

Defect engineering and growth optimization of single crystal large area hexagonal boron nitride
and graphite using atmospheric pressure and high temperatures

By

Thomas Paul Poirier Jr.

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DOCTOR OF PHILOSOPHY

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Abstract

In this study, the growth of large area single crystal graphite and hexagonal boron nitride (hBN) through atmospheric pressure and high temperature metal flux precipitation (APHT) is optimized using process parameters ranging from source material purity to cover gas composition. The effects of each of these parameters were assessed with a variety of characterization techniques including Raman spectroscopy, X-ray diffraction (XRD), and defect sensitive etching (DSE). Additionally, defects are intentionally introduced into these materials to engineer their electronic and optical properties. Graphite was doped with boron while hBN was prepared with boron vacancies and doped with carbon.

To maximize graphite crystal grain size and minimize its defect density, the source carbon concentration, temperature, and cover gas (N_2 or Ar) were optimized. The optimum starting source composition to grow graphite single crystals was 5.8 wt.% carbon in iron. At temperatures <1400 °C, graphite crystals were $\sim 20\%$ smaller than those grown at temperatures above 1400 °C. Defect sensitive etching (DSE) revealed that nitrogen leads to larger etch pits but significantly fewer in quantity compared to argon. Boron-doped and undoped graphite crystals were of comparable quality, showing no additional strain due to boron. The addition of a small amount of silicon (0.25 at. %) consistently produced larger graphite crystals.

Like graphite, high quality large area single crystal hBN was pursued through APHT process parameters like temperature, cover gas, time, source material, and crucible materials. Compared to previous studies, larger (6 mm^2) and *thicker* ($>80\text{ }\mu\text{m}$) hBN single crystals were grown by hydrogen-rich crystal growth and standard crystal growth and *tripling the dwell time in hot pressed boron nitride (HPBN) crucibles*, respectively. To determine the temperature at which

the hBN crystals begin to form, a series of experiments was conducted in which the nitrogen source was switched from $^{15}\text{N}_2$ enriched to natural nitrogen during the crystal growth process. In this manner, it was determined that when cooling from an initial temperature of 1550 °C, the majority of the hBN crystals formed at 1508 °C. Source materials such as traditional Ni-Cr or Fe and new flux compositions including Ga and Cu, were explored for hBN. Ga reduced the surface tension of the metal flux sufficiently for the metal to occupy more area of the crucible, directly allowing more area for hBN growth; however, Ga_2O_3 posed a challenge at Ga concentrations >15 wt. %. Gallium also significantly reduced vapor pressure of the metal flux, eliminating metal condensation onto the crystal surface. Copper proved useful for producing thin films with lower quality than hBN precipitated from other transition metals.

Boron vacancies in hBN was created by neutron irradiation, causing the ^{10}B isotope to undergo transmutation to ^7Li . This study used boron-10 and nitrogen-15 isotopically enriched $\text{h}^{10}\text{B}^{15}\text{N}$. The ^7Li is ejected from the lattice site, resulting in either an absence of electrons or leaving its valence electrons behind. The former is known as the V_B^0 or neutral boron vacancy. The latter is known as the negatively charged boron vacancy (V_B^-), which has useful quantum sensing properties. Different fluences of neutrons and annealing conditions proved effective for optimizing the photoluminescence (PL) brightness from the V_B^- and thus the signal integrity which are vital for magnetic sensing. Lower fluences and post-irradiation annealing temperatures of 600 °C to improve these properties proved best.

hBN was doped with carbon in three ways: flux addition, diffusive annealing, and ion implantation. Carbon induces numerous electronic changes to hBN permitting a wide range of applications and property changes. After hBN:C was grown using fifteen different carbon concentrations from 0.25 to 2.32 wt. % carbon, the crystals themselves did not change appearance,

but their photoluminescence spectral properties changed. Diffusively doped hBN:C was obtained at 1700°C, lower than previously observed, leading to yellow crystals, and saturation was reached after 9 hours of annealing. In both methods, the most abundant defect was the carbon dimer, $C_B C_N$; however, other signatures in addition to this dimer appeared in diffusive annealing. Ion implantation generated a wide array of spectral light emission signatures between 500 and 800 nm in wavelength that could not be assigned without further characterization due to the convolution of photoluminescent peaks.

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Preface

This dissertation is broken into six main chapters focusing on the crystal growth optimization and defect creation in graphite (chapter 1, with publication) and hexagonal boron nitride (chapter 3). Investigations pertaining to hBN doping are more developed and are hence given their own chapters (four and five) following that of pure hBN.

Each chapter is organized into a general introduction of the material, a discussion of the pure materials properties, and its applications. Next, the steps to optimize specific crystal properties, either by modifying the crystals growth process or through defect engineering, are described. Finally, the results and conclusions are stated.

Dedication

I'd like to thank my friends and family for being the pillars upon which this research could be conducted with such fervor. I'd like to thank Dr. Edgar for his encouragement and endless perseverance in the search for wafer-sized crystals. I'd also like to thank my colleagues for being not only great scholars, but great friends:

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I'd like to dedicate the formatting of this document to Dylan M. Evans. (Legally required)

And lastly, to my girlfriend who was there the whole way: Ishi.

Chapter 1 - Two-dimensional materials

Contributions to the field

In this dissertation, novel large scale >5 square millimeter bulk single crystals of high-quality bulk graphite and hexagonal boron nitride (hBN) with thicknesses of 20 and 100 micrometers, respectively, are presented. This contrasts with typical hBN and graphite layers grown with a nanometer thickness, with a <10 square micron single crystal size, and with lower crystal quality. Therefore, this research investigates materials exclusively made at Kansas State University that enable high quality electrical (field effect transistors), optoelectronic (white and ultraviolet light emitting diodes), quantum (magnetometry), and nanophotonic (light confinement) devices.

In addition to large scale growth of these crystalline materials, defect engineering is demonstrated with boron doping of graphite for lithium-ion batteries, the controlled creation of negatively charged boron vacancies through neutron irradiation of isotopically enriched $h^{10}B^{15}N$ for quantum sensing, and exploration of carbon doped hBN through in-situ and diffusion doping mechanisms for single photon emitters and optically active spin defects. These methods result in significantly less damage to the crystal lattice, thereby improving defect lifetime and stability. Additionally, ion implantation was explored to fabricate more diverse defects in $h^{10}BN$ than thermodynamic doping.

Background

Two-dimensional (2D) materials are layers that are single atoms thick that do not have dangling surface bonds. As the dimensionality of materials decreases, their properties deviate further from classical physics and begin to exhibit quantum behavior. Their properties are highly anisotropic and rarely seen in bulk three-dimensional materials [1]. These materials exist in a variety of compositions. Examples include transition metal dichalcogenides (TMDs) like WSe_2 [2], pure carbon (graphene) [3], and hexagonal boron nitride (hBN) [4]. They have a wide range of properties that span from insulating to conducting, both thermally and electrically. Their diverse properties enable a wide range of potential applications including photovoltaic conversion of sunlight [5], ballistic electron transport [6], and nanophotonics [7].

2D materials can be combined to produce interfaces without dangling bonds held together by weak van der Waals forces. Because dangling bonds cause energy losses via phonon/photon scattering, more efficient devices are possible using 2D materials [8]. Once materials are on the atomic scale, new quantum properties emerge which lead to unique device applications [9].

2D materials are synthesized by a wide variety of methods. For example, WSe₂ thin films can be deposited by reactive sputtering of tungsten in gaseous H₂Se [10]. Graphene is precipitated from methane dissolved in copper foil [11]. hBN layers are often deposited on a substrate by reacting triethyl borane, borazine, or diborane with nitrogen or ammonia [4].

The quality of these materials is commonly assessed with spectroscopic techniques such as Raman spectroscopy, X-ray diffraction (XRD), or photoluminescence (PL). Though many 2D materials are synthesized as monolayers (a single atom sheet) or few layers, the quality and scalability can be improved.

For instance, hBN grown by chemical vapor deposition (CVD), requires 3 minutes per monolayer [12]. If thin films are desired, then this method is acceptable; however, for films thicker than 1 micrometer (3,000+ layers), a faster growth method is needed. There is significant control in some of these techniques for maximizing crystal area [13] or crystallinity, but that alone doesn't permit niche changes 2D materials need for all types of applications. These methods work well for large area monolayers, but bulk production can be upscaled and provide higher quality material. If bulk production can be achieved, then the methods shown by Nobel Prize winner Andre Geim *et al* [14] in tandem with technology [15] could create thousands of these monolayers with ease for solid-state devices.

Applications

2D materials have potential in several regimes of the energy industry [16]. 2D materials can serve as devices using their individual properties [17], or they can be combined via stacking [18] or direct epitaxial growth [19]. Each individual material's properties can be engineered to permit diverse applications. Typical applications for 2D materials include sensors [20], memory [21], and optics [22]. In the case of graphene (few-layer derivative of graphite) and hBN, applications are abundant due to their unique properties discussed in their respective chapters.

Graphene

As a sensor, graphene can be functionalized to selectively detect organic molecules from gases [23]. The pi-pi interactions between graphene and aromatic molecules allow for strong physisorption to the surface. Additionally, graphene-gold composites can be used to monitor pathogens like cholera using surface plasmon resonance (SPR) [24], an optical technique that measures the change in refractive index as molecules bond to the graphene surface [25]. Graphene's sensitivity in transduction permits many other types of sensors that convert concentration to current [26].

Power demand through data storage (memory) is a persistent issue in computers. The lifetime and stability of memory types are key to power management and performance. Digital memory has evolved from punch cards [27] to now quantum level storage [21]. Graphene has the potential to play a part in digital memory via spintronics [28], devices that use electron spin instead of charge to store information. Applying voltages via ferromagnetic metal electrodes (like iron, cobalt, or nickel [29]) controls the spin state of the graphene electrons. Since there are only 2 spin states $\pm(\pm\frac{1}{2})$, one of these states is defined as the ground state (0) and the excited state (1), forming a binary translation. The electrodes measure the spintronic orientations through spin valves. Should the electron spins be different (anti-parallel), then current is met with high resistance as well as the contrary (parallel/low resistance) [30],[31]. Hence, if the spin orientation can be controlled through modulated current, then these states can be correlated to bit values, which are the fundamental units of memory. These low-dimensionality spintronics use significantly less power than current commercial memory storage devices. Graphene serves as a stable platform for spin-modulated memory and is predominant component of 2D devices for these reasons.

Graphene is also used in optoelectronics [32]. Graphene is a plasmonic material; its surface charges can be controlled with light [33]. Plasmonic graphene is used in optoelectronics as a waveguide [34] for efficient directional control of waves, which are commonly used in communication devices (phone, radio, satellite, etc.) and medical oncology [35]. The manner in which plasmons disperse in graphene can be used as a sensor [36] or as an infrared waveguide to direct light to specific points [37]. The challenges frequently faced within these fabricated devices are impurities and defects [38]. Defects can degrade device sensitivity or hinder lifetime performance. Hence, minimizing defects or having precise control over them is of the utmost importance.

Hexagonal boron nitride

hBN is another 2D material like graphene. However, its electrical properties are vastly different. hBN is an insulator, ultrawide-bandgap semiconductor, due to its 5.955 eV (208 nm) bandgap [39]. Despite its ultraviolet (UV) wavelength bandgap, hBN can serve in similar device applications as graphene. hBN can be a sensor or indicator for specific chemical species [40],[41] or a memory switch through electrical resistance [42], [43]. hBN serves as a waveguide for infrared light as well as in optoelectronics [44] because hBN is transparent to visible light. hBN commonly serves as an electronic insulator/encapsulation in numerous 2D heterostructures [45],[46].

As a sensor, hBN nanosheets serve as functional electrochemical sensors for several analytes using electrochemistry [47]. Examples such as peroxide or dopamine induce a change in the solution conductivity depending on analyte concentration.

In memory, hBN can be a flexible memristor [42] through resistive switching [43] where resistance dictates the ON/OFF (0 or 1) state. When a certain potential threshold is crossed, hBN becomes conductive through migration of atoms in adjacent layers. These deformities are reversible by applying potential in the opposite direction. This bilateral migration of atoms makes hBN memory devices energy efficient.

hBN layers are often employed as a 2D insulator [48], one of the most vital components in any electronic device. Some example devices using hBN as a dielectric include 2D photodiodes [49], light-emitting diodes [50], field effect transistors [51], and synaptic emulators [52].

hBN is transparent to the human eye, but it interacts with infrared (IR) light. This interaction can be used for hyper lensing with IR [53]. hBN also serves as a UV lasing material based on its ultra large bandgap [54].

2D materials' lack of dangling bonds minimizes losses to phonon/photon scattering, thus maximizing the efficiency of 2D electronics, paving the way for highly condensed devices. Therefore, producing high quality 2D materials is paramount in addition to large quantities. The versatility of 2D materials is orders of magnitude higher when their defect types and densities are controlled. The following chapters focus on the bulk growth of high-quality graphite and hBN single crystals with controlled properties.

Chapter 2 - Bulk graphite single crystals grown with controlled defect densities and isotope concentrations at atmospheric pressure from a metal flux.

Background

Graphite is a crystalline hexagonal lattice of sp^2 -bonded carbon atoms with an alternating stacking order of ABAB, also known as Bernal stacking. Each layer within the graphite lattice is only bound to adjacent layers by van der Waals (vdW) forces resulting in a low interlayer shear strength [55]. The unit cell of bilayer graphite is shown in in Figure 2.1.

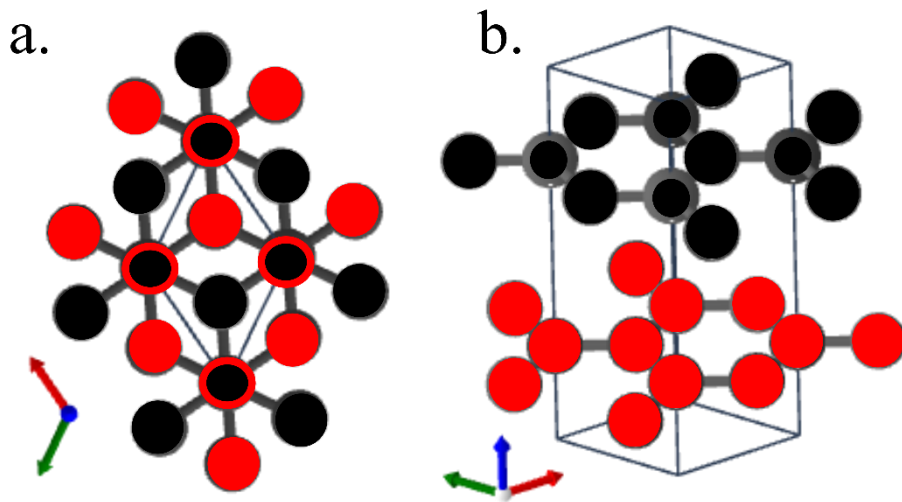


Figure 2.1. (a) c-axis and (b) skewed view of graphite crystal stacking structure [56]. Red circles denote carbon atoms in the lower layer and black circles denote those in the upper layer. Black circles inside of red circles denote overlapping atoms.

Graphite is metallic [56] and anisotropic, with differing properties within a layer (in-plane, perpendicular to Fig. 2.1a), versus between layers (out-of-plane upward arrow Fig 2.1b).

Crystalline graphite has high in-plane thermal [57] and electrical [58] conductivities of $2000 \frac{W}{m K}$ and $1 \times 10^6 \frac{S}{m}$, respectively. These values are significantly lower for out-of-plane conductivities

($0.7 \frac{W}{m \cdot K}$ [59] and $200 \frac{S}{m}$ [60]), highlighting graphite's anisotropy. Graphite crystals are stable with moderately low bulk reactivity; they remain unoxidized at temperatures up to 500 °C [61] in ambient air. When less than three isolated layers of graphite are stacked together this creates a unique material derived from graphite: graphene [3].

Graphene is a special material because of its extremely high in-plane thermal [62] and electrical conductivity [63] of $\sim 5000 \frac{W}{m \cdot K}$ and $1.46 \pm 0.82 \times 10^6 \frac{S}{m}$ respectively (nearly double those of graphite). Graphene's high electrical conductivity is due to the ballistic transport: of its electrons: they travel through the crystal lattice without collisions [64].

Graphene is more susceptible to oxidation than bulk graphite, undergoing oxidation at temperatures as low as 500°C [65]. Graphene also hosts a myriad of unique physical properties as a monolayer. Some of these properties include fluid electrons [66], reflectionless electron tunneling (Klein paradox) [67], unconventional quantum hall effect [68], superconductive “magic twist” angle of bilayer graphene [69], and the foundation of stacked 2D material heterostructures [70].

