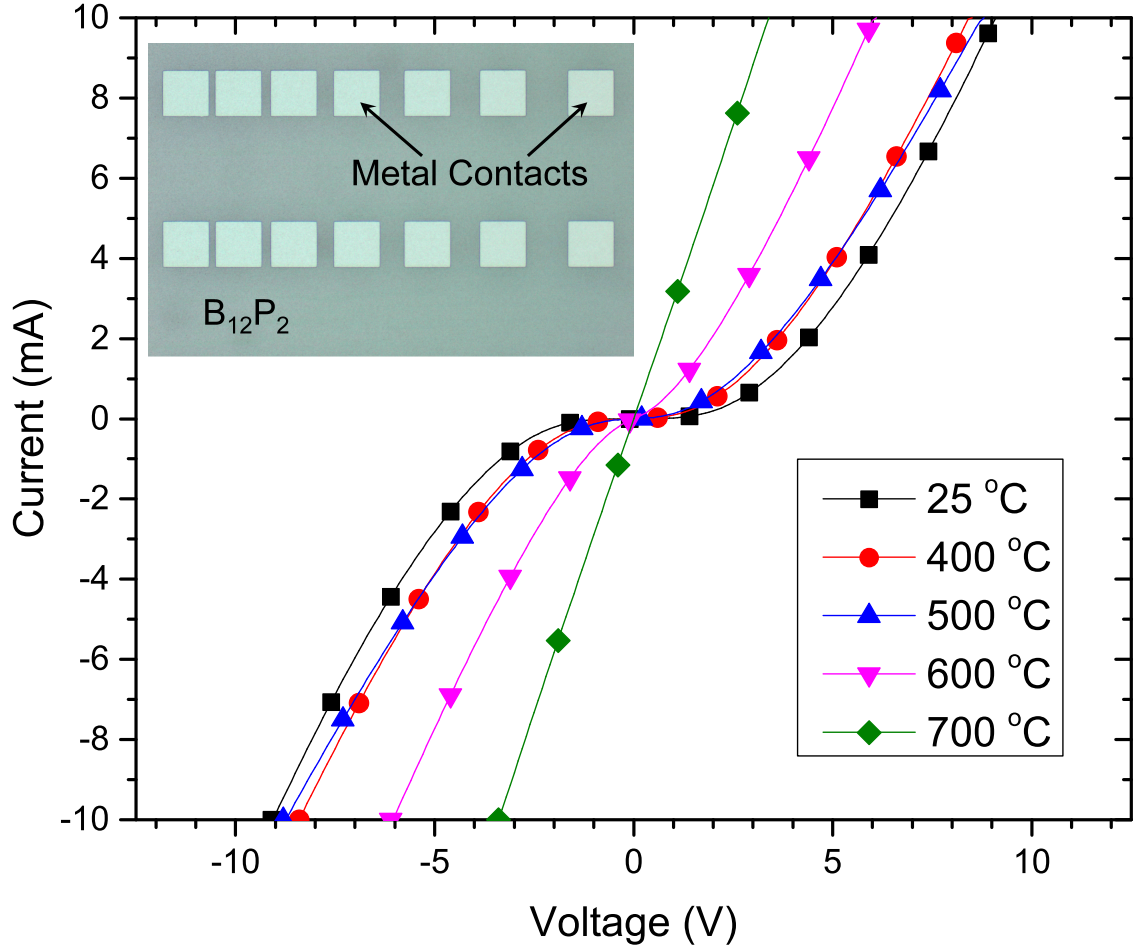


Figure 4.1: The progression of the current-voltage curve for Cr/Pt contacts with a spacing of $10\ \mu\text{m}$ as they are annealed at subsequently higher temperatures, as indicated in the legend. Inset is an optical micrograph of two sets of TLM patterns. Each metal pad is nominally $100 \times 100\ \mu\text{m}^2$.

corresponding to non-intermixed Cr and Pt layers. Also, sharp B and P edges can be identified. The signals of the Cr, P, and B edges (roughly located at 1.36, 1.05, and 0.35 MeV, respectively) are shifted to energies lower than the surface peak energies denoted by arrows in Figure 4.3 because they are not located at the sample surface but are buried beneath other layers. After annealing, Cr, Pt, P and B peaks are dramatically broadened. The large Pt shift to lower energies (i.e., to larger depths from the sample surface) represents its diffusion through the Cr layer to the underlying $B_{12}P_2$. The broadening of the Cr peak is consistent with such inter-diffusion. Both B and P edges are shifted to higher energies,

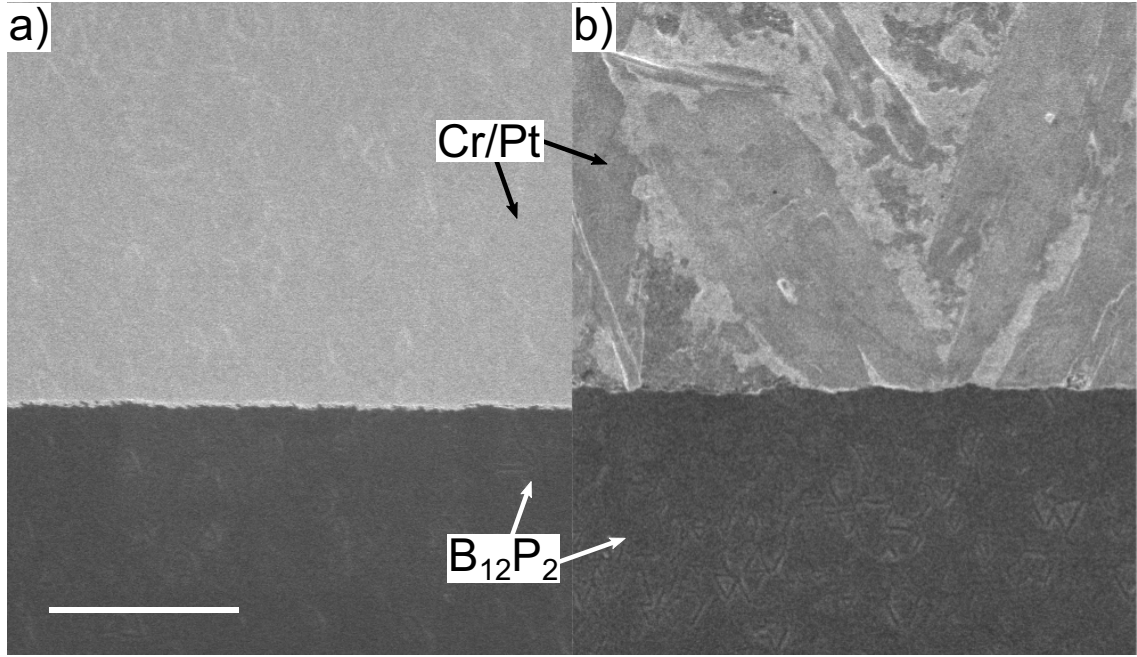


Figure 4.2: SEM micrograph of Cr/Pt contact edges a) before annealing and b) after annealing at 700 °C for 30 s. The contact is smooth and uniform prior to annealing, and the morphology of the contact becomes much rougher after the anneal. The scale bar is 6 μm .

indicating that not only does B₁₂P₂ react with Cr/Pt, but both B and P atoms are mobile at 700 °C and rapidly diffuse toward the surface. P diffuses completely to the sample surface, as evidenced by a peak at 1.20 MeV, corresponding to scattering from P atoms at the sample surface. In addition to the morphology change, the large amount of mixing and fast diffusion of the species involved at this temperature are consistent with the formation of a liquid eutectic.

After annealing at 700 °C for 30 s, the specific contact resistance was $2 \times 10^{-4} \Omega\text{cm}^2$. In an attempt to further lower the contact resistance, the contacts were annealed repeatedly at 700 °C in 30 s increments. Higher annealing temperatures were avoided to prevent dewetting and lateral spreading of the contact. After annealing for two cumulative minutes at 700 °C, the contact resistance did not decrease but rather slightly increased to $3 \times 10^{-4} \Omega\text{cm}^2$ with no further change in surface morphology.

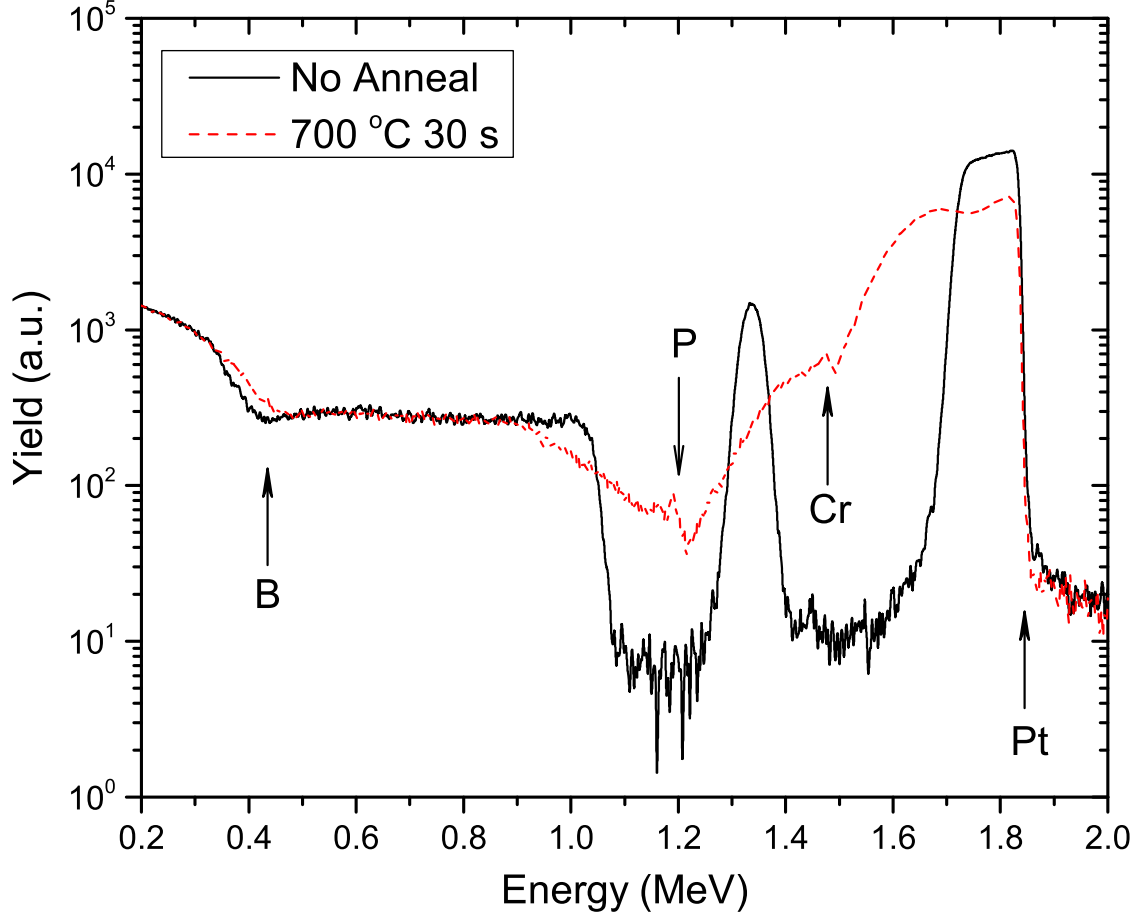


Figure 4.3: Semi-log plot of RBS spectra for Cr/Pt contacts before any heat treatment and after annealing at 700 °C for 30 s. The positions of the surface peaks of Pt, Cr, P, and B are denoted by arrows.

The minimum specific contact resistance for Cr/Pt to $B_{12}P_2$ in this study is similar to the minimum values of $\sim 2\text{-}3 \times 10^{-4} \Omega\text{cm}^2$ reported by Wang *et al.*⁶¹ for Cr/Pt contacts to $B_{12}As_2$. In both studies, the lowest contact resistance is attained after annealing at 700 °C for 30 s. $B_{12}P_2$ and $B_{12}As_2$ could be expected to behave similarly due to their similar structure and comparable band gaps of 3.35²⁰ and 3.37 eV,¹¹⁴ respectively. Also, since both materials are largely composed of B, the contact resistances may also be dominated by B-Cr and B-Pt interactions, thus masking differences between each material. In contrast, however, Cr/Pt contacts to $B_{12}As_2$ are suggested to be ohmic before annealing,⁶¹ while Cr/Pt contacts to $B_{12}P_2$ only become ohmic after annealing at 700 °C.

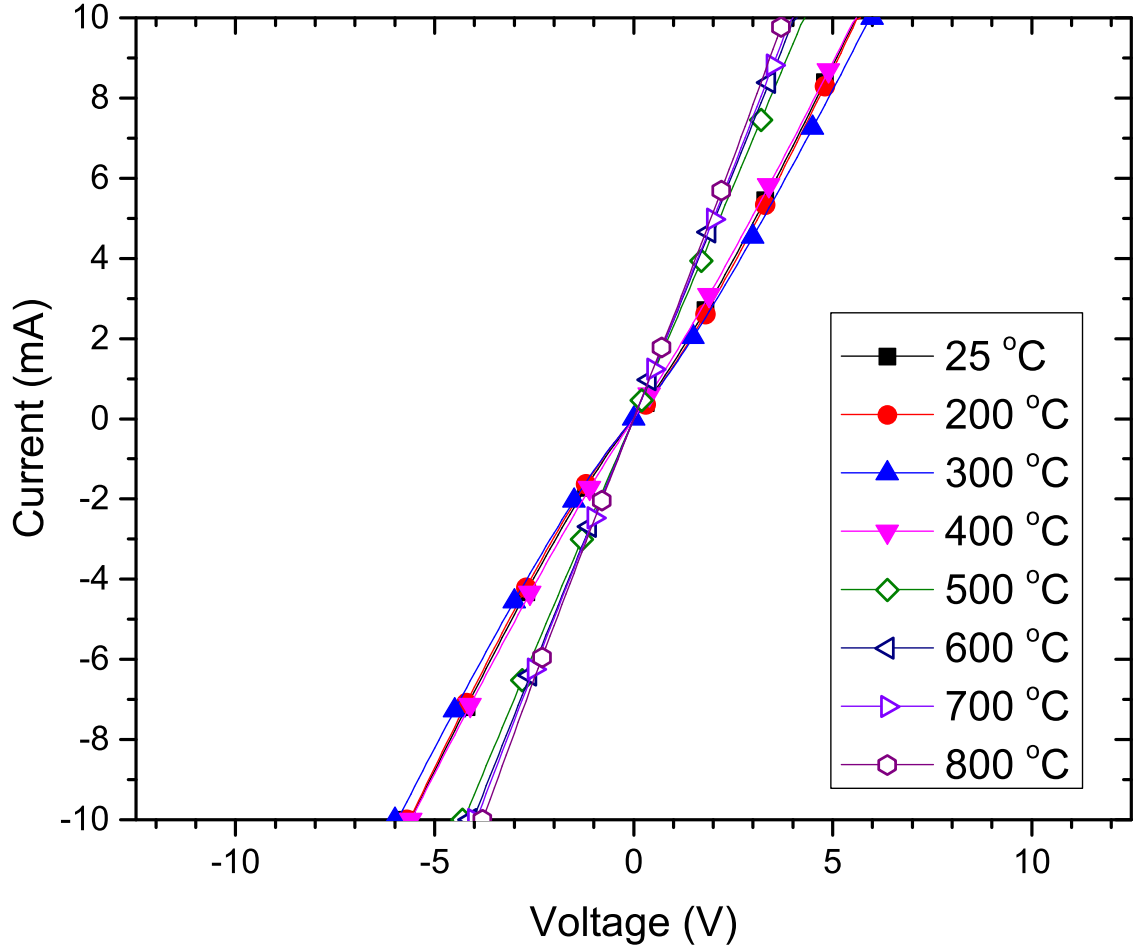


Figure 4.4: *The progression of the current-voltage curve for different annealing temperatures for Ni/Au contacts with a spacing of 10 μm . After annealing at 500 $^{\circ}\text{C}$ for 30 s, the curves become steeper (open markers), a result of reducing the contact resistance.*

4.4.2 Ni/Au Contacts

The Ni/Au contacts were annealed sequentially at 200, 300, 400, 500, 600, 700, and 800 $^{\circ}\text{C}$ for 30 s at each temperature. As can be seen in Figure 4.4, the contacts are ohmic before any annealing. The annealing progression of the I - V curve can be broken into two regimes. In the first regime, annealing up to 400 $^{\circ}\text{C}$ causes essentially no change in the I - V curve. A step change in the I - V characteristics occurs after annealing at 500 $^{\circ}\text{C}$ for 30 s marking a second regime where the specific contact resistance decreases by an order of magnitude. Subsequently higher temperature anneals, however, do not drastically affect

the I - V curve. This effect is better illustrated in Figure 4.5, showing the specific contact resistance as a function of anneal temperature, with specific contact resistance values of ~ 2 - $4 \times 10^{-3} \Omega \text{cm}^2$ and ~ 1 - $4 \times 10^{-4} \Omega \text{cm}^2$ in the low and high temperature regimes, respectively. The specific contact resistance is only slightly lowered by annealing above 500 °C. Such a step-like change in the annealing temperature range of 400-500 °C is most likely due to a metal-semiconductor interfacial reaction.

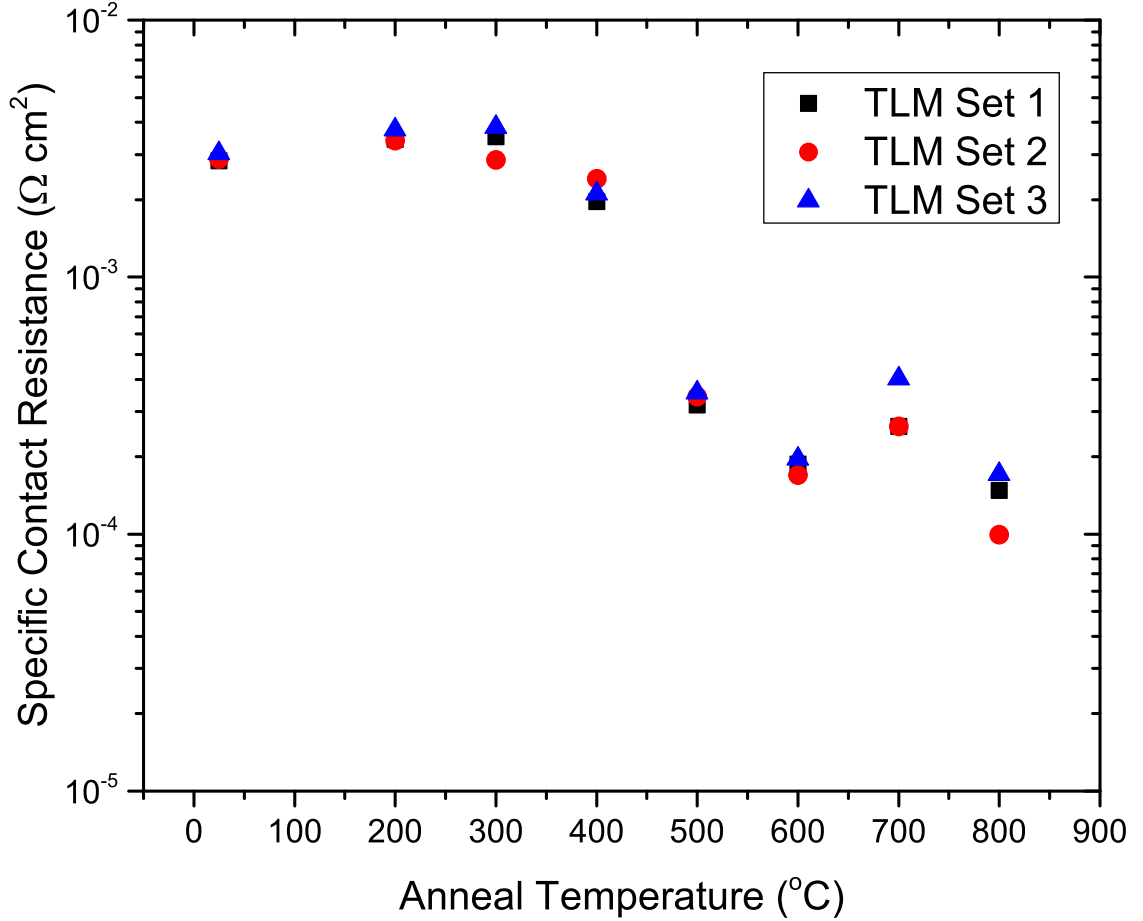


Figure 4.5: *The change in the specific contact resistance of Ni/Au contacts as a function of anneal temperature. Three sets of TLM patterns were tested after each anneal.*

After annealing at 800 °C for 30 s, the metal contacts display visible signs of reaction with B_{12}P_2 around the edges of contact pads. Figure 4.6 shows the edge of a Ni/Au contact prior to annealing and the edge of two contacts originally spaced 5 μm apart after annealing

at 800 °C for 30 s. The edge of the contacts clearly diffuses outward, and droplets form around the periphery, suggesting that the edge reaches a eutectic during the annealing. From the Ni-Au phase diagram,¹¹⁵ the droplets at the edge cannot be a result of a eutectic caused solely by the metals since the Ni-Au eutectic is above 950 °C. Therefore the metal must be reacting with the underlying $B_{12}P_2$. Since none of the binary phase diagrams of the elements of interest have eutectics below 850 °C,^{116,117} the droplets must be a three or more component mixture. The center of the contact remains intact but has speckles over the surface (Figure 4.6(b)). This may be caused by Ni diffusion and segregation at the sample surface, which is common for Ni/Au contacts on other materials such as GaN.^{118,119,120,121}

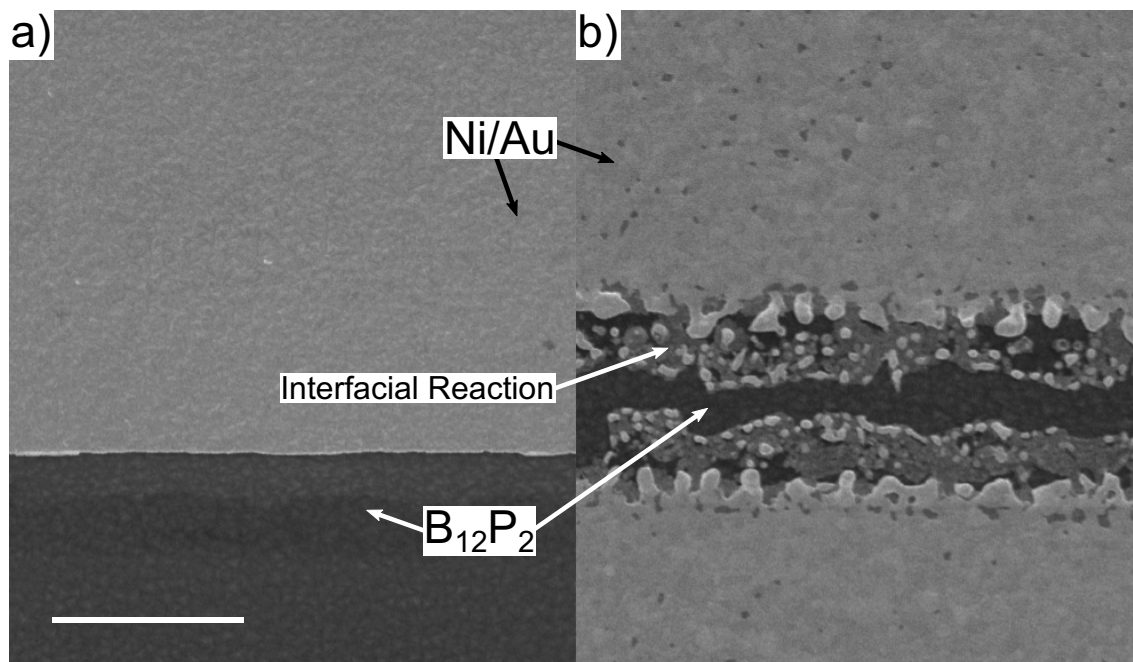


Figure 4.6: SEM micrograph of a) Ni/Au contact edges before annealing and b) space between two Ni/Au contacts originally 5 μm wide after annealing at 800 °C for 30 s. The edges of the contacts become rough and spread outward after annealing. The scale bar is 6 μm .

To further investigate the interfaces in the Au/Ni/ $B_{12}P_2$ system, RBS was performed on a sample before any heat treatment and after the 500 °C anneal, which caused a major change in the I - V characteristics. The RBS spectra are shown in Figure 4.7. Before annealing, the

spectrum reflects non-intermixed layers of Au and Ni on $B_{12}P_2$. Again, the Ni, P and B peak edges (roughly located at 1.45, 1.0, and 0.32 MeV, respectively) are shifted to lower energies since those elements are located beneath the sample surface. During annealing, Au and Ni layers inter-diffuse, as indicated by the broadening of the Au peak to lower energies and the Ni peak to higher energies. In addition, after the anneal, a small, sharp Ni peak is present at the energy corresponding to the sample surface, confirming Ni diffusion to the surface of the contact. A slight broadening of the Ni peak to lower energies after the 500 °C anneal suggests lateral non-uniformity in the Ni layer thickness. This is consistent with SEM observations (Figure 4.6(b)). The fact that RBS signals from B and P are unchanged upon annealing at 500 °C indicates that the reaction layer thickness and diffusion length of these elements must be less than ~ 25 nm—the detection limit of this RBS measurement. In spectra taken after anneals up to 800 °C (not shown), the P peak is shifted to higher energies and confirms an increase of the reaction layer thickness.

The above results show that annealing at 500 °C for 30 s is sufficient to lower the Ni/Au contact resistance without spreading of the metal contacts along the $B_{12}P_2$ surface. This anneal temperature is also low enough to avoid the annealing-induced reduction in sheet resistivity reported by Wang *et al.*⁶¹ while still attaining reasonably low contact resistances. Hence, annealing at 500 °C for 30 s is the optimum procedure in this study.

4.4.3 Comparison of Ni/Au and Cr/Pt Contacts

Ni/Au and Cr/Pt contacts differ in several key ways. First, unlike Cr/Pt, the as-deposited Ni/Au contacts are ohmic. The measured sheet resistance between the Cr/Pt sample and Ni/Au sample are not significantly different, and variations in the $B_{12}P_2$ conductivity cannot be attributed for the difference in conduction. In fact, the sheet resistance for the Ni/Au film is slightly greater ($3.2 \times 10^3 \Omega/\square$ vs. $1.8 \times 10^3 \Omega/\square$ for Cr/Pt). One possible explanation for the difference in the conduction mechanism for the as-deposited condition is that Ni has a higher work function than Cr (as shown in Table 4.1) and lowers the barrier height. A

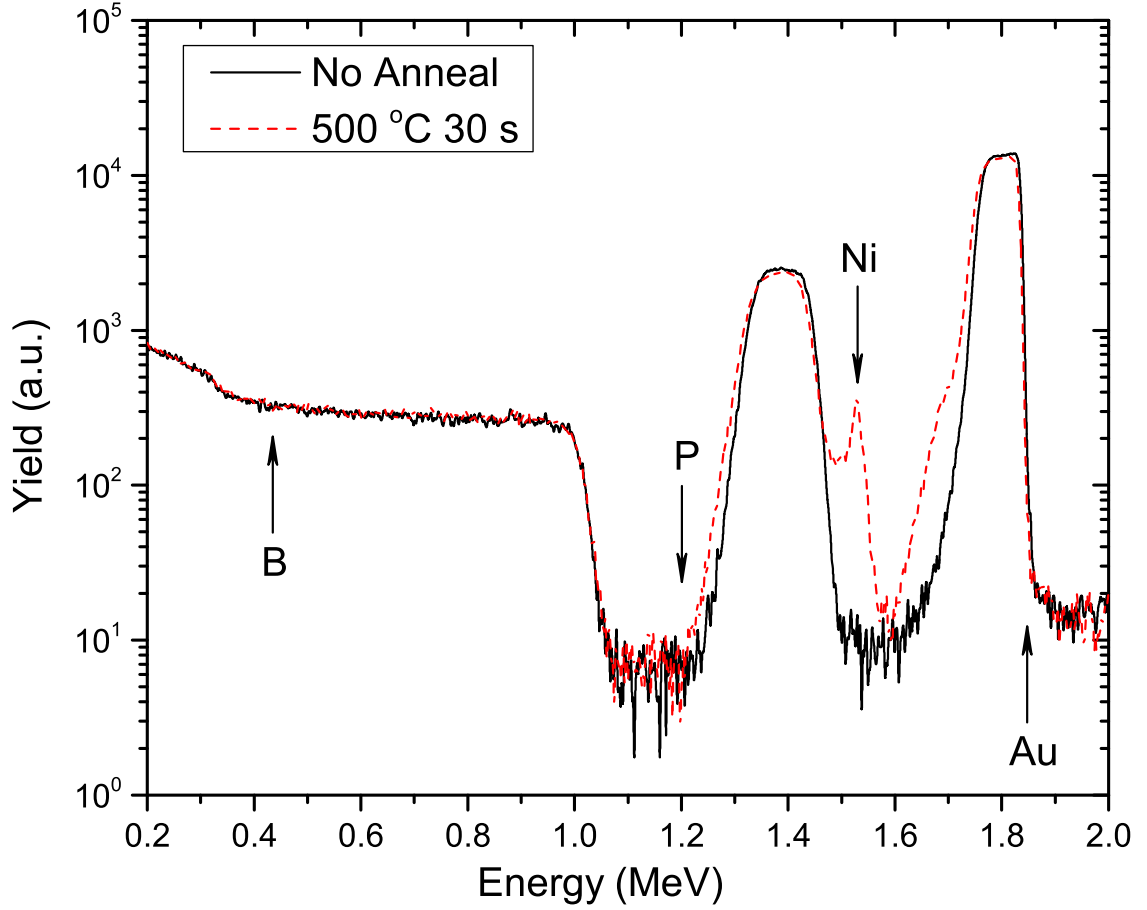


Figure 4.7: *Semi-log plot of RBS spectra for Ni/Au contacts before any heat treatment and after annealing at 500 °C for 30 s. The positions of the surface peaks of Au, Ni, P, and B are denoted by arrows.*

second explanation is that Cr is more susceptible to oxidation (for instance, from residual water vapor in the metal evaporation system) and could form an oxide barrier between $B_{12}P_2$ and Cr. Another difference between the Ni/Au and Cr/Pt contacts is the alloying characteristics necessary for low resistance contacts. The Cr/Pt contacts not only need to react with the surface of $B_{12}P_2$ to become ohmic, but the contacts must react to a much greater degree than Ni/Au to achieve a specific contact resistance on the order of $10^{-4} \Omega\text{cm}^2$. Further, Cr/Pt contacts redistribute both B and P throughout the depth of the contact. At 500 °C, B and P are essentially immobile in the Ni/Au system.