Graphite is a naturally occurring mineral [71] that has been used for many technologies. However, natural graphite is unsuitable for solid devices because it is full of impurities and extended defects that cause strain [72] and diminish its properties [73]. The types of defects include impurities such as Si, Al, Mg, and Ca, vacancies, and Stone-Wales defects [72],[74]. An impurity substituted on a lattice site is shown in (Figure 2.2a/b) stretching out-of-plane and distorting in-plane bonds (Fig. 2.2c/d). These defects can combine and overlap in the same location such as a double substitution. Each permutation of defects has a significant impact on the crystal lattice that can be detected and quantified by optical spectroscopy techniques such as Raman or XRD. These defects can also be seen by high-resolution transmission electron microscopy (HRTEM) [75].

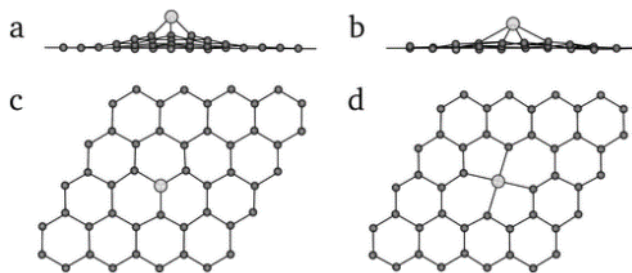


Figure 2.2. Substitutional defect with metal atom in (a) side view and (c) top view. A larger atom occupying two carbon sites in (b) side view and (d) top view. The small dark circles represent carbon atoms; large light gray circles represent defect species atoms [72].

For graphite specifically, the sp^2 -bonded carbon-12 atoms exhibit an active intralayer vibrational frequency of 1580 cm^{-1} (or wavenumbers) [76]. This creates an intense Raman scattering labeled the “G-Peak”. Example Raman spectra from high purity graphite powder and a graphite crystal are plotted in Figure 2.3. Note the absence of the D-peak for bulk APHT graphite crystal.

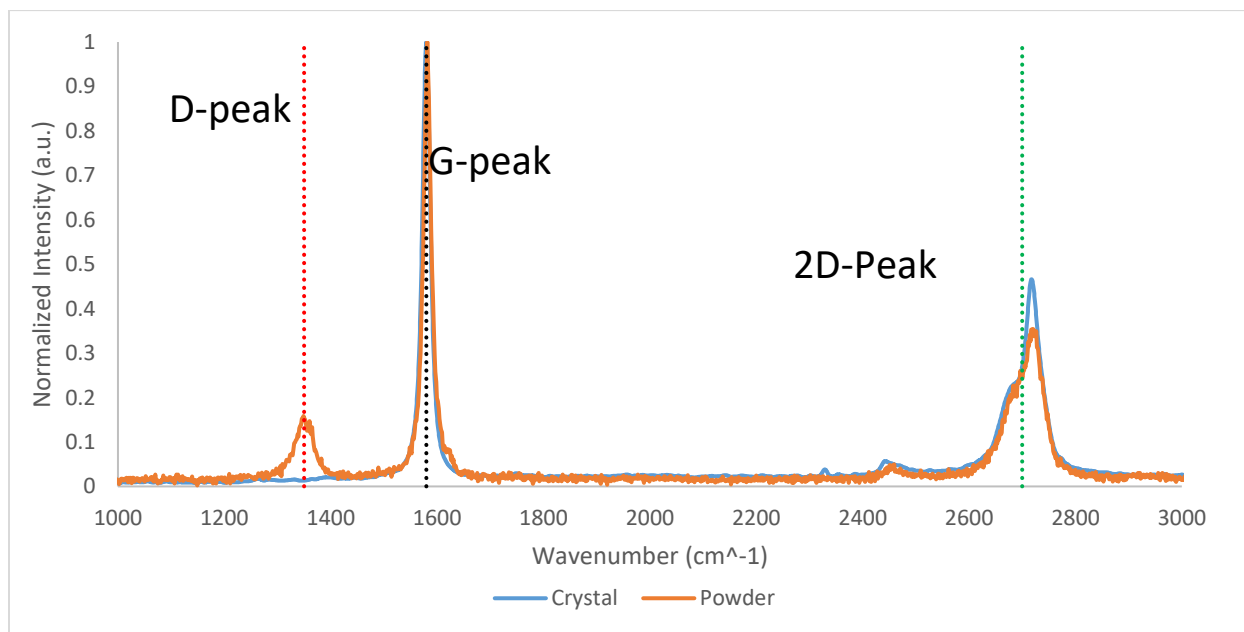


Figure 2.3. Raman spectra of graphite powder from commercial vendor [77] (orange) and graphite crystal (blue) showing three common peaks each indicated by a dashed line. From left to right: the D-peak at 1350 cm^{-1} , the G-peak at 1580 cm^{-1} , and the 2D-peak at 2750 cm^{-1} .

There are three main peaks present in the graphite Raman spectra: with increasing wavenumber, they are the D-peak at $\sim 1350\text{ cm}^{-1}$, G-peak, and 2D-peak at $\sim 2500\text{ cm}^{-1}$. The last is a propagation of the original D-peak. Typically, more defects correlate to a higher intensity D-peak and a wider G-peak due to induced strain interfering with the vibrational modes. This strain is quantified by the full width at half maximum (FWHM) of the G-peak. Similar measurements of quality can be made using XRD patterns of crystalline materials. Since graphite has a hexagonal unit cell, standard XRD reveals the 002, 004, and 006 crystal planes. Much like the G-peak in Raman, any of the peaks in XRD for graphite can be assessed by its FWHM. Figure 2.4 illustrates a typical diffraction pattern for the same powder (blue) and crystalline graphite (orange) from Figure 2.3.

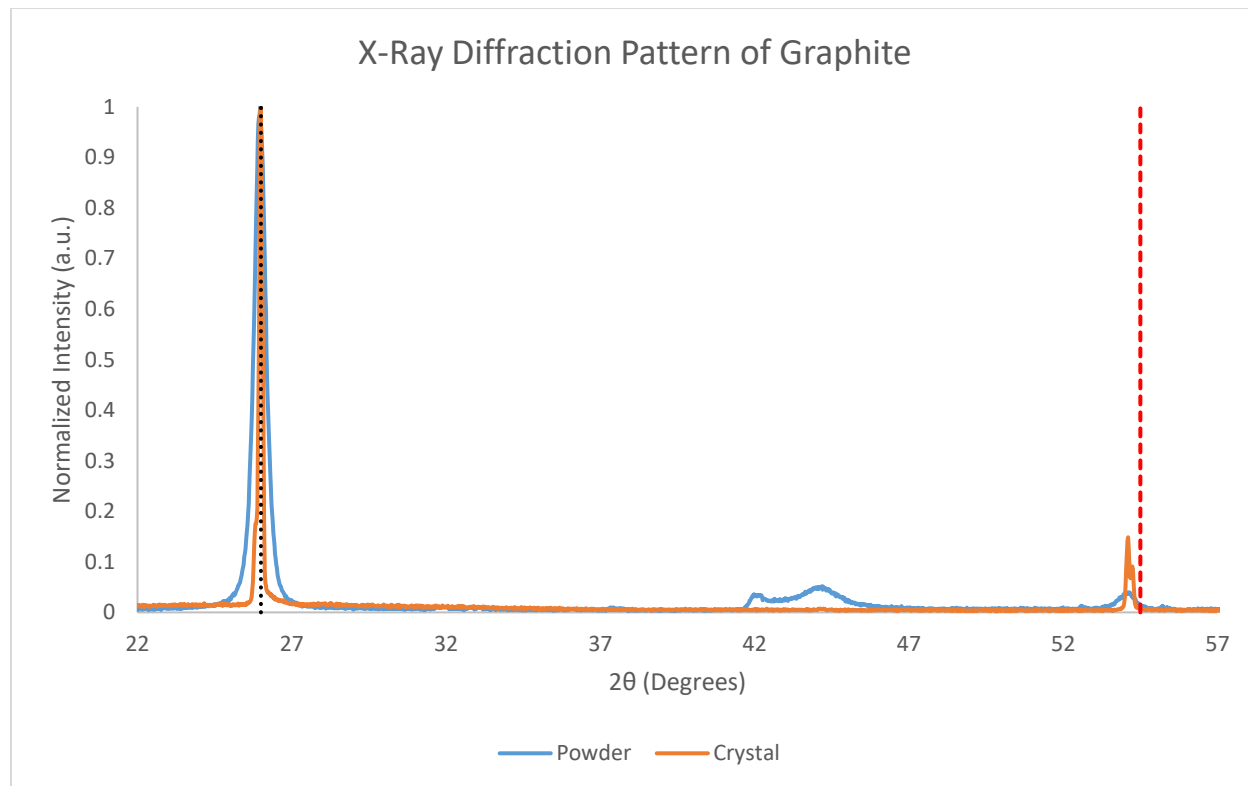


Figure 2.4. X-Ray Diffraction pattern of graphite powder (blue) and crystal (orange) with the (002) and (004) planes marked by dashed lines at 26.5 and 54.5 degrees.

Defects like those shown in Figure 2.2 are revealed in XRD [78] via distortion of these crystal planes resulting in strain indicated by the width of the 002 peaks at 26° in Figure 2.4. Note that the powder has a much broader 002 peak and 100 and 101 planes diffracting at 42° and 45° [79] due to the presence of defects. In some applications, defects are extremely undesirable as they change the performance and possibly ruin the desired properties. However, they can also introduce new properties that have applications elsewhere. Some examples of beneficial defects are boron [80]–[83], nitrogen [84], or more niche species. Each carries their own benefits and hinderances to crystalline graphite and much more so to graphene.

Applications

Graphite's general applications range from mechanical lubricant [85] to dissipating thermal energy [86] and modulating neutrons [87],[88]. Graphite powder is a good solid lubricant because of its atomically smooth surface and ease of delamination. The lack of dangling bonds leads to clean interfaces thus minimizing friction between layers. Due to graphite's high thermal conductivity, it readily conducts heat away from hot zones reducing thermal strain and prevents overheating on high power equipment and devices [89]. This facilitates higher power devices that generate deleterious heat. Graphite is employed to slow neutrons with a cross capture area of 3-5 mbarns [90] and small atomic radii acting as a mesh filter [91]. However, impurities play a crucial role in the service time of the graphite. As graphite gains more impurities from various modification processes like intercalation, aerosolization, and composite formation, it loses crystallinity.

Crystallinity describes continuous crystal planes known as grains. Graphite samples with a low density of grain boundaries can be categorized as highly crystalline. The inverse is also true. Below in Figure 2.5 is a depiction of what is meant by grain size.

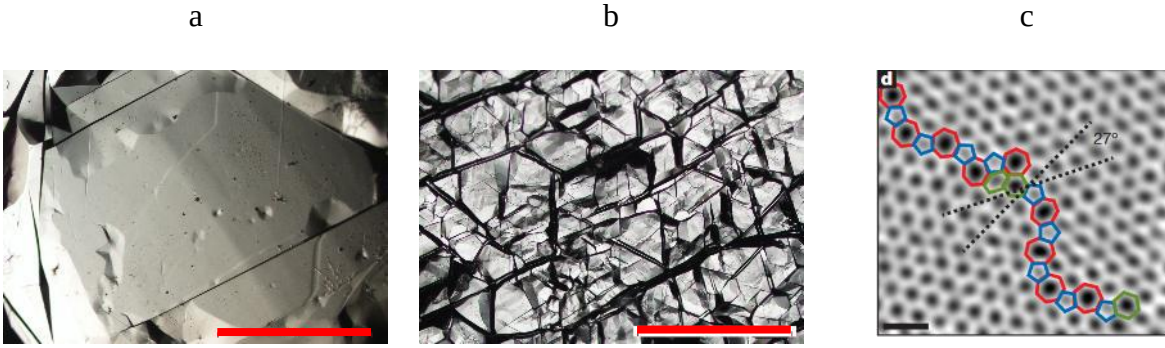


Figure 2.5. Optical photographs of large (a) and small (b) graphite crystal grains and (c) HRTEM image of graphene grain boundary [92]. Scale bars are (a, b) 1000 μm and (c) 5 $\text{\AA}$.

Electronics have evolved from bulky macrostructures down to quantum scale devices, and as such, defects in 2D materials become more problematic. As the defect densities increase, the electrical and thermal properties of crystalline graphite decrease due to scattering and vibrational losses [93],[94]. Hence, if bulk crystalline graphite can be synthesized with few defects, then it becomes a valuable resource for electronic implementation.

Few-defect bulk single crystal graphite

Graphite crystal without defects is extremely useful for high performance devices and conductors. Large area bulk graphite single crystals are highly sought by researchers around the world. Large area single crystal *graphene* is commonly made by chemical vapor deposition in which methane or another hydrocarbon gas is dissolved into a rolling copper sheet and reprecipitated via cooling [11]. The resulting film area is limited only by the size of the reactor but is typically only 1-5 atom layers thick with FWHM of 33 cm^{-1} . In this chapter, large area (6 mm^2) bulk ($\sim 20\text{ }\mu\text{m}$ thick) single crystal graphite is precipitated using a facile method known as atmospheric pressure high temperature (APHT) metal flux growth. The investigation of several parameters and uncommon characterization as functions of growth conditions were extensively investigated [95]. In short, this study demonstrates that there are many variables that impact crystal

growth and that they must be carefully considered depending on the desired crystal properties. Additionally, this study details the ease of isotopic enrichment of graphite which showed preferential clustering of similar carbon isotopes [96].

Atmospheric pressure high temperature metal flux growth

The APHT method is a means of precipitating crystalline materials from a molten metal solution via slow cooling [97]. The metal-carbon source is selected such that the mixture will be saturated with carbon at the highest operating temperature, known as the dwell temperature. As the solution cools from the dwell temperature, the carbon solubility decreases. Upon equilibrating, the solution precipitates graphite crystals in this case. When precipitated near thermodynamic equilibrium by slow cooling crystal nucleation is controlled. In the case of graphite, the metal solvent is typically iron due to its low cost and high carbon solubility, and the solute is some form of carbon, whether it be amorphous carbon powder or graphitic pellets.

Avoiding oxidation is a key challenge to the APHT method [98]–[100]. Therefore, the furnaces are purged by evacuating air to high vacuum (<80 mTorr), backfilling to 500 torr of inert gases (N_2 or Ar), then evacuated to the same vacuum. The furnaces are purged twice at ambient temperature before beginning temperature controls. The process is described in depth in Ref. [95].

Advantages of APHT method

The APHT growth method offers three key advantages: safety, simplicity, and high crystal quality.

The method is relatively safe. The main danger is the furnace's high temperature. A carbon-fiber composite heating element resistively heats a small section of a stainless-steel box chamber to high temperatures shown below in Figure 2.6.

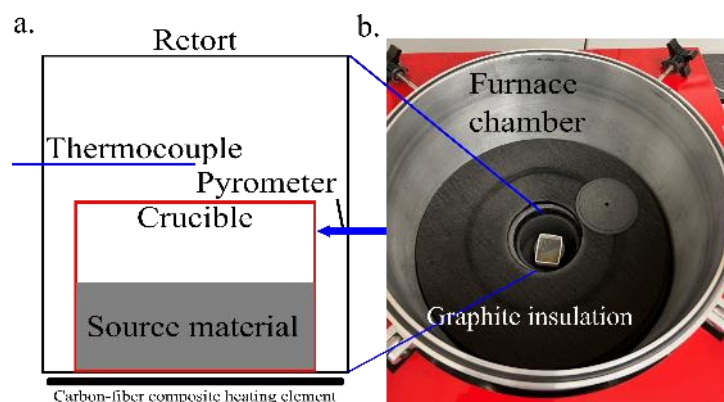


Figure 2.6. (a) Cross-sectional illustration of loaded sample and (b) top-down view of furnace chamber interior

The heating element is held in place by four graphite nuts to two graphite rods connected to the power supply/controller. The five layers of separation (retort/block insulation/foam insulation/chamber body/red shell box) from the hot zone provide protection for the operator. Another advantage is the operational pressures. As the name applies, the furnace is heated while slightly above atmospheric pressure (850 Torr) reducing equipment requirements and potential pressurized gas hazards.

Apart from operational advantages, APHT metal flux growth has minimal materials complexity. Materials such as iron shots and graphite pellets can be loaded into a crucible and placed at the center of the retort and with the chamber lid closed. The chamber is evacuated by a dry-scroll roughing pump and a turbomolecular pump to $\leq 10^{-5}$ mbar and purged with an inert gas (typically nitrogen).

Another key advantage of the APHT method is that it produces high quality crystals. Methods such as chemical vapor deposition (CVD) [101], molecular beam epitaxy (MBE) [102], high pressure graphitization (HPG) [103], steel refining (Kish) byproduct [104], and even naturally occurring graphite [105] produce graphite crystals with lower crystallinity than APHT. APHT produces high quality single crystal graphite in bulk ($>1 \text{ mm}^2$ area, $>20 \text{ }\mu\text{m}$ thickness).

Disadvantages of APHT Method

Despite the simplicity of the APHT method, it comes with drawbacks. One such drawback is the obscurity of the growth process due to the furnace enclosures. Aside from the enclosure in Figure 2.6, blackbody radiation of the heated materials further prevents direct observation. This prevents in situ spectroscopic techniques to help understand the nucleation and growth of graphite crystals. Another drawback is that the source materials can only be prepared at the beginning, *i.e.*, no in-situ changes can be made once the source materials are loaded. The full report of the optimization of graphite growth via APHT [95] is reproduced on the next page with formatting changes to the original publication in MDPI to suit this dissertation.

Article

Controlled Growth of Large-Area Graphite Single Crystals at Atmospheric Pressure and High Temperature from a Metal Flux

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precipitated from a saturated iron–carbon solution by slowly cooling (4 °C/h) from a maximum temperature to reduce the carbon solubility. The graphite flakes were >25 square millimeters in area and >10 microns thick, with individual crystal grains as large as 1.2 mm². The crystals were (0002) oriented, as determined by X-ray diffraction. The high structural quality of the graphite crystals was verified by Raman spectroscopy. For graphite with the natural distribution of carbon isotopes, the G-peak at 1580 cm^{−1} was narrow (~12 cm^{−1}) and the defect peak (D-peak) was absent. To demonstrate the process versatility, graphite crystals enriched in the ¹³C isotope were grown at 5 degrees of enrichment. The Raman G-peak linearly shifted from 1580 cm^{−1} to 1520 cm^{−1} for graphite crystals enriched from 1 to 99% ¹³C. The etch pit densities from defect-sensitive etching ranged from 0 to 1.6 × 10⁸ per cm². The process was refined by examining the grain size and quality as functions of the carbon concentration in the starting sources, the carrier gas composition, and maximum temperature. The simplicity of this process suggests it can be scaled to produce very large graphite crystals that would be suitable for a wide range of technologies.

Keywords: graphite; crystal; optimization; characterization; growth; solvent; atmospheric pressure; high-temperature

Abstract

In this study, the growth of high-quality graphite single crystals from a molten metal flux at atmospheric pressure was optimized. The crystals were

controlled in graphite crystals from these sources. Monolayers or a few layers of graphene are synthesized by CVD on metal substrates [6] and the thermal conversion of silicon carbide single crystals [7], but their quality is lower than that produced by the exfoliation of bulk graphite. While there is a plethora of literature on iron–carbon solutions, due to its importance to the manufacture of steel, there have been surprisingly few studies on graphite crystal growth from molten metal solutions. The focus of most prior studies was on steel production with little attention to Kish graphite. The most detailed study was conducted by Austerman [8] nearly sixty years ago. He found supersaturation of an iron flux with carbon produced a variety of macrostructures of graphite.

Graphite's weak interplane attraction also allows layers to be easily separated into monolayer graphene via mechanical exfoliation [9]. Aside from being an ultra-thin material (0.334 nm thick), graphene's properties are enhanced beyond that of normal graphite, including low density, high surface-area-to-volume ratio, ultra-high electron mobility (200,000 cm²/Vs), thermal conductivity (5000 Wm/K), high optical transparency (97.4%), and enhanced mechanical properties [9–11]. These properties make graphene suitable for growing industries such as electric vehicles, lightweight electronics, transistors, and energy storage such as in rechargeable batteries [12–14]. The high Young's modulus (1 TPa) lends itself to applications in high-performance flexible electronics such as flexible photovoltaic cells or LED displays [15]. Graphene also finds applications in data storage, logic gates, and magnetic field sensors through the use of spintronics [16]. Graphene is attractive for spintronics due to its long electron spin diffusion lengths, long spin lifetimes, and difference in nuclear spins between the ¹²C (nuclear spin 0) and ¹³C (nuclear spin 1/2) isotopes [17–19]. Recently, we have demonstrated that ¹³C doping in ¹²C graphite leads to splitting of the Landau level transitions under an out-of-plane magnetic field [20]. In addition, isotopically pure graphite exhibits enhanced thermal conductivity due to the reduction in phonon scattering by the isotope mass differences of natural carbon (99 at% ¹²C, 1 at% ¹³C) [21].

The present study optimizes graphite crystal growth around quality, single grain area, and isotopic enrichment from a molten metal solution, specifically iron. The process conditions examined include the mass fraction of carbon, cover gas composition, and maximum temperature. The quality of the graphite crystals was assessed by Raman spectroscopy, 002 XRD diffraction, and defect-sensitive etching (DSE). Single crystal grain sizes were measured by optical microscopy. These parameters point towards the ideal conditions to produce large-area graphite crystals while minimizing unintentional/undesired defects.

Materials and Methods

Metal Flux Growth

Transition metals (including Fe, Ni, and Co) are all suitable solvents for carbon. Iron was selected for these experiments because of its relatively low cost. In these experiments, mixtures of carbon (99.995%) and iron (99.99%) were heated in an alumina (99.9%) crucible under an inert gas. The temperature control schedule was varied between each optimization experiment set. Essentially, the iron is melted and the carbon dissolves into the melt, forming an iron–carbon solution. It is then slowly cooled, causing the carbon to supersaturate and precipitate from the solution, forming bulk graphite crystals on the metal surface. Graphite crystals were then mechanically exfoliated

from the ingot using thermal release tape. Figure 1, below, is the temperature control schedule for maximum temperature optimization with an inset depicting the resulting graphite crystals on an iron boule.

Five graphite samples of various isotopic concentrations were synthesized by varying the ratio of natural carbon and graphite powder that was enriched to 99% with the ^{13}C isotope. These samples contained 1%, 20%, and 60%, and two samples contained 99% ^{13}C .

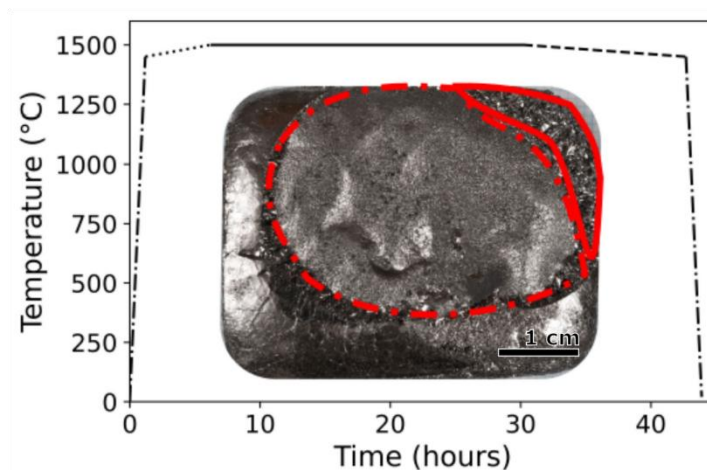


Figure 1. A representative time–temperature profile employed to grow graphite crystals. Different segment styles indicate a change in the process as follows: heat up, slow heat, dwell, slow cool, and quench. Inset: a macrograph of graphite crystals on an iron boule with large (solid outline) and small graphite crystal regions (dashed outline).

Grain Size Measurements

Optical microscope images of typical exfoliated graphite flakes are shown in Figure 2. Figure 2a presents an isotopically enriched ^{13}C graphite flake and arrows distinguish visible defects along the surface in Figure 2b. A parallel for natural graphite crystals is shown in Figure 2c,d. Graphite flakes were exfoliated from the boule surface, then imaged with objectives varying from 25 to 1000× magnification. The topology of the crystal flake consisted of large flat facets separated by wrinkles, cracks, and grain boundaries. Individual grain sizes were measured by using the polygon feature of ImageJ software (version 1.54d) [22] over grains enclosed by grain boundaries. To collect statistics on the single grain areas within an experiment, 10 isolated flakes were imaged with flat, unobscured, and distinguishable grains. An example is provided below in Figure 2c. Several examples are provided in Appendix A.

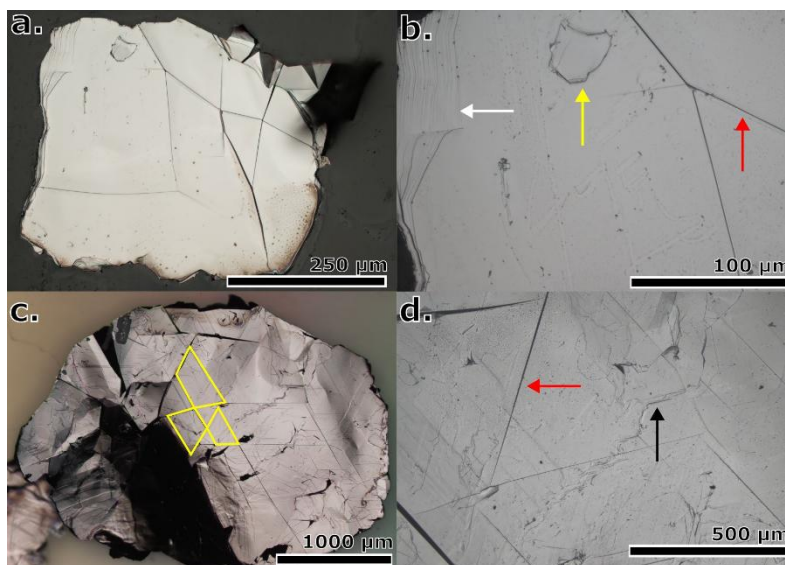


Figure 2. (a) Exfoliated ^{13}C graphite crystal flake grown under the following conditions: 5.8 carbon-13 wt.%, nitrogen gas, and a 1500 °C dwell temperature; (b) surface image of same crystal. (c) Demonstration of grain counting and measuring (yellow trapezoids) on natural carbon equivalent to (a) with (d) surface texture image. White arrows point to steps, yellow arrows to defects, red arrows to grain boundaries, and black arrows to folds visible on the surface.

In Figure 2c is a graphite flake with polygons tracing grain boundaries. The grain size was quantified by averaging the area within >100 of these polygons across ~10 graphite flakes per experiment. Some common features are distinguished with arrows in Figure 2b,d. The grain boundaries traced were required to meet specific criteria: visible at 50× magnification, enclosed within the exfoliated flake (to exclude discontinuous grains around the perimeter), not enveloped by another grain (similar to the feature indicated by the yellow arrow in Figure 2b), and not shadowed by topography (similar to the lower right section of Figure 2c).

Raman Analysis

The crystal quality and isotope concentrations in the graphite flakes were verified by Raman spectroscopy. Spectra were taken at room temperature with a Bruker 2 Senterra employing a 532 nm laser with a power of 20 mW collected in backscattering configuration. This instrument exhibited a signal-to-noise ratio of >25 when measuring a pristine silicon standard. Two spectral regions were analyzed. The first region is the “G-peak” which is between 1520 cm^{-1} (for ^{13}C -enriched graphite) and 1580 cm^{-1} (for graphite with the natural distribution of isotopes). Apart from normalization when comparing multiple spectra, there was no post-processing of the data. The full-width at half-maxima (FWHM) of the G-peak is indicative of the crystal quality and the exact peak position shifts with isotopic concentration. The second region is the “D-peak”, or defect peak, whose intensity is indicative of the defect concentration in the graphite [23]. The G-peaks were fit with Lorentzian curves to obtain the FWHM.

Three isotopically enriched graphite samples were mapped using a 31 × 31-point Raman scan across a 15 × 15 μm region to test for consistency across the surface of the sample. The FWHM of each point was determined with a Python program (version 3.9), creating a statistical distribution of peak widths that can be compared across different samples. Raman mapping was performed at room temperature using a Horiba LabRAM HR800 Confocal Raman

Microscope system (Horiba Jobin Yvon, Villeneuve d'Ascq, France) that is equipped with a thermoelectrically cooled CCD detector. A 532 nm laser and a 100× objective lens was used. Laser power was kept at 6.8 mW during Raman mapping. A 600 grooves/mm grating was used which corresponds to an instrument resolution of $\sim 2 \text{ cm}^{-1}$. This instrument exhibited a signal-to-noise ratio of >400 throughout all measurements.

X-Ray Diffraction Analysis

In addition to Raman spectroscopy, Cu K α X-ray diffraction (XRD) patterns from 10 to 80° were collected for all optimization experiments using a Rigaku Miniflex Tabletop XRD (Rigaku Corporation, Tokyo, Japan) at 30 mA. Similar to Raman spectroscopy, the quality of the graphite crystals was quantified with the XRD FWHM of the 0002 peak. Narrow diffraction peaks are further evidence of crystal integrity.

Defect-Sensitive Etching

The dislocation density of graphite crystals was assessed using DSE. A combination of 40 wt.% NaOH and 60 wt.% KOH was mixed in a crucible heated to 450 °C. The molten solution was poured onto a room temperature stainless steel plate before being aliquoted into small cubes. Graphite crystals were placed into an aluminum foil vessel atop a heating plate. The heating plate was heated to 490 °C before adding a pellet of the etchant mixture. The mixture reacted with graphite at surface defect sites, producing etch pits. Durations from 30 s to 600 s were tested to maximize defect quantity without the etch pits overlapping each other. The graphite crystals were etched for the optimal time of 280 s. The crystals were then quenched to room temperature in water to remove the alkali hydroxide [24]. Patel and Bahl [25] demonstrated that the resulting etch pits correlate with edge and screw dislocations. The morphologies of these pits are pointed termination and some can have flat termination as illustrated in Figure 3 below.

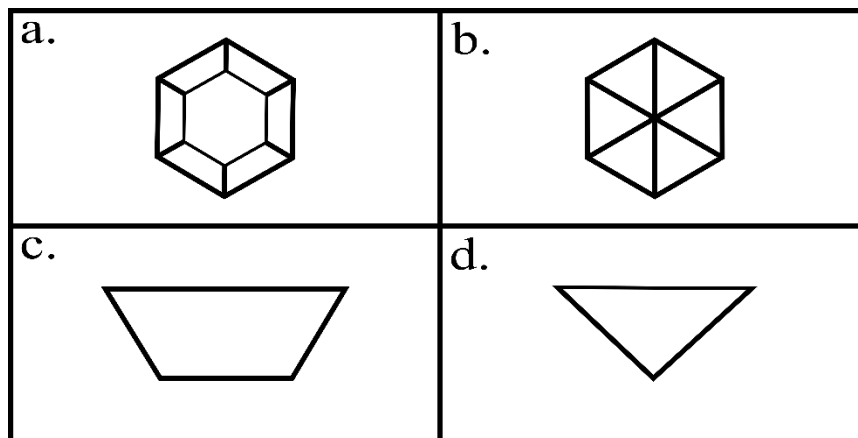


Figure 3. Drawing of typical topology of graphite etch pits (a) flat-bottomed pits with (c) cross-sectional view and (b) pointed-bottom pits with (d) cross-sectional view.

Edge dislocations occur when there is an additional crystal plane that terminates midlattice perpendicular to the Burgers vector inducing tensile strain [17]. A screw dislocation occurs when an atom in a lattice is slightly displaced, causing interlayer shift parallel to the Burgers vector [26].

The area of the pits was determined using the ImageJ software [22]. The etch pits in five representative regions were imaged from each etched graphite flake. The average area of pits was weighed with the number of pits used to represent each sample's overall etch pit size.

$$A_{\text{sample etch}} = \frac{\sum_{i=1}^5 \hat{A}_{\text{pit},i} * N_{\text{pit},i}}{5} \quad (1)$$

The etch pit density was calculated by dividing the number of etch pits over the crystal area encompassed in each image. To illustrate the etch pits in detail, scanning electron microscope (SEM) images were taken using a Zeiss Gemini SEM 500 with an acceleration voltage of 0.5 kV and aperture of 20 μm using the InLens detector (ZEISS, Jena, Germany).

Crystal Growth Optimization

The goal of these experiments was to optimize the process to produce large-area crystals of high quality. The relevant parameters investigated included the carbon mass percent, cover gas composition, and maximum temperature. The graphite crystal quality was assessed with the FWHM of the XRD (0002), Raman D-peak FWHM, and DSE etch pit densities. All experiments were performed using a R.D. Webb Red Devil Graphite (R. D. Webb, North Kingstown, RI, USA) insulated box furnace.

The temperature profile for the *carbon composition* experiments consisted of a heating to 1500 $^{\circ}\text{C}$ at 75 $^{\circ}\text{C/h}$ in an argon atmosphere and holding for 24 h. Then the molten metal solutions were cooled at 4 $^{\circ}\text{C/h}$ to 1350 $^{\circ}\text{C}$ and finally quenched at 75 $^{\circ}\text{C/h}$ to room temperature. The carbon solubility in molten iron is 6.67 mass percent [27]. Eight experiments were conducted to ascertain the carbon mass percent that maximizes the grain size and quality of the precipitated graphite. The graphitic carbon mixed with iron shots was varied from 2.1 to 6.7 mass percent. These compositions represent the lowest possible composition and saturation in iron, respectively, for graphite precipitation. The composition that produced the largest grain size average was then used for both the cover gas experiments and the maximum temperature experiments.