4.5 Conclusion

Cr/Pt and Ni/Au ohmic contacts to p -type $B_{12}P_2$ were developed. Cr/Pt contacts became ohmic after annealing at 700 °C for 30 s with a specific contact resistance of $2 \times 10^{-4} \Omega\text{cm}^2$. RBS demonstrates that Cr, Pt, B, and P intermix before ohmic conduction is achieved. Ni/Au contacts, however, are ohmic in the as-deposited condition and have a specific contact resistance of $3 \times 10^{-4} \Omega\text{cm}^2$ after annealing at 500 °C for 30 s. RBS indicates that the reaction layer between Ni and $B_{12}P_2$ is less than ~ 25 nm thick and that Ni diffuses to the sample surface. Ni/Au contacts display superior properties than Cr/Pt contacts, including ohmic conduction prior to annealing, better thermal stability, and a similar contact resistance at a lower anneal temperature that is also below the observed temperature that causes a reduction in sheet resistance in icosahedral borides.

In future work, increasing the dopant level in $B_{12}P_2$ may aid in reducing the specific contact resistance. Si, a p -type dopant in $B_{12}As_2$, could be co-evaporated with Ni. Alternatively a thin Si film could be evaporated prior to Ni evaporation. While sintering the contact, Si may diffuse into the $B_{12}P_2$ directly beneath the contact, locally increase the doping concentration, and lower the contact resistance. Such a scheme may become even more important when creating ohmic contacts to $B_{12}P_2$ that has a lower background doping level.

Chapter 5

Identification and Quantification of Impurities Using Secondary Ion Mass Spectrometry

5.1 Introduction

Impurities strongly influence the electronic properties of a semiconductor. Foreign atoms in the crystal can act as dopants, introduce deep levels in the bandgap that can trap charge carriers, or become scattering sites that lower the charge carrier mobility, μ . While appropriate impurities, which lie near the conduction or valence band (see Figure 5.1), must be intentionally introduced to modulate the carrier concentration and thus the material's conductivity, background doping must be minimized as background impurities can compensate intentionally added dopants. Intentional doping must overcome the background level to change the conductivity of the crystal so that the desired conductivity can be controlled over a wide range. Further, impurities that create deep energy levels can reduce the effective carrier concentration and shorten the lifetime of carriers, interfering with device performance. Even impurities that are not effective dopants and which do not form deep levels can still act as scattering sites and reduce the mobility. Therefore, control over impurities in the growth of B_{12}P_2 is essential to improving the crystal quality and the fabrication of devices.

In this study, impurities in the B_{12}P_2 films were identified and quantified by secondary ion mass spectrometry (SIMS). The data shows that C, Si, and O are present in very high amounts and that C and Si originating from the 4H-SiC substrate and graphite susceptor are the likely impurities causing large hole concentrations which are greater than $1 \times 10^{18} \text{ cm}^{-3}$. Replacing known impurity sources with higher purity and more stable materials reduced the O and C concentrations, but the Si, C, and O background impurity concentrations were still $> 1 \times 10^{18} \text{ cm}^{-3}$. C impurity in the Zr susceptor is likely the remaining source of C, and Zr metal may reduce the SiO_2 components of the reactor thus releasing Si. The O source is still unknown.

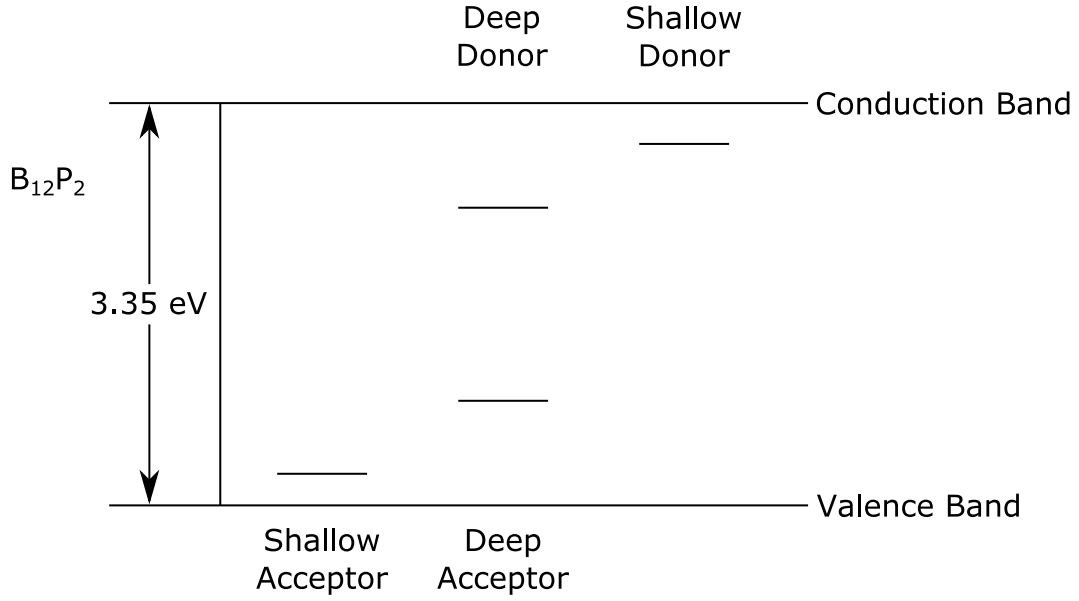


Figure 5.1: A schematic of the conduction and valence band in $B_{12}P_2$ depicting the relative positions of shallow and deep donors and acceptors. Shallow donors and acceptors are desired as dopants because the ionization energy is low and the carriers can be ionized at moderate temperatures.

5.2 Overview of Secondary Ion Mass Spectrometry (SIMS)

SIMS is a common technique to measure small impurity concentrations in thin films. Advantages of SIMS include impurity detection capabilities down to parts per billion, the ability to measure impurity concentrations as a function of depth from the film surface, and a wide dynamic range of detection (up to 6 orders of magnitude). SIMS works by bombarding a solid surface with a beam of positively charged ions (typically Cs^+) or negatively charged ions (typically O^-). As seen in Figure 5.2, the primary ions from the ion beam impact the sample surface, the sample atoms are sputtered in a spray of neutral and ionized atoms (secondary ions)). Some elements are more easily ionized by positive ions while others are more readily ionized by negative ions. Thus, depending on the impurity element of interest, the correct ion beam must be selected. After being ejected from the surface, the secondary

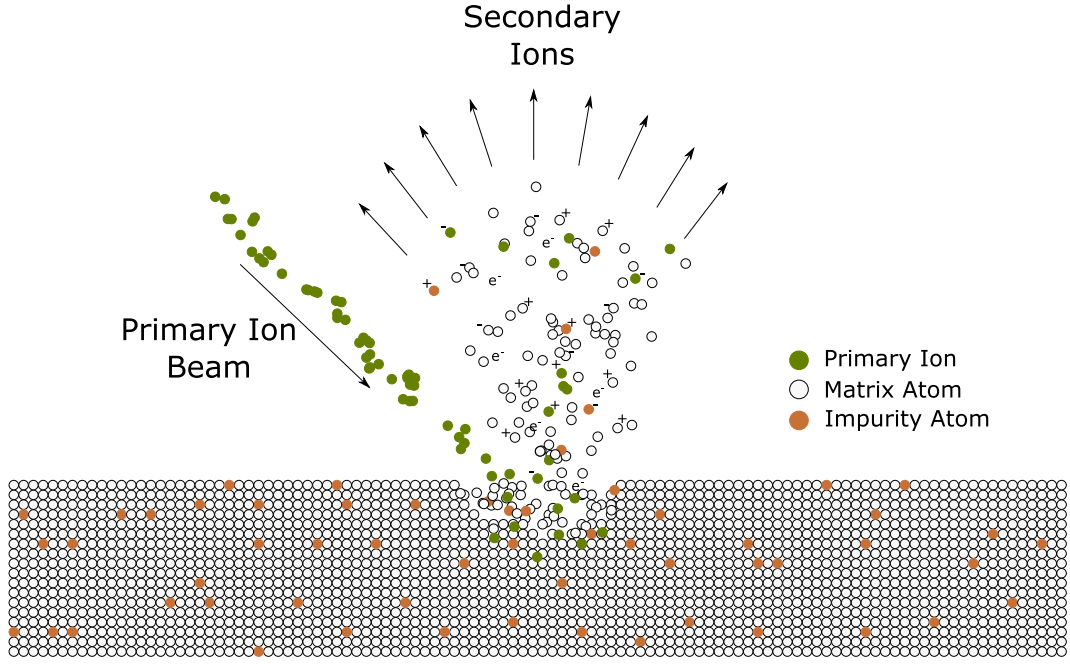


Figure 5.2: A schematic of the physical process of sputtering a sample surface during SIMS. A primary beam (Cs^+ or O^- in this study) sputters the sample surface, generating secondary ions of the matrix material (B and P in this study) and of impurities atoms.

ions are then accelerated to a mass spectrometer where the ions are sorted by their atomic mass and then counted. Depth profiles can be generated by correlating the start and end of the sputter time to the sputtered depth which can be measured using standard profilometry techniques. To quantify the concentration of impurities in the material (e.g. in atoms/cm^3), the count rate in the mass spectrometer must be calibrated. This is typically done by creating standards samples with a known concentration of impurities. By sputtering the standard, the count rate of that impurity can be calibrated to the known impurity concentration in that material. Details on standard creation are discussed in section 5.5.

5.3 Survey of Background Impurities

Before intentional impurities can be introduced into the crystal, the background impurities must be identified so that they can be reduced, sequestered, or eliminated. SIMS was used

Table 5.1: *List of 22 impurity species surveyed and the impurities detected in $B_{12}P_2$ films grown at 1250 and 1450 °C.*

Species Surveyed	Species Detected
H, C, O, F, Si, S, Cl, Li, Na, Mg, Al, K, Ca, Ti, Cr, Fe, Ni, Co, Cu, Zr, Mo, In	H, C, O, F, Si, S, Cl, Al

to survey for a broad range of impurities in $B_{12}P_2$ grown on 4H-SiC. Ideally, the background impurity concentrations should be below the SIMS detection limit. SIMS surveys (Figure 5.3) were taken on a sample grown at 1250 °C and one at 1450 °C to cover the entire temperature range of $B_{12}P_2$ growth and to determine whether the introduction or incorporation of any impurity is a function of the growth temperature. For this initial survey, the spectra were not calibrated to a standard and the absolute concentrations (cm^{-3}) are unknown. However, these spectra still provide information on the presence of the impurities and the relative change in concentration between the two surveyed samples.

Of the 22 impurity species surveyed, only H, C, O, Si, Al, F, Cl, and S were detected in the films (see Table 5.1). The SIMS survey profiles of H, C, O, Si, and Al elements are shown in Figure 5.3 and possible sources of these impurities are depicted in Figure 5.4. The concentrations of H, O, Cl, F, and S were the same at the two growth temperatures. On the other hand, the C and Si concentrations increase by more than an order of magnitude from 1250 to 1450 °C, and a modest increase in the Al concentration near the $B_{12}P_2$ -SiC interface is seen in the film grown at 1250 °C over that of the 1450 °C-grown film. There are two possible explanations why more C and Si impurities were present in the films grown at 1450 °C. C and Si may more readily locate within the crystal lattice at higher temperatures, i.e. the solubility of these impurities increases with temperature, or the impurity source sheds more material at elevated temperatures. The most obvious source of C and Si is the SiC

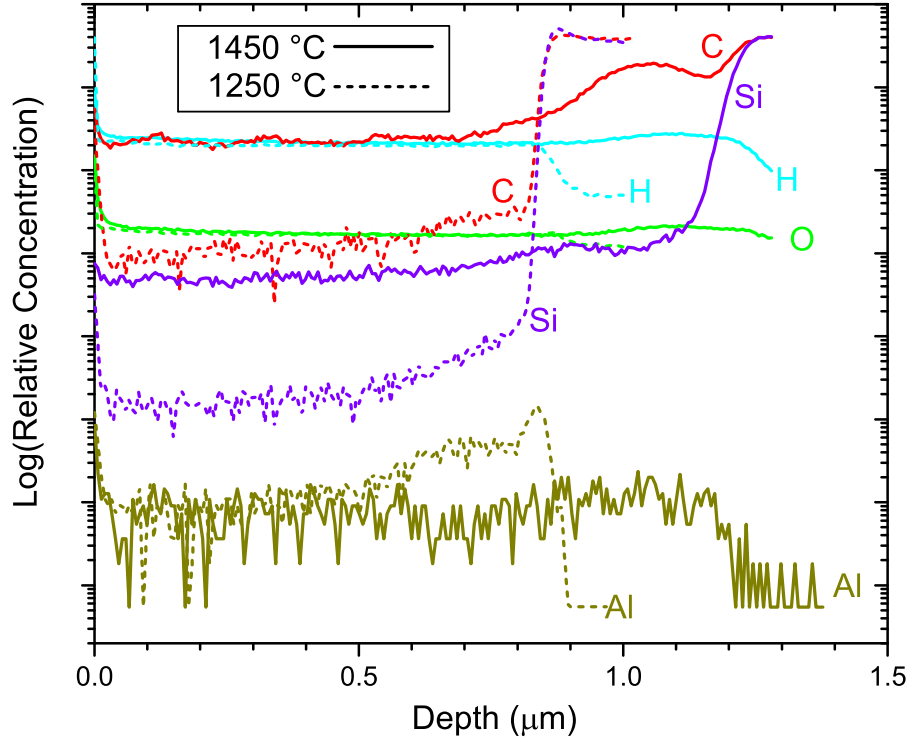


Figure 5.3: The SIMS depth profile of H, C, O, Si, and Al are shown from the 22-element SIMS survey taken on $B_{12}P_2/4H\text{-}SiC$ samples grown at 1250 and 1450 °C.

substrate although the C could originate from the susceptor or the H_2 gas and the Si from the quartz walls, gas distributor tube, or alumina insulation.

The only two sources for Al impurity are the alumina insulation surrounding the susceptor and the alumina thermocouple sheath located downstream of substrates. H is incorporated into the film from either the carrier gas or from incomplete dissociation of BH_x or PH_x precursor molecules. F, Cl, and S may be from residue of dissolved solids in the water used to clean the dump tube or from trace amounts of impurities in the insulation.

5.4 Effect of Impurities in $B_{12}P_2$

Little is known about the electronic effects of impurities in $B_{12}P_2$, but all reports have indicated $B_{12}P_2$ to be *p*-type. According to Emin,³² group IV elements such as C or Si can dope $B_{12}P_2$ by substitution of P atoms. Kumashiro, *et al.*^{25,26} attributed the *p*-type conductivity

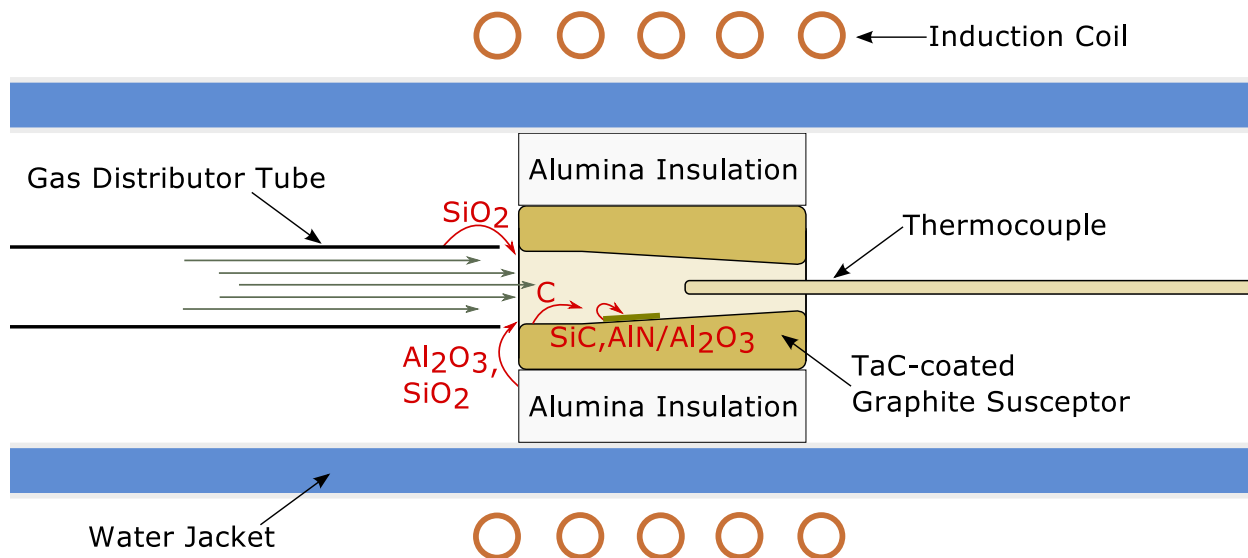


Figure 5.4: Possible sources for many of the detected elements in $B_{12}P_2$ films.

of their $B_{12}P_2$ films grown on Si substrates to Si auto-doping, with concentrations as high as 10^{22} cm^{-3} . Xu, *et al.*⁶⁰ was even able to control the *p*-type conductivity of $B_{12}As_2$ by 4 orders of magnitude through *in situ* Si doping during growth. Although the effect of Al doping is unknown, other alumino-boride compounds with B_{12} icosahedra have exhibited *n*-type conductivity, including $AlMgB_{14}$ ^{122,123} and $Y_xAl_yB_{14}$.^{66,67} Maruyama, *et al.*⁶⁶ has even demonstrated *p-n* control by changing the Al composition in $Y_xAl_yB_{14}$. Emin³² has speculated that O does not substitutionally dope $B_{12}P_2$ *n*-type by locating on a P site because O does participate in bonding in the “interstitial” chain. S, being another group VI element, may behave similarly to O as it also forms another icosahedral boride semiconductor: $B_{12}S_{2-x}$ ⁶² (details on the bonding in icosahedral borides is found in section 1.3.1). H could play an interesting role in conjunction with other impurities. H is known to passivate dangling bonds in amorphous Si,¹²⁴ B dopants in crystalline Si,^{125,126,127} C dopants in *p*-type GaAs,¹²⁸ Mg donors in GaN,^{129,130,131,132} and possibly even *p*-type dopants in icosahedral borides.^{60,61} The effect of halogens (F, Cl, etc.) in $B_{12}P_2$ is unknown.

5.5 SIMS Standards Fabrication

To measure the absolute concentration of impurities present, quantification through calibration of SIMS profiles using standards is necessary. Since standards are not readily available for $B_{12}P_2$, standards were created by ion implantation. By implanting a known and controlled amount of an impurity into the $B_{12}P_2$ matrix, the count rate of the ion mass spectrometer can be calibrated to the concentration profile generated by the implant.

C, Si, O, Al, and N were selected for further analysis by quantified SIMS depth profiles. C and Si were selected because they are clearly present and can strongly influence the electronic and material properties of $B_{12}P_2$. Also, the SiC substrate can be identified whether or not it is a source of C and Si by quantifying the amount of C and Si in $B_{12}P_2$ grown on AlN/sapphire substrates. Although the electronic implications of O, Al, or N doping in $B_{12}P_2$ is unknown, the AlN/sapphire substrate could be a source for each of the impurities. Moreover, a quantified comparison between these impurities in films grown on AlN/sapphire and SiC can help identify whether these impurities originate from the substrate or from other sources such as the alumina insulation.

One challenge to creating a SIMS standard for a novel material was to choose a dose that created an appropriate concentration. Ideally, the amount of species implanted would generate a maximum concentration that was at least ten times higher than the background concentration. The background concentration was unknown in these initial samples, but were assumed to be high for C, Si, and O. Therefore, large implantation doses were required. However, the implant dose cannot be arbitrarily large because the concentration could exceed the solid solubility limit of the species in $B_{12}P_2$ and precipitate into a second phase causing a large error in the standard. Even more, large doses could also severely damage the $B_{12}P_2$ crystal lattice or even create an amorphous region at the depth of the implant.

Two approaches were taken to mitigate the need to implant a large dose in the $B_{12}P_2$ standards. The first was to implant particular species into samples that have a lower background of that impurity. To illustrate, C and Si were implanted into films grown

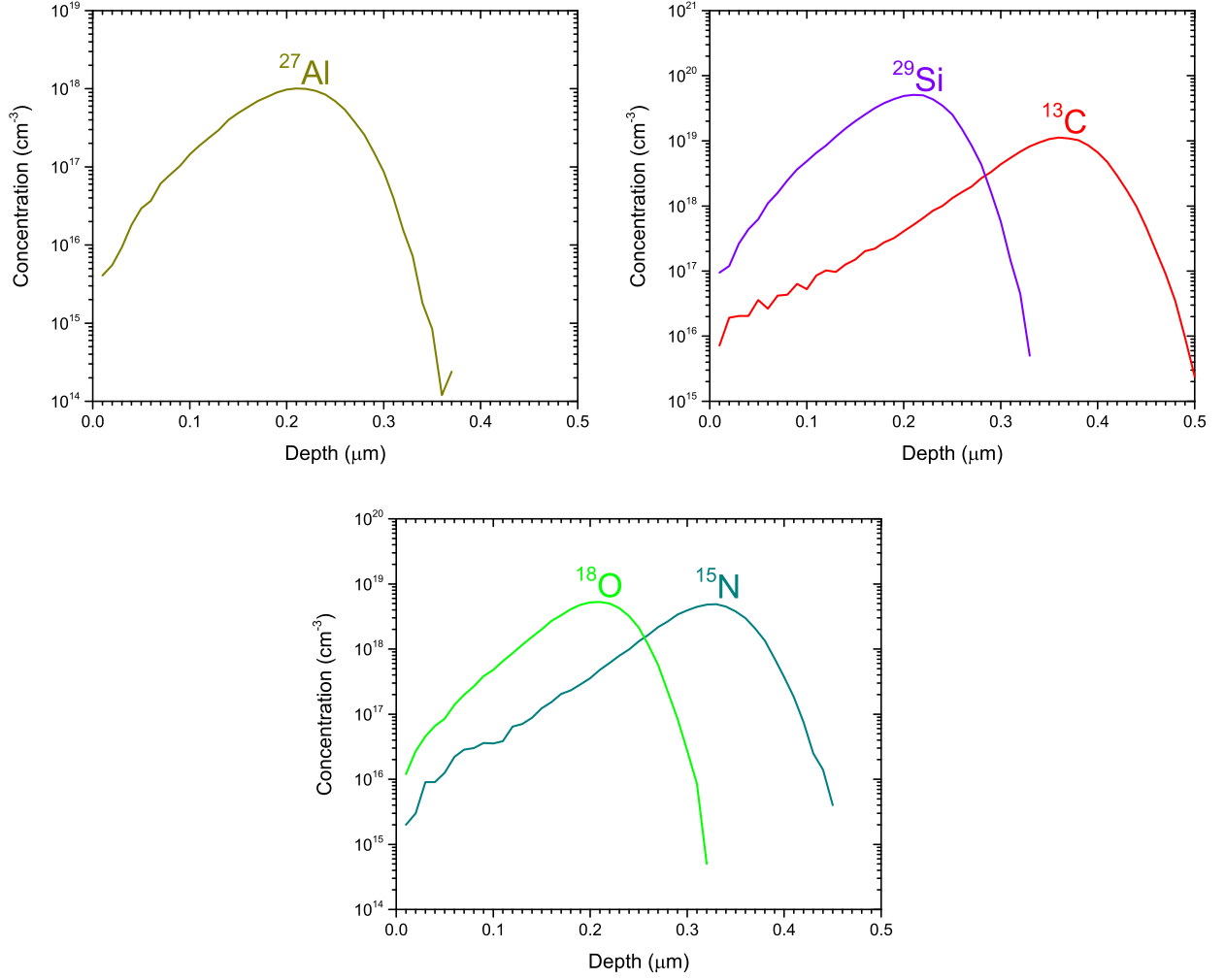


Figure 5.5: *Simulated ion implantation concentration profiles into $B_{12}P_2$ using SRIM and the energies listed in Table 5.2.*

on AlN/sapphire substrate which most likely had the lowest C and Si background concentrations. Similarly, Al and N were implanted into $B_{12}P_2$ films grown on SiC substrates. The other approach to reduce the implant dose needed was to implant minority isotopes of the species of interest. Since the isotope of a given element does not affect its chemical behavior, any isotope can be chosen. By selecting a minority isotope, the implanted dose no longer needed to be ten times greater than the total background of the impurity. Instead only a concentration ten times greater than the background of the minority isotope. For example, the background O concentration was assumed to be large at 10^{20} cm^{-3} . Then,

the background ^{18}O was assumed to be $2 \times 10^{17} \text{ cm}^{-3}$ because the mole fraction of ^{18}O in naturally abundant O is 2.05×10^{-3} . Thus, only a concentration of $\approx 2 \times 10^{18} \text{ cm}^{-3}$ of ^{18}O was implanted into the standard. Moreover, this only increases the total amount of O in the sample by 2% and should not change the chemical makeup of the B_{12}P_2 film. When the films are profiled, naturally abundant O is measured and then calibrated using the ^{18}O standard. The implanted species are summarized in Table 5.2.

To design and predict the implantation and concentration profile for the species studied, SRIM calculations were made. SRIM is a common simulation package that predicts the transport and stopping of high energy ions impacting matter (solid, liquid, or gas) and is frequently used to predict the depths at which ions stop in semiconductors after ion implantation. The simulations are based on the interaction of ions colliding with target atoms and require that the stoichiometry and density of the target material (B_{12}P_2 in this case) as well as the ion and ion energy to be known. The simulated profiles are shown in Figure 5.5. Three B_{12}P_2 films were used for standards and are summarized in Table 5.2. In films that were implanted with two species, the peak implantation concentration was placed at separate depths for each impurity to prevent any interaction between the implanted species. The implanted depths were controlled by increasing or decreasing the ion implantation energy.

5.6 Quantification of Background Impurities and Possible Sources

Three B_{12}P_2 samples were analyzed to quantify the concentration of background C, Si, O, N, and Al: B_{12}P_2 grown on AlN/sapphire at 1250 °C, B_{12}P_2 grown on 4H-SiC at 1250 °C, and B_{12}P_2 grown on 4H-SiC at 1450 °C. All films were grown for 15 min at 100 torr using flow rates of 6 sccm PH_3 (100%), 80 sccm B_2H_6 (1% in balance H_2), and 3500 sccm of H_2 .

Table 5.2: SIMS standards were made by implanting Al and minority isotopes of C, Si, O, and N into $B_{12}P_2$ films grown at 1250 °C. The substrates, isotopes, natural abundance mole fraction, dose, ion implantation energy, and maximum concentration from implant are shown.