Two different gases were used to determine whether the *cover gas composition* affects crystal growth: ultra-high purity (UHP) nitrogen (99.99%) and UHP argon (99.99%). The temperature schedule was different from the composition experiments for consistency between the two. The schedule began with heating to 1450 $^{\circ}\text{C}$ at 1200 $^{\circ}\text{C/h}$, then to 1500 $^{\circ}\text{C}$ at 600 $^{\circ}\text{C/h}$. The flux was held at that temperature for 24 h. Once this dwell was over, the furnace was cooled to 1000 $^{\circ}\text{C}$ and dwelled for 24 h before being quenched to room temperature via natural cooling. To find the *optimal temperature*, the temperature schedule was a heating ramp to a varied dwell temperature (X). Initially the chamber was heated to $X-50$ $^{\circ}\text{C}$ at 1200 $^{\circ}\text{C/h}$, then to X $^{\circ}\text{C}$ at 600 $^{\circ}\text{C/h}$. The furnace was held at X $^{\circ}\text{C}$ for 24 h followed by cooling at 4 $^{\circ}\text{C/h}$ to $X-50$ $^{\circ}\text{C}$. After this, the furnace was quenched to room temperature at 1200 $^{\circ}\text{C/h}$. X was evaluated from 1125 $^{\circ}\text{C}$ to 1550 $^{\circ}\text{C}$ in increments of 25 $^{\circ}\text{C}$ (i.e., $X \in [1125, 1550 \text{ }^{\circ}\text{C}]$, $\Delta X = 25 \text{ }^{\circ}\text{C}$).

Results and Discussion

Grain Size Optimization

A collection of box plots representative of each parameter in the optimization experiment set is presented in Figure 3. The grain size is measured against the independent variables in the left column, while the associated temperature schedules are shown on the right abbreviated from 1000 °C along the y-axis.

Figure 3a illustrates graphite grain size as a function of the initial amount of carbon loaded. Since 2.1 wt.% did not produce crystals that could be exfoliated, it was omitted from the figure. Due to the high standard deviation, no correlations can be confidently drawn. There are a wide range of factors that can influence nucleation such as surface energies or impurities in the molten solution. The former would cause these high-energy surface points to serve as a premature nucleation site. Impurities could be either insoluble, having a similar impact as undissolved carbon, or an impurity serving as a defect in the precipitated graphite inducing strain and leading to the formation of grain boundaries. On the right, the y-axis begins at 1000 °C to highlight the cooling step following the dwell. The maximum grain size was recorded at 5.8 wt.% carbon composition; therefore, it was selected as the composition for the remaining experiments. There was no statistical correlation between the cover gas and crystal grain area (Figure 4b). This is unsurprising given neither gas is expected to react with carbon nor iron in the molten metal solution. Consequently, nitrogen was arbitrarily selected as the cover gas for the final set of optimization experiments.

In Figure 4c, the maximum temperature was varied from 1550 °C to 1125 °C—below which the solution was no longer molten. Smaller crystals did form at lower temperatures; however, they were significantly smaller than those formed at higher temperatures. Crystals grown at 1250 °C produced significantly smaller grains ($900 \mu\text{m}^2$) than others, likely an outlier. The grain area increases with temperatures up to 1400 °C. This implies the existence of an optimum temperature for grain size. The temperature versus time profile is different for each experiment set, disqualifying comparison between the different test variables.

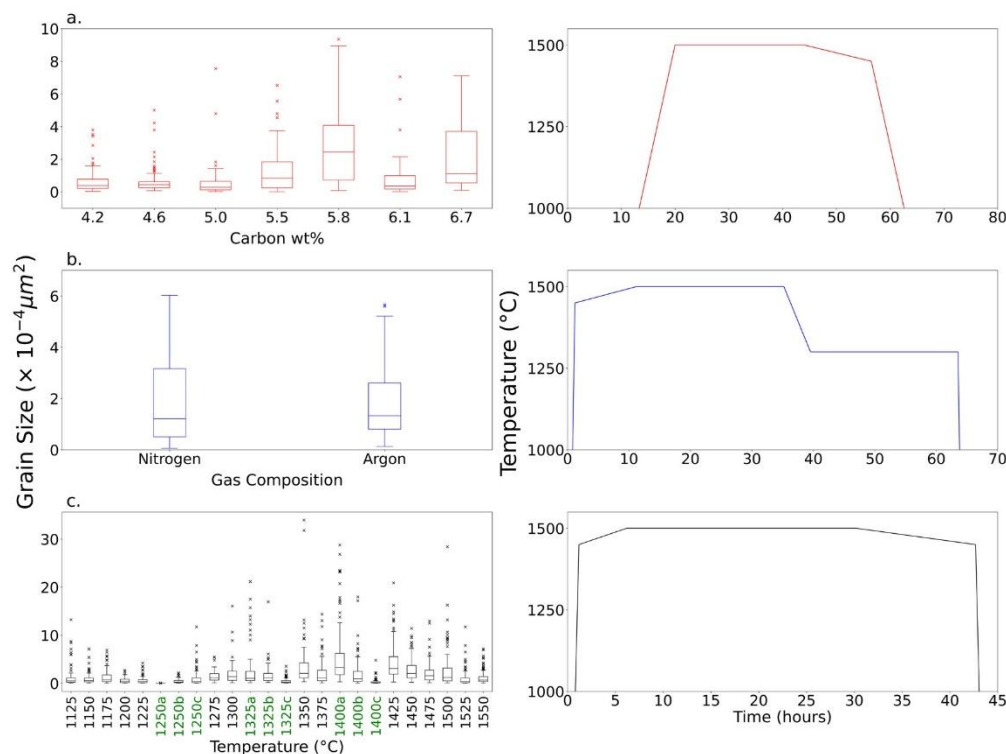


Figure 4. Box plots of average graphite crystal grain size (scaled down by 10^4) versus (a) carbon wt.%, (b) cover gas, (c) and maximum dwell temperature with corresponding temperature schedules (**right**). Green labels in (c) indicate experiments that were repeated to examine variance.

Raman Analysis

3.2.1. Optimization Characterization

Single Raman spectra were taken from three different flakes and averaged together to represent each experiment. Regardless of the process conditions, none of the graphite crystals grown in this study exhibited a D-peak. The FWHM and position of the G-peak remained consistent around 14 cm^{-1} at 1580 cm^{-1} for all experiments. The only exception to this observation is the compositional optimization which showed a linear decrease in FWHM from 15.6 at 4.2 carbon wt.% to 14.2 at 6.7 wt.% C. The abundance of carbon may prevent certain intrinsic defects like Stone–Wales or other sources of strain.

3.2.2. Isotopic Enrichment

The graphite crystals were high-quality even with variation in the carbon isotopes, as indicated by Raman spectroscopy (Figure 5). Regardless of ^{12}C to ^{13}C ratio, none of the graphite crystals had the “D-peak” at 1350 cm^{-1} . Narrow graphite “G-peaks” indicate a low crystal strain and a high degree of crystallinity [21,28]. The FWHM of the Raman G-Peak broadens when the graphite contains isotope mixtures. An isotopically pure sample has an FWHM of 12.2 cm^{-1} for both carbon isotopes, whereas a mixture of 40% ^{12}C /60% ^{13}C has a peak width of 20.8 cm^{-1} , due to isotopic disorder. Isotopically pure graphite has superior phonon transport properties and functions better as a thermal and electrical conductor [21,28,29]. The G-peak shift is sensitive to isotopic concentration in the graphite due to the mass differences between carbon isotopes changing the vibrational frequency of the crystal bonds. Crystals with a 1% ^{12}C content have a G-peak shift of 1520 cm^{-1} , and crystals with a 99% ^{12}C content have a G-peak shift of 1580 cm^{-1} . Figure 5c shows that the G-peak shift is linear with respect to isotopic concentration, allowing isotopic concentration to be readily determined by Raman spectroscopy.

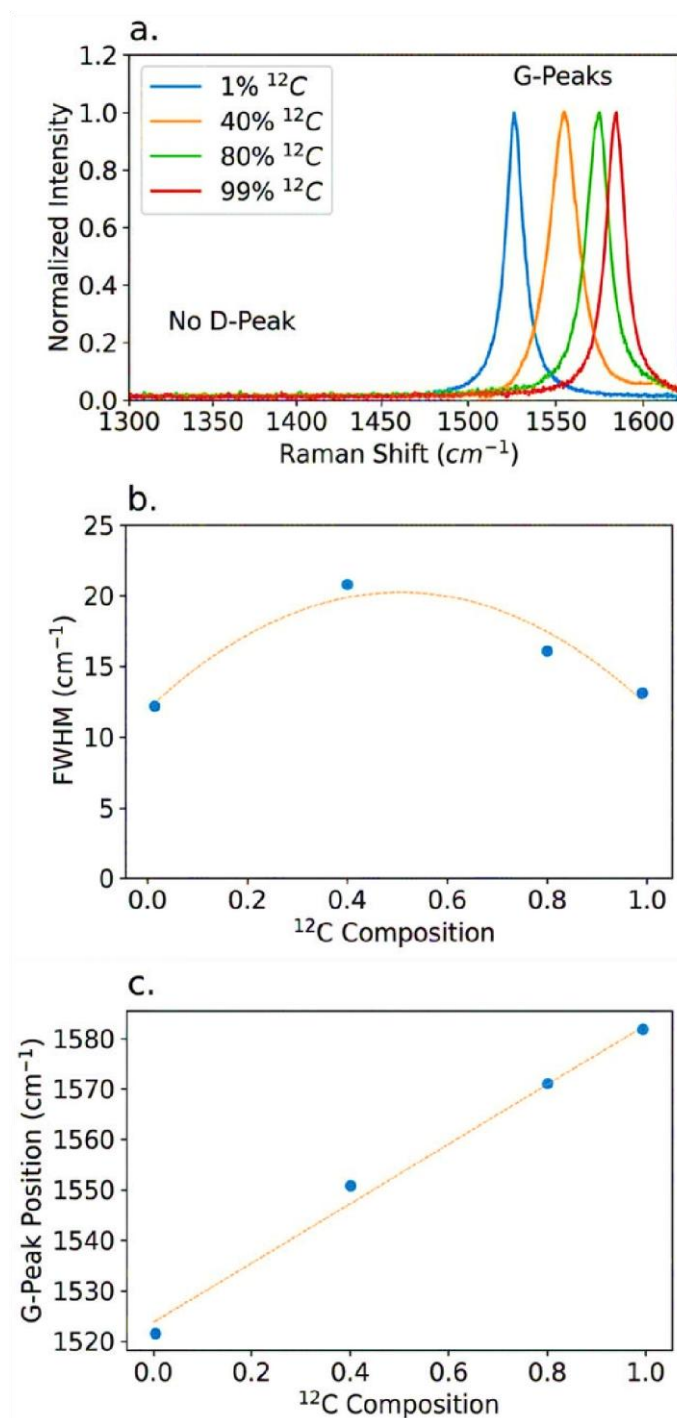


Figure 5. (a) Raman spectra of isotopically enriched graphite of different isotopic purities normalized to their G-peaks. (b) G-peak FWHM as a function of isotope concentration. (c) G-peak shift as a function of isotopic purity.

Raman mapping was used to test for consistency across the crystal surface. In total, 960 measurements were taken in a $15 \times 15 \mu\text{m}$ grid across samples of varying isotopic concentration, and histograms of the G-peak FWHM are shown in Figure 6. Overall, the variance of the FWHM is small, indicating a high degree of sample uniformity. The isotopically mixed samples showed a larger standard deviation in the peak width than isotopically

pure samples. This indicates that the isotopically pure samples are more uniform across the sample surface than the isotopically mixed samples. Pairing the increased non-uniformity with the wider median FWHM, isotopically mixed graphite shows a higher propensity for defect inclusions in the crystal structure.

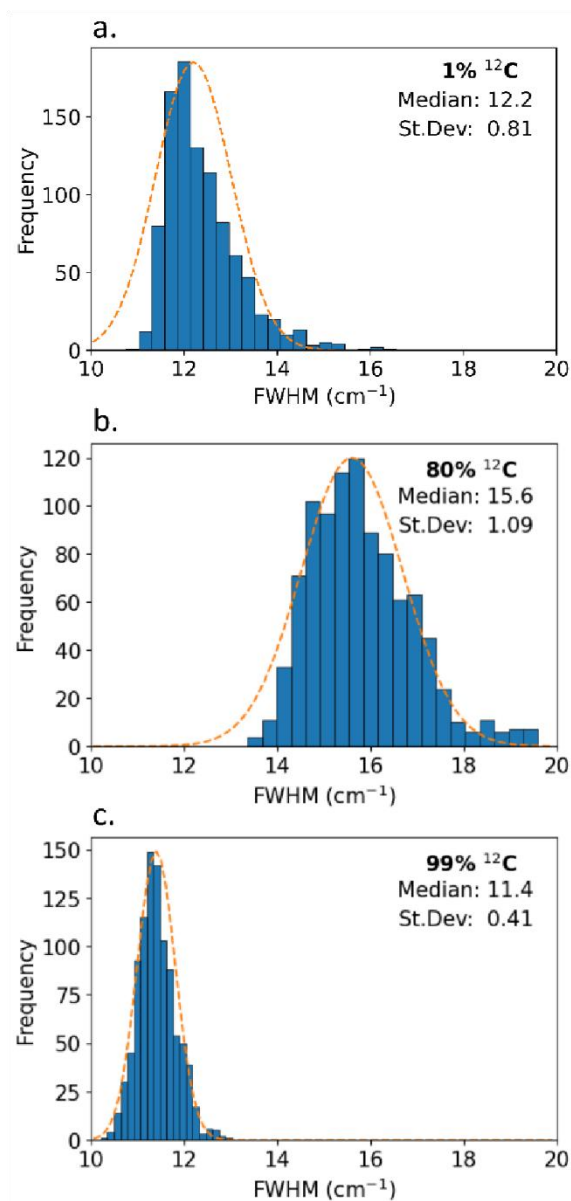


Figure 6. Histograms of the G-peak FWHM of 960 measurements mapped across (a) 1% ¹²C, (b) 80% ¹²C, and (c) 99% ¹²C graphite single crystals.

X-Ray Diffraction

XRD patterns were taken from exfoliated graphite crystals except for the 2.1 weight percent carbon source from which no crystals could be exfoliated. Crystal quality was comparable across all conditions, regardless of the source carbon weight percent. Figure 7a illustrates the existence of a non-optimal range producing very disordered crystals from 4.6 to 5.8 wt.% C in Fe. The narrow 002 plane diffraction pattern at 26° seen in Figure 5b was typical of crystals grown outside the 4.6–5.8 wt.% C in Fe range. These results oddly contradict the Raman FWHM analysis,

suggesting that there may be defects along the c-direction which would appear below the sensitivity range of the Raman microscope used in this work ($>100\text{ cm}^{-1}$).

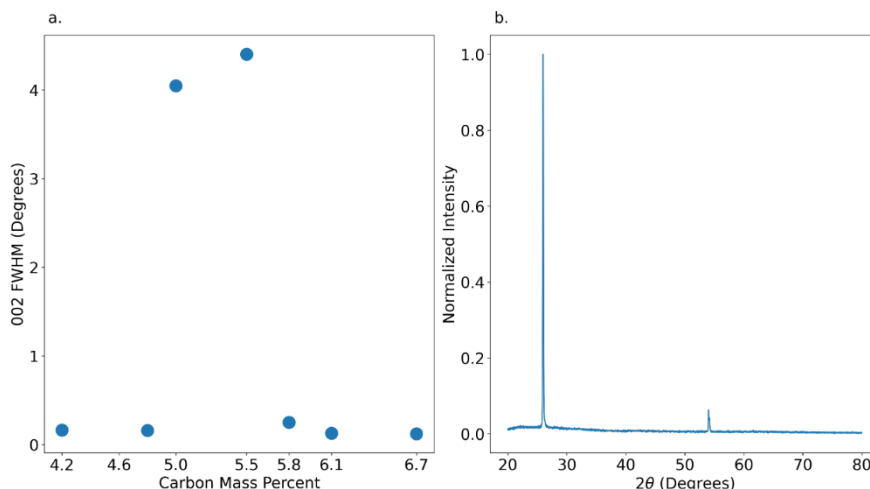


Figure 7. (a) Graphite XRD 002 peak FWHM versus the initial carbon composition and (b) normalized exfoliated graphite sample XRD pattern of sample grown from a 6.1 wt.% carbon solution.

Unexpectedly, there is no relation between 002 FWHM and temperature or cover gas composition. It was expected that as the crystals grew larger, more defects would be present due to the larger sample volume. As the defect quantity increases, so too does the strain in the crystal bulk reflected by the increasing FWHM. The cover gas composition did not have a significant impact on the diffraction patterns. The nitrogen and argon samples both had 002 FWHMs of 0.12° . A similar trend was noted in the temperature optimization series, with all but one sample oscillating around $0.12 \pm 0.02^\circ$.