Substrate	Isotope	Natural Abundance (Mole Fraction)	Dose (Ions/cm ²)	Implantation Energy (keV)	Concentration Maximum (cm ⁻³)
SiC	²⁷ Al	1.00	1.2×10^{13}	150	1.0×10^{18}
AlN/Al ₂ O ₃	¹³ C	0.0108	1.2×10^{14}	190	1.1×10^{19}
	²⁹ Si	0.0469	5×10^{14}	190	5.1×10^{19}
SiC	¹⁸ O	0.00205	5×10^{13}	110	5.4×10^{18}
	¹⁵ N	0.00364	5×10^{13}	190	6.3×10^{17}

5.6.1 Effect of Temperature on Background Impurities in $B_{12}P_2$ Films Grown on 4H-SiC.

Impurity depth profiles in $B_{12}P_2$ films grown at 1250 and 1450 °C on 4H-SiC can be found in Figure 5.6. The C and Si concentrations are high, ranging from $\approx 1 \times 10^{19}$ - 3×10^{20} cm⁻³. Like the survey, the concentration of both C and Si are lower at the lower growth temperature. As expected, the O concentration is very high at 2 - 3×10^{20} cm⁻³ but does not change as a function of temperature, consistent with the surveyed samples. The amount of N in both films is near the detection limit of the mass spectrometer and is the lowest concentration impurity studied in this comparison.

At 1450 °C, the C and Si concentrations track perfectly together, indicating that the source of both impurities is the SiC substrate, either by gaseous auto-doping or by diffusion through the film. The concentration of both elements is nearly an order of magnitude

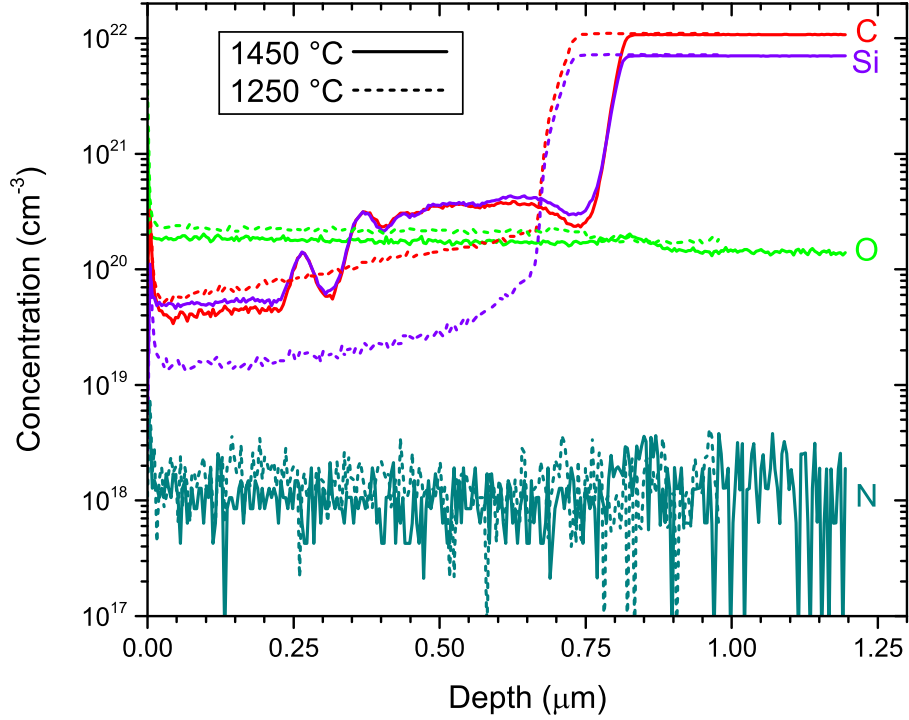


Figure 5.6: Quantified SIMS depth profiles for $B_{12}P_2$ films grown on $4H$ -SiC at $1250\text{ }^{\circ}\text{C}$ and $1450\text{ }^{\circ}\text{C}$. C, Si, and O concentrations are high while N levels are near the detection limit.

smaller at the surface compared to near the film-substrate interface. This could be an effect of segregation of the impurities in different regions of the films. Or, since $B_{12}P_2$ at this temperature grows as individual islands that coalesce, the C and Si could be released from exposed substrate between $B_{12}P_2$ islands. As the islands merge together, the substrate is effectively sealed off and the amount of C and Si that is released into the film is reduced. Another possibility is that $B_{12}P_2$ islands re-emerge during sputtering (either due to voids near the film-substrate interface or from initial surface roughness) and the SiC is partially exposed before all of the $B_{12}P_2$ is sputtered away.

At $1250\text{ }^{\circ}\text{C}$, the Si concentration was reduced throughout the film thickness and was lowered by about a factor of three near the surface. While the C concentration is also reduced near the substrate interface, the surface concentration is not lower, suggesting that there is either another source of carbon other than the substrate, or that C more readily

incorporates into $B_{12}P_2$ at 1250 °C than Si.

5.6.2 Effect of Substrate on Impurities in $B_{12}P_2$ Grown at 1250 °C

Impurities of $B_{12}P_2$ films grown on both SiC and AlN/sapphire substrates were compared to determine whether the substrates auto-dope the $B_{12}P_2$ and to help identify other sources of the impurities. The SIMS depth profiles of $B_{12}P_2$ grown at 1250 °C on SiC and AlN/sapphire are shown in Figure 5.7.

Despite being grown on a nitride substrate, the nitrogen concentration in the $B_{12}P_2$ film grown on AlN/sapphire does not have a higher N concentration than in the film grown on SiC and remains near the detection limit. N may have a low solid solubility in $B_{12}P_2$. The O concentration is marginally higher in the $B_{12}P_2$ film on AlN/sapphire which may be within the measurement error but could also be caused by etching of the sapphire substrate. The O source in the $B_{12}P_2$ film grown on SiC must be eliminated to ensure that the high O levels in the AlN/sapphire film is from the substrate. The O may originate from a number of sources. The insulation could be slowing etching in the reducing atmosphere, adsorbed oxygen gas or water molecules in the highly porous insulation could be slowly released during growth, or there may be a small leak in the vacuum system.

Si contamination is drastically reduced by nearly two orders of magnitude from $\approx 2 \times 10^{19} \text{ cm}^{-3}$ to $\approx 2 \times 10^{17} \text{ cm}^{-3}$ by growing on AlN/sapphire substrates, indicating that even at the relatively low growth temperature of 1250 °C, there is still significant Si auto-doping from the SiC substrate. The Si concentration is reduced nearly to the detection limit close to the film surface of the film grown on the AlN/sapphire substrate. The small amount of Si near the film/substrate interface could be caused by etching of the alumina insulation or by the gas distributor tube, which may become hot due to its close proximity to the susceptor.

While C is also strongly reduced by a factor of 2-3 from $\approx 6 \times 10^{19} \text{ cm}^{-3}$ to $\approx 2 \times 10^{19} \text{ cm}^{-3}$ at the film surface by growing on AlN/sapphire, there is still severe C contamination

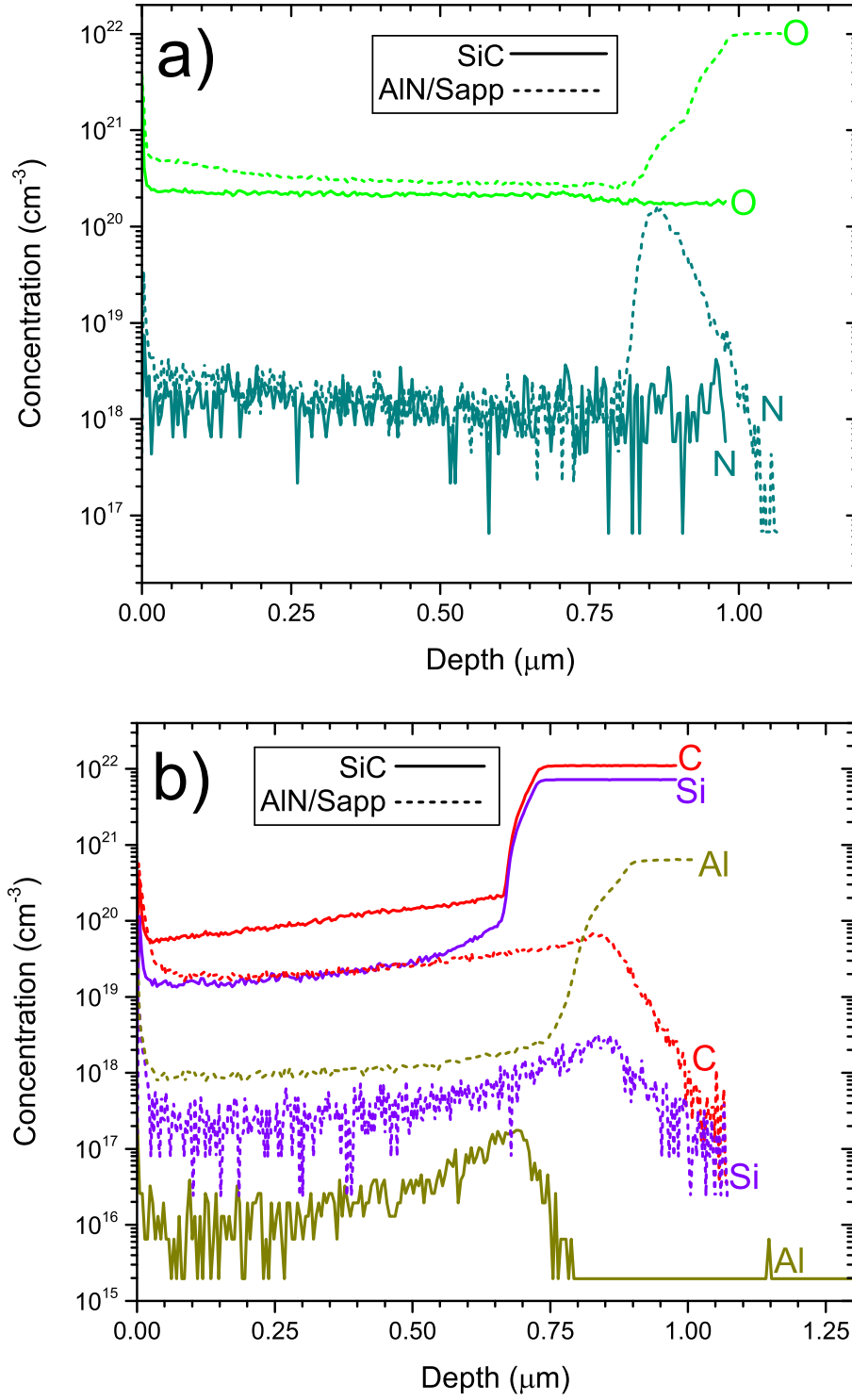


Figure 5.7: SIMS depth profiles of a) O and N and b) C, Si, and Al in $B_{12}P_2$ grown on 4H-SiC and AlN/sapphire substrates at 1250 °C.



Figure 5.8: *Heavily used, TaC-coated graphite susceptors are shown. In the left image, cracks in the TaC coating are visible. In the right image, exposed graphite can be seen after the TaC-coating has flaked off on the top left corner and the top edge.*

with concentrations greater than $2 \times 10^{19} \text{ cm}^{-3}$. Clearly another C source other than the SiC substrate is present in the system. The most obvious possible source is the susceptor, which is made from graphite coated by TaC. While TaC is extremely resistant to chemical attack by H_2 at high temperatures, even minuscule cracks in the $\sim 30 \text{ }\mu\text{m}$ TaC coating will expose the graphite to the carrier gas and produce gaseous hydrocarbons. Even more, after heavy usage, the TaC can even begin to flake off as seen in Figure 5.8. Another possible source of C could be the H_2 gas itself, which is manufactured from the steam reformation of methane. However, the palladium membrane purifier is capable of producing 99.99999% pure H_2 and was helium leak checked to ensure proper function. Thus, the susceptor is the most likely source.

In contrast to C and Si, the Al concentration was much higher in B_{12}P_2 films grown on AlN/sapphire. Thus, its source must be the substrate. The Al could be from either the AlN or from the sapphire, which caused the Al concentration to be $1 \times 10^{18} \text{ cm}^{-3}$. The depth profile remains relatively flat throughout the thickness of the film, and may be caused from constant auto-doping from continuous etching of the sapphire on the bottom of the substrate or by rapid diffusion of Al through the B_{12}P_2 . Consistent with the SIMS survey, Al is also found in B_{12}P_2 films grown on SiC and likely originates from the alumina insulation. In

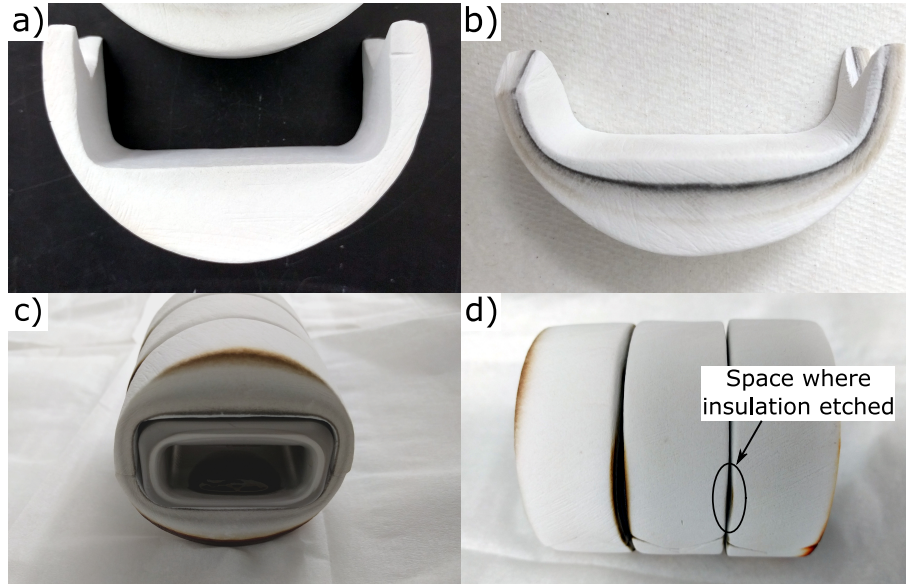


Figure 5.9: *Pristine alumina insulation is shown in a). Used alumina insulation is shown in b). A TaC-coated graphite susceptor is shown inside alumina insulation in c). A side view of the alumina rings is shown in d) where a gap between the rings caused by etching of the alumina can be seen.*

fact, the alumina insulation appears to react with the process gases as is seen in Figure 5.9 b). In Figure 5.9 a), an unused piece of alumina is shown and is uniformly bright white. After using the insulation, a dark ring appears a few millimeters from where the susceptor makes contact to the insulation (Figure 5.9 b) and c)). Furthermore, visible signs of material removal can even be seen Figure 5.9 d). While the effect of Al doping in $B_{12}P_2$ is unknown, its concentration in films grown on AlN/sapphire is still an order of magnitude lower than C in $B_{12}P_2$ on AlN/sapphire and nearly two orders of magnitude lower than C in $B_{12}P_2$ on SiC. Therefore, in terms of auto-doping control, AlN/sapphire is a superior substrate to 4H-SiC.

5.7 Effect of Impurities on the Carrier Concentration

As mentioned in section 5.4, Si and C are expected to be p -type dopants in $B_{12}P_2$. Thus, the concentration of C and Si measured in the films should control the number of electron-

holes in the material, i.e. larger amounts of these impurities should manifest as higher hole concentrations. To measure the hole concentration, Hall Effect measurements were taken on the samples as a function of the growth temperature. The films were grown on semi-insulating 4H-SiC miscut 4° to the $(11\bar{2}0)$ with a nominal thickness of $1\text{ }\mu\text{m}$. The films were then fabricated into a $5\times 5\text{ mm}^2$ square Van der Pauw geometry. $1000/1000\text{ }\text{\AA}$ Ni/Au ohmic contacts were evaporated onto the corners of the sample and annealed at $500\text{ }^\circ\text{C}$ for 30 seconds. Details on Ni/Au ohmic contacts to B_{12}P_2 can be found in Chapter 4.

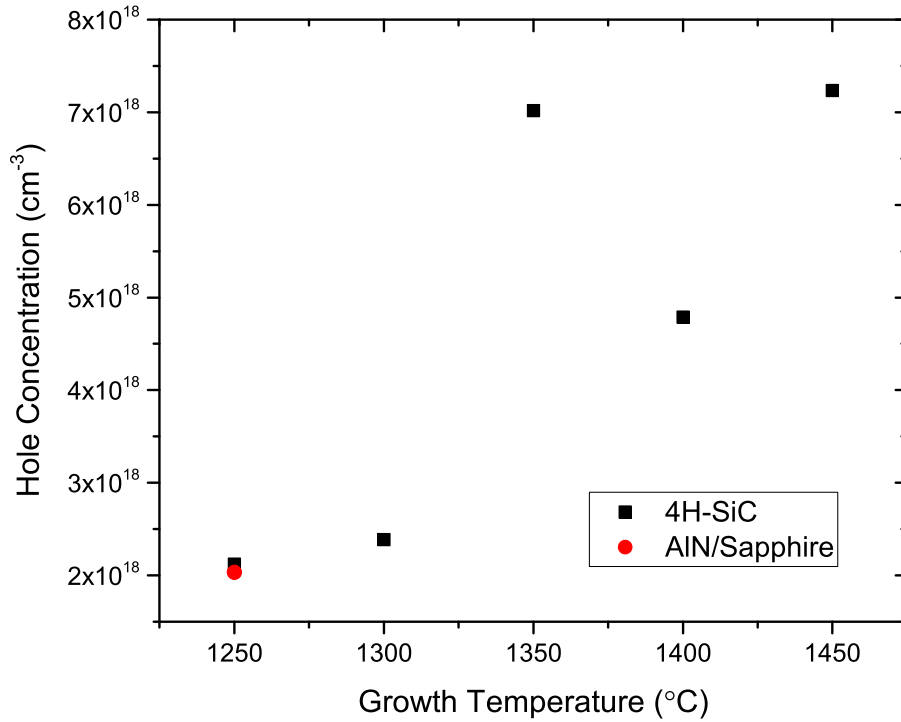


Figure 5.10: The hole concentration at room temperature as measured by Hall Effect for B_{12}P_2 films grown on 4H-SiC at different growth temperatures. The hole concentration for B_{12}P_2 grown on AlN/sapphire is also shown. As the growth temperature increases, the carrier concentration also increases because more Si and C are incorporated into the films at higher growth temperatures. These films were all grown using a TaC-coated graphite susceptor.

As seen in Figure 5.10, the hole concentration generally increases as the growth temperature is increased for films grown on 4H-SiC. This agrees with the SIMS data showing that C and Si concentrations in the film increase at higher growth temperatures. The high

hole concentration in the film grown on AlN/sapphire indicates that C is the likely *p*-type dopant in that film because the Si concentration is low ($<5 \times 10^{17} \text{ cm}^{-3}$). Another possibility is that native defects in the material are introducing holes.

5.8 Efforts and Methods to Reduce Impurities

5.8.1 Susceptor

Since the predominant residual impurities in B_{12}P_2 and their potential sources have been identified, steps can be taken to remove the sources of contamination.

The most egregious impurity is C, which is likely originating from the graphite susceptor in addition to the 4H-SiC. The graphite material should be modified or replaced with another material that is ideally C-free. The susceptor material must meet several criteria:

- Because the susceptor is heated inductively via an RF-coil, the material must be electrically conductive.
- The material must be refractory, i.e. it cannot decompose, melt or substantially sublime near the growth temperature (1250-1450 °C).
- The material cannot form a low melting eutectic with B or P (e.g. Pt forms eutectics at 790 °C and 588 °C with B and P, respectively).
- The material cannot contain C or evolve C at high temperatures.
- The material must be stable in H_2 gas at the growth temperature.

One path to creating a low-C susceptor would be to sequester the graphite by using a more robust and C-free coating such as pyrolytic boron nitride. Pyrolytic boron nitride is a common coating for graphite susceptors, has a similar atomic structure to graphite and is well-suited as a coating because it is extremely pure, boron is not a contaminant, and the



Figure 5.11: *a) a graphite susceptor coated with pyrolytic boron nitride. A boron nitride-painted graphite susceptor is shown b) before and v) after heating. The pyrolytic boron nitride film buckles and delaminates from the graphite on the inside of the susceptor. After heating, the boron nitride paint also buckles and delaminated on the interior of the susceptor.*

SIMS analysis presented earlier shows that nitrogen does not incorporate into the growing $B_{12}P_2$ film. Replacing the TaC coating with pyrolytic coating was the first attempt to create a new low-C susceptor. Although pyrolytic boron is commonly used to coat graphite, the interior of the tubular susceptor could not be coated without the boron nitride film buckling and delaminating from the graphite (see Figure 5.11 a)). The delamination is presumably due to differences in the coefficient of thermal expansions of the two materials. For the susceptor geometry used in this CVD system, pyrolytic boron nitride could not be used.

Boron nitride paint was also tested to try to sequester C from the graphite. The paint was water-based and used alumina as a binder. Figure 5.11 b) shows a freshly painted graphite susceptor. However, after heating the susceptor to the growth temperature, the painted film began to crack and then buckle and delaminate as the susceptor was cooled (Figure 5.11 c)). Like the pyrolytic boron nitride, the boron nitride paint was unsuitable.

Another path to create a low-C susceptor would be to replace graphite with a material that does not contain C at all. Some possible replacements include B, Zr, ZrB_2 , ZrN, TiB_2 , or a TiB_2 /BN composite. A high-purity boron susceptor would be ideal. However, solid boron blocks are not commercially available and machining the material would be difficult. ZrB_2 and TiB_2 blocks are commercially available but use carbon as a binder. ZrN blocks are not commercially available but Zr is easily procured and can be nitrided by heating in

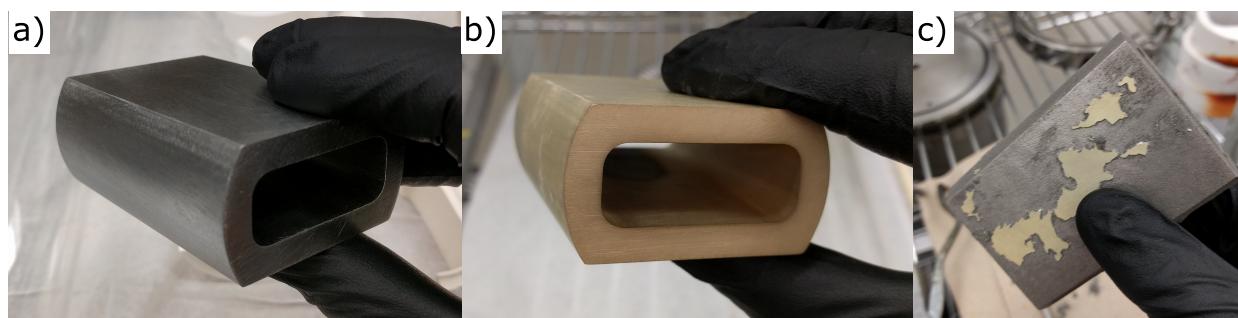


Figure 5.12: a) an unused, polished Zr susceptor. b) a Zr susceptor nitride in N_2 at 1500 °C for two hours. c) a photograph of the remaining ZrN coating on the Zr susceptor after exposing the susceptor to H_2 gas at room temperature.

a N_2 atmosphere. TiB_2/BN composite blocks are also commercially available and use no binder.

Zr was selected as a possible susceptor material because it has a high melting point of 1855 °C, it can be easily purchased and machined, and the surface can be conformally nitrided by heating in nitrogen and thus forming a refractory coating. Furthermore, if Zr reacts with B, then ZrB_2 would form which should also be a refractory coating. A nitrided Zr susceptor was tested as a graphite replacement. A polished Zr susceptor (Figure 5.12 a)) was nitrided at 1500 °C for two hours in a N_2 atmosphere (Figure 5.12 b)). The coating was conformal and uniform over the entire susceptor. Next, the susceptor was loaded into the CVD system to be heated in a H_2 atmosphere. Upon exposure to H_2 gas at room temperature, the nitride coating immediately crumbled and turned into powder (Figure 5.12 c)). Only spots of the ZrN coating remained. It was hypothesized that the H_2 reacted with the Zr/ZrN interface in small cracks in the brittle ZrN coating forming ZrH_2 , another brittle compound. The stress between the two brittle materials caused the coating to break apart and crumble off of the susceptor. A ZrN coating on Zr is not a compatible material to use in an H_2 atmosphere and could not be used to deposit $B_{12}P_2$.

Since the ZrN coating was unstable in H_2 , pure Zr metal was tested as a susceptor. While the susceptor could be heated in H_2 , the Zr absorbed and reacted with H_2 . As the susceptor was heated, it formed ZrH_2 and then decomposed back to Zr above 820 °C and

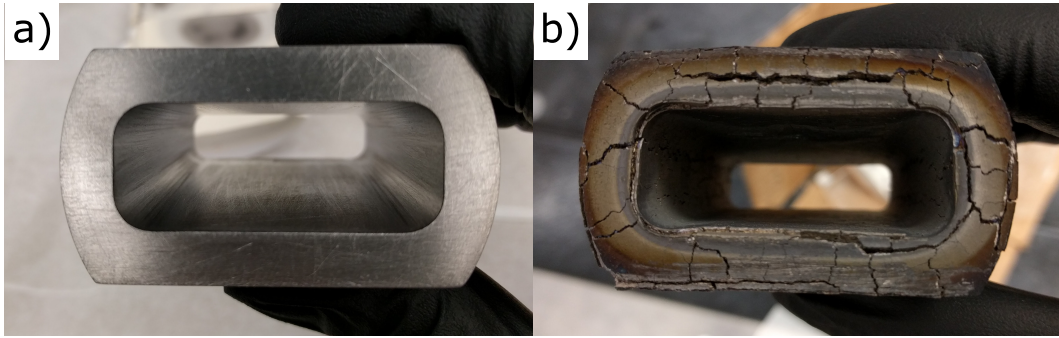


Figure 5.13: *a) an unused, polished Zr susceptor. b) a Zr susceptor heated three times in H_2 showing severe cracks due to hydrogen embrittlement.*

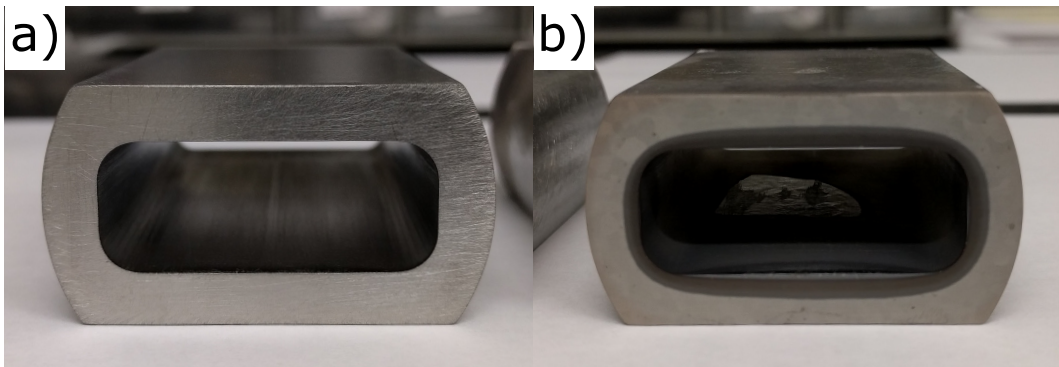


Figure 5.14: *a) an unused, polished Zr susceptor. b) a Zr susceptor heating and cooled in Ar and used to deposit $B_{12}P_2$ films. No signs of hydrogen embrittlement are evident.*

then reformed ZrH_2 again after cooling to below $820\text{ }^{\circ}\text{C}$. These phase transitions caused so much stress in the material that deep cracks and crevices started to split the susceptor. A pristine, polished Zr susceptor is shown in Figure 5.13 a). After heating the susceptor three times above $820\text{ }^{\circ}\text{C}$, the susceptor was damaged beyond usability as is seen in Figure 5.13 b).

To avoid forming ZrH_2 , an alternate approach to heating the Zr was tested. By heating the Zr susceptor in Ar until the susceptor was above the decomposition temperature of ZrH_2 and then switching the atmosphere to H_2 , ZrH_2 should never form. Once the atmosphere has been converted to H_2 the substrates can be etched and the $B_{12}P_2$ film deposited. After the deposition is complete, the atmosphere can be switched back to Ar, and the susceptor can be cooled back to room temperature without forming ZrH_2 or deteriorating the susceptor.

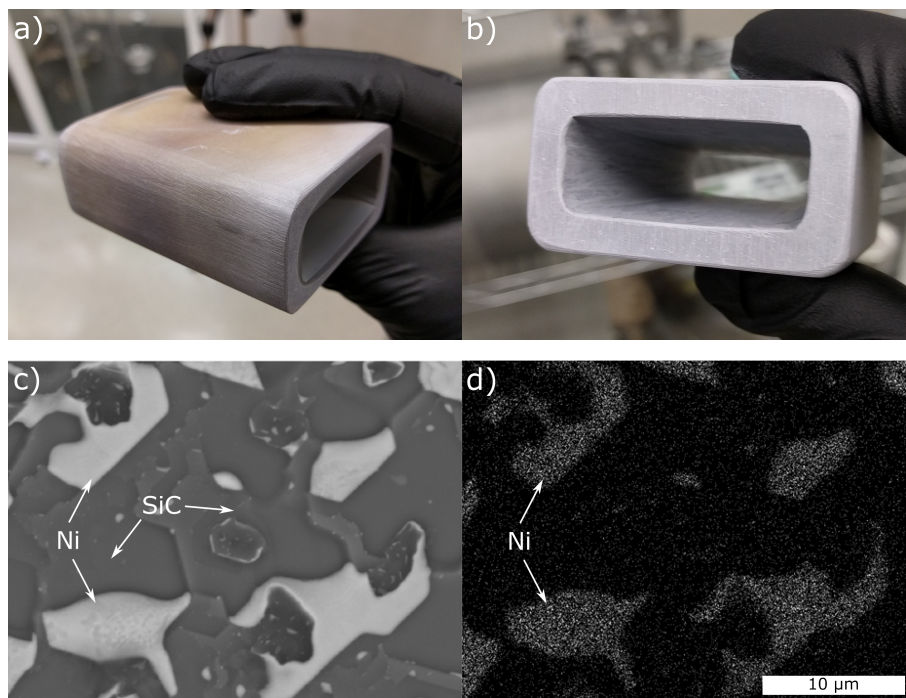


Figure 5.15: A TiB_2/BN composite susceptor is shown in a) and b). c) an SEM micrograph of a substrate used for B_{12}P_2 epitaxy with the TiB_2/BN susceptor. d) an EDS map of Ni metal in the SEM micrograph.

Images of the susceptor before and after using the alternate heating approach are shown in Figure 5.14 where a) is the unused susceptor and b) is the used susceptor.

A TiB_2/BN composite was selected as another alternate C-free susceptor material. The material was selected because B is not a contaminate and N incorporation into B_{12}P_2 is low. Even though TiB_2 is a stable refractory material, the primary concern when using the composite was that Ti might be released if H_2 etched the susceptor. A block of the composite was machined and filed into a susceptor which is shown in Figure 5.15 a) and b). After depositing a trial B_{12}P_2 film on 4H-SiC, metal droplets were observed on the backside and the top edges of the 4H-SiC substrate. The metal droplets catalytically etched the surface into faceted steps and islands as can be seen in Figure 5.15 c). Energy-dispersive X-ray spectroscopy (EDS) revealed that the metal droplets were composed of Ni. An EDS map of the substrate surface near the top edge is seen in Figure 5.15 d) illustrating the metal droplets composition. The source of the Ni is uncertain as the manufacturer of the

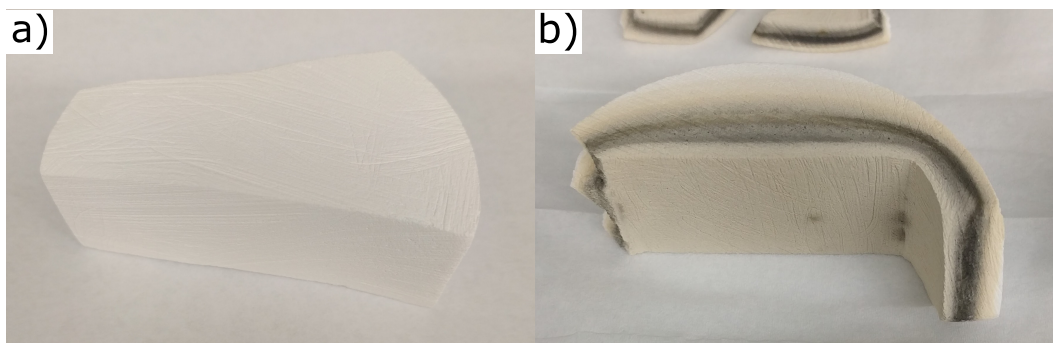


Figure 5.16: *a) an unheated piece of yttria-stabilized zirconia. b) a piece of yttria-stabilized zirconia insulation after being used in $B_{12}P_2$ epitaxy.*

composite states that no binder is used. Ni may possibly be an impurity in the composite or that the files used to make the susceptor contaminated the surface with Ni.

5.8.2 Insulation

The alumina insulation was another source of O, Si, and Al impurities in the $B_{12}P_2$ films. To eliminate both Si and Al from the insulation material, the alumina insulation was swapped with yttrium-stabilized zirconia insulation. Yttria and zirconia are both more stable in reducing H_2 atmospheres than either silica or alumina and therefore should be more chemically robust while simultaneously removing large amounts of Si and Al in contact with the hot susceptor. Furthermore, Zr is not an additional impurity atom if used with the Zr susceptor.

The yttria-stabilized zirconia insulation was tested using the Zr susceptor to reduce impurities during $B_{12}P_2$ growth. Like the alumina insulation, the insulation started out as a very bright white before being used (Figure 5.16 a)) and then formed a dark ring a few millimeters from where the susceptor makes contact with insulation (Figure 5.16 b)). Although yttria and zirconia are more stable than alumina, the material does appear to react with the process gases.

5.8.3 SIMS on B₁₂P₂ Films Grown Using Zirconium Susceptor and Yttria-stabilized Zirconia Insulation

To reduce the amount of Si and C in B₁₂P₂, films were grown on AlN/sapphire substrates with a Zr susceptor using the Ar heat up and cooled down process in conjunction with the yttria-stabilized zirconia insulation. The films were grown for 15 min at 1250 °C and 100 torr using flow rates of 6 sccm, 80 sccm, and 3500 sccm of PH₃ (100%), B₂H₆ (1% in balance H₂) and H₂, respectively. Since the insulation has a high surface area for moisture to adsorb and therefore could be an O source, the insulation was stored in an oven to drive off as much residual moisture as possible to try to reduce O in the system.

A B₁₂P₂ film grown with the Zr susceptor and yttria-stabilized insulation was analyzed by SIMS and compared to the B₁₂P₂ film grown on AlN/sapphire using the TaC coated graphite susceptor with alumina insulation. The SIMS depth profiles are shown in in Figure 5.17. Apart from the susceptor, the insulation, and the atmosphere during heating and cooling, the growth conditions were the same. The solid lines in Figure 5.17 represent data from the films grown using the Zr susceptor and the dotted lines represent data from the films grown using the TaC coated graphite susceptor.

Near the sample surface the Al concentration in the film grown using the Zr susceptor is similar to that grown using the TaC/graphite susceptor. The AlN/sapphire substrate has already been identified as the primary Al source and since the same substrate was used for both films, the amount of Al should be similar. Near the AlN interface, the Al concentration is higher in the film using the Zr susceptor. The B₁₂P₂ film was held at temperatures above 1000 °C longer than the film using TaC/graphite. This is in part due to the slower cooling rate because Zr has a higher thermal mass but also because of the time needed to switch from H₂ to Ar gas flow before cooling to room temperature. The extended amount of time at high temperature may allow Al to diffuse more into the B₁₂P₂ film.

O is reduced by a factor of two ($\approx 4 \times 10^{20} \text{ cm}^{-3}$ to $\approx 2 \times 10^{20} \text{ cm}^{-3}$) compared to the film grown on the TaC/graphite susceptor with the alumina insulation. The reduction could be

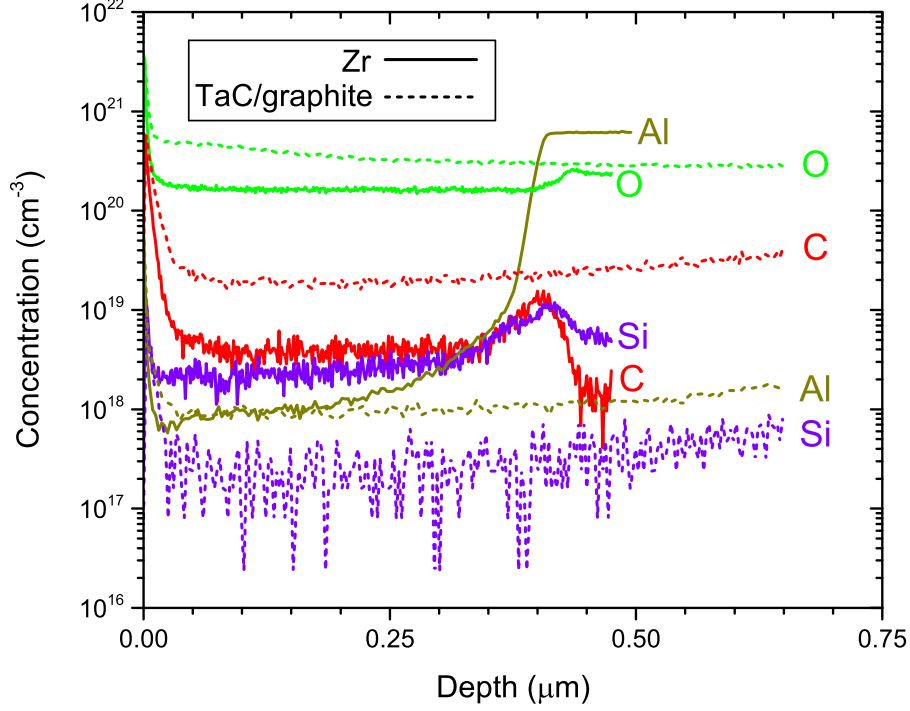


Figure 5.17: SIMS profiles of Al, Si, C, and O in $B_{12}P_2$ films grown on AlN/sapphire substrates using a TaC-coated graphite susceptor with alumina insulation (dotted lines) and using a Zr susceptor and yttria-stabilized zirconia insulation (solid lines).

caused by less etching or outgassing of the yttria-stabilized zirconia insulation. Another possibility is that the Zr susceptor itself gettered some of the O in the system since Zr has a strong O affinity. Zr also likely became a sink for both B and P, which may be responsible for the much thinner $B_{12}P_2$ film compared to films grown using the TaC/graphite susceptor. Nonetheless, the O concentration is still extremely high and more effort is needed to reduce that impurity.

C is reduced by a factor of five or more ($\approx 2 \times 10^{19} \text{ cm}^{-3}$ to $\approx 4 \times 10^{18} \text{ cm}^{-3}$) and is likely a result of removing graphite from the system. However, the C concentration is still at $\approx 4 \times 10^{18} \text{ cm}^{-3}$, which is still very high and should be further decreased. Although the amount of C in the system was greatly reduced, the Zr susceptor still contains C as an impurity (most metals do). From the manufacturer, the Zr 702 alloy used to make the susceptor contains a maximum of 0.05 wt% C, which is equivalent to 0.38 atomic % C. In

absolute terms, this is still a substantial amount of C. Without a coating on the susceptor, the C may be free to diffuse to the surface and enter the carrier gas and thus continue to dope the $B_{12}P_2$ film.

The amount of Si in the $B_{12}P_2$ film increased by about an order of magnitude from $2 \times 10^{17} \text{ cm}^{-3}$ to $\approx 2 \times 10^{18} \text{ cm}^{-3}$ when using the Zr susceptor and yttria-stabilized zirconia insulation. The Zr metal likely contains negligible amounts of Si and is not suspected to be a Si source. The yttria-stabilized zirconia contains less Si than the alumina insulation. Perhaps small amounts of Zr evaporate in the system. If evaporated Zr atoms come into contact with the distributor tube or other quartz components of the CVD system, they could reduce the SiO_2 to form ZrO_2 and release the Si into the carrier gas. If any Zr did evaporate during the film deposition, it did not incorporate into the $B_{12}P_2$ films as no Zr or Hf (the largest impurity in Zr 702) was detected during the SIMS analysis.

Using the Zr susceptor and the yttria-stabilized zirconia insulation had a profound impact on the electrical resistivity of the $B_{12}P_2$ film. From Hall Effect measurements, films grown using the TaC/graphite susceptor had resistivities on the orders of $\approx 0.1\text{-}10 \text{ } \Omega\text{-cm}$. However, the films grown using the Zr susceptor were so resistive that Hall Effect could not be measured. As is illustrated in Figure 5.18, measuring the current-voltage curve between two $100 \times 100 \text{ Ni/Au}$ contacts spaced $\sim 6 \text{ } \mu\text{m}$ apart resulted in resistances of hundreds of $G\Omega$'s.

5.9 Possible Routes to *n*-type Conductivity

Icosahedral boride compounds, especially boron carbides, are known for their *p*-type conductivity and difficulty in effectively doping them *n*-type. However, Mori, *et al.*^{68,69,70} has achieved considerable success in creating homologous *n*-type borides to $B_{12}P_2$, such as $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$ (where *RE* stands for rare earth). Maruyama, *et al.*^{66,67} was able to produce both *p*-type and *n*-type conductivity in $Y_xAl_yB_{14}$, another

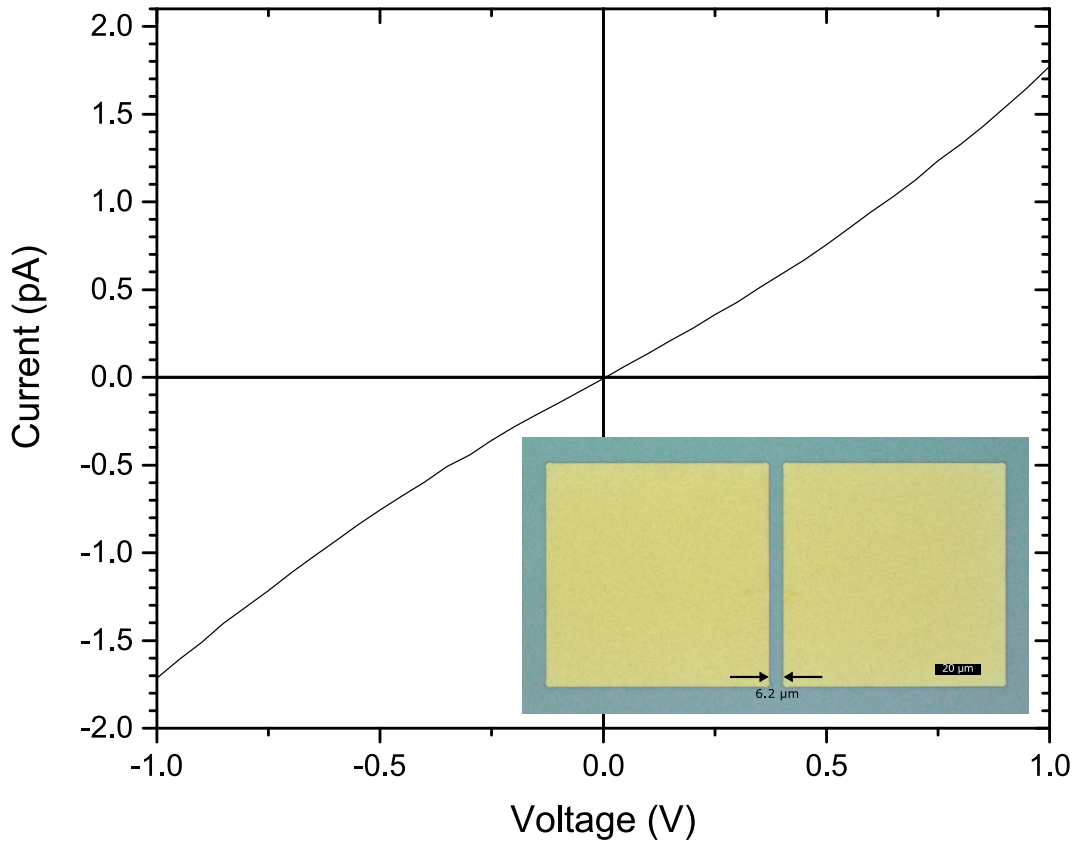


Figure 5.18: *Current-voltage relationship between the two Ni/Au contacts shown in the inset of a $B_{12}P_2$ film grown on AlN/sapphire using the Zr metal susceptor. The extremely high resistance prevented Hall Effect measurements to determine carrier concentration.*

B_{12} icosahedra-containing boride. Other compounds have exhibited n -type conductivity as well: Mg_2B_{14} ,¹³³ and $AlMgB_{14}$.^{122,123} While none of these compounds have the same crystal structure as $B_{12}P_2$, n -type conductivity can clearly be achieved with compounds containing boron icosahedra. Still, even more semiconducting boride compounds exist, including $Li_2B_{12}C_2$ ¹³⁴ and $LiB_{12}PC$ ¹³⁵ which is also a wide band gap semiconductor (3.08 eV¹³⁵). These materials suggest that Li could possibly be an interstitial n -type dopant in $B_{12}P_2$.

The compounds mentioned above could possibly inform attempts to dope $B_{12}P_2$ n -type. The easiest way to survey many potential n -type dopants would be to ion implant $B_{12}P_2$ films with low hole background concentrations. To date, neither Al, Y, Mg, nor Li doping of $B_{12}P_2$ have been tested.

5.10 Conclusions and Future Work

Background impurities species and possible sources were identified in $B_{12}P_2$ films using SIMS. 22 elements were surveyed on $B_{12}P_2$ films grown on 4H-SiC and H, C, O, F, Si, S, Cl, and Al were detected. To quantify the concentration of the impurities in the $B_{12}P_2$ films, SIMS standards were fabricated by ion implantation of Al and minority isotopes of C, Si, O, and N. By analyzing $B_{12}P_2$ films grown at 1250 and 1450 °C, Si and C were found to increase in concentration with increasing temperature and emanate from the 4H-SiC substrate. Hall Effect measurements showed that the increase in Si and especially C contributed to the increased hole concentrations at higher growth temperatures. By comparing $B_{12}P_2$ films grown on 4H-SiC and AlN/sapphire substrates at 1250 °C, Si was confirmed to originate from the 4H-SiC substrate and that Al originated from the AlN/sapphire substrate. Since the C concentration was still high ($>1 \times 10^{19} \text{ cm}^{-3}$) in the film grown on AlN/sapphire, the graphite susceptor was identified as another C contamination source. To reduce the amount of C in the CVD system, new susceptors were designed and tested. To reduce the amount of Si and Al in the system, yttria-stabilized zirconia insulation was also tested in place of the alumina insulation. By using a Zr metal susceptor in conjunction with the yttria-stabilized zirconia insulation, the amount of C in the films was reduced by a factor of 5 to $4 \times 10^{18} \text{ cm}^{-3}$ and the amount of O was reduced by a factor of 2 to $2 \times 10^{20} \text{ cm}^{-3}$. Si contamination increased by about a factor of 10 to $2\text{-}3 \times 10^{18} \text{ cm}^{-3}$ which could be due to Zr metal reducing the quartz in the system.

More work should be done to further reduce the amount of C, Si, and O in the $B_{12}P_2$ films, ideally below the detection limit of SIMS. This could include using a susceptor made from pure TaC or ZrC which may release less C than the Zr metal susceptor. Alternatively the reactor geometries could be changed so that pyrolytic boron nitride susceptors could be used. The reactor could also be designed so that insulation could be eliminated from the system since it is a likely source of O contamination. After the background impurities of $B_{12}P_2$ are sufficiently reduced, *n*-type doping could be explored by *in situ* doping during

growth or by ion implantation of elements such as Al, Y, Mg, or Li.

Chapter 6

Irradiation Response on the Electrical Transport Properties of $p\text{-B}_{12}\text{P}_2$ and $p\text{-4H-SiC}$

6.1 Introduction

$B_{12}P_2$ is reported to self-heal from radiation damage from high-energy electrons (β 's); no structural defects were detected in TEM micrographs taken after irradiation.^{6,7} This absence of defect agglomeration in $B_{12}P_2$ after irradiation to a fluence of 1×10^{23} electrons/cm² of 400 keV electrons was attributed to a “self-healing” mechanism. Defects may still be present because TEM cannot resolve the arrangement of atoms within the boron icosahedra. However, performing simulations, Huber, *et al.*¹³⁶ found that certain types of Frenkel pairs have low energy barriers for recombining, supporting the claim that $B_{12}P_2$ may indeed self-heal.

Electrical measurements may provide additional evidence on the radiation hardness of $B_{12}P_2$, as they are more sensitive to irradiation-induced damage of the material. Measuring the electrical response to irradiation have been limited by the need for large, high quality crystals. In this study, the radiation hardness of $B_{12}P_2$ hetero-epitaxial films was evaluated by Hall Effect measurements. Hall Effect provides measurements of the carrier concentration, resistivity, and carrier mobility. By varying the temperature, additional information and insight can be gained, including dopant ionization energy, amount of compensating centers, conduction mechanism, and the dominant type of carrier scattering. As a point of reference, a *p*-type 4H-SiC film was characterized in tandem with the $B_{12}P_2$ film. 4H-SiC was chosen because it is a conventional semiconductor that is generally regarded as radiation hard.

Hall Effect measurements were measured after successive irradiation from α particles emitted from ^{210}Po decay over fluences of 1×10^{11} - 1×10^{13} α /cm². The data shows that radiation-induced defects in 4H-SiC compensate holes, reduce the hole mobility, cause carrier hopping, and form defect bands. For $B_{12}P_2$, the background defect level before irradiation is high enough to cause an impurity/defect band to form, cause hopping conduction, and mask any of radiation-induced defects at low fluences. At high fluences, the resistivity increases in $B_{12}P_2$ because the mobility decreases and the impurity band becomes more pronounced,

suggesting that defects are accumulating in the material. The high levels of preexisting background defects levels from impurities and hetero-epitaxy-induced dislocations may form complexes with irradiation-induced defects and therefore interfere or prevent “self-healing.”

6.2 Experimental Approach

Hall Effect measurements were chosen to evaluate the radiation response of high-energy α -particle bombardment because important properties such as the carrier concentration, carrier mobility, and carrier compensation can be extracted from the measurements. Further, $B_{12}P_2$ films can be readily fabricated into a Van der Pauw geometry for the measurement. p - $B_{12}P_2$ and a companion p -4H-SiC were fabricated into devices for the Hall Effect measurements. Diagrams of the sample are depicted in Figure 6.1. Details on the implementation of the Van der Pauw approach to Hall Effect measurements can be found elsewhere.¹³⁷ For the 4H-SiC sample, the intrinsic layer of the sample was assumed to electrically isolate the p -layer from the substrate (the i -layer had a quoted carrier density of $8 \times 10^{14} \pm 50\%$). Ni/Au contacts were made to $B_{12}P_2$ as described in Chapter 4. Contacts to p -4H-SiC were made by evaporating 100/1500/500/2000 Å of Ti/Al/Pt/Au and annealed at 950 °C for 120 s. The room temperature Hall Effect properties of the 4H-SiC and $B_{12}P_2$ films prior to any irradiation can be found in Table 6.1. The $B_{12}P_2$ sample used in this study was selected because of its similar hole concentration to the 4H-SiC companion sample and because of its good hole mobility compared with other grown samples.

The electrical properties of the 4H-SiC sample were measured over the temperature range of 100-400 K. At 100K the hole concentration almost reached $1 \times 10^{12} \text{ cm}^{-3}$, nearly the lower bound of what was measurable with the equipment used. 400 K was the highest temperature that the measurement system can operate. $B_{12}P_2$ was measured over the temperature range of 128-400 K. 128 K was the lower bound because Hall measurements below that temperature yielded a non-linear relationship between the Hall coefficient and the magnetic field.

Table 6.1: *The electrical transport properties of the Van der Pauw samples used in this study at room temperature prior to irradiation.*

	p -4H-SiC	p -B ₁₂ P ₂
Hole Concentration [p] (cm ⁻³)	2.25×10^{17}	2.74×10^{17}
Mobility [μ] (cm ² /Vs)	55.6	2.35
Resistivity [ρ] (Ω cm)	0.50	9.73

Table 6.2: *Properties of the ^{210}Po source used to irradiate the samples in this study.*

	α energy	Half-life	Activity	Daughter Isotope
^{210}Po	5.3 MeV	138.4 days	≈ 2.5 mCi	^{206}Pb

6.2.1 ^{210}Po Source

The samples were irradiated by a commercial ^{210}Po α -emitting source (Figure 6.2) to test the radiation response. The properties of the ^{210}Po isotope are listed in Table 6.2. The source consisted of a thin plate of ^{210}Po sealed with a precious metal coating. The α -particles escape from the source through a 0.7 inch diameter window. To irradiate the samples, the window of the ^{210}Po source was placed directly over the samples. The activity of the source was approximately 2.5 mCi.

While the energy of the α -particles emitted from ^{210}Po are all 5.3 MeV, their actual energy distribution leaving the source varies due to self-shielding. The particle energy is also attenuated as they pass through the air. Further, because the α -particles are ejected from plate at random angles, α 's reaching the samples at shallow angles travel longer distances

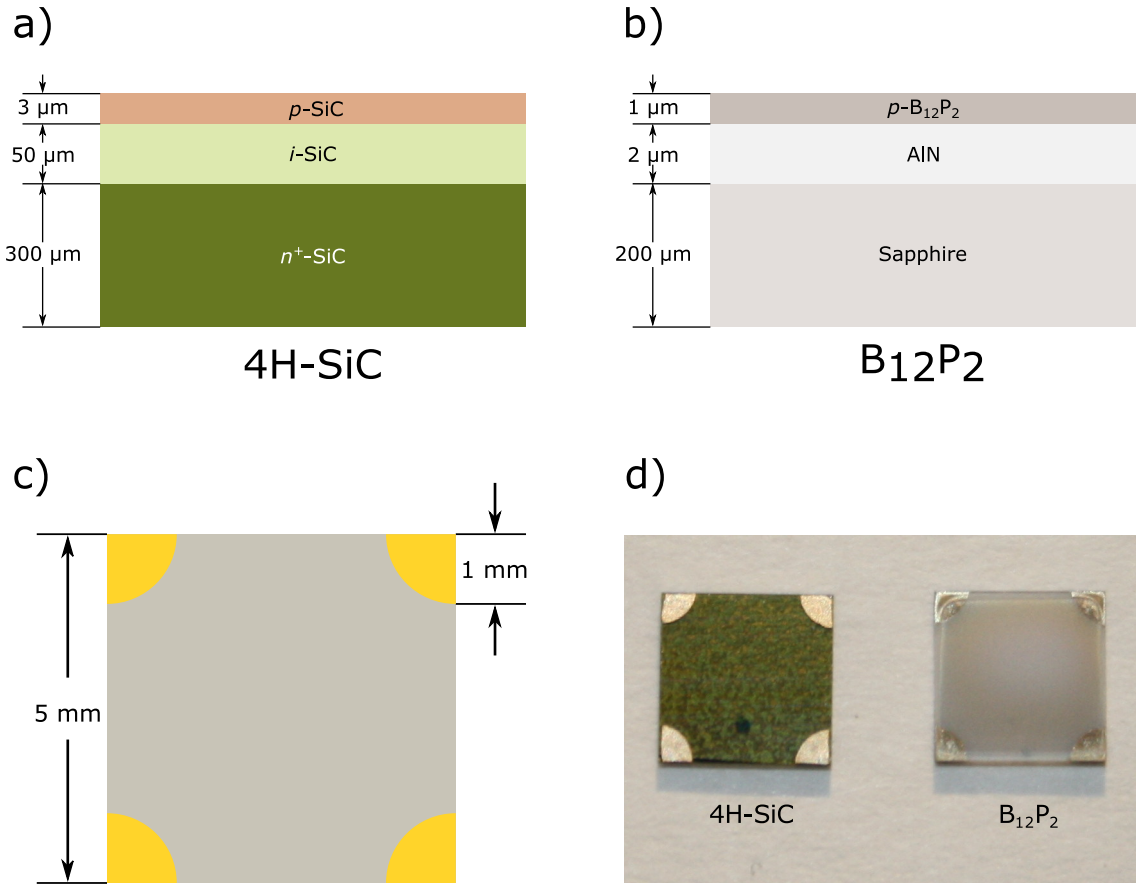


Figure 6.1: a) the epitaxial structure of p -4H-SiC. b) the hetero-epitaxial structure of the $B_{12}P_2$ sample used in this study. c) a schematic of the Van der Pauw geometry used. d) a photograph of the 4H-SiC and $B_{12}P_2$ Van der Pauw samples.

through air and are therefore more strongly attenuated than those that impact the samples at normal angle.