Defect-Sensitive Etching

DSE revealed etch pit densities ranging from 0 to 1.6×10^8 pits/cm². The absence of etch pits in some of the compositional optimization experiments indicates pristine crystals with minimal high-energy sites susceptible to etching. The density of these pits can be correlated with the abundance of edge and screw dislocations due to defects. Hence, the etch pit density can be correlated with defect density along the surface since the etching is surface-sensitive. An example of such dislocations is provided in Figure 8 below.

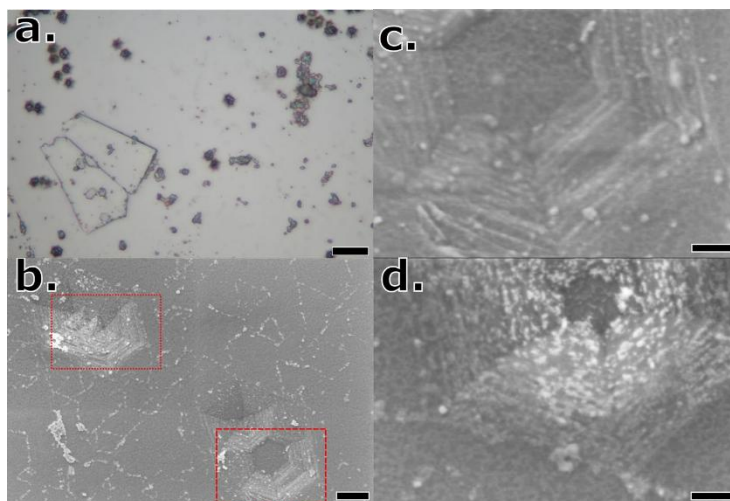


Figure 8. (a) Etch pits on graphite crystal at 1000× magnification. (b) Etch pits in the shape of hexagons with flat (dashed box) and pointed bases (dotted box) captured in SEM. (b) SEM image of flat DSE etch pits and (c) pointed etch pits. Scale bars are (a) 10 μm (b) 300 nm and (c,d) 100 nm.

As shown in Figure 8a, there are several facets to the defects present as previously shown in Figure 2. These DSE etch pits varied in diameter; hence, it is insightful to look into how the optimization parameters can affect their size. Additional samples were etched to reveal potential trends with respect to growth conditions throughout the growth optimization experiments summarized in Figure 9. There did not appear to be any consistent trend regarding the location of these pits. They seemed to have no preference for macroscopic defects like grain boundaries or wrinkles. Occasionally, these pits would have a crystallographic arrangement relative to each other, but more often they had no apparent preference. Etch pits observed across the optimization experiments are shown in Figure 9.

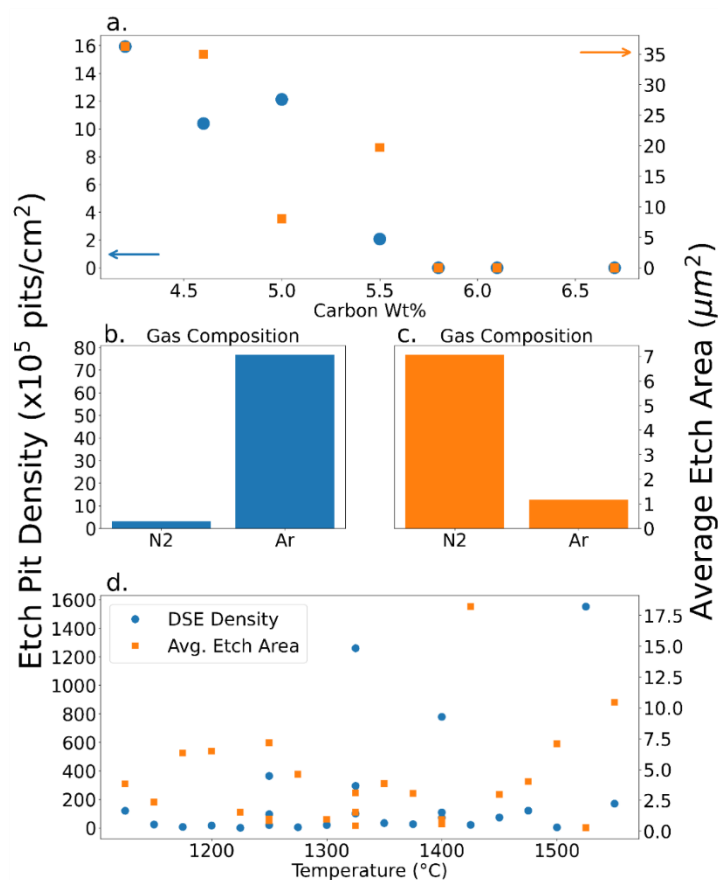


Figure 9. Effects of (a) initial carbon weight %, (b,c) cover gas composition, and (d) maximum process temperature on dislocation frequency per unit area (left y-axis, blue circles), pit area (right y-axis, orange squares) of individual samples.

The etch pit density dropped to zero as for an initial carbon concentration greater than 5.8 wt. %. An explanation may be that the oversaturation of the solvent minimizes surface defects. Another possible explanation is that the etchant's surface sensitivity outweighs that of XRD. This means that, despite having a narrower 002 diffraction peak, there may be more defects than accounted for along the surface specifically.

DSE shows that growing graphite crystals in nitrogen induces larger defects (Figure 9c) but fewer instances (Figure 9b). The reason remains unclear. A theory is that the solubilization of nitrogen in iron at elevated temperatures [30] possibly interferes with the way that graphite is precipitated, inducing specific defect sizes. Since nitrogen is more reactive than argon, it could be that nitrogen is more likely to decorate these defects when they form, thus increasing the area over which the surface energy is relatively higher than in the chemically inert argon.

In Figure 9d, crystals grown at different maximum temperatures show little correlation with defect topology. From the data provided, there can be no correlation confidently claimed between defects in graphite crystals and the temperature at which they are grown. Since smaller crystals are grown at lower temperatures, it is not unreasonable to expect fewer defects due to the lack of bulk defects produced.

Conclusions

The largest graphite single crystal grain was grown with a 5.8 wt.% carbon source at 1400 °C under a nitrogen atmosphere. It was 18% larger ($3.4 \times 10^5 \mu\text{m}^2$) than the second largest crystal grown under other conditions ($2.8 \times 10^5 \mu\text{m}^2$). The optimized APHT solvent growth method produces high-quality bulk graphite with a Raman G-peak FWHM of less than 10 cm^{-1} and XRD (0002) diffraction peaks FWHM as low as 0.03° . These graphite crystals are also large with grain sizes on the order of 1.2 square millimeters. Furthermore, these grains are relatively thick compared to film methods resulting in $>10 \mu\text{m}$ thick freestanding crystals. This synthesis method also allows for good control of isotopic enrichment as demonstrated in the shift of the G-peak.

In conclusion, the optimal conditions for graphite growth coincide with those reported by Austerman et al. [8]; however, contrary to their findings, nitrogen was more favorable for graphite growth under the same conditions: the average grain size was 25% larger ($2.5 \times 10^5 \mu\text{m}^2$ versus $2.0 \times 10^5 \mu\text{m}^2$). The conditions to grow the largest-area graphite crystal grains are a 5.8 wt.% carbon mixture heated to 1400 °C under a nitrogen atmosphere, though there will be a few large dislocations relative to other conditions. However, to minimize dislocations, the same composition could be heated to 1500 °C and produce less consistent but larger crystal grains. Therefore, the metal flux method can be tailored to produce crystals with moderate control over their dislocations and grain sizes without jeopardizing quality. Future investigations over controlled nucleation will lead to the scalable growth of large graphite single crystals via the metal flux method.

Author Contributions: Conceptualization, J.H.E., T.P. and D.E.; methodology, T.P.; software, T.P. and D.E.; validation, J.H.E.; formal analysis, T.P., D.E., M.L.S., G.Y. and R.H.; investigation, T.P., D.E., I.T., G.Y. and R.H.; resources, J.H.E.; data curation, T.P., D.E., G.Y. and R.H.; writing—original draft preparation, T.P., D.E. and J.H.E.; writing—review and editing, T.P., D.E. and J.H.E.; visualization, T.P. and D.E.; supervision, J.H.E. and P.B.A.; project administration, J.H.E.; funding acquisition, J.H.E. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Dataset available on request from the authors.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

XRD	X-ray diffraction
FWHM	Full-width at half-maximum
SEM	Scanning electron microscope
CVD	Chemical vapor deposition
DSE	Defect-sensitive etching

Appendix A

Appendix A.1. Grain Counting Example Images

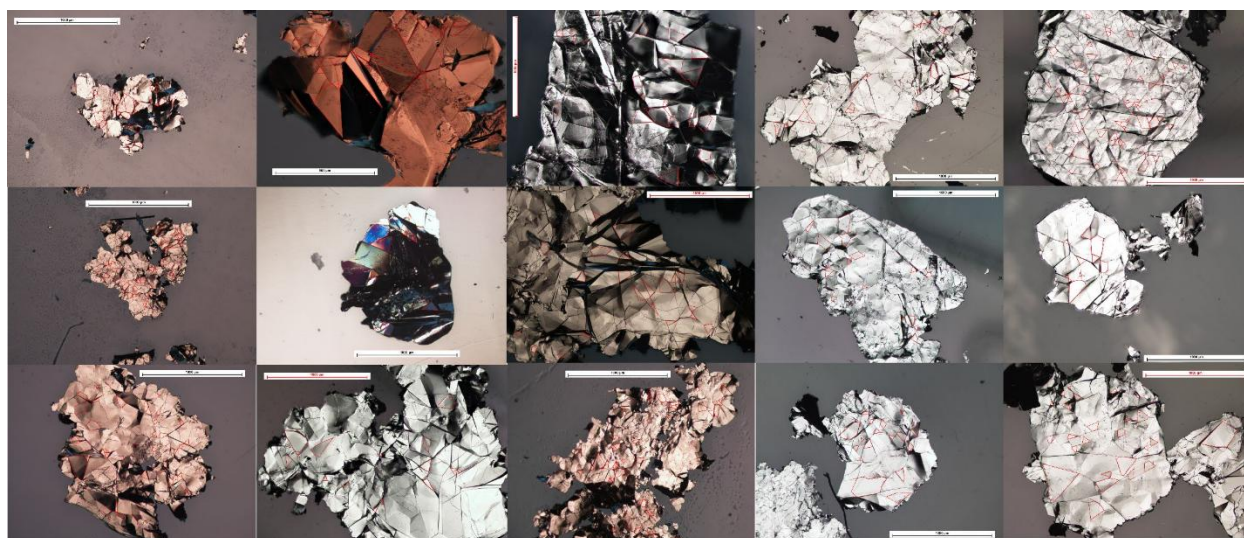


Figure A1. Total of 15 images from grain size measurement dataset. Red polygons encompass what are considered single grains. The area of these grains is calculated by ImageJ using the scale bar to define distance per pixel.

Appendix A.2. Defect-Selective Etching Example Images

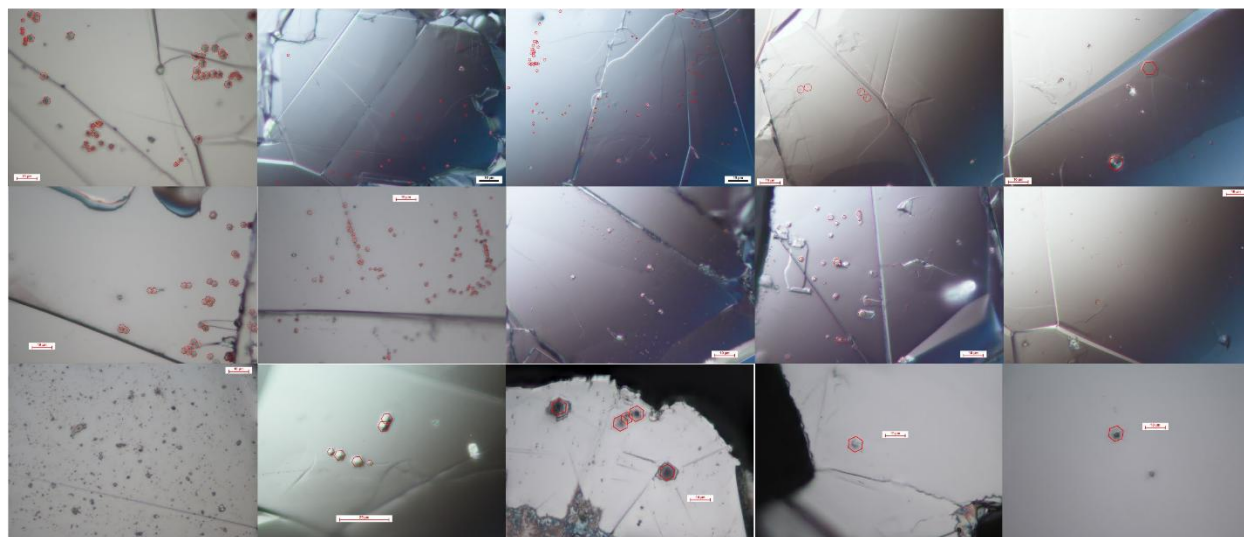


Figure A2. Total of 15 images from defect-sensitive etching measurement dataset. Red hexagons encompass what are considered individual etch pits. The diameter of the etch pits is calculated by the diagonal of the hexagons and the area is calculated by ImageJ using the scale bars in each image.

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Defect-controlled bulk single crystal graphite

Impurity doping of the graphite crystals is easy with the APHT method. The APHT method allows for controllable dissolution of certain impurities into the same flux that precipitates the graphite. In doing so, these impurities incorporate into the crystals [106]. The impurities/defects are more stable due to the thermodynamic equilibrium used in ATHP during slow cooling. Several elements have been successfully incorporated into graphite including B, N, Si, Ti [107], and Zr [108]. Here APHT graphite is attempted by including B and Si with the source solids and N through flux composition and temperature controls.

Boron-doped graphite

Boron-doped graphite (BDG) increases lithium-ion batteries (LIBs) discharge capacity by 15-20% [109]. BDG is a p-type doped material with a higher hole carrier density than pristine graphite that can halve its resistivity [79]. This is attributed to the reduced layer spacing due to the difference in electrostatic surface potentials of the boron dopants and graphitic carbons in adjacent layers [110]

Doping experiments were conducted using 0.1 and 0.6 weight percent boron powder among the source materials in APHT growth. No significant deviations from standard graphite could be detected by XRD or Raman, as shown in Figure 2.7.

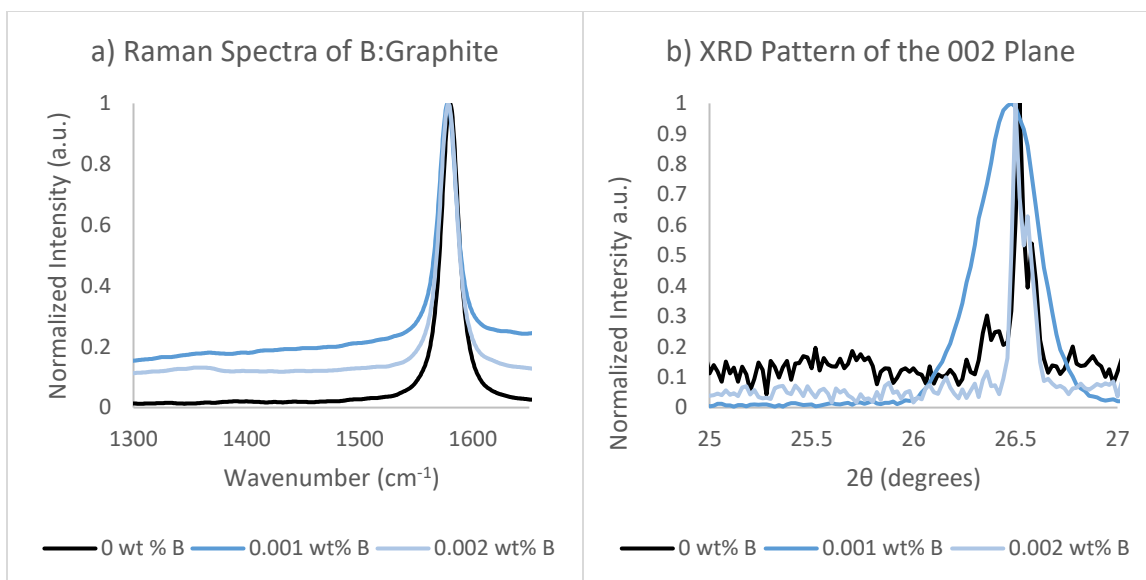


Figure 2.7. Normalized (a) Raman spectra and (b) XRD patterns of B-doped graphite crystals. Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) performed at South Dakota State University (SDSU) revealed that with 0.001 wt. % B in source materials produced 0.001 at. % boron concentration in the upper layers of the graphite. The orders of magnitude lower concentration in the crystals from the source materials reflect the purification of the crystal growth process. XRD suggests that the quality worsened with an increase in 002 peak width.