The energy distribution of emitted α 's were measured using a silicon *pin* diode as a detector. However, the activity of the source was so high that placing the silicon *pin* diode directly under the source saturated the detector. For the purposes of measuring the α energy distribution only, an aluminum foil was placed over the window and a hole was poked in it to reduce the number of α 's reaching the detector (the foil was removed before irradiating the Hall samples). The energy distribution of α 's emitted through the hole in the foil was then measured via the silicon *pin* diode detector. The maximum energy of the α 's was about 4 MeV; however, the spectrum is broad and many lower energy α 's were detected. By using

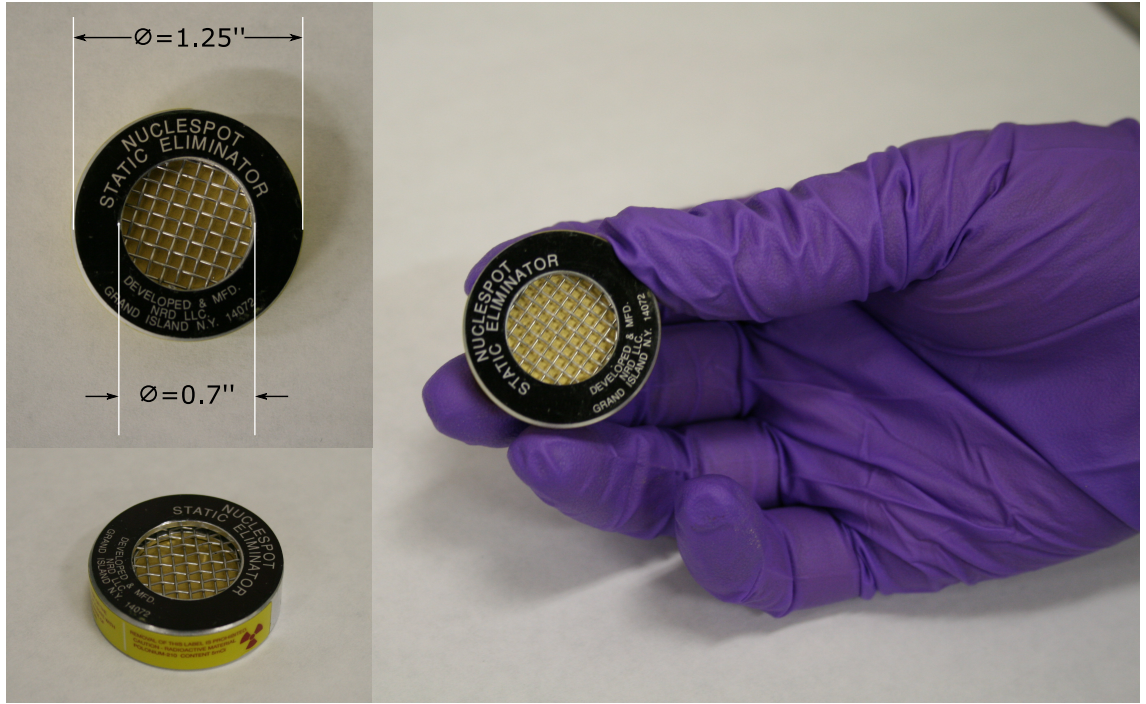


Figure 6.2: Photographs of the ^{210}Po α -emitter used for irradiation.

a the hole in the foil to decrease the number of α 's reaching the silicon diode, the source was slightly collimated. This collimation likely attenuates the signal on the lower energy portion of the spectrum because the low energy α 's are likely leaving the source at shallow angles and are more likely to be blocked by the foil.

To better understand how the α -irradiation will damage the different epitaxial layers in the samples, SRIM simulations were used to create vacancy generation depth profiles in B_{12}P_2 and 4H-SiC (Figure 6.4). Two vacancy distribution types were simulated. First, ion implantation of 3.8 MeV He^+ ions in to both 4H-SiC and B_{12}P_2 were simulated (red profiles in Figure 6.4). These monoenergetic He^+ ions are perfectly collimated are incident normal to the sample surface. Preliminary 3.8 MeV He^+ ion implantation experiments into 4H-SiC were completed before testing with the ^{210}Po source and are discussed further below. As can be seen in Figure 6.4, most of the damage occurs at the end of the ion track where the ions come to a stop. Since all of the ion trajectories terminate deep in the material, little damage occurs near the surface. The broad, second type of vacancy profile is the simulated

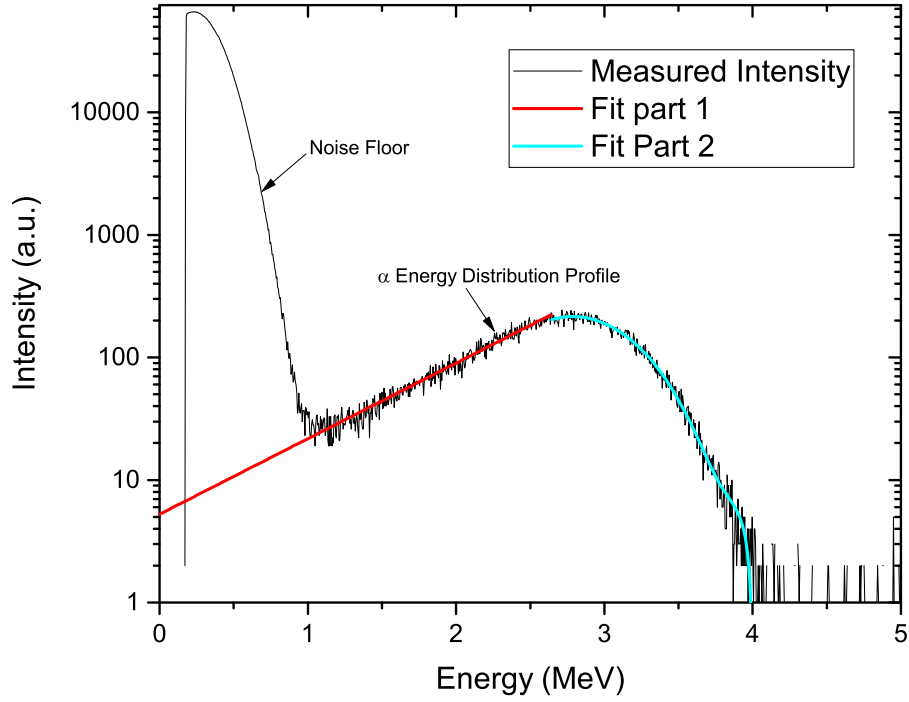


Figure 6.3: The spectrum of α energies being emitted from the ^{210}Po as measured through a pin hole through a foil. The intensity at lower energies likely reduced due to collimation of the pin hole. Fits made to the energy distribution are shown as red and cyan lines.

damage distribution in 4H-SiC and B_{12}P_2 from α particles emitted from the ^{210}Po source. The method for simulating the vacancy profile from the ^{210}Po is described in the following.

Simulating the damage profile for the ^{210}Po source is more complicated than for the ion implantation case because the α 's not only vary in energy but also in the impinging angle relative to the surface of the sample. To create the profiles in Figure 6.4, several assumptions were made prior to running the simulations:

1. From MCNP simulations of the source, the angle of incidence of the α 's were assumed to only be in the range of 30-90° relative to the sample surface (90° representing a normal to the sample surface).¹³⁸
2. The energy spectrum was assumed to be the same as that in Figure 6.3 which was measured through a pin hole. The energy spectrum was fitted by two functions and the lower energy fit was extrapolated to 0 MeV.

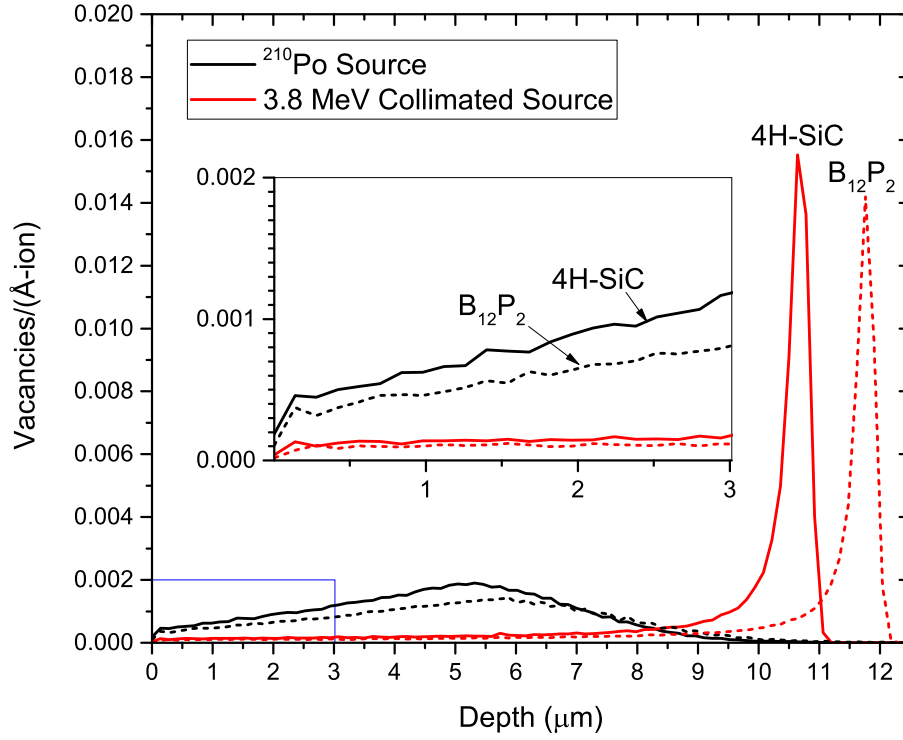


Figure 6.4: Radiation damage profiles of high-energy α -particles impinging on 4H-SiC (solid lines) and $B_{12}P_2$ (dashed lines) as simulated using SRIM. The collimated source is representative of a high-energy ion implantation. Most of the damage is at the end of the ion track. For the simulated ^{210}Po source, the damage profile is more evenly distributed because the ends of the ion tracks terminate throughout the first 10 μm in depth due to the variety of energy and angles of the α 's emitted from the source. The inset is a zoomed-in view of the damage profile near the surface as outlined by the blue rectangle.

3. Since α 's impinging the sample at shallow angles must travel further through air before reaching the sample surface, the angle of the α 's was assumed to linearly correlate with the α energy. That is, α 's reaching the surface at an angle of 30° have the lowest energy (0 MeV) and α 's impinging the surface at a normal have energies of 4 MeV.

The simulation results are shown in Figure 6.4. The damage profile is extremely broad in comparison to the ion implantation profile. The spectrum is also shifted to shallower depths within the sample. The broadening and shifting of the damage towards the surface is caused by the α trajectories terminating at different depths within the material due to the variety of α energies and impinging angles (particles impinging at a shallow angle do not

penetrate as far as a particle impinging at a normal to the surface). Although the cumulative number of vacancies per ion/ α for the ^{210}Po source is smaller than for the collimated source (the area under the curve is smaller), the amount of damage near the surface according to the simulation is up to ten times greater. Since the Hall Effect measurements in this study only measure the p -type layers at the surface (top 3 μm for 4H-SiC and top 1 μm for B_{12}P_2), radiation damage should be more severe and therefore easier to measure from the ^{210}Po source as compared to ion implantation. As mentioned previously though worth reiterating, the energy profile used in this simulation (Figure 6.3) is likely attenuated at low energies. Therefore, the damage near the surface is likely being underestimated in the simulated damage profiles for the ^{210}Po source Figure 6.4. The actual amount of damage at the surface should be even higher in comparison to the ion implanted damage.

6.2.2 Determining Appropriate Fluences for Evaluating Radiation Hardness

Let us first consider 4H-SiC since it is a conventional semiconductor and will provide a basis and a point of comparison for evaluating B_{12}P_2 . The characteristic behaviour of a p -type semiconductor undergoing band-type conduction as a function of reciprocal temperature can be qualitatively represented by Figure 6.5. Because 4H-SiC is a wide bandgap semiconductor and because of the large ionization energy of Al dopants in 4H-SiC (even at 400 K not all of the acceptors are ionized), the experiments for this study reside solely in the carrier freeze-out regime. Carrier compensation influences the low temperature behavior of the freeze-out rate of the majority carriers, and this will be used to investigate the effects of α -irradiation.

The carrier freeze-out region of Figure 6.5 can be modeled by the following:

$$\frac{p(p + N_D) - n_i^2}{N_A - N_D - p + \frac{n_i^2}{p}} = \frac{N_V}{g} \exp\left(\frac{-E_A}{kT}\right) \quad (6.1)$$

where p is the hole concentration as a function of temperature, N_A is the acceptor con-

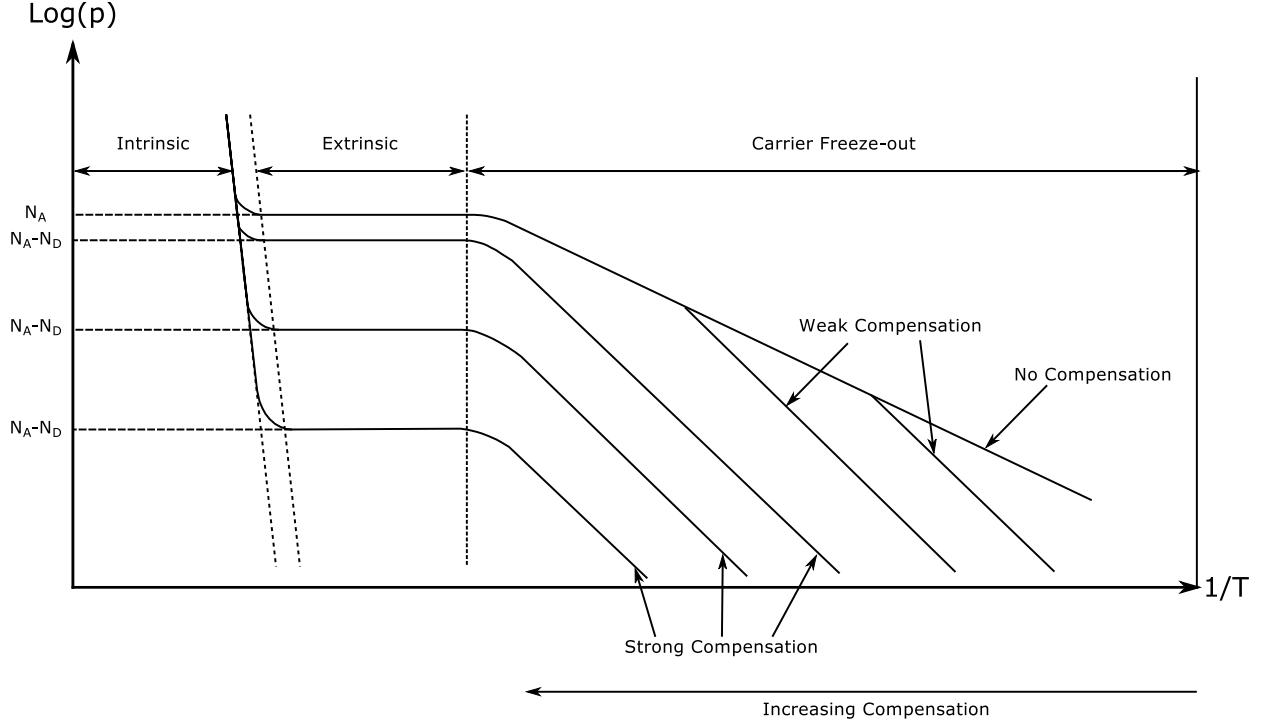


Figure 6.5: A qualitative plot of the hole concentration versus reciprocal temperature of an ideal band-conducting semiconductor with various amounts of compensation.

centration, N_D is the donor concentration, n_i is the intrinsic carrier concentration, N_V is the effective density of states, g is the degeneracy factor (typically taken as 4), E_A is the ionization energy of acceptors above the valence band, k is Boltzmann's constant, and T is temperature in Kelvin.¹³⁹ For wide bandgap semiconductors such as 4H-SiC and $B_{12}P_2$, n_i^2 is negligible for the doping concentrations and temperatures in this study ($n_i \approx 0.3 \text{ cm}^{-3}$ at 400 K for 4H-SiC) and Eq. 6.2 simplifies to:

$$\frac{p(p + N_D)}{N_A - N_D - p} = \frac{N_V}{g} \exp\left(\frac{-E_A}{kT}\right) \quad (6.2)$$

By measuring the carrier concentration as a function of reciprocal temperature and fitting the data to Eq. 6.1 via least squares regression, values for N_A , N_D , and E_A can be determined. This model was applied to the p -layer in SiC before irradiating (see Figure 6.6), where $N_A = 1.62 \times 10^{20} \text{ cm}^{-3}$, $N_D = 1.26 \times 10^{13} \text{ cm}^{-3}$, and $E_A = 0.256 \text{ eV}$ were the opti-

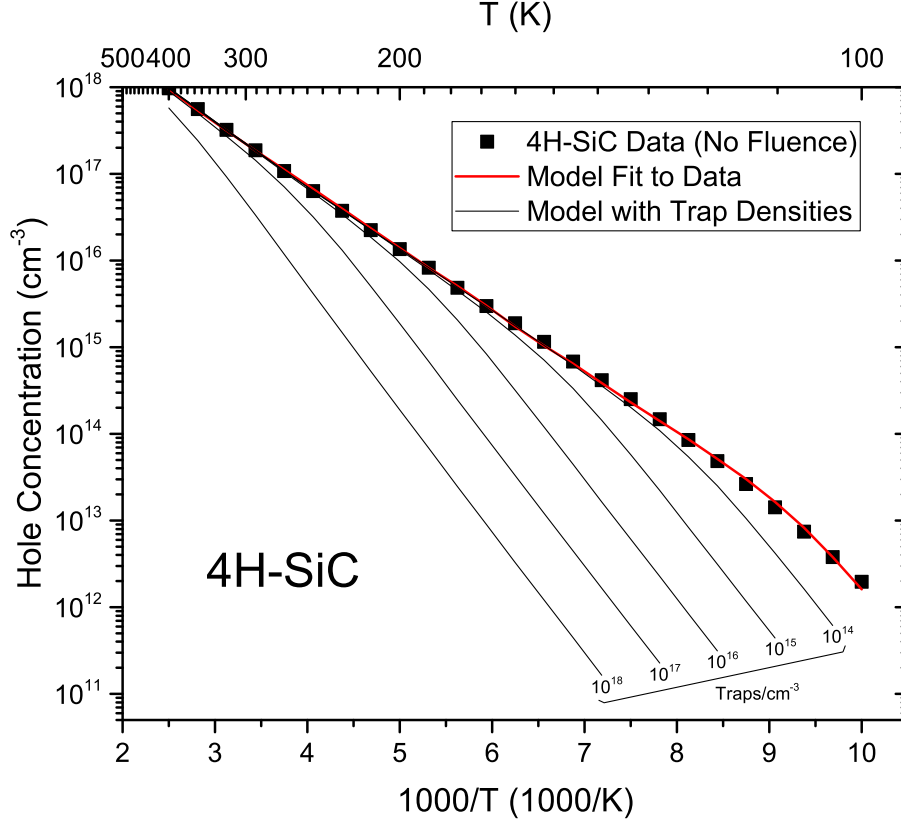


Figure 6.6: The hole concentration versus reciprocal temperature of *p*-4H-SiC before irradiation. The black squares are the measured data point. The red curve is a least squares fit of Eq. 6.2 to the measured data. The black curves are the projected hole concentrations as modeled by Eq. 6.2 after introducing increasing concentration of traps in the material.

mally fit parameters. The model (red curve) fits reasonably although the activation energy is higher than the reported values of 0.190-0.230 eV.^{140,141,142}

As the SiC is irradiated, deep levels within the bandgap are expected to form which can trap carriers.^{143,144} As a first-order approximation of the effect that the traps will have on the carrier concentration, N_D in Eq. 6.2 may be interpreted to be any compensating center—including traps—rather than just donors. Keeping N_A and E_A constant and systematically varying N_D to simulate trap generation, p can be solved for iteratively. The changes in the $\text{Log}(p)$ versus T^{-1} due to trap generation were estimated and are shown as black curves in Figure 6.6. As higher and higher traps densities are inserted into the model, the carrier concentration decreases as carriers are trapped in addition to being frozen-out.

The model and Figure 6.5 are in good agreement.

An estimate of the fluences needed from the ^{210}Po source to damage 4H-SiC enough to create measurable changes in the freeze-out curve is beneficial. Understanding how much time the sample needs to spend under the source is essential because the changes seen in Figure 6.6 are on a logarithmic scale. If the fluences required are too great, the irradiation time could take weeks, months, or longer. If the fluences required are so low that the time needed under the source is milliseconds, then controlled fluences are difficult to implement. The desired fluences need to match with the ^{210}Po activity to ensure an appropriate time scale.

To coarsely estimate how many traps are generated as a function of fluence, 4H-SiC samples of the same structure as in Figure 6.1 were implanted with 3.8 MeV He^+ . The implanted ions were used as surrogates for accelerated fluences of α particles. The hole concentrations were measured at room temperature by Hall Effect after fluences of 10^{12} , 10^{14} , and 10^{15} ions/ cm^2 . The carrier density remaining after irradiation at room temperature, p_ϕ , can be expressed by Eq. 6.3 using the concept of a “carrier removal rate”:¹⁴⁵

$$p_\phi = p_0 \exp\left(\frac{-R_{C,p}\phi}{p_0}\right) \quad (6.3)$$

where p_0 is the effective carrier concentration before irradiation (taken at room temperature), $R_{C,p}$ is the carrier removal rate in the p -layer, ϕ is the fluence (α/cm^2). $R_{C,p}$ was estimated to be $R_C \times \left(\frac{\text{Vacancies in } p\text{-layer}}{\text{Total Vacancies}}\right)$, where R_C is the carrier removal rate averaged over the entire length of the ion track. The fraction of dislocations in the p -layer is a small portion of the total vacancies generated because the ions are collimated and most of the vacancies are generated at the end of the ion track. Using a damage distribution profile from SRIM simulations (see Figure 6.4), the fraction of total vacancies generated in the p -layer was estimated to be 0.0425. Knowing p_0 , p_ϕ , and ϕ , R_C can be fit to Eq. 6.3 by a least squares fit, resulting in a value of $1.59 \times 10^4 \text{ cm}^{-1}$ ($R_{C,p} = 1.59 \times 10^4(0.0425) = 676 \text{ cm}^{-1}$). Since the ^{210}Po α -source does not produce a monoenergetic, collimated beam of α particles but

α -rays emanating over wide angular distribution and a large energy distribution (see Figure 6.4), the ion tracks of many of the α particles will terminate in the p -layer, thus damaging the p -layer at a faster rate than for the implanted samples. Therefore, the damage from the ^{210}Po source should enhance $R_{C,p}$ by a factor of 5-10 or more. Note: the purpose of determining a carrier removal rate here is not to produce a precise model but a model that is good enough to estimate the fluences needed within a range of several orders of magnitude.

For a given fluence from the ^{210}Po source, the trap density produced was assumed to simply be $p_0 - p_\phi$, or:

$$N_{Traps} = p_0 - p_0 \exp\left(\frac{-R_{C,p}\phi}{p_0}\right) \quad (6.4)$$

Using a multiplier of 10 on $R_{C,p}$ and a value of $2.2 \times 10^{11} \text{ cm}^{-3}$ for p_0 , fluences of 1×10^{11} - $1 \times 10^{13} \alpha/\text{cm}^2$ produce calculated trap densities of 3×10^{14} - $3 \times 10^{16} \text{ traps/cm}^3$. As is seen in Figure 6.6, trap concentrations of these amount should produce strong, measurable changes in the freeze-out characteristics of p -type 4H-SiC. With a ^{210}Po source with an activity of $\approx 2.5 \text{ mCi}$, the required irradiation time for a fluence of $10^{11} \alpha/\text{cm}^2$ is approximately 2.4 hours and for $10^{13} \alpha/\text{cm}^2$ is approximately 10 days, each of which are quite manageable to implement.

6.3 Results and Discussion

6.3.1 Observed Changes in p vs. T^{-1} after Irradiation

B_{12}P_2 and 4H-SiC were irradiated with the ^{210}Po source for fluences up to $1 \times 10^{13} \alpha/\text{cm}^2$. As is seen in Figure 6.7, large changes in the carrier concentration of the 4H-SiC sample are observed at low temperatures. The behavior of p versus T^{-1} does not adhere to the projected curves of Eq. 6.2, which predict that the carrier concentration should decrease monotonically as the temperature is cooled and as the fluences are increased. After irradiating, the carrier

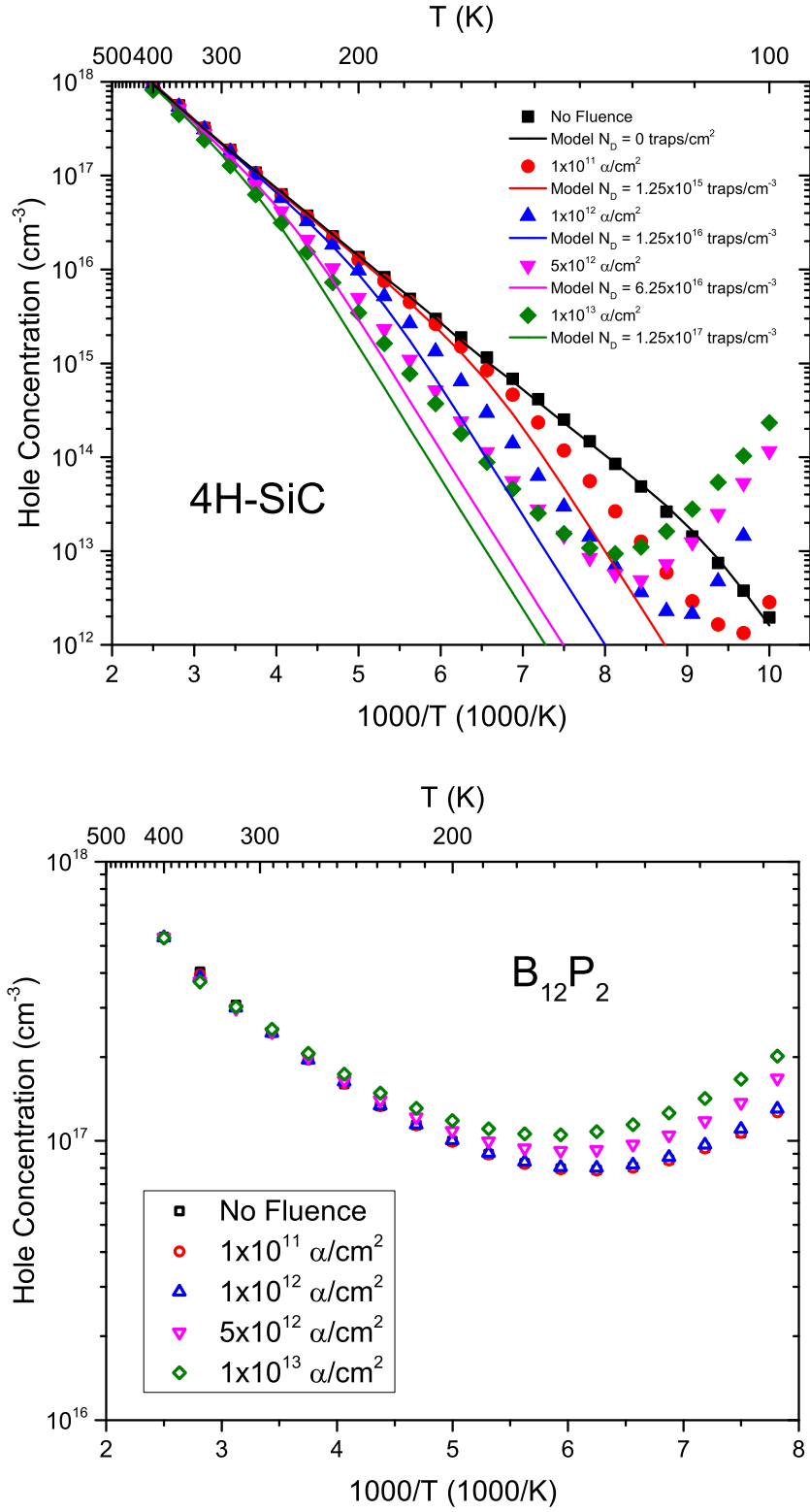


Figure 6.7: The upper plot shows the hole concentration in 4H-SiC versus reciprocal temperature after various levels of irradiation by the ²¹⁰Po source. The solid lines are best fits to the data of the projected hole concentrations after the introduction of traps according to Eq. 6.2. At low temperatures and high fluences, the model is no longer able to fit the data because hopping conduction dominates. The lower plot is the carrier concentration of B₁₂P₂ versus reciprocal temperature.

concentration decreases at high and intermediate temperatures but begins to increase at sufficiently low temperatures. The upward bending of the curves begins at increasingly higher temperatures and carrier concentrations for successively larger fluences. Upward bending of the p versus T^{-1} curves is a hallmark of impurity band conduction.^{146,147}

The solid curves in Figure 6.7 were fit to the data (symbols) using Eq. 6.2 by holding N_A and E_A constant using values optimized for the un-irradiated curve and changing N_D to fit the data from 400K to the lowest temperature possible. N_D was assumed to scale linearly with the fluence, and N_D 's of 1.25×10^{15} , 1.25×10^{16} , 6.25×10^{16} , and 1.25×10^{17} traps/cm³ correspond to fluences of 1×10^{11} , 1×10^{12} , 5×10^{12} , 1×10^{13} α /cm², respectively. At higher temperatures, the carrier concentration is modeled satisfactorily by Eq. 6.2. However, at intermediate temperatures and especially at low temperatures, the model breaks down and is no longer able to predict the carrier concentration. Thus, the assumptions made when using Eq. 6.2 do not apply at low temperatures after irradiation. Eq. 6.2 assumes that the carrier transport is of band-type conduction. Also, the analysis in section 6.2.2 assumed that radiation-induced defects consisted of only hole traps and that each trap effectively compensated a single hole. In reality, various traps may form that have difference energies below the bandgap (e.g. i center = $E_V + 0.53$ eV, L center $\approx E_V + 0.24$ eV, EH6/7 center = $E_C - 1.55$ eV)^{148,144,143} whose ionization is temperature dependent. Further, at high enough defect concentrations, conduction mechanisms other than band conduction may arise.