Nitrogen-doped graphite

Contrary to BDG, nitrogen-doping of graphite (NDG) adds more electron carriers (increases n), reduced interfacial tension, and improves the charge transfer speed [111]. NDG also exhibits greater surface activity, and the ability to hydrogen bond with larger molecules. A challenge with nitrogen doping in APHT grown graphite is the low nitrogen solubility in metal solvents. Initially iron-carbon binary mixtures were heated under nitrogen. However, there was no evidence from Raman nor XRD that any nitrogen had been incorporated into the graphite (Figure 2.8). Chromium has a high nitrogen solubility relative to other transition metals [112], so chromium was mixed with iron for a total composition of 79 wt. % Fe and 21 wt. % Cr in a graphite crucible, with the goal of increasing nitrogen incorporation into the graphite crystal. Additionally,

higher temperatures up to 1600 °C were employed to increase nitrogen dissociation into the melt. Despite these efforts, ToF-SIMS from SDSU showed no detectable nitrogen incorporation.

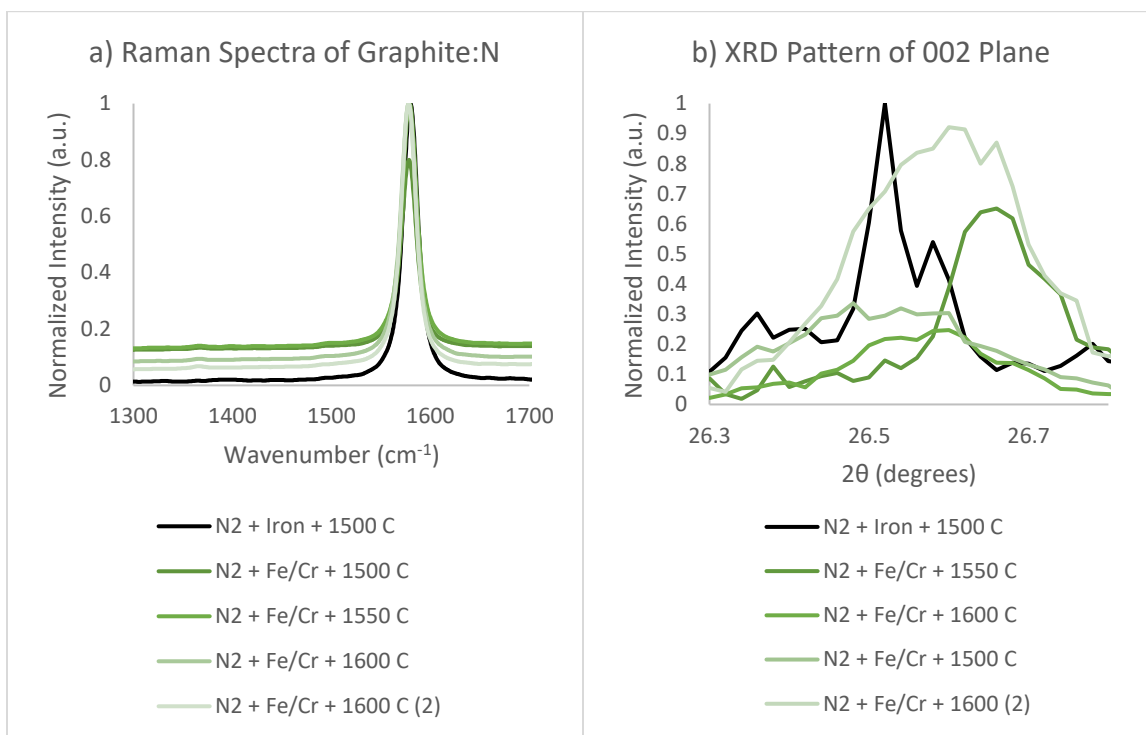


Figure 2.8. Raman spectra and XRD pattern of N-doped graphite crystals with varying experiment conditions (Gas + Solvent + Temperature)

Note there is still no D-peak at 1350 cm⁻¹ in the Raman spectra nor is there any change in the position or the FWHM of the G-peak at 1580 cm⁻¹. The XRD suggests that there is lattice shrinkage similar to the boron indicated by the shift of the 002 peak to higher angles.

Silicon-doped graphite

Lastly, silicon doping was attempted at four different silicon concentrations. Silicon assists with charge retention and improves lithium-ion battery service lifetimes [113]. Since Si is in the same element group as carbon, its valence should match well despite the increase in atomic radius [114]. Again, Raman and XRD showed no broadening of the G-peak and 002 diffraction plane nor the appearance of a D-peak presented in Figure 2.9.

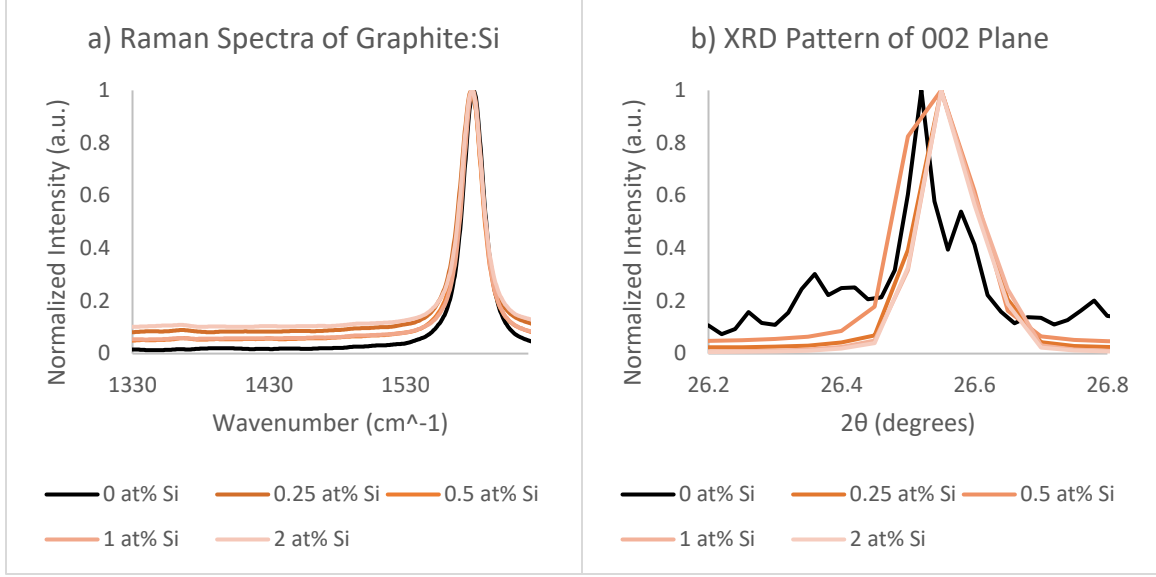


Figure 2.9 - Raman spectra and XRD pattern of Si-doped graphite crystals

For graphite crystals grown with any Si, the position of the (002) XRD peak shifts from 26.5° to 26.55°. This corresponds to a decrease in the d_{002} -spacing according to Bragg's Law (Equation 2.1).

$$d = \frac{n\lambda}{2 \sin \theta} \quad (2.1)$$

Where n is the order of diffraction (1), λ is the wavelength of the copper x-rays (1.54 Å), and θ is one half the angular the peak position in the diffraction pattern (one half of 26.5° and 26.55° in this case). This shows that with Si doping the d_{002} -spacing in graphite decreases from 3.357 Å to 3.353 Å contrary to the study of silicon doping of graphene by Liu et al [115]. The consistently smaller lattice constant indicates that the bonding landscape between layers has changed. A possible explanation is that: like boron doping, there is an interlayer charge difference causing attraction between layers proposed by DFT [116] or the Si atoms may be sp^3 bonding with each other since there is no D-peak in the Raman spectra. The latter is unlikely as there is no characteristic peak of silicon at 521 cm⁻¹.

Conclusion and Contribution

In conclusion, graphite single crystals have been grown under controlled growth conditions like carbon concentration, maximum growth temperature, and cover gas (N_2 or Ar) to optimize grain size up to 1.2 mm^2 and defect density (0 defects per μm^2). Defect engineering to tailor the conductive properties without compromising crystal quality was conducted with notable changes in XRD patterns of graphite especially in the case of alloying chromium to enhance nitrogen dissolution into the flux. Large area graphite crystals of up to 6mm^2 were also grown using the optimized temperature control ($1400\text{ }^\circ\text{C}$ max temperature for 24 hours under nitrogen) with 80 grams of low-carbon iron dissolved into a graphite crucible acting as a source.

Chapter 3 - Defect control of large area and bulk single crystal APHT grown hBN

Background

Hexagonal boron nitride (hBN) is an allotrope of the boron nitride family commonly referred to as “white graphite”. Other allotropes include cubic, rhombohedral, and wurtzite boron nitride. hBN is homologous to graphite in that sp^2 -bonded alternating boron and nitrogen atoms arranged in a hexagonal lattice as shown in Figure 3.1.

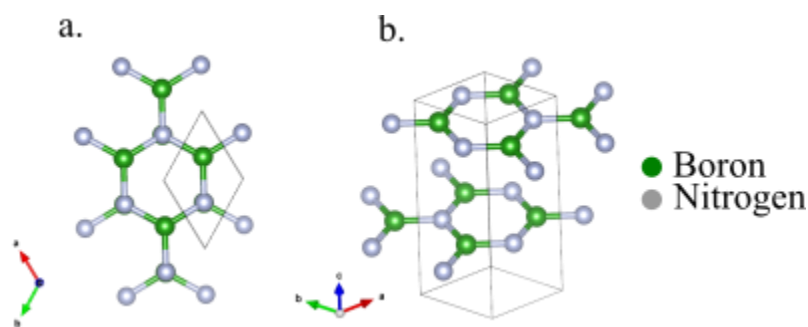


Figure 3.1. (a) Top-down and (b) skewed view of bilayer hexagonal boron nitride [117]

Contrary to graphite, however, hBN follows AA' stacking. This means that the layers overlap with one another as in Figure 3.1a but lie in opposite directions (Figure 3.1b). The boron atoms are directly aligned with the nitrogen atoms in the adjacent layers along the c -axis (blue arrow in Fig. 3.1b).

Despite having similar anisotropic crystal structures, hBN and graphite have very different electrical properties. Graphite is metallic (i.e. no bandgap) where hBN is a “wide-bandgap” semiconductor (borderline insulator) with a bandgap of 5.955 eV [39]. hBN doesn't have a special monolayer moniker like graphene; however, it has unique properties as a monolayer material [118]. hBN has low electrical conductivity $1 \times 10^{-11} \frac{S}{m}$ [119], but its thermal conductivity is

exceptional compared to other dielectrics at $420 \frac{W}{mK}$ [120] like SiO_2 , SiN , or AlN with thermal conductivities of 1.3 [121], 9 [122], and $310 \frac{W}{mK}$ [123] respectively. hBN also offers the benefits of being highly anisotropic as a 2D material. hBN is less reactive than graphite, showing no change in air up to 1000 °C [4]. hBN is entirely synthetic in origin since the B-N bonding energy is so strong at -57.62 eV [124] and more spontaneously forms oxides. hBN demonstrates intriguing phenomena such as hyperbolic phonon-polaritons (HPhP) [125]. When hBN vibrates at certain frequencies, its surface charges invert causing a detectable ripple-like wave or a PhP. The hyperbolic nature of the PhPs stems from the asymptotic nature of the Reststrahlen bands. These are narrow ranges of energy in which light of certain wavelengths exhibits complete internal reflection in a material [126]. hBN does this for long infrared (8 and 12 μm wavelengths), a common wavelength in heat sensors [127]. HPhPs also allow light to be hyper-confined beyond optical limitations governed by diffraction [128].

Another feature that distinguishes hBN from other 2D materials is its Raman spectrum with a single characteristic peak, known as the E_{2G} peak, at 1367 cm^{-1} [129]. hBN lacks a D-peak regardless of strain due to the strength of its oscillation. A typical Raman spectrum for hBN using a 532 nm laser is presented in Figure 3.2.

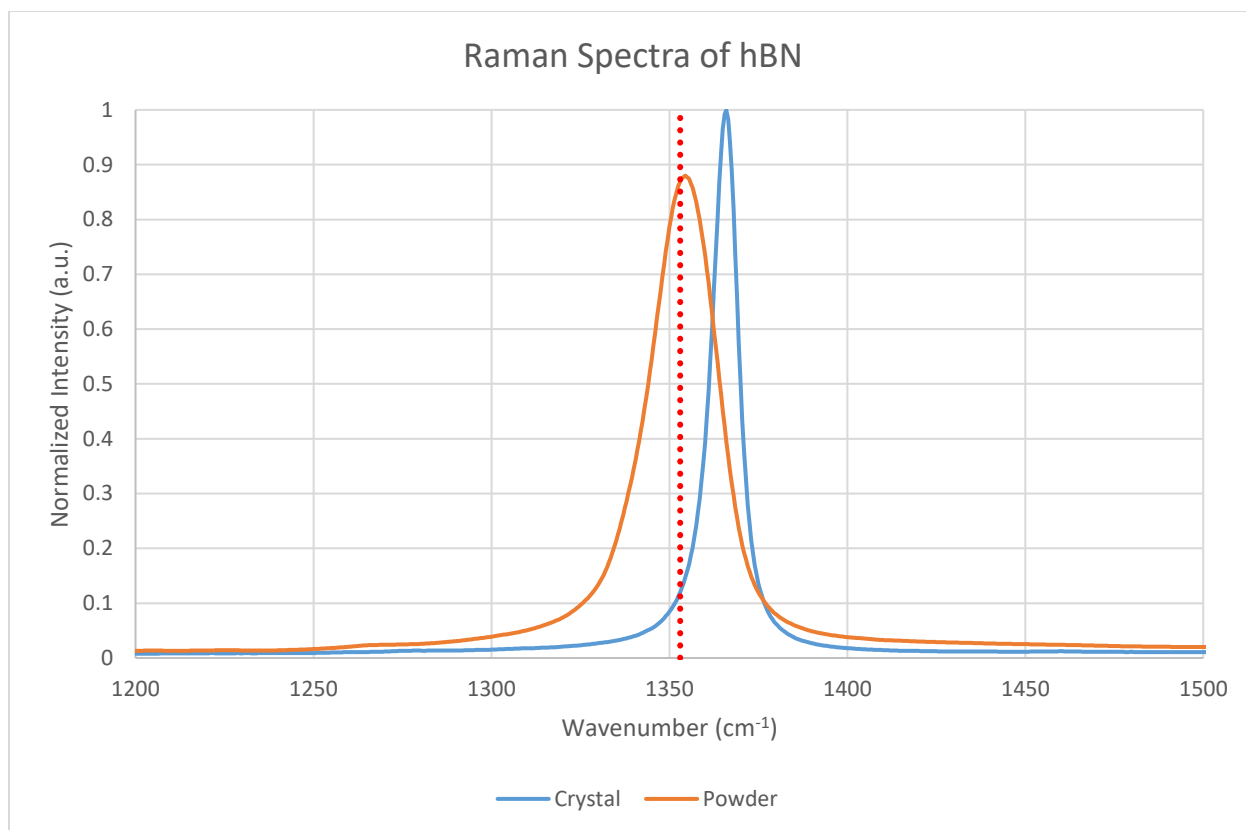


Figure 3.2. Raman spectra of hBN powder from commercial vendor (orange) and hBN crystal (blue). The E_{2G} peak is the red dashed line.

Since there is no D-peak for quantifying the presence of defects, the only metric is the FWHM of the E_{2G} peak. This is a key factor for qualitatively describing hBN like the G-peak of graphite. Another parallel, stemming from the homologous structure of hBN to graphite, is the XRD spectrum of hBN. In standard XRD, the 002 plane diffracts at 26° as shown in Figure 3.3.