For the B₁₂P₂ sample (bottom of Figure 6.7), hole concentration versus T^{-1} cannot be modeled by Eq. 6.2 even before irradiation. As the sample is cooled, the carriers do freeze-out to a temperature of about 160 K; however, similarly to the irradiated 4H-SiC, the hole concentration begins to increase below ≈ 160 K, indicating that impurity band conduction may be present. The B₁₂P₂ film is insensitive up to fluences of 1×10^{12} α /cm². Like in SiC, fluences of 5×10^{12} to 1×10^{13} α /cm² increase the upward bending of the $\text{Log}(p)$ versus T^{-1} behavior. The insensitivity of the curves at the lower fluences is likely a result of large amount of defects already present in the material masking any effects of radiation damage.

More discussion on the irradiation effects on $B_{12}P_2$ is provided in section 6.3.5.

6.3.2 Origin and evidence of hopping conduction in $B_{12}P_2$ and 4H-SiC

As discussed in Chapter 1 section 1.4.3, the conduction mechanism in $B_{12}P_2$ can be either band or hopping type conduction. If hopping conduction predominates, then the conductivity should follow Mott's law:¹⁴⁹

$$\sigma = \sigma_0 \exp \left(- \left(\frac{T_0}{T} \right)^{\frac{1}{4}} \right) \quad (6.5)$$

and plotting $\log(\sigma)$ versus $T^{-\frac{1}{4}}$ should result in a linear relationship. Indeed, Figure 6.8 demonstrates such a relationship. The lines in Figure 6.8 are linear fits to the data. Thus, the $B_{12}P_2$ film used in this study conducts by a hopping conduction mechanism and conducts this way over the entire temperature range measured and for all fluences. The large amounts of impurities present in the film (see Chapter 4) is the most likely the origin of the hopping conduction. Impurity atoms introduce localized states into the bandgap. Other point defects and dislocations could also add localized states into the bandgap and contribute to the hopping conduction.

4H-SiC is a conventional band-type conducting semiconductor. For low doping, band conduction is expected to dominate, and carrier freeze-out is expected as the temperature of the material is decreased. At high doping levels, hopping conduction may be possible, especially at low temperatures. Further, adding sufficient defect levels into the material may cause hopping conduction through the introduction of disorder and more localized states into the bandgap. Since hopping conduction has been observed in electron-irradiated *p*-type silicon¹⁵⁰ and ion-implanted GaAs,¹⁵¹ a similar effect may occur in α -irradiated 4H-SiC. As was done with $B_{12}P_2$, the $\log(\sigma)$ was plotted versus $T^{-\frac{1}{4}}$ to check for evidence of hopping conduction (Figure 6.9).

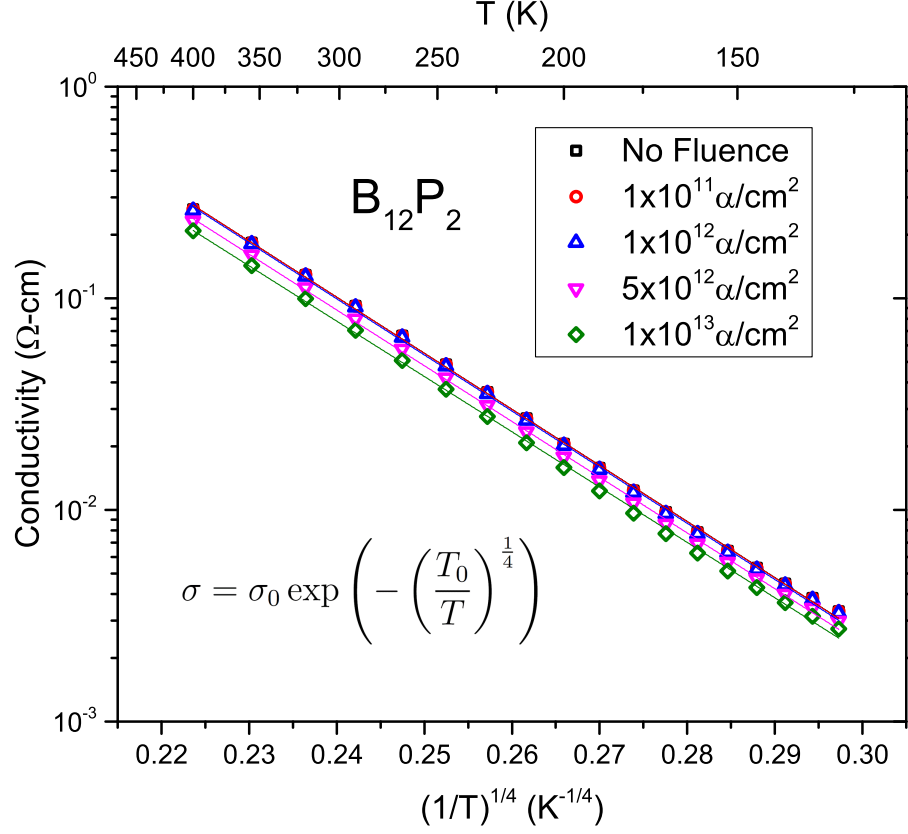


Figure 6.8: A semi-log plot of the conductivity of $B_{12}P_2$ versus $T^{-\frac{1}{4}}$. The lines are linear fits to the data. The strong linear relationship indicated that $B_{12}P_2$ conducts via a hopping mechanism.

In the lower plot of Figure 6.9, the conductivity of the SiC is plotted from 100-400 K in a semilog plot versus $T^{-\frac{1}{4}}$. Lines have been fitted to portions of each curve in the plot, representing plausible regions where hopping conduction is taking place. For better clarity, only the linear segments are plotted for each curve the upper portion of Figure 6.9. For each fitted line, the coefficient of determination (R^2) was 0.999. For no fluence, only the last four data points could be fitted linearly to $R^2=0.999$. With so few points, there is not strong evidence for hopping conduction in un-irradiated SiC. However, as the fluence is increased the portion of the curve that is linear becomes successively larger and begins at higher and higher temperatures, suggesting that hopping conduction is present in irradiated 4H-SiC.

At higher temperatures, $\text{Log}(p)$ versus $T^{-\frac{1}{4}}$ is not linear and the material clearly does

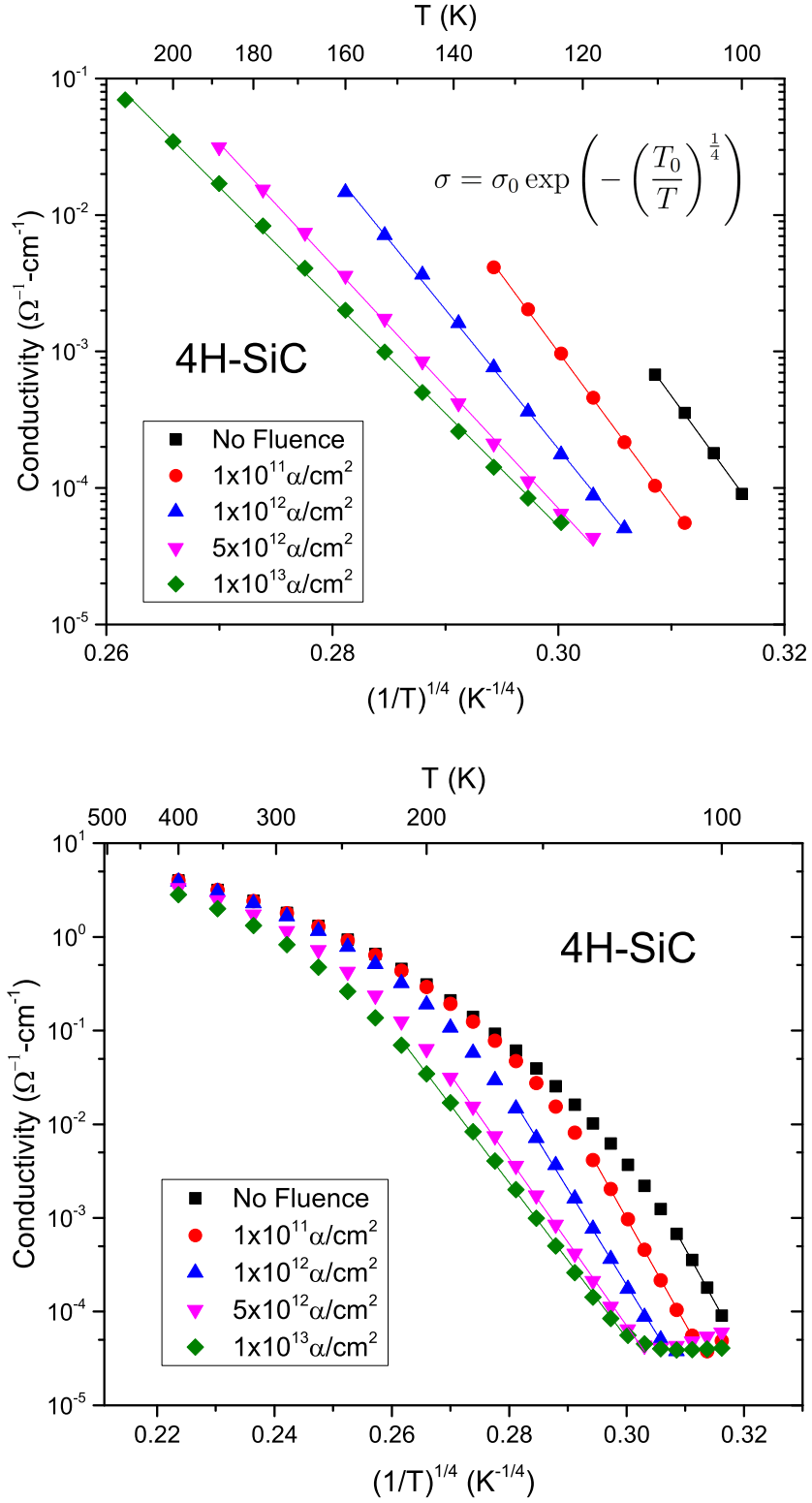


Figure 6.9: The upper plot is a semi-log plot of the p -4H-SiC versus $T^{-\frac{1}{4}}$ after various fluences. The linear relationship suggests that p -4H-SiC conducts via hopping at these data points. The full data set is plotted in the lower plot.

not conduct via hopping. As discussed previously, Eq. 6.2 adequately models the carrier concentration in 4H-SiC at all temperatures for un-irradiated SiC but only at increasingly higher temperatures as the fluences are increased. Hence, for un-irradiated 4H-SiC, the conduction mode is band conduction over the entire temperature range, while band conduction only dominates at higher temperatures after irradiation. In fact, Eq. 6.2 no longer models p vs. $T^{-\frac{1}{4}}$ accurately at temperatures just before the onset of the hopping conduction regime.

The conduction in irradiated 4H-SiC can be explained by a superposition of band conduction and hopping conduction. At high temperatures, a large number of p -type dopant atoms are ionized, much larger than the number of trap levels. In this regime, some carriers are trapped and can conduct via thermally assisted hopping. However, the number of carriers that can conduct through the valence band are greater and their mobilities are larger, and thus their contribution to the conductivity dominates. As the temperature is lowered and more carriers are frozen-out of the valence band, the hopping conduction contribution becomes more prominent and begins to dominate at sufficiently high fluences and low temperatures.

As seen in Figure 6.7 the carrier concentration begins to rise at low enough temperatures in the irradiated 4H-SiC. In this regime, hopping conduction no longer dominates as there may not be enough energy for thermally assisted hopping. The high levels of damage may start to form defect bands within the material in which the holes can conduct. Bands of this type are only half-filled and behave like a poor metal.¹⁴⁷ The carrier concentration for B₁₂P₂ also begins to rise with reciprocal temperature after reaching a minimum although the conduction still follows Mott's law. At high enough doping/defect concentrations, the defect band can merge into the valence band, which may be the case for this B₁₂P₂ sample.

6.3.3 Effect of Irradiation on Mobility

In typical band-conducting semiconductors, lattice or phonon scattering processes are the dominate carrier scattering mechanism such that as the temperature increases the carriers

are scattered by more and more phonons and the mobility decreases.¹⁵² As the temperature is decreased, there are fewer phonons and ionized impurity scattering begins to dominate. At lower temperatures, carriers are moving more slowly and can further interact with the electric field of ionized impurities enhancing scattering.

For un-irradiated 4H-SiC, the mobility dependence on the temperature (Figure 6.10) exactly follows that as determined by Koizumi, *et al.*:¹⁵³ holes are scattered by neutral impurities at temperatures of ≈ 100 K; acoustic scattering dominates to ≈ 200 K; and optical-phonon scattering dominates above ≈ 250 K. As the sample is irradiated, other scattering mechanisms are introduced which lower the mobility over the entire temperature range. Irradiation-induced defects could introduce both ionized and/or neutral scattering sites. At a fluence of 5×10^{12} α/cm^2 and higher, the slope at high temperature of the $\text{Log}(\mu)$ versus $\text{Log}(T)$ curve in Figure 6.10 changes, suggesting that another scattering effect is becoming comparable to phonon scattering at high temperatures. At the highest fluences, the mobility sharply drops off at ≈ 130 K which coincides with the minima in the carrier concentration. The drop in mobility is consistent with the onset of impurity band conduction.¹⁴⁷

The B_{12}P_2 log-log μ versus T plot in Figure 6.10 increases monotonically over the entire measured temperature range, suggesting that phonon mediated scattering is not the dominate scattering mechanism but that ionized impurity scattering predominates. Further, since the transport of hopping carriers is thermally assisted, increases in temperature are expected to increase the mobility in hopping conductors. At high enough temperatures, however, the mobility should saturate and phonon scattering can begin to dominate dominate.⁵⁶ As with 4H-SiC, the mobility of the B_{12}P_2 sample decreases with increasing fluence. The decrease in mobility could be caused by the introduction of vacancies or formation of defect complexes with the impurity atoms present in the film.

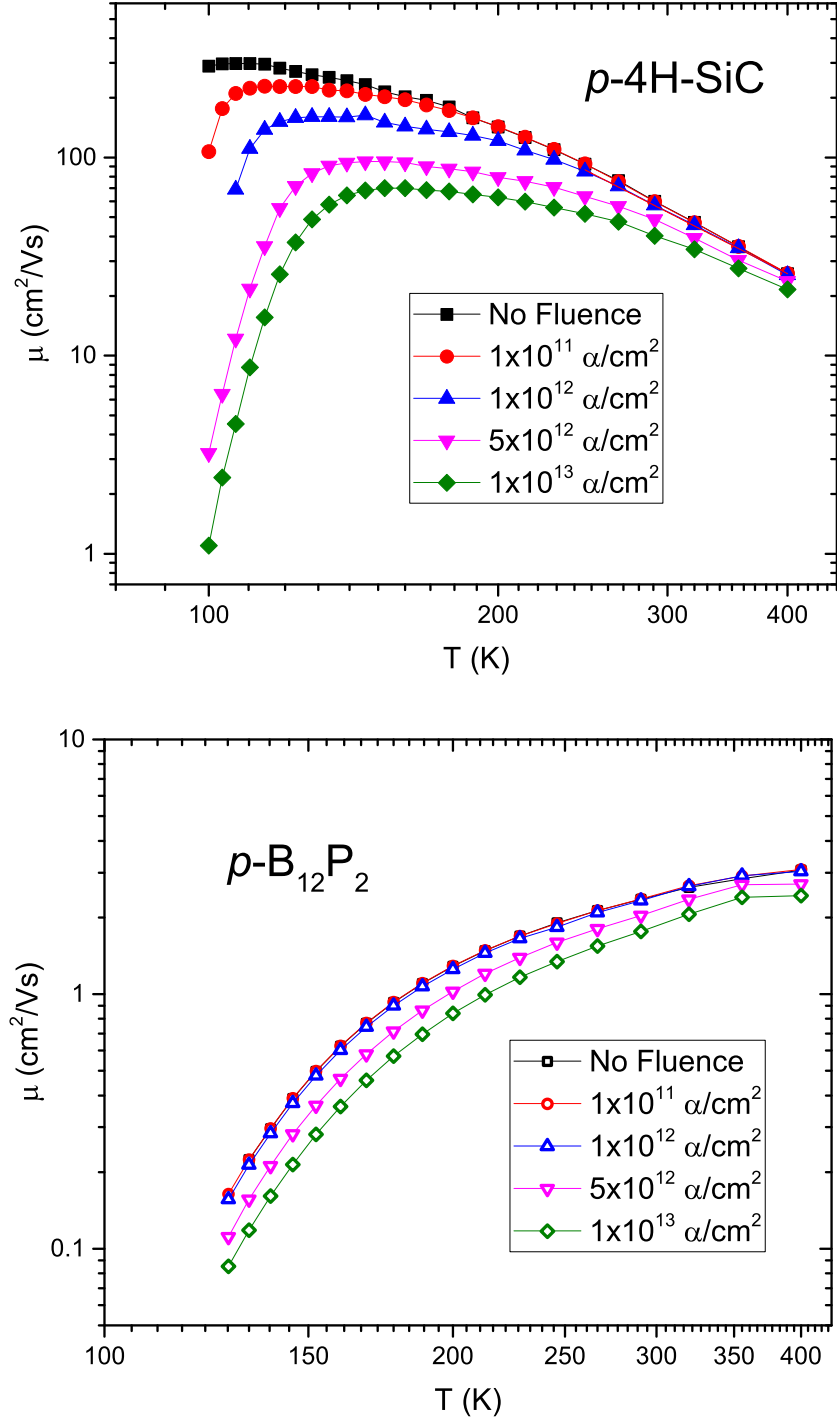


Figure 6.10: A log-log plot of the hole mobility (μ) versus temperature for $p\text{-4H-SiC}$ (top) and $p\text{-B}_{12}\text{P}_2$ (bottom) after successive irradiation with the ^{210}Po source. In both materials, the mobility decreases after each subsequent fluence.

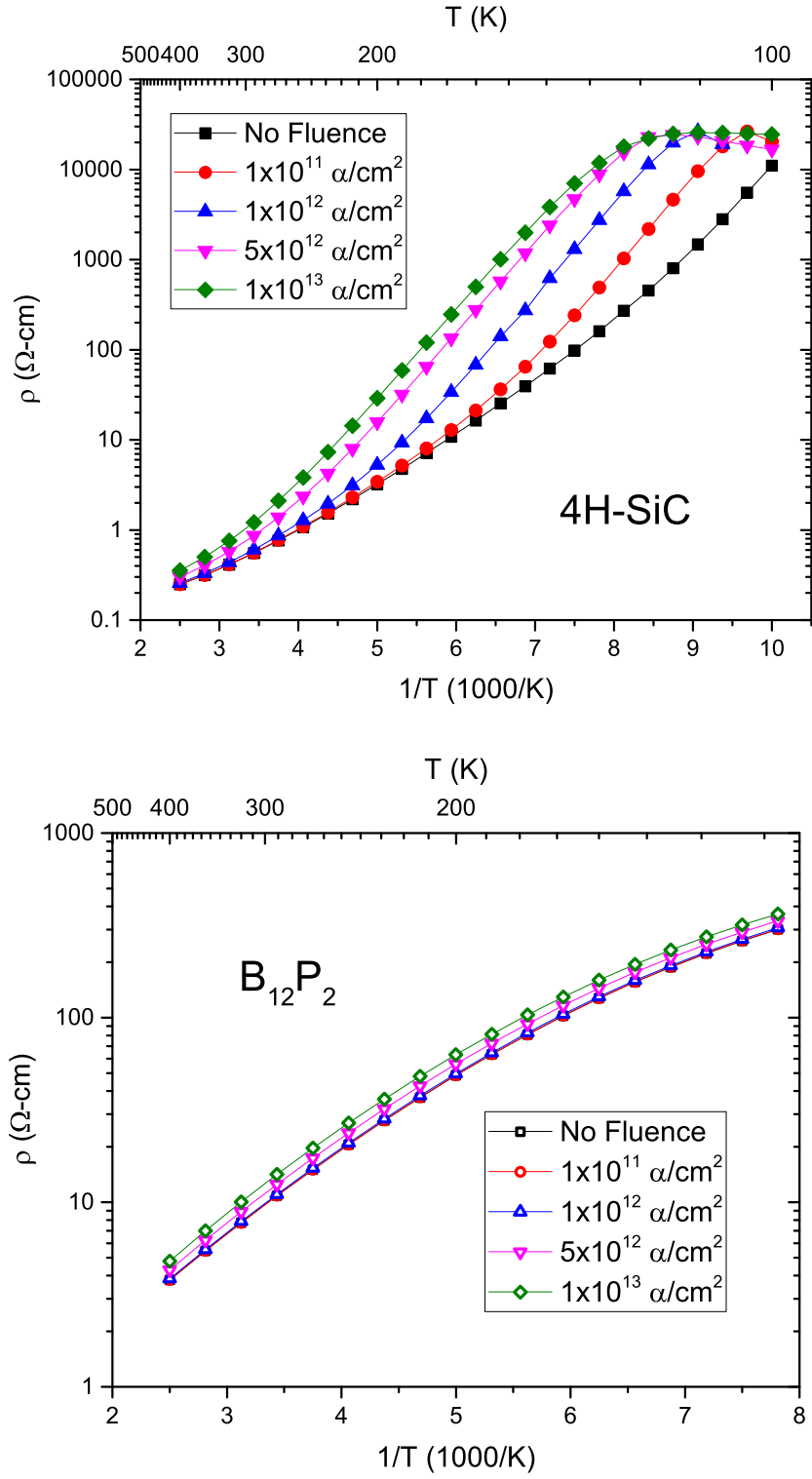


Figure 6.11: A semi-log plot of the resistivity (ρ) versus reciprocal temperature for *p*-4H-SiC (top) and *p*- B_{12}P_2 (bottom) after successive fluence from the ^{210}Po source.

6.3.4 Effect of Irradiation on Resistivity

In Figure 6.11, the resistivity of 4H-SiC is plotted versus reciprocal temperature for each fluence. As the temperature is decreased and holes freeze-out, the resistivity increases as expected. After irradiation, electron-hole traps form, removing carriers and adding scattering sites that increase the resistivity. The resistivity in the irradiated curves reach a plateau at about 10 k Ω -cm. At successively higher fluences, this plateau is reached at increasingly higher temperatures. The curves start to plateau at the minima in the $\text{Log}(p)$ versus T^{-1} plots and the onset of the mobility drop-off and is a consequence of impurity band conduction.^{146,147}

The resistivity of B₁₂P₂ increases as the temperature of the sample is decreased and is depicted in Figure 6.11. From 400-160 K the resistivity increase is at least in part due to carrier freeze-out but also increases because the mobility is rapidly decreasing (Figure 6.10). Below 160 K, the increase of resistivity is solely a result of the mobility decreasing. After irradiation, the resistivity increases only because the mobility is decreasing due to the irradiation.

6.3.5 Discussion

At a glance, it may appear that since the changes in the electrical and transport properties in B₁₂P₂ are smaller than that for 4H-SiC, B₁₂P₂ is more radiation hard than 4H-SiC. However, the starting material of the 4H-SiC is of far better quality than the B₁₂P₂. The B₁₂P₂ sample used here has high levels of impurities and is grown on a non-native substrate (unlike the 4H-SiC), which results in large amounts of dislocations. In many ways, the transport properties of the un-irradiated B₁₂P₂ qualitatively resembles the irradiated 4H-SiC.

For example, the hole concentration versus T^{-1} curve resembles that of the 4H-SiC after it has been irradiated to a fluence of 1×10^{13} α/cm^2 (Figure 6.7). To make the comparison easier, select hole concentration versus T^{-1} curves of B₁₂P₂ and 4H-SiC have been plotted together in Figure 6.12. The onset of the upward bending of the hole concentration versus

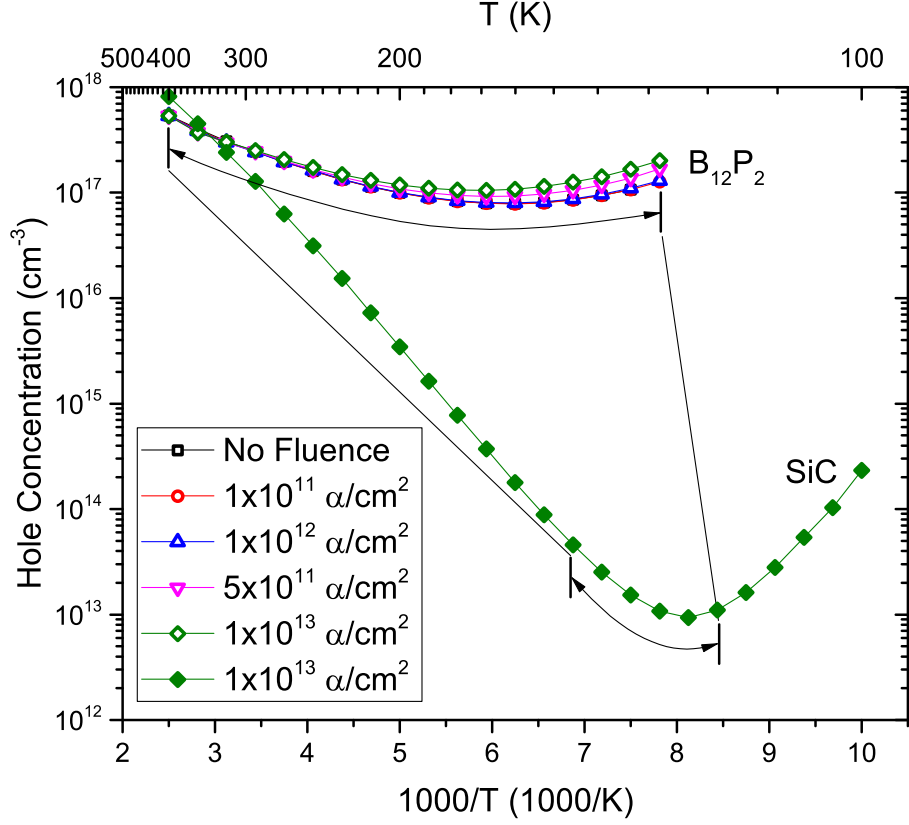


Figure 6.12: The hole concentration for $B_{12}P_2$ and $4H\text{-SiC}$ are plotted in the same plot. The characteristic bending of the $B_{12}P_2$ curves resemble those of the irradiated $4H\text{-SiC}$ at transition between hopping and impurity band conduction. The denoted data points for both $B_{12}P_2$ and $4H\text{-SiC}$ are the same as those denoted in Figure 6.13.

T^{-1} curve (impurity band conduction) in un-irradiated $B_{12}P_2$ begins at hole concentrations which are orders of magnitudes higher than for $4H\text{-SiC}$ at the highest fluence. If the $4H\text{-SiC}$ were to be irradiated further to even higher fluences, the hole concentration versus T^{-1} curve should resemble the un-irradiated $B_{12}P_2$ curve more and more. The hopping conduction should begin at higher and higher temperatures, and the onset of impurity band conduction should also occur at higher temperatures. $B_{12}P_2$ has been reported to be capable of being a hopping or a band conductor, or possibly a superposition of the two mechanisms. This $B_{12}P_2$ sample may begin to conduct by band conduction at higher temperatures, just as the irradiated $4H\text{-SiC}$ transitions from hopping to band conduction at increasingly higher temperatures. If the $B_{12}P_2$ material quality could be improved through

the elimination of impurities and the reduction of hetero-epitaxy-induced dislocations, the conduction may then be dominated by band conduction at the temperatures studied here. The un-irradiated hole concentration versus T^{-1} curve may more closely resemble that of the 4H-SiC with hopping conduction and impurity band conduction only occurring at low temperatures. For a pristine $B_{12}P_2$ crystal, the hole concentration versus T^{-1} curve may follow Eq. 6.2 at all temperatures like un-irradiated 4H-SiC.

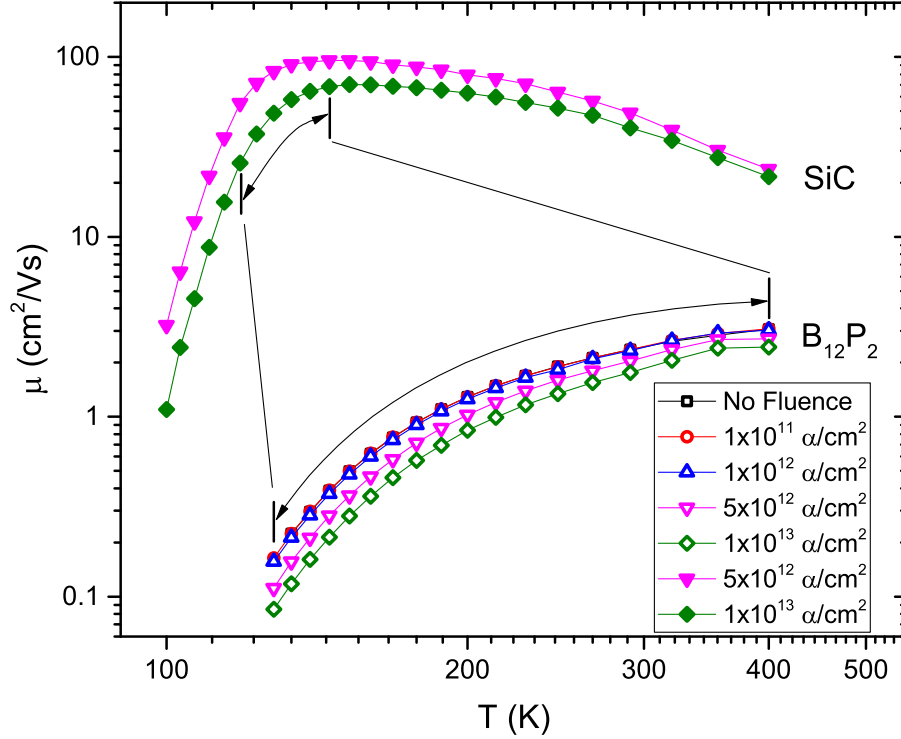


Figure 6.13: The mobility of $B_{12}P_2$ and 4H-SiC plotted together. The mobility of $B_{12}P_2$ resembles that of the irradiated 4H-SiC. The denoted data points for both $B_{12}P_2$ and 4H-SiC are the same as those denoted in Figure 6.12.

Another example of how un-irradiated $B_{12}P_2$ resembles the irradiated 4H-SiC sample is shown in Figure 6.13. The denoted sections of the curves correspond to the denoted sections in Figure 6.12, i.e. the same temperature range is denoted for $B_{12}P_2$ and 4H-SiC in each figure. The mechanisms that are causing the change in mobility (and carrier concentration) may be the same ones at play in each material.

In this study, there is no evidence to support the claim that $B_{12}P_2$ self-heals or is immune

to radiation damage from α decay from ^{210}Po . In the sample tested, the change in the hole concentration versus T^{-1} curve and the reduction in hole mobility suggests that defects are accumulating in B_{12}P_2 in contrast to the TEM analysis reported in the literature.^{6,34} It is possible that electrically active defects in the B_{12}P_2 are unobservable by TEM analysis since atomic positions within the boron icosahedra are not resolvable. Only large, gross changes in the crystal structure should be resolvable by TEM imaging, and that is why an electrical transport measurement approach was used in this study. Unfortunately, this B_{12}P_2 sample had high impurity concentrations and likely large dislocation densities, which makes any definitive claims about the radiation hardness of B_{12}P_2 difficult. “Self-healing” could be circumvented by large concentrations of impurities or dislocations in the crystal. For example, irradiation-induced Frenkel defects may not recombine but rather react with impurity atoms to form stable impurity-defect complexes or the defects could interact with a nearby dislocation and contribute to the lattice disruption there. Defect complexes and dislocations will no doubt negatively affect the electrical transport in B_{12}P_2 . Ideally, this experiment should be reproduced with a better quality film or, even better, a high quality bulk crystal.

Another possibility for why B_{12}P_2 accumulated defects in this study is that B_{12}P_2 may not be able to self-heal from α radiation damage. The reported “self-healing” of B_{12}P_2 was for β particles which are of lower energies than α ’s and can transfer less energy to atoms within the crystal lattice due to the smaller mass. This experiment could be repeated with a β emitter in future experiments.

6.4 Conclusions and Future Work

To measure the effect of α radiation on p -type B_{12}P_2 and 4H-SiC, epitaxial layers of each material were irradiated by α particles from a ^{210}Po source, and the electrical transport properties were measured by temperature dependent Hall Effect after successive fluences over

the range of 1×10^{11} - 1×10^{13} α/cm^2 . In 4H-SiC, the α radiation induced hole compensation, a reduction in hole mobility, carrier hopping, and a defect band to form. The background defect levels in B_{12}P_2 before irradiation were high enough to form an impurity or defect band which caused hopping conduction and mask any radiation damage at low fluences. After higher α fluences, the mobility in B_{12}P_2 was reduced and the impurity band becomes more pronounced. The temperature dependence of transport properties of 4H-SiC after irradiation qualitatively resemble those of the un-irradiated B_{12}P_2 film indicating that the starting defect level concentration in B_{12}P_2 is very large. Irradiation-induced defects in B_{12}P_2 may be a result of background impurities and defects forming complexes with vacancies that are produced from the α irradiation and therefore interfere or circumvent “self-healing.”

Since the background defect levels in B_{12}P_2 were so large, the irradiation experiments should be repeated with higher quality films. Ideally, the carrier concentration would be the same but other impurities in the crystal would be decreased and the concentration of dislocation would be reduced. With low defect levels, B_{12}P_2 may conduct purely by band conduction, even at low temperatures. Furthermore, radiation-induced Frenkel pairs may be able to recombine without the influence of growth-induced defects. If radiation-induced defects do form, Hall Effect measurements on better quality B_{12}P_2 crystals will be more sensitive to defect generation (as was the case for 4H-SiC in this study).

Another method for probing the effect of irradiation on B_{12}P_2 or 4H-SiC is measuring the minority carrier lifetime as a function of fluence. High minority carrier lifetimes are desired for radioisotope batteries. Even if the carrier concentration is largely unaffected, a drastic drop in the minority carrier lifetime could be devastating to the output power of a device. The lifetimes in epitaxial B_{12}P_2 films could be measured via photoconductance decay or by short-circuit current-open-circuit voltage decay in pn junctions.

To better understand the number of defects and their position within the bandgap after successive irradiation, other measurements could be taken. If a pn junction could be made, then deep-level transient spectroscopy (DLTS) could be used. If the films could be grown

with a very low background carrier concentration (high resistivity), the thermally stimulated current (TSC) could be used. Cryogenic photoluminescence could also be measured on $B_{12}P_2$ films which has the advantage of not needing a device, not needing extremely high resistivity material, and can probe defect levels throughout the entire bandgap.

The ultimate test for measuring the radiation hardness and longevity of $B_{12}P_2$ would be to fabricate a pn junction and measure the output power under a radioisotope over time. Such a device could be easily compared to 4H-SiC and other semiconductor devices.

This study focused on α radiation which is far more damaging than β radiation in part due to the higher energies of α emitters and in part due to heavy mass of an α in comparison to a β . Perhaps $B_{12}P_2$ can “self-heal” to β irradiation but not to α irradiation. The experiments in this study and the experiments outlined as future work could be repeated using a β emitter.

Chapter 7

Conclusions and Future Work

7.1 Summary

The reported “self-healing” of $B_{12}P_2$ could make feasible radioisotope batteries employing high-energy radioisotopes with longer device lifetimes than batteries made from conventional semiconductor materials. This dissertation demonstrates improved $B_{12}P_2$ epitaxial growth, fabrication of ohmic contacts to p - $B_{12}P_2$, reduced impurities in the films grown, and tested how α radiation from a ^{210}Po source affected the transport properties of $B_{12}P_2$.

Using chemical vapor deposition, $B_{12}P_2$ was deposited over the temperature range of 1250-1450 °C using B_2H_6 (1% in H_2), PH_3 , and H_2 on 4H-SiC substrates. From X-ray diffraction, the epitaxial relationship was established as $(0001)[1\bar{1}00]_{B_{12}P_2} \parallel (0001)[1\bar{1}00]_{4H-SiC}$ or using the equivalent rhombohedral indices for $B_{12}P_2$: $(111)[1\bar{2}1]_{B_{12}P_2} \parallel (0001)[1\bar{1}00]_{4H-SiC}$. 1300 °C was the optimum growth temperature in this study as determined by X-ray diffraction rocking curves about the (0003) $B_{12}P_2$ peak. 4H-SiC substrates with a standard miscut to the (11 $\bar{2}$ 0) produced $B_{12}P_2$ films that had a twin density of 30% while 4H-SiC substrates miscut to the (1 $\bar{1}$ 00) produced $B_{12}P_2$ films with suppressed twin densities of less than 1%.

Before testing the electrical properties of $B_{12}P_2$ in response to α irradiation, ohmic contacts were developed and the background impurity concentrations were evaluated by SIMS. Two different ohmic contacts were developed to $B_{12}P_2$: Cr/Pt (500/1000 Å) and Ni/Au (1000/1000 Å). The best ohmic contact tested was Ni/Au annealed in Ar at 500 °C for 30 s. Secondary ion mass spectrometry revealed high concentrations of Si, C, and O impurities. Si and C, which are p -type dopants, were reduced by replacing the TaC-coated graphite susceptor with Zr metal and the 4H-SiC substrate with an AlN/sapphire substrate. The effects of α irradiation on $B_{12}P_2$ were compared to p -4H-SiC by temperature-dependent Hall Effect to understand how the transport properties change. The high background defect density made it difficult to assess conclusively whether $B_{12}P_2$ “self-heals” from α irradiation damage.

7.2 Future Work

Much work must still be done before the radiation hardness of $B_{12}P_2$ can be fully evaluated and long-lasting $B_{12}P_2$ radioisotope batteries can be fabricated. Outlined here are steps that could be taken improve $B_{12}P_2$ growth and ways to characterize both the material quality and to evaluate the radiation hardness of $B_{12}P_2$.

7.2.1 $B_{12}P_2$ Crystal Growth

The extent to which α or β radiation damage to $B_{12}P_2$ can be tested hinges on the starting quality of the $B_{12}P_2$ crystal. Thus, improving $B_{12}P_2$ crystal growth should be the highest priority in future work. The crystal growth in this study was far from comprehensive and much more could be done to further improve $B_{12}P_2$ hetero-epitaxy on 4H-SiC.

As was discussed in Chapter 3, the substrate surface plays a large role in how the epitaxial film nucleates and propagates. The etched 4H-SiC substrate surfaces in this dissertation were hillocked; however, the surface should ideally be atomically smooth with atomic steps. Substrate surface preparation should be optimized and can be characterized by AFM imaging for different surface preparation techniques and conditions. The surface preparation should be optimized by adjusting the *in-situ* H_2 etch temperature and etch time as well as the introduction of PH_3 over the substrates.

After the surface preparation is optimized, a technique for improved $B_{12}P_2$ nucleation should be developed. The best growth conditions for nucleation may be extremely different than those used for growth of thick films as the surface energy near a hetero-epitaxial interface may be very different than the surface of a thick film. Ideally, since the 4H-SiC substrates are stepped, $B_{12}P_2$ will nucleate only at step edges, and then the steps will grow continuously in step flow growth. After establishing conditions for a good nucleation and buffer layer growth, then the conditions for continuing to grow the film should be optimized to ensure continued step-flow epitaxial growth. The process parameters that will need to

be adjusted include the growth temperature, absolute precursor flow rates, the PH_3 partial pressure, the III/V ratio, and the carrier gas flow rate.

Hetero-epitaxy on substrates other than 4H-SiC should also be explored. AlN/sapphire templates were used in this work for evaluating impurities, but growth on AlN/sapphire should be further researched, and the same surface preparations and growth optimizations described for 4H-SiC should also be performed with this substrate. Other templated growth techniques could also be explored, such as B_{12}P_2 growth on microstructured pillar arrays.¹⁵⁴ If B_{12}P_2 bulk crystals were available, then films could be grown homo-epitaxially which would prevent any auto-doping, and should greatly lower the dislocation density in the films assuming that the bulk crystal is of high quality.

Further improvements to decrease the background doping of B_{12}P_2 must also be made. While replacements for the graphite susceptor, substrate, and insulation were made in an effort to reduce the amount of impurities in the B_{12}P_2 films, these efforts were limited by maintaining the same reactor geometry and setup. With an appropriate reactor geometry, such as the vertical CVD furnace depicted in Figure 7.1, the insulation can be moved downstream or even eliminated from the design to eliminate it as an impurity source. Furthermore, pyrolytic boron nitride could not be used as a coating on the graphite susceptor in this study because the film buckled and delaminated on the interior surface of the tubular susceptor. Pyrolytic boron nitride adheres extremely well to the outside faces of graphite. With the susceptor geometry shown in Figure 7.1, pyrolytic boron nitride only needs to coat the outside of the susceptor. Even if cracks eventually form in the coating, there is no part of the susceptor upstream of the substrate and C contamination should therefore be low. Switching to a completely new reactor geometry would require optimizing the growth condition from scratch. Before building such a reactor, any design would benefit from simulations of the fluid, heat, and mass transport using modeling software.

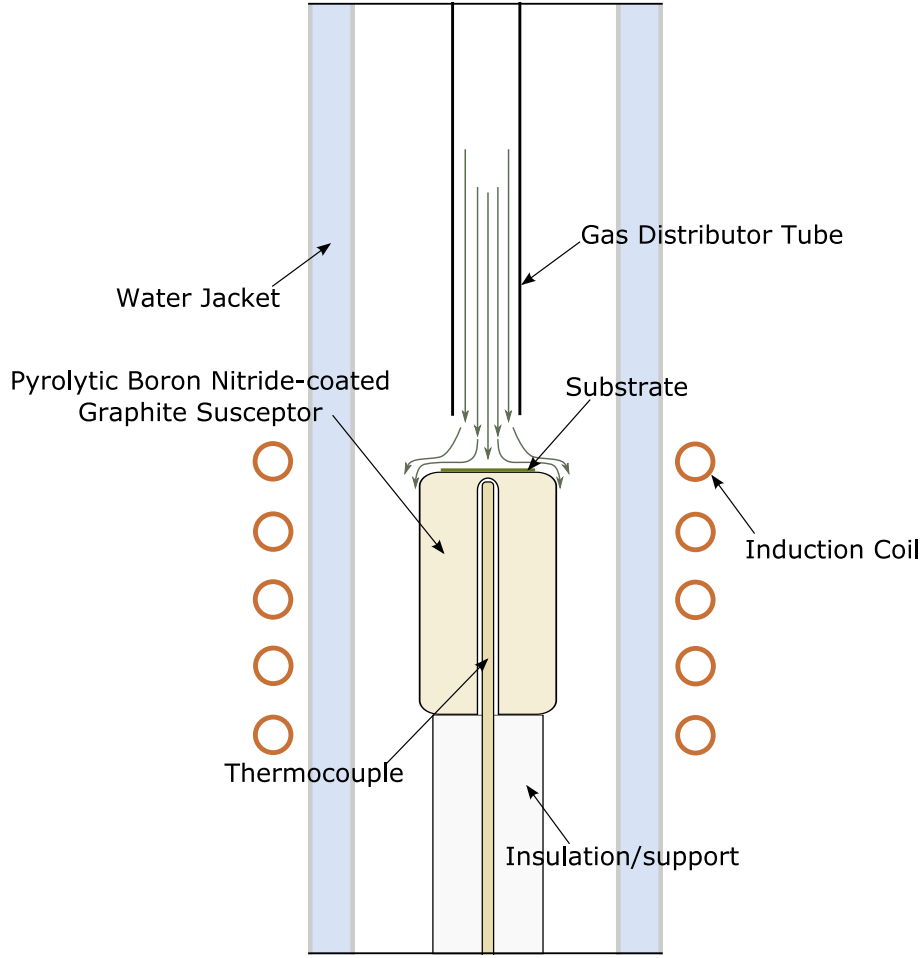


Figure 7.1: A proposed schematic of a vertical chemical vapor deposition system for future $B_{12}P_2$ epitaxial growth. The substrate rests on the end of a pyrolytic boron nitride-coated graphite susceptor. Contamination from the susceptor and insulation should be suppressed as any potential impurities will be swept downstream and away from the substrate and growing film.

7.2.2 Doping $B_{12}P_2$

Once smooth, high purity epi-layers can be reliably grown, the $B_{12}P_2$ film can be doped either *in-situ* during growth or by ion implantation. As with $B_{12}As_2$, $B_{12}P_2$ could be doped *p*-type with Si by using SiH_4 as a dopant source. Although *n*-type $B_{12}P_2$ has not been created, Al, Y, Mg, and Li were suggested as possible *n*-type dopant atoms in Chapter 5. Al and Mg could possibly be doped *in-situ* using compounds routinely used in metalorganic chemical vapor deposition (MOCVD) of III-nitrides such trimethylaluminum or triethylaluminum for

Al or bis(cyclopentadienyl)magnesium for Mg. However, these compounds could potentially also be a C source which may compensate n -type doping if incorporated into the $B_{12}P_2$ crystal. Ion implantation offers more flexibility in choosing which elements that can be tested as a dopant because virtually any element can be implanted with extremely high purity. Many dopant atoms could be tested via ion implantation, including but not limited to Al, Y, Mg, and Li. Ion implantation and activation of any dopants in $B_{12}P_2$ — p -type or n -type—is completely unexplored.

7.2.3 Materials Characterization

In-depth materials characterization of $B_{12}P_2$ should be done as the crystal growth is improved to both characterize defects formed during growth and to evaluate the radiation hardness of $B_{12}P_2$. If crystals with high enough quality can be grown, Rutherford backscatter channeling experiments can measure crystal lattice damage before and after irradiation. Cryogenic photoluminescence (PL) could also be used to characterize the presence of radiation damage by detecting deep levels within the bandgap. Ionization energies of dopant atoms in $B_{12}P_2$ could also be measured via temperature-dependent PL.

Some basic properties of $B_{12}P_2$ still have not been measured and should be done in future work. For example, the electron affinity of $B_{12}P_2$ is unknown, but this property is essential to understanding how bands align in heterojunction diodes. Another unmeasured property of $B_{12}P_2$ is its coefficient of thermal expansion (CTE). Although it may be similar to that measured for $B_{12}As_2$, knowing this property can greatly inform how strain and defects form in hetero-epitaxy.

7.2.4 Electrical Characterization

As demonstrated in Chapter 6, the high concentration of impurities and background defects limited the amount of electrical characterization that could be done on irradiated $B_{12}P_2$. If the impurity background and the concentration of defects can be reduced, many electrical

measurement techniques can be used to characterize the crystal quality, defects present, dopant levels, device performance, and radiation hardness.

Hall Effect measurements can provide direct information about the carrier type, carrier concentration, carrier mobility, and—if measured as a function of temperature—compensating dopant concentration and dopant ionization energies. The carrier type and concentration are important to evaluate so that they can be controlled and device stacks can be designed and fabricated. Characterizing the ionization energy of different dopants is essential to assessing the suitability of different dopant atoms and their substitutional lattice positions. The mobility is strongly affected by the crystal quality and thus can be an indirect measure of it. Temperature-dependent mobility measurements can also provide information on the carrier scattering mechanisms. As thoroughly discussed in Chapter 6, Hall Effect can also be a powerful tool to measure radiation damage.

Minority carrier lifetime measurements (e.g. via photoconductance decay) give insight into the crystal quality and the defects present, but also if α or β radiation damage are creating recombination centers. Techniques such as deep-level transient spectroscopy can measure defect energy levels and concentrations if the levels are near the valence band or conduction band and if a pn junction or Schottky diode can be made. Thermally stimulated current can also provide similar information and can be used with either a pn junction or a highly resistive film or bulk crystal.

7.2.5 $B_{12}P_2$ Device Processing and Microfabrication

Many semiconductor microfabrication processes need to be thoroughly developed for $B_{12}P_2$. Examples include dry etching for mesa isolation, native oxide removal, surface passivation, and Schottky contact formation. Ideally, diodes (pn homojunctions, pn heterojunctions, and Schottky diodes) should be developed as the final goal is to create a radioisotope battery. Proof-of-concept, power-generating diodes should be tested with both α and β emitters to characterize the power output and device longevity.

7.2.6 α and β Irradiation Experiments

The irradiation experiments in this work used high-energy α particles to test the radiation hardness of $B_{12}P_2$. α emitter radioisotope batteries are desirable because they have potentially higher power densities over devices that employ β emitters. However, future experiments should also be performed with β emitters as the literature reports $B_{12}P_2$ to “self-heal” from β damage. While β ’s generally have lower energies and radioisotope batteries made from them have theoretically lower power densities, the advantages of using β irradiation include the lower likelihood for lattice damage and the lack of He atom accumulation in the semiconductor lattice.

7.3 Outlook

If impurities can be reduced and the film quality of $B_{12}P_2$ crystals improved, more definitive characterization of the radiation hardness or “self-healing” of $B_{12}P_2$ can be made. Impurity reduction during the CVD growth of $B_{12}P_2$ is certainly achievable in the near term. Improved epitaxy will be an ongoing process which could last decades, and full maturity of $B_{12}P_2$ epitaxy would require the efforts of many researchers. However, a strong reduction in the background impurity concentrations and modest improvements in the crystal quality would be enough to get better preliminary electrical measurements of the effect of irradiation on $B_{12}P_2$ and should be pursued.

This work has contributed to advancing epitaxial crystal growth and electrical characterization of $B_{12}P_2$. The steps needed to improve $B_{12}P_2$ crystal growth so that its radiation hardness can be fully evaluated have been clarified, bringing $B_{12}P_2$ radioisotope batteries closer to reality.

References

- [1] Panasonic. <https://na.industrial.panasonic.com/sites/default/pidsa/files/ncr18650b.pdf>. Accessed: October 2016.
- [2] *Handbook of Aviation Fuel Properties*, p. 71. CRC, 1983.
- [3] R. Duggirala, A. Lal, and S. Radhakrishnan, *Radioisotope thin-film powered microsystems*, vol. 6, ch. 2, p. 14. Springer Science & Business Media, 2010.
- [4] A. H. Smith, “Progress in photovoltaic energy conversion,” *NASA Report*, no. 66, p. 15406, 1965.
- [5] L. C. Olsen, P. Cabaay, and B. J. Elkind, “Betavoltaic power sources,” *Physics Today*, vol. 65, no. 12, p. 35, 2012.
- [6] M. Carrard, D. Emin, and L. Zuppiroli, “Defect clustering and self-healing of electron-irradiated boron-rich solids,” *Physical Review B*, vol. 51, no. 17, p. 11270, 1995.
- [7] D. Emin, “Unusual properties of icosahedral boron-rich solids,” *Journal of Solid State Chemistry*, vol. 179, no. 9, pp. 2791–2798, 2006.
- [8] W. Ehrenberg, C. S. Lang, and R. West, “The electron voltaic effect,” *Proceedings of the Physical Society. Section A*, vol. 64, no. 4, p. 424, 1951.
- [9] P. Rappaport, “The electron-voltaic effect in p-n junctions induced by beta-particle bombardment,” *Physical Review*, vol. 93, no. 1, p. 246, 1954.
- [10] W. G. Pfann and W. Van Roosbroeck, “Radioactive and photoelectric p-n junction power sources,” *Journal of Applied Physics*, vol. 25, no. 11, pp. 1422–1434, 1954.

- [11] Widetronix. www.widetronix.com/products. Accessed: October 2016.
- [12] C. Thomas, S. Portnoff, and M. Spencer, “High efficiency 4H-SiC betavoltaic power sources using tritium radioisotopes,” *Applied Physics Letters*, vol. 108, no. 1, p. 013505, 2016.
- [13] City Labs. www.citylabs.net. Accessed: October 2016.
- [14] BetaBatt. www.betabatt.com. Accessed: October 2016.
- [15] Qynergy. www.qynergy.com/technologies. Accessed: October 2016.
- [16] M. A. Prelas, C. L. Weaver, M. L. Watermann, E. D. Lukosi, R. J. Schott, and D. A. Wisniewski, “A review of nuclear batteries,” *Progress in Nuclear Energy*, vol. 75, pp. 117–148, 2014.
- [17] G. A. Slack and K. E. Morgan, “Some crystallography, chemistry, physics, and thermodynamics of $B_{12}O_2$, $B_{12}P_2$, $B_{12}As_2$, and related alpha-boron type crystals,” *Journal of Physics and Chemistry of Solids*, vol. 75, no. 9, pp. 1054–1074, 2014.
- [18] G. A. Slack and K. E. Morgan, “Crystallography, semiconductivity, thermoelectricity, and other properties of boron and its compounds, especially B_6O ,” *Solid State Sciences*, 2015.
- [19] O. A. Golikova, N. E. Solovev, Y. A. Ugai, and V. A. Feigelman, “Electrophysical properties of α -rhombohedral boron,” *physica status solidi (a)*, vol. 86, no. 1, pp. K51–K54, 1984.
- [20] G. A. Slack, T. F. McNelly, and E. A. Taft, “Melt growth and properties of B_6P crystals,” *Journal of Physics and Chemistry of Solids*, vol. 44, no. 10, pp. 1009–1013, 1983.
- [21] O. A. Golikova, “Electron transport in boron-rich borides,” in *MRS Proceedings*, vol. 97, p. 17, Cambridge Univ Press, 1987.

- [22] T. Akashi, T. Itoh, I. Gunjishima, H. Masumoto, and T. Goto, “Thermoelectric properties of hot-pressed boron suboxide (B_6O).,” *Materials Transactions*, vol. 43, no. 7, pp. 1719–1723, 2002.
- [23] Y. Gong, Y. Zhang, M. Dudley, J. H. Edgar, P. J. Heard, and M. Kuball, “Thermal conductivity and seebeck coefficients of icosahedral boron arsenide films on silicon carbide,” *Journal of Applied Physics*, vol. 108, no. 8, p. 084906, 2010.
- [24] R. Nagarajan, Z. Xu, J. H. Edgar, F. Baig, J. Chaudhuri, Z. Rek, E. A. Payzant, H. M. Meyer, J. Pomeroy, and M. Kuball, “Crystal growth of $B_{12}As_2$ on SiC substrate by CVD method,” *Journal of Crystal Growth*, vol. 273, no. 3, pp. 431–438, 2005.
- [25] Y. Kumashiro, T. Yokoyama, K. Sato, Y. Ando, S. Nagatani, and K. Kajiyama, “Electrical and thermal properties of $B_{12}P_2$ wafers,” *Journal of Solid State Chemistry*, vol. 154, no. 1, pp. 33–38, 2000.
- [26] Y. Kumashiro, H. Yoshizawa, and K. Shirai, “Preparation of rhombohedral boron phosphide wafer by CVD process,” *JJAP series*, vol. 10, pp. 166–167, 1994.
- [27] D. He, Y. Zhao, L. Daemen, J. Qian, T. Shen, and T. Zerda, “Boron suboxide: as hard as cubic boron nitride,” *Applied Physics Letters*, vol. 81, no. 4, pp. 643–645, 2002.
- [28] V. Mukhanov, O. Kurakevych, and V. Solozhenko, “Thermodynamic model of hardness: particular case of boron-rich solids,” *Journal of Superhard Materials*, vol. 32, no. 3, pp. 167–176, 2010.
- [29] X. Guo, J. He, Z. Liu, Y. Tian, J. Sun, and H. T. Wang, “Bond ionicities and hardness of $B_{13}C_2$ -like structured B_yX crystals ($X= C, N, O, P, As$),” *Physical Review B*, vol. 73, no. 10, p. 104115, 2006.
- [30] B. Morosin, A. Mullendore, D. Emin, and G. Slack, “Rhombohedral crystal struc-

- ture of compounds containing boron-rich icosahedra,” in *Boron-Rich Solids*, vol. 140, pp. 70–86, AIP Publishing, 1986.
- [31] I. Higashi, M. Kobayashi, J. Bernhard, C. Brodhag, and F. Thévenot, “Crystal structure of B_6O ,” in *Boron-rich solids*, vol. 231, pp. 201–204, AIP Publishing, 1991.
 - [32] D. Emin, “Bonding and doping of simple icosahedral-boride semiconductors,” *Journal of Solid State Chemistry*, vol. 177, no. 4, pp. 1619–1623, 2004.
 - [33] H. C. Longuet-Higgins and M. d. V. Roberts, “The electronic structure of an icosahedron of boron atoms,” in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 230, pp. 110–119, The Royal Society, 1955.
 - [34] D. Emin, “Icosahedral boron-rich solids,” *Physics Today*, vol. 40, no. 1, pp. 55–62, 1987.
 - [35] L. Spinar and C. Wang, “The crystal structure of tridecaboron diphosphide,” *Acta Crystallographica*, vol. 15, no. 10, pp. 1048–1049, 1962.
 - [36] F. V. Williams and R. A. Ruehrwein, “The preparation and properties of boron phosphides and arsenides,” *Journal of the American Chemical Society*, vol. 82, no. 6, pp. 1330–1332, 1960.
 - [37] T. Kobayashi, K. Susa, and S. Taniguchi, “Syntheses of BP under high pressures,” *Materials Research Bulletin*, vol. 9, no. 5, pp. 625–631, 1974.
 - [38] J. L. Peret, “Preparation and properties of the boron phosphides,” *Journal of the American Ceramic Society*, vol. 47, no. 1, pp. 44–46, 1964.
 - [39] P. Yang and T. Aselage, “Synthesis and cell refinement for icosahedral boron phosphide $B_{12}P_2$,” *Powder Diffraction*, vol. 10, no. 04, pp. 263–265, 1995.