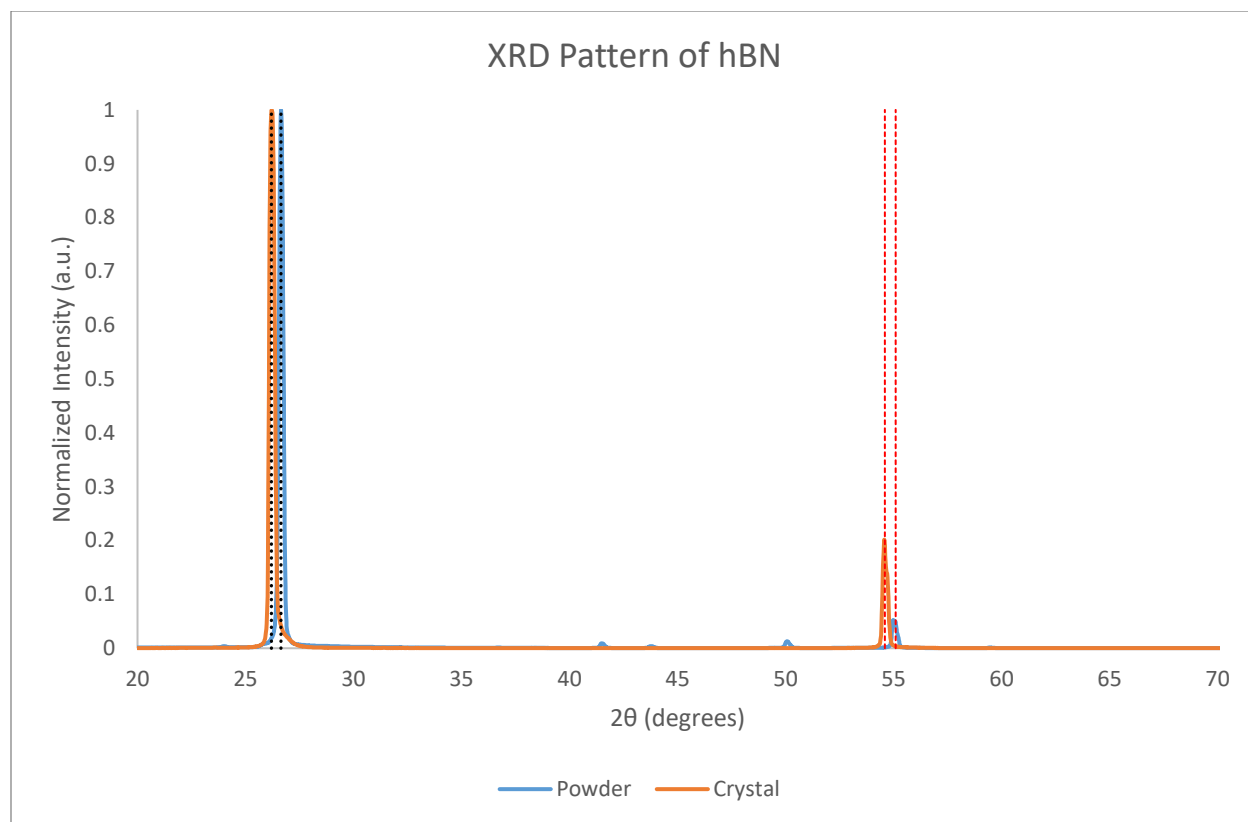


Figure 3.3. X-Ray diffraction pattern of hBN powder (blue) and crystal (orange) with (002) and (004) planes marked by dashed lines at 26.5 and 55 degrees.

Just like graphite, hBN defects can be monitored somewhat quantitatively by shifts or broadening of the 002 peak [130],[131]. Note the difference in intensity of the 004 peak between crystal and powder; this means that the crystal is more structured than the powder as expected. The position of the hBN crystal's 002 and 004 peaks being left of the powder indicates a more compact crystal structure (smaller d -spacing) which aligns with expectations.

Applications

hBN and graphite powder pressed ceramics have similar applications Both are used in lubricant additives [132] for their 2D structure and heat sinks [133] due to their high thermal conductivity. However, hBN is used in neutron detection [134] due to the large thermal neutron capture cross-section of boron-10. The large band gap is employed as a 2D dielectric in electronic devices [17]. It is often layered with graphene to make heterostructures like field effect transistors

(FETs) [135] and photodiodes (PDs) [136]. As mentioned previously, defects can play a critical role in each of these applications. For instance, perfectly crystalline hBN is an ideal heat dissipator and electrical insulator, making it great for assisting graphene in ballistic electron transport without building up too much heat [137]. Pristine thick hBN is also useful in nanophotonics [138],[139]: the nanoscale control of light. However, as defects become more abundant in the lattice, these properties diminish exponentially. Therefore, highly crystalline hBN is very desirable for a variety of applications.

Defects in hBN are similar to those found in graphite crystals. hBN crystals grown via APHT are shown in Figure 3.4 where large grains are separated by grain boundaries. Some grain boundaries follow crystallographic directions; however, others can additively disrupt the growth resulting in Figure 3.4c. At grain boundaries Stone-Wales (SW) structural defects are common. Examples of SW defects are shown below in Figure 3.4f (red and yellow polygons) alongside microscope images of hBN crystal grains.

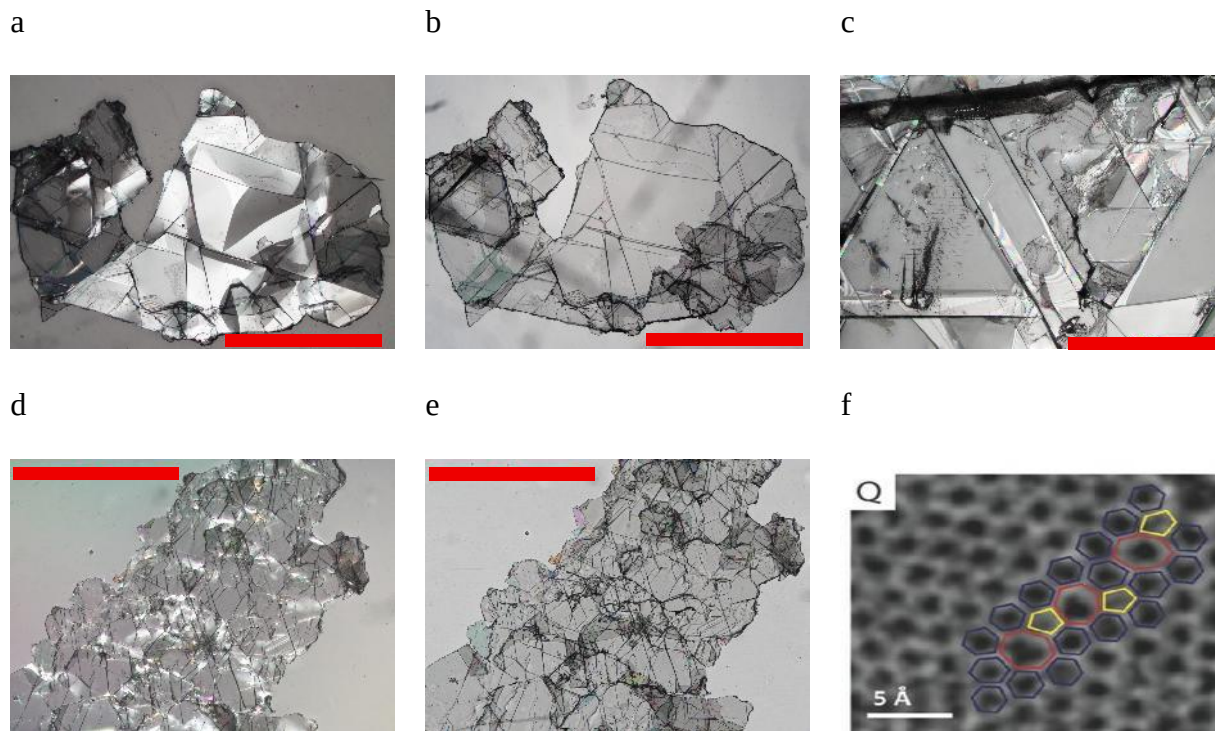


Figure 3.4. Microscopic image of a large grain hBN crystal flake grown via APHT in (a) reflection and (b) transmission at 25x magnification. (c) Macroscopic structural defects in hBN crystal. Microscope images of a small grain hBN crystal flake in (d) reflection and (e) transmission at 50x magnification. (f) HRTEM image of hBN defects, yellow and red polygons are Stone-Wales defects while the blue hexagons illustrate the induced strain on surrounding bonds [140]. Scale bars are (a, b) 2000 μm and (c, d, e) 1000 μm .

In addition to SW defects, hBN also exhibits defects between layers where atoms will connect out of plane [140] and contains grain boundaries in bulk crystalline form as shown in Fig. 3.4a. In parallel with all other 2D materials, these structural defects severely impact the performance of devices made with hBN due to phonon scattering causing energy loss.

Thick and large area hBN crystals have a variety of applications. Hence, if large defect-free single crystals can be produced, then they can host tens of thousands of devices on a single crystal (much like silicon). Therefore, the goal of this section is to demonstrate the growth of square millimeter area and dozens of micrometers thick hBN crystals with minimal defects.

Few-defect bulk single crystal hBN via APHT method

All the hBN crystals discussed in this chapter were grown similarly to the graphite discussed in the previous chapter; that is via the AHP method. This process differs from the graphite crystal growth in the source materials: carbon is substituted by boron; iron remains or is substituted with a mixture of 1:1 nickel and chromium by mass. This solvent was chosen after several others were tested by previous graduate students: B. Clubine [141], T. Hoffman [142], and E. Janzen [143]. The nickel serves as a boron solvent but lacks suitable nitrogen solubility. Chromium increases the dissolution of gaseous nitrogen into the metal solvent. Other solvents such as gallium are discussed later.

Experimental apparatus

The APHT method for hBN involves 5 different furnaces depending on the property desired. The first of them is the same furnace discussed in Chapter 2 henceforth called the Webb furnace (Figure 2.6). Second is a molybdenum heatshield vertical chamber furnace with tungsten heating elements. This furnace is named by the brand: Thermal Technologies furnace shown below in Figure 3.5. Lastly, three furnaces are horizontal alumina tube furnaces with MoSi₂ heating elements (Figure 3.6).



Figure 3.5 - Thermal Technologies Furnace equipped with tungsten heating elements and lined with stainless-steel heat shields

In all these furnaces, argon is used to purge out air to reduce the possibility of forming metal oxides as a common nucleation promoter. In two of the horizontal tube furnaces, H_2 is used in addition to Ar in a 1:19 volumetric ratio as “Forming Gas” (FG).

The three horizontal alumina tube furnaces are CM brand. All three have a 4x2 array of $MoSi_2$ resistive heating elements that heat the central 20” of the tube or reaction volume. The first is a 1.25” diameter CM horizontal alumina tube furnace (SCM) fitted with O-ring compression

threaded endcaps (see Figure 3.6). The temperature is controlled via Eurotherm 2116i/3116 controller and a Type-B (Pt/Rh-Pt) alumina insulated thermocouple. Gas is supplied from a manifold of 3 mass flow controllers for N₂, H₂, and Argon. The SCM was used for nearly all isotopically enriched hBN growths as well as the ¹³C doping experiments discussed in Chapter 5.



Figure 3.6. A closed horizontal alumina tube furnace with MoSi₂ resistive heating elements (not shown) used to grow hBN via APHT. Gas is supplied through the left side of the tube and flow is controlled using the valve on the right or a butterfly valve to regulate the pressure.

The second CM horizontal alumina tube furnace uses 2" diameter tubes and requires alumina insulation at both ends of the metal box or furnace body. This furnace is capable of being tilted while in operation up to 30° hence it is labeled the tilting CM furnace or TCM for short. This furnace is equipped with forming gas (5% H₂ in Ar) and N₂ mass flow controllers. It is primarily used in Chapter 5. A picture of the TCM is provided in Figure 3.7.



Figure 3.7 - Image of TCM apparatus. Gas is provided from the left and exhausted on the right.

The last CM horizontal alumina tube furnace uses 3.5" tubes and requires additional internal alumina insulation. The large diameter tubing bestows the name large CM furnace (LCM). This furnace was used to test solvents, owing to its high throughput, discussed later in this chapter. This furnace is adorned with chilled water lines around each end to prevent heating damage to the endcaps. An image of the LCM is shown in Figure 3.8.



Figure 3.8 - Image of LCM apparatus. Gas is supplied from the left and pumped out on the right. Pure hydrogen was available for this furnace as opposed to forming gas.

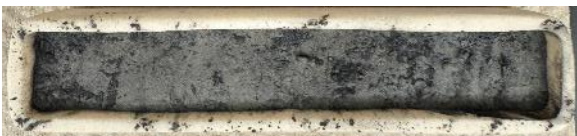
Experimental design

All procedures for APHT included purging with nitrogen to sweep out residual oxygen. Two purge cycles using a mixture of 4:1 N_2 and argon/FG to 500 torr preceded a backfill to 860 Torr of the desired gases (N_2 /FG/ H_2). Ingot formation, a key step for removing adsorbed air and

pre-existing oxides [144], is done under a backfill of 90% Ar and 10% H₂. Whereas crystal growth is performed under a backfill of 90% N₂ and 10% H₂/FG.

Crystal growth for hBN involves two main steps: ingot formation and crystal growth. Ingots are formed from powder, shots, or droplets of source materials mixed in a crucible of alumina or hot-pressed boron nitride (HPBN). A perforated alumina/HPBN lid is set atop the crucible to minimize metal deposition along the furnace tube caused by source evaporation. The original source materials have a high surface area to volume ratio making them prone to oxygen adsorption. Typically, the sources are coated with a thin surface oxide. The powder mixture is loaded into a furnace and melted at 1550 °C for both Ni-Cr or Fe-based mixtures. Once cooled to room temperature the ingot is unloaded and checked for oxidation or abnormalities. An example of the source material before and after of ingot formation is provided below in Figure 3.9.

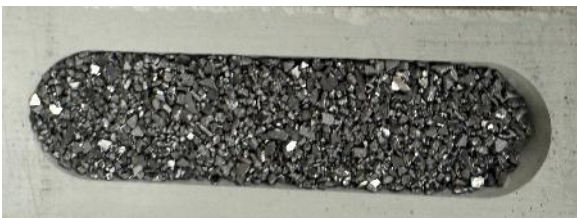
A



B



c



d



Figure 3.9 - Source materials (B, Ni, Cr) loaded into an alumina (a) crucible and (b) unloaded after ingot formation. Source material (Fe) loaded into a (c) HPBN crucible and (d) unloaded after ingot formation.

Temperature controls

The two processes used in the growth of hBN have different temperature-time profiles (Figure 3.10).

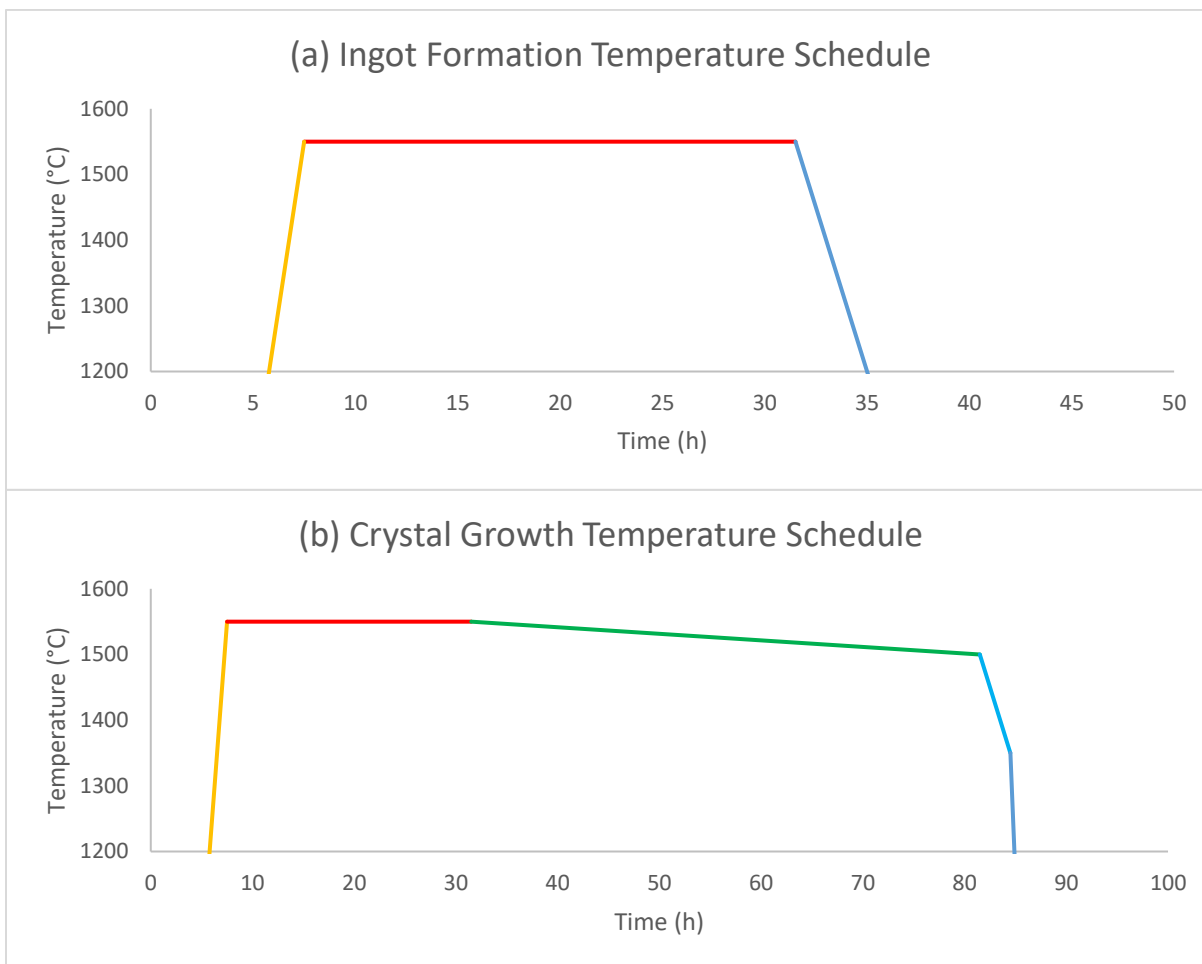


Figure 3.10. Ingot formation temperature schedule (top) and crystal growth temperature schedule (bottom). Orange segments are heat up, reds are dwell, green is slow-cool, and blues are quench steps. The y-axes are broken to highlight the differences between green and blue steps.