- [40] V. A. Mukhanov, P. S. Sokolov, O. Brinza, D. Vrel, and V. L. Solozhenko, “Self-propagating high-temperature synthesis of boron subphosphide $B_{12}P_2$,” *Journal of Superhard Materials*, vol. 36, no. 1, pp. 18–22, 2014.
- [41] V. L. Solozhenko, V. A. Mukhanov, P. S. Sokolov, Y. Le Godec, K. A. Cherednichenko, and Z. Konôpková, “Melting of $B_{12}P_2$ boron subphosphide under pressure,” *High Pressure Research*, vol. 36, no. 2, pp. 91–96, 2016.
- [42] G. A. Slack, D. W. Oliver, and F. Horn, “Thermal conductivity of boron and some boron compounds,” *Physical Review B*, vol. 4, no. 6, p. 1714, 1971.
- [43] R. A. Burmeister and P. E. Greene, “Synthesis and crystal growth of B_6P ,” *Transactions of the Metallurgical Society of AIME*, vol. 239, no. 3, pp. 408–413, 1967.
- [44] P. Yang and T. L. Aselage, “Crystal growth of $B_{12}P_2$,” *JJAP series*, vol. 10, pp. 130–131, 1994.
- [45] Y. Kumashiro, T. Yokoyama, J. Nakahura, K. Hatsuda, H. Yoshida, and J. Takahashi, “Thermoelectric properties of boron and boron phosphide film,” in *MRS Proceedings*, vol. 242, p. 629, Cambridge Univ Press, 1992.
- [46] Y. Kumashiro, T. Yokoyama, J. Nakamura, and J. Takahashi, “Semiconducting properties of boron phosphide thin films by MBD process,” *JJAP series*, vol. 10, pp. 168–169, 1994.
- [47] M. Takigawa, M. Hirayama, and K. Shohno, “Hetero-epitaxial growth of lower boron phosphide on silicon substrate using PH_3 - B_2H_6 - H_2 system,” *Japanese Journal of Applied Physics*, vol. 12, no. 10, p. 1504, 1973.
- [48] T. Takenaka and K. Shohno, “Double-layer epitaxial growth of Si and $B_{13}P_2$ on Si substrates and some electrical properties of Si layers,” *Japanese Journal of Applied Physics*, vol. 13, no. 8, p. 1211, 1974.

- [49] K. Shohno, M. Takigawa, and T. Nakada, “Epitaxial growth of BP compounds on Si substrates using the B_2H_6 - PH_3 - H_2 system,” *Journal of Crystal Growth*, vol. 24, pp. 193–196, 1974.
- [50] P. Groot, J. H. F. Grondel, and P. J. Van der Put, “Chemical vapour deposition of boron phosphides using bromide reactants,” *Solid State Ionics*, vol. 16, pp. 95–98, 1985.
- [51] T. L. Aselage, “Preparation of boron-rich refractory semiconductors,” in *MRS Proceedings*, vol. 97, p. 101, Cambridge Univ Press, 1987.
- [52] Y. Kumashiro, H. Yoshizawa, and T. Yokoyama, “Epitaxial growth of rhombohedral boron phosphide single crystalline films by chemical vapor deposition,” *Journal of Solid State Chemistry*, vol. 133, no. 1, pp. 104–112, 1997.
- [53] P. Lu, J. H. Edgar, J. Pomeroy, M. Kuball, H. M. Meyer, and T. Aselage, “Growth of rhombohedral $B_{12}P_2$ thin films on 6H-SiC (0001) by chemical vapor deposition,” in *MRS Proceedings*, vol. 799, pp. Z2–10, Cambridge Univ Press, 2003.
- [54] Y. Kumashiro, T. Yokoyama, and Y. Ando, “Thermoelectric properties of boron and boron phosphide CVD wafers,” in *Thermoelectrics, 1998. Proceedings ICT 98. XVII International Conference on*, pp. 591–594, IEEE, 1998.
- [55] R. Schmechel and H. Werheit, “Evidence of the superposition of drude type and hopping type transport in boron-rich solids,” *Journal of Solid State Chemistry*, vol. 133, no. 1, pp. 335–341, 1997.
- [56] Y. Zhang, *Epitaxial growth of icosahedral boron arsenide on silicon carbide substrates: improved process conditions and electrical properties*. PhD thesis, Kansas State University, 2011.

- [57] C. Frye, J. Edgar, I. Ohkubo, and T. Mori, “Seebeck coefficient and electrical resistivity of single crystal $B_{12}As_2$ at high temperatures,” *Journal of the Physical Society of Japan*, vol. 82, no. 9, p. 095001, 2013.
- [58] H. Werheit, U. Kuhlmann, K. Shirai, and Y. Kumashiro, “Interband transitions and phonon spectra of Si-doped $B_{12}P_2$,” *Journal of Solid State Chemistry*, vol. 133, no. 1, pp. 140–144, 1997.
- [59] H. Werheit, U. Kuhlmann, K. Shirai, and Y. Kumashiro, “Optical properties of $B_{12}P_2$,” *Journal of alloys and compounds*, vol. 233, no. 1, pp. 121–128, 1996.
- [60] Z. Xu, J. H. Edgar, D. C. Look, S. Baumann, R. Bleiler, S. H. Wang, and S. E. Mohny, “The effect of Si doping on the electrical properties of $B_{12}As_2$ thin films on (0001) 6H-SiC substrates,” *Journal of Applied Physics*, vol. 101, no. 5, pp. 053710–053710, 2007.
- [61] S. H. Wang, E. M. Lysczek, B. Liu, S. E. Mohny, Z. Xu, R. Nagarajan, and J. H. Edgar, “Cr/Pt ohmic contacts to $B_{12}As_2$,” *Applied Physics Letters*, vol. 87, no. 4, pp. 042103–042103, 2005.
- [62] O. Sologub, Y. Matsushita, and T. Mori, “An α -rhombohedral boron-related compound with sulfur: Synthesis, structure and thermoelectric properties,” *Scripta Materialia*, vol. 68, no. 5, pp. 289–292, 2013.
- [63] H. Bolmgren and T. Lundström, “The crystal structure of a new boron selenide, $B_{12}Se_{2-x}B_x$,” *Journal of alloys and compounds*, vol. 202, no. 1, pp. 73–76, 1993.
- [64] H. Werheit, K. De Groot, W. Malkemper, and T. Lundström, “On n-type β rhombohedral boron,” *Journal of the Less Common Metals*, vol. 82, pp. 163–168, 1981.
- [65] H. Werheit, R. Schmechel, V. Kueffel, and T. Lundström, “On the electronic properties

- of β -rhombohedral boron interstitially doped with 3D transition metal atoms,” *Journal of alloys and compounds*, vol. 262, pp. 372–380, 1997.
- [66] S. Maruyama, Y. Miyazaki, K. Hayashi, T. Kajitani, and T. Mori, “Excellent p-n control in a high temperature thermoelectric boride,” *Applied Physics Letters*, vol. 101, no. 15, p. 152101, 2012.
 - [67] S. Maruyama, A. Prytuliak, Y. Miyazaki, K. Hayashi, T. Kajitani, and T. Mori, “Al insertion and additive effects on the thermoelectric properties of yttrium boride,” *Journal of Applied Physics*, vol. 115, no. 12, p. 123702, 2014.
 - [68] T. Mori, T. Shishido, and K. Nakajima, “Doping effects in rare-earth borides,” *Journal of Electronic Materials*, vol. 38, no. 7, pp. 1098–1103, 2009.
 - [69] T. Mori and T. Nishimura, “Thermoelectric properties of homologous p-and n-type boron-rich borides,” *Journal of Solid State Chemistry*, vol. 179, no. 9, pp. 2908–2915, 2006.
 - [70] T. Mori, T. Nishimura, W. Schnelle, U. Burkhardt, and Y. Grin, “The origin of the n-type behavior in rare earth borocarbide $Y_{1-x}B_{28.5}C_4$,” *Dalton Transactions*, vol. 43, no. 40, pp. 15048–15054, 2014.
 - [71] J. Varley, V. Lordi, A. Miglio, and G. Hautier, “Electronic structure and defect properties of B_6O from hybrid functional and many-body perturbation theory calculations: A possible ambipolar transparent conductor,” *Physical Review B*, vol. 90, no. 4, p. 045205, 2014.
 - [72] Y. Gong, M. Tapajna, S. Bakalova, Y. Zhang, J. H. Edgar, M. Dudley, M. Hopkins, and M. Kuball, “Demonstration of boron arsenide heterojunctions: A radiation hard wide band gap semiconductor device,” *Applied Physics Letters*, vol. 96, no. 22, pp. 223506–223506, 2010.

- [73] Y. Zhang, H. Chen, M. Dudley, Y. Zhang, J. H. Edgar, Y. Gong, S. Bakalova, M. Kuball, L. Zhang, D. Su, *et al.*, “Mechanism for improved quality $B_{12}As_2$ epitaxial films on (0001) 4H-SiC substrates by tilting toward $[1\bar{1}00]$ direction,” in *MRS Proceedings*, vol. 1246, pp. 1246–B04, Cambridge Univ Press, 2010.
- [74] Y. Zhang, H. Chen, M. Dudley, Y. Zhang, J. H. Edgar, Y. Gong, S. Bakalova, M. Kuball, L. Zhang, D. Su, *et al.*, “Elimination of degenerate epitaxy in the growth of high quality $B_{12}As_2$ single crystalline epitaxial films,” in *MRS Proceedings*, vol. 1307, pp. mrsf10–1307, Cambridge Univ Press, 2011.
- [75] B. Padavala, C. D. Frye, Z. Ding, R. Chen, M. Dudley, B. Raghothamachar, N. Khan, and J. H. Edgar, “Preparation, properties, and characterization of boron phosphide films on 4H-and 6H-silicon carbide,” *Solid State Sciences*, vol. 47, pp. 55–60, 2015.
- [76] C. E. Whiteley, M. J. Kirkham, and J. H. Edgar, “The coefficients of thermal expansion of boron arsenide ($B_{12}As_2$) between 25 °C and 850 °C,” *Journal of Physics and Chemistry of Solids*, vol. 74, no. 5, pp. 673–676, 2013.
- [77] Y. Okada and Y. Tokumaru, “Precise determination of lattice parameter and thermal expansion coefficient of silicon between 300 and 1500 K,” *Journal of Applied Physics*, vol. 56, no. 2, pp. 314–320, 1984.
- [78] R. R. Reeber and K. Wang, “Lattice parameters and thermal expansion of important semiconductors and their substrates,” in *MRS Proceedings*, vol. 622, pp. T6–35, Cambridge Univ Press, 2000.
- [79] H. Chen, G. Wang, M. Dudley, L. Zhang, L. Wu, Y. Zhu, Z. Xu, J. H. Edgar, and M. Kuball, “Defect structures in $B_{12}As_2$ epitaxial layers grown on (0001) 6H-SiC,” *Journal of Applied Physics*, vol. 103, no. 12, p. 123508, 2008.
- [80] Y. Zhang, H. Chen, M. Dudley, Y. Zhang, J. H. Edgar, Y. Gong, S. Bakalova, M. Kuball, L. Zhang, D. Su, *et al.*, “Growth mechanisms and defect structures of

- B₁₂As₂ epilayers grown on 4H-SiC substrates,” *Journal of Crystal Growth*, vol. 352, no. 1, pp. 3–8, 2012.
- [81] W. M. Vetter, R. Nagarajan, J. H. Edgar, and M. Dudley, “Double-positioning twinning in icosahedral B₁₂As₂ thin films grown by chemical vapor deposition,” *Materials Letters*, vol. 58, no. 7, pp. 1331–1335, 2004.
 - [82] J. Michael, T. Aselage, D. Emin, and P. Kotula, “Structural variants in attempted heteroepitaxial growth of B₁₂As₂ on 6H-SiC (0001),” *Journal of materials research*, vol. 20, no. 11, pp. 3004–3010, 2005.
 - [83] T. Stoto, L. Zuppiroli, and J. Pelissier, “Absence of defect clusters in electron irradiated boron carbide,” *Radiation effects*, vol. 90, no. 3-4, pp. 161–170, 1985.
 - [84] G. Li, J. K. Abbott, J. D. Brasfield, P. Liu, A. Dale, G. Duscher, P. D. Rack, and C. S. Feigerle, “Structure characterization and strain relief analysis in CVD growth of boron phosphide on silicon carbide,” *Applied Surface Science*, vol. 327, pp. 7–12, 2015.
 - [85] B. Padavala, C. D. Frye, X. Wang, B. Raghothamachar, and J. H. Edgar, “CVD growth and properties of boron phosphide on 3C-SiC,” *Journal of Crystal Growth*, vol. 449, pp. 15–21, 2016.
 - [86] T. Chu, J. Jackson, A. Hyslop, and S. Chu, “Crystals and epitaxial layers of boron phosphide,” *Journal of Applied Physics*, vol. 42, no. 1, pp. 420–424, 1971.
 - [87] B. Padavala, *Epitaxy of boron phosphide on AlN, 4H-SiC, 3C-SiC and ZrB₂ substrates*. PhD thesis.
 - [88] V. Ramachandran, M. F. Brady, A. R. Smith, R. M. Feenstra, and D. W. Greve, “Preparation of atomically flat surfaces on silicon carbide using hydrogen etching,” *Journal of Electronic Materials*, vol. 27, no. 4, pp. 308–312, 1998.

- [89] F. Owman, C. Hallin, P. Mårtensson, and E. Janzen, “Removal of polishing-induced damage from 6H-SiC (0001) substrates by hydrogen etching,” *Journal of crystal growth*, vol. 167, no. 1, pp. 391–395, 1996.
- [90] Q. An and W. A. Goddard III, “Boron suboxide and boron subphosphide crystals: Hard ceramics that shear without brittle failure,” *Chemistry of Materials*, vol. 27, no. 8, pp. 2855–2860, 2015.
- [91] L. S. McCarthy, N. Q. Zhang, H. Xing, B. Moran, S. DenBaars, and U. K. Mishra, “High voltage AlGaN/GaN heterojunction transistors,” *International Journal of High Speed Electronics and Systems*, vol. 14, no. 01, pp. 225–243, 2004.
- [92] D. Kapolnek, X. H. Wu, B. Heying, S. Keller, B. P. Keller, U. K. Mishra, S. P. DenBaars, and J. S. Speck, “Structural evolution in epitaxial metalorganic chemical vapor deposition grown GaN films on sapphire,” *Applied Physics Letters*, vol. 67, no. 11, pp. 1541–1543, 1995.
- [93] M. Wilhelm, M. Rieth, M. Brandl, R. A. Wibowo, R. Hock, and P. Wellmann, “Optimization of growth parameters for growth of high quality heteroepitaxial 3C-SiC films at 1200 °C,” *Thin Solid Films*, vol. 577, pp. 88–93, 2015.
- [94] Y. Zhang, *Growth Mechanisms and Defect Structures of $B_{12}As_2$ Epilayers*. PhD thesis.
- [95] J. O. Song, J.-S. Ha, and T.-Y. Seong, “Ohmic-contact technology for GaN-based light-emitting diodes: Role of p-type contact,” *Electron Devices, IEEE Transactions on*, vol. 57, no. 1, pp. 42–59, 2010.
- [96] Y. Ino, S. Nishimura, M. Hirai, S. Matsumoto, and K. Terashima, “Characteristics of ohmic contacts to n-type boron phosphide,” *Japanese Journal of Applied Physics*, vol. 52, no. 3R, p. 031201, 2013.

- [97] Y. Kumashiro, T. Yokoyama, T. Sakamoto, and T. Fujita, "Preparation and electrical properties of boron and boron phosphide films obtained by gas source molecular beam deposition," *Journal of Solid State Chemistry*, vol. 133, no. 1, pp. 269–272, 1997.
- [98] S. N. L'vov, V. F. Nemchenko, P. S. Kislyi, T. S. Verkhoglyadova, and T. Y. Kosolapova, "The electrical properties of chromium borides, carbides, and nitrides," *Soviet Powder Metallurgy and Metal Ceramics*, vol. 1, no. 4, pp. 243–247, 1962.
- [99] J. E. Macintyre, ed., *Dictionary of Inorganic Compounds (v. 1-5)*, p. 3082. Chapman and Hall/CRC, 1 ed., 1992.
- [100] H. Okamoto, "B-Cr (boron-chromium)," *Journal of Phase Equilibria*, vol. 24, no. 5, pp. 480–480, 2003.
- [101] M. Venkatraman and J. P. Neumann, "The Cr-P (chromium-phosphorus) system," *Journal of Phase Equilibria*, vol. 11, no. 5, pp. 430–434, 1990.
- [102] B. Predel, "B-Pt (boron-platinum)," in *B-Ba C-Zr* (O. Madelung, ed.), vol. 5B of *Landolt-Bornstein - Group IV Physical Chemistry*, pp. 1–3, Springer Berlin Heidelberg, 1992.
- [103] H. Okamoto, "The P-Pt (phosphorus-platinum) system," *Journal of Phase Equilibria*, vol. 11, no. 5, pp. 511–513, 1990.
- [104] M. D. Smolin, V. G. Grebenkina, Y. M. Goryachev, L. I. Panov, and E. I. Shvartsman, "Electrophysical properties of nickel boride phases," *Soviet Powder Metallurgy and Metal Ceramics*, vol. 21, no. 8, pp. 662–665, 1982.
- [105] I. Shirotani, E. Takahashi, N. Mukai, K. Nozawa, M. Kinoshita, T. Yagi, K. Suzuki, T. Enoki, and S. Hino, "Electrical conductivity of nickel phosphides," *Japanese Journal of Applied Physics*, vol. 32, no. S3, p. 294, 1993.

- [106] N. Kobayashi, Y. Kumashiro, P. Revesz, J. Li, and J. W. Mayer, “Thermal and ion beam induced reactions in Ni thin films on BP (100),” *Applied Physics Letters*, vol. 54, no. 19, pp. 1914–1915, 1989.
- [107] R. I. Stearns and P. E. Greene, “Phase stability regions of boron phosphides in the Ni-B-P system,” *Journal of The Electrochemical Society*, vol. 112, no. 12, pp. 1239–1240, 1965.
- [108] U. Nwagwu, “Flux growth and characteristics of cubic boron phosphide,” Master’s thesis, Kansas State University, 2012.
- [109] T. L. Chu, M. Gill, and R. K. Smeltzer, “Growth of boron monophosphide crystals with the accelerated container rotation technique,” *Journal of Crystal Growth*, vol. 33, no. 1, pp. 53–57, 1976.
- [110] D. K. Schroder, *Semiconductor Material and Device Characterization*, ch. 3, pp. 133–199. Wiley-Interscience, 2 ed., 1993.
- [111] F. A. Padovani and R. Stratton, “Field and thermionic-field emission in Schottky barriers,” *Solid-State Electronics*, vol. 9, no. 7, pp. 695–707, 1966.
- [112] D. Eastman, “Photoelectric work functions of transition, rare-earth, and noble metals,” *Phys. Rev. B*, vol. 2, pp. 1–2, Jul 1970.
- [113] M. Venkatraman and J. P. Neumann, “The Cr-Pt (chromium-platinum) system,” *Journal of Phase Equilibria*, vol. 11, no. 1, pp. 16–21, 1990.
- [114] P. B. Klein, U. Nwagwu, J. H. Edgar, and J. A. Freitas Jr, “Photoluminescence investigation of the indirect band gap and shallow impurities in icosahedral $B_{12}As_2$,” *Journal of Applied Physics*, vol. 112, no. 1, p. 013508, 2012.
- [115] T. A. Hall and A. A. Johnson, “The solidus and liquidus lines in the Au-Ni phase diagram,” *Journal of the Less Common Metals*, vol. 141, no. 1, pp. L19–L22, 1988.

- [116] H. Okamoto, “Ni-P (nickel-phosphorus),” *Journal of Phase Equilibria*, vol. 21, no. 2, pp. 210–210, 2000.
- [117] O. Teppa and P. Taskinen, “Thermodynamic assessment of Ni-B phase diagram,” *Materials Science and Technology*, vol. 9, no. 3, pp. 205–212, 1993.
- [118] H. W. Jang, S. Y. Kim, and J.-L. Lee, “Mechanism for ohmic contact formation of oxidized Ni/Au on p-type GaN,” *Journal of Applied Physics*, vol. 94, no. 3, pp. 1748–1752, 2003.
- [119] A. Motayed, A. V. Davydov, L. A. Bendersky, M. C. Wood, M. A. Derenge, D. F. Wang, K. A. Jones, and S. N. Mohammad, “High-transparency Ni/Au bilayer contacts to n-type GaN,” *Journal of Applied Physics*, vol. 92, no. 9, pp. 5218–5227, 2002.
- [120] Y. Koide, T. Maeda, T. Kawakami, S. Fujita, T. Uemura, N. Shibata, and M. Murakami, “Effects of annealing in an oxygen ambient on electrical properties of ohmic contacts to p-type GaN,” *Journal of Electronic Materials*, vol. 28, no. 3, pp. 341–346, 1999.
- [121] J.-K. Ho, C.-S. Jong, C. C. Chiu, C.-N. Huang, K.-K. Shih, L.-C. Chen, F.-R. Chen, and J.-J. Kai, “Low-resistance ohmic contacts to p-type GaN achieved by the oxidation of Ni/Au films,” *Journal of Applied Physics*, vol. 86, no. 8, pp. 4491–4497, 1999.
- [122] Y. Tian, G. Li, J. Shinar, N. L. Wang, B. A. Cook, J. W. Andereg, A. P. Constant, A. M. Russell, and J. E. Snyder, “Electrical transport in amorphous semiconducting AlMgB₁₄ films,” *Applied Physics Letters*, vol. 85, no. 7, p. 1181, 2004.
- [123] T. Fujima, H. Arimatsu, S. Miura, S. Yokoyama, and K.-I. Takagi, “n-p type variation in thermoelectric AlMgB₁₄-based materials by raw material mixture ratio,” *Solid State Sciences*, 2015.
- [124] R. A. Street, *Hydrogenated amorphous silicon*. Cambridge University Press, 2005.

- [125] J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lucovsky, “Hydrogen localization near boron in silicon,” *Applied Physics Letters*, vol. 46, no. 4, pp. 421–423, 1985.
- [126] J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, “Neutralization of shallow acceptor levels in silicon by atomic hydrogen,” *Physical Review Letters*, vol. 51, no. 24, p. 2224, 1983.
- [127] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in crystalline semiconductors*, vol. 16. Springer Science & Business Media, 2013.
- [128] B. Clerjaud, F. Gendron, M. Krause, and W. Ulrici, “Electronic level of interstitial hydrogen in GaAs,” *Physical review letters*, vol. 65, no. 14, p. 1800, 1990.
- [129] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, “P-type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI),” *Japanese Journal of Applied Physics*, vol. 28, no. 12A, p. L2112, 1989.
- [130] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, “Hole compensation mechanism of p-type GaN films,” *Japanese Journal of Applied Physics*, vol. 31, no. 5R, p. 1258, 1992.
- [131] W. Götz, N. M. Johnson, J. Walker, D. P. Bour, H. Amano, and I. Akasaki, “Hydrogen passivation of Mg acceptors in GaN grown by metalorganic chemical vapor deposition,” *Applied Physics Letters*, vol. 67, no. 18, pp. 2666–2668, 1995.
- [132] S. J. Pearton, C. R. Abernathy, and F. Ren, “Electrical passivation in hydrogen plasma exposed GaN,” *Electronics Letters*, vol. 30, no. 6, pp. 527–528, 1994.
- [133] S. Bakalova, R. Speller, R. J. Lacey, C. Frost, and M. Kuball, “Novel n-type Mg_2B_{14} on silicon diode: Demonstration of a thermal solid state neutron detector,” *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, vol. 700, pp. 140–144, 2013.

- [134] N. Vojteer and H. Hillebrecht, “ $\text{Li}_2\text{B}_{12}\text{C}_2$ and $\text{LiB}_{13}\text{C}_2$: Colorless boron-rich boride carbides of lithium,” *Angewandte Chemie International Edition*, vol. 45, no. 1, pp. 165–168, 2006.
- [135] N. Vojteer, V. Sagawe, J. Staufer, M. Schroeder, and H. Hillebrecht, “ LiB_{12}PC , the first boron-rich metal boride with phosphorussynthesis, crystal structure, hardness, spectroscopic investigations,” *Chemistry-A European Journal*, vol. 17, no. 11, pp. 3128–3135, 2011.
- [136] S. Huber, E. Gullikson, C. Frye, J. Edgar, R. van de Kruijs, F. Bijkerk, and D. Prendergast *Chemistry of Materials*, Submitted 2016.
- [137] L. Van der Pauw, “A method of measuring specific resistivity and hall effect of discs of arbitrary shape,” *Philips Res. Rep.*, vol. 13, pp. 1–9, 1958.
- [138] J. Murphy. personal communication.
- [139] D. K. Schroder, *Semiconductor Material and Device Characterization*, ch. 2, pp. 100–104. Wiley-Interscience, 2 ed., 1993.
- [140] I. G. Ivanov, A. Henry, and E. Janzén, “Ionization energies of phosphorus and nitrogen donors and aluminum acceptors in 4H-silicon carbide from the donor-acceptor pair emission,” *Physical Review B*, vol. 71, no. 24, p. 241201, 2005.
- [141] M. Ikeda, H. Matsunami, and T. Tanaka, “Site effect on the impurity levels in 4H, 6H, and 15R SiC,” *Physical Review B*, vol. 22, no. 6, p. 2842, 1980.
- [142] N. Kuznetsov and A. Zubrilov, “Deep centers and electroluminescence in 4H-SiC diodes with a p-type base region,” *Materials Science and Engineering: B*, vol. 29, no. 1, pp. 181–184, 1995.
- [143] A. Lebedev, V. Kozlovski, N. Strokan, D. Davydov, A. Ivanov, A. Strelchuk, and

- R. Yakimova, “Radiation hardness of wide-gap semiconductors (using the example of silicon carbide),” *Semiconductors*, vol. 36, no. 11, pp. 1270–1275, 2002.
- [144] A. Lebedev, *Silicon Carbide: Materials, Processing & Devices (Optoelectronic Properties of Semiconductors and Superlattices)*, ch. 8. CRC Press, 2003.
- [145] S. Onoda, T. Ohshima, T. Hirao, K. Mishima, S. Hishiki, N. Iwamoto, K. Kojima, and K. Kawano, “Decrease of charge collection due to displacement damage by gamma rays in a 6H-SiC diode,” *IEEE Transactions on Nuclear Science*, vol. 54, no. 6, pp. 1953–1960, 2007.
- [146] H. Fritzsche, “Resistivity and hall coefficient of antimony-doped germanium at low temperatures,” *Journal of Physics and Chemistry of Solids*, vol. 6, no. 1, pp. 69–80, 1958.
- [147] K. Seeger, *Semiconductor Physics: An Introduction*, ch. 6, pp. 210–212. Springer-Verlag, 5 ed., 1991.
- [148] T. Kimoto and J. A. Cooper, *Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices and Applications*, ch. 5. Wiley-IEEE Press, 2014.
- [149] N. Mott, “Charge transport in non-crystalline semiconductors,” in *Festkörperprobleme 9*, pp. 22–45, Springer, 1969.
- [150] S. Kouimtzi, “Hopping conduction in electron-irradiated boron-doped silicon,” *Journal of Physics: Condensed Matter*, vol. 1, no. 8, p. 1437, 1989.
- [151] Y. Kato, T. Shimada, Y. Shiraki, and K. Komatsubara, “Electrical conductivity of disordered layers in GaAs crystal produced by ion implantation,” *Journal of Applied Physics*, vol. 45, no. 3, pp. 1044–1049, 1974.
- [152] S. Sze, *Semiconductor Devices Physics and Technology*, ch. 3, pp. 49–51. Wiley, 2 ed., 2002.

- [153] A. Koizumi, J. Suda, and T. Kimoto, “Temperature and doping dependencies of electrical properties in Al-doped 4H-SiC epitaxial layers,” 2009.
- [154] C. V. Falub, H. von Känel, F. Isa, R. Bergamaschini, A. Marzegalli, D. Chrastina, G. Isella, E. Müller, P. Niedermann, and L. Miglio, “Scaling hetero-epitaxy from layers to three-dimensional crystals,” *Science*, vol. 335, no. 6074, pp. 1330–1334, 2012.