Each segment of these schedules is important to the successful growth of high-quality, large area, and thick hBN crystals. First, the furnace is heated at 200 °C/hr. (orange) to the dwell temperature. Second, during the dwell (red) the temperature is held at 1550 °C for 24 hours to fully homogenize the solution. Third, either the furnace is quenched (blue) at 100 °C/hr. to room temperature for ingot formation or slow cooled (green) for crystal growth at 1 °C/hr. Following

the slow cool, the crystal growth undergoes a fast cool (light blue) at 50°C/hr. before concluding with a quench (blue) at 100 °C/hr. to room temperature.

An ingot formed in an alumina crucible is depicted below in Figure 3.11a and the resulting boule with hBN on top after crystal growth is shown in Figure 3.11b.

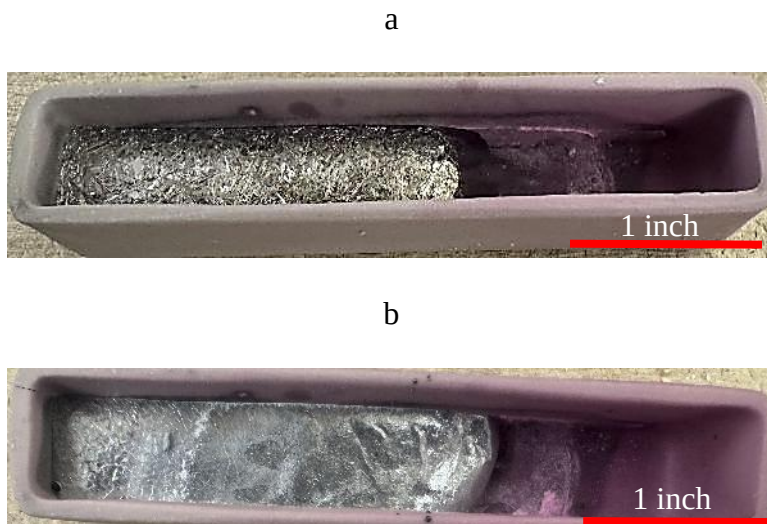
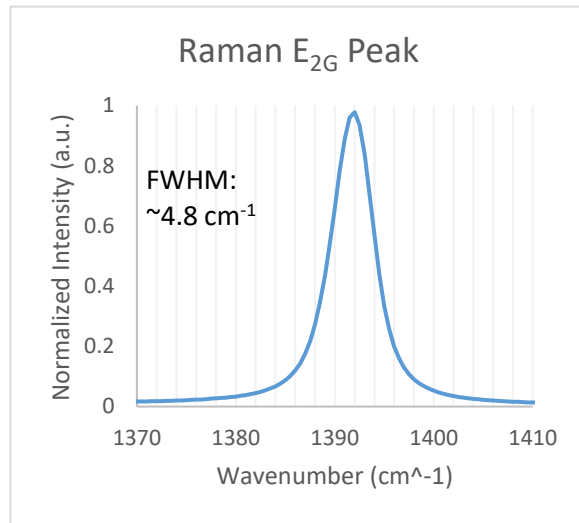


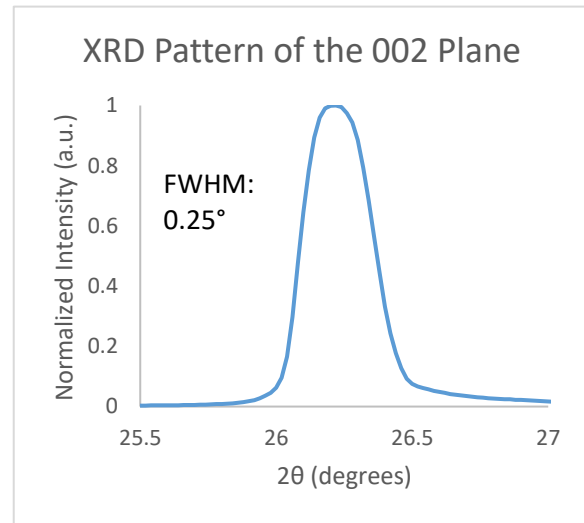
Figure 3.11. Macroscopic image of ingot after formation (top) and hBN atop metal boule after crystal growth (bottom).

In Fig. 3.11a, the metal shows a different topography prior to crystal growth. The ingot has a very rough texture and several reflective facets. In Fig. 3.11b, the surface becomes much flatter with a somewhat uniform topography and much finer texture. This indicated that the hBN laminates the ingot surface. Free standing hBN crystals are isolated using thermal release tape and rinsing with solvents, identical to [95]. Crystals using the previously discussed equipment vary in size, thickness, and defect density. The largest single grains of hBN produced in these investigations was 6 mm² shown in Figure 3.12 alongside the corresponding Raman spectra and XRD patterns.

a



b



c



d

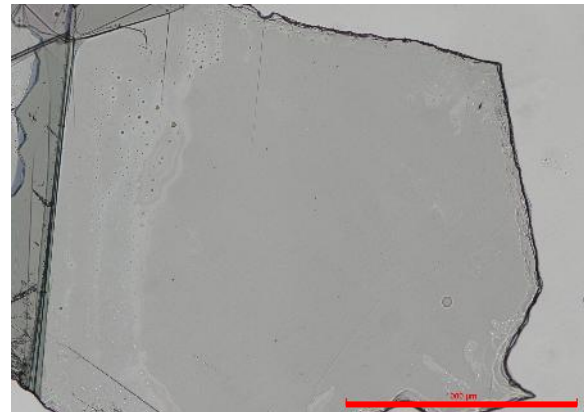


Figure 3.12 - (a) Raman spectra of largest single crystal grown and (b) XRD pattern of the same crystal. FWHM of the E_{2G} and 002 peaks are shown. Microscope images in (c) reflection and (d) transmission at 50x magnification. $h^{10}\text{BN}$ was grown with 3.72 wt. % ^{10}B (98% enriched), 48.14 wt. % Ni, and 48.14 wt. % Cr source materials. Scale bars are 1000 μm .

In Figure 3.12a and b, narrow peaks of $\text{FWHM} < 10 \text{ cm}^{-1}$ indicate the high quality of the $h^{10}\text{BN}$ crystal relative to other methods [145]. In addition to large area grains, thick crystals composed of perfectly aligned layers are highly desirable for optical confinement [125],[126]. While this is difficult to achieve due to nitrogen dissolution limitations once hBN covers the surface of the solution [143], the thickest hBN crystal grown reached more than 100 microns, as confirmed with microscopy.

An optical microscope first focuses on the top face of the crystal, and then the hBN/metal interface. From the change in the fine focus the thickness of the hBN crystal was approximated.

Following exfoliation of the crystals, the flake (cluster of single grains) of the same crystal was mounted perpendicular to the microscope stage so that the crystal thickness can be measured directly. These three images are presented below in Figure 3.13.

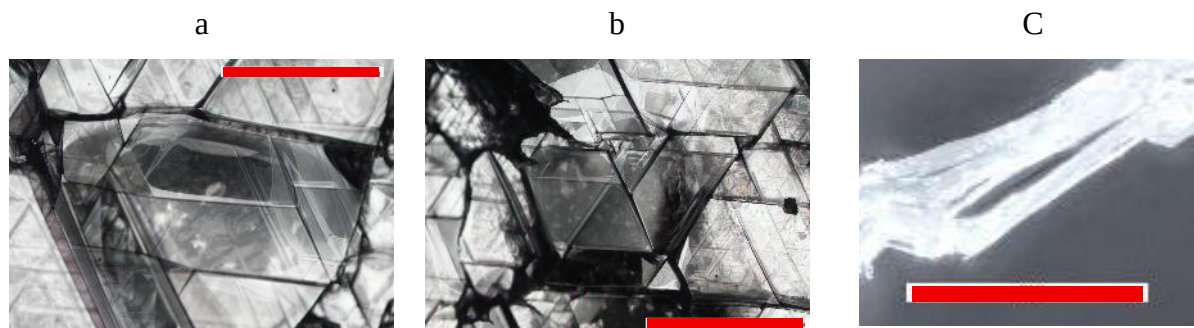


Figure 3.13 - (a) Focus on the top surface of hBN crystal, (b) focus on the metal surface in same location, and (c) thickness measurement of perpendicularly mounted flake. Scale bars for (a, b) are 1000 μm and (c) 200 μm . hBN was grown with 50 wt. % Ni, 50 wt. % Cr loaded into a 4" diameter HPBN crucible. Scale bars are (a, b) 1000 and (c) 200 μm .

The depth measured using the micron stage adjustment was 115 microns. The thickness measured with perpendicular mounting was 112 microns in good agreement. This is the thickest single hBN crystal ever produced experimentally. The Raman and XRD patterns for this experiment taken from another crystal that was ~80 microns thick are presented in Figure 3.14.

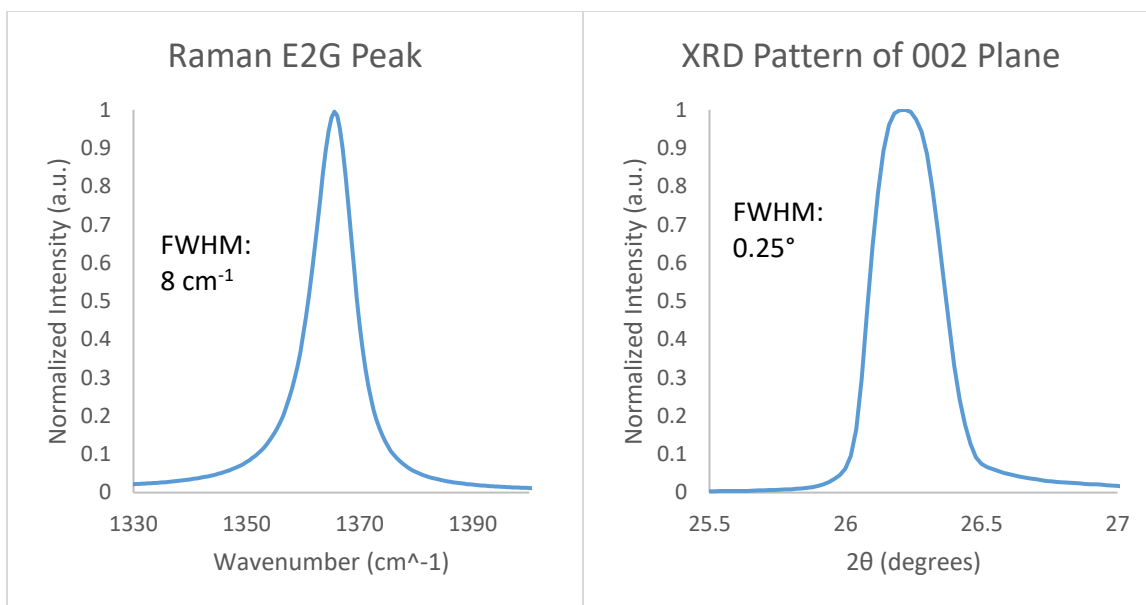


Figure 3.14 - Raman spectra and XRD pattern of thick hBN crystals. FWHM are displayed adjacent to the relevant peaks.

The rounding in the 002 plane occurs due to saturation of the detector. The raw intensities were near the maximum detection limit for the diffractometer used, another indication of degree of crystallinity. The asymmetry of the peak is likely due to the topography of the flakes analyzed.

Solvent exploration for APHT hBN growth

Despite the tremendous performance and reliability of the Ni-Cr alloy solvent, there are many improvements that could be made to APHT hBN growth. If the crystal production is dependent on the unoccupied solvent surface area, then this should be maximized. The metal solvent's high surface tension causes them to minimize their surface areas by forming into geometries with the lowest surface area to volume ratios: spheres. Since the metal is heavy it cannot form perfect spheres but attempts to do so by forming a rounded and thicker end. Examples of such behavior are shown in Figure 3.15.



Figure 3.15 - (a) Typical hBN ingot geometry and (b) side profile of the same hBN growth ingot as (a). Scale bars are 0.5 inches.

Additionally, metal condensing on the alumina lid covering the crucibles is also a problem because if these droplets gain sufficient mass, they fall and then etch the hBN crystal. Some examples are provided in Figure 3.16.

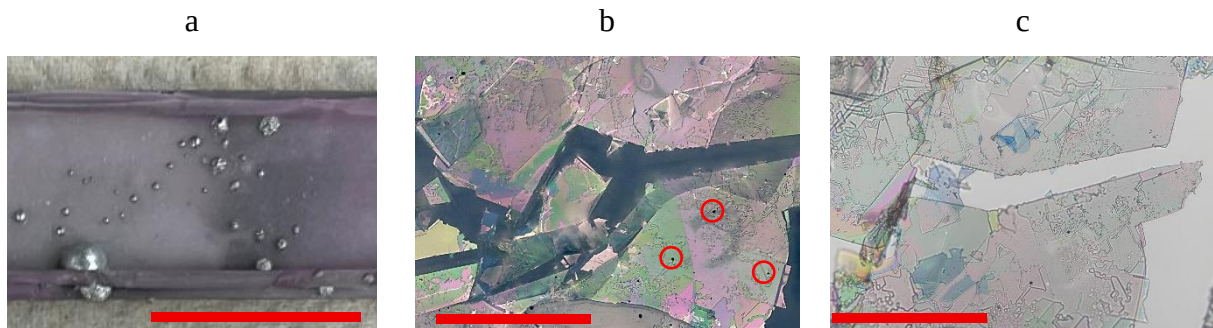


Figure 3.16 - (a) Metal droplets often formed on the crucible lid, (b) etch paths due to metal re-deposition on the hBN surface, and (c) metal etching tracks in transmission. Black dots (circled) are trapped between layers. Scale bars are (a) 1 inch and (b, c) 250 μm .

Similarly, these metal inclusions can induce macroscopic changes and strain. Some crystals with these obvious defects are shown in Figure 3.17.



Figure 3.17 - Macroscopic defects caused by metal re-deposition on the hBN crystal in (a) reflection and (b) transmission. Scale bar is (a) 1000 μm and (b) 500 μm .

Synchrotron measurements performed by the National Institute of Standards and Technology (NIST) confirmed that these inclusions are from the metal solvent with diffraction peaks corresponding to chromium and nickel.

Addition of gallium

To maximize the available surface area, other metals were introduced as surfactants to help the metal solvent occupy the full space of the crucibles (improved wetting). Gallium was tested due to its improved wetting of copper via reduction [146]. However, gallium is very easily oxidized when not in a reductive environment. This oxidation increases nucleation density leading to smaller crystals. Selected compositions, tabulated in Table 3.1, were tested involving Ga, Ni, and Cr over the course of 13 total compositions. They will be identified by their gallium content.

The mass of gallium was systematically evaluated depending on whether the flux “wet” the alumina crucible and the size/quality of the hBN crystals that grew. Crucible wetting is defined in this study as the percentage of the area of the crucible that the flux covered. While the goal is to maximize coverage, it must be balanced with the crystal size and quality. Since gallium is a liquid metal near room temperature, it will lower the surface tension of the molten metal and reduce spherical geometries governed by surface energy. Gallium spontaneously forms oxide films under ambient conditions [146] therefore it cannot be a dominant component of the flux or the oxide will induce excessive nucleation leading to smaller crystals along the same surface. Balancing these aspects made for an optimization experiment series around gallium and our common flux: Ni-Cr.

Table 3.1 – Compositions of metal flux with gallium (10g total mass)				
Ga (wt.%)	Ni (wt.%)	Cr (wt.%)	B (wt.%)	Results
5.31	45.35	45.33	4.01	Comparable crystal size/quality, but no metal wetting.
10.51	42.79	42.71	3.99	Comparable crystal size/quality, but no metal wetting (Figure 3.18a-d)
15.25	40.39	40.40	3.96	Smaller than average crystal sizes, but metal wetting evident (Figure 3.18e-h)
21.10	37.44	37.48	4.03	Metal wetting, but heavily oxidized forming powder sized crystals.

97.72	0	0	2.28	Heavily oxidized surface with powder sized crystals.
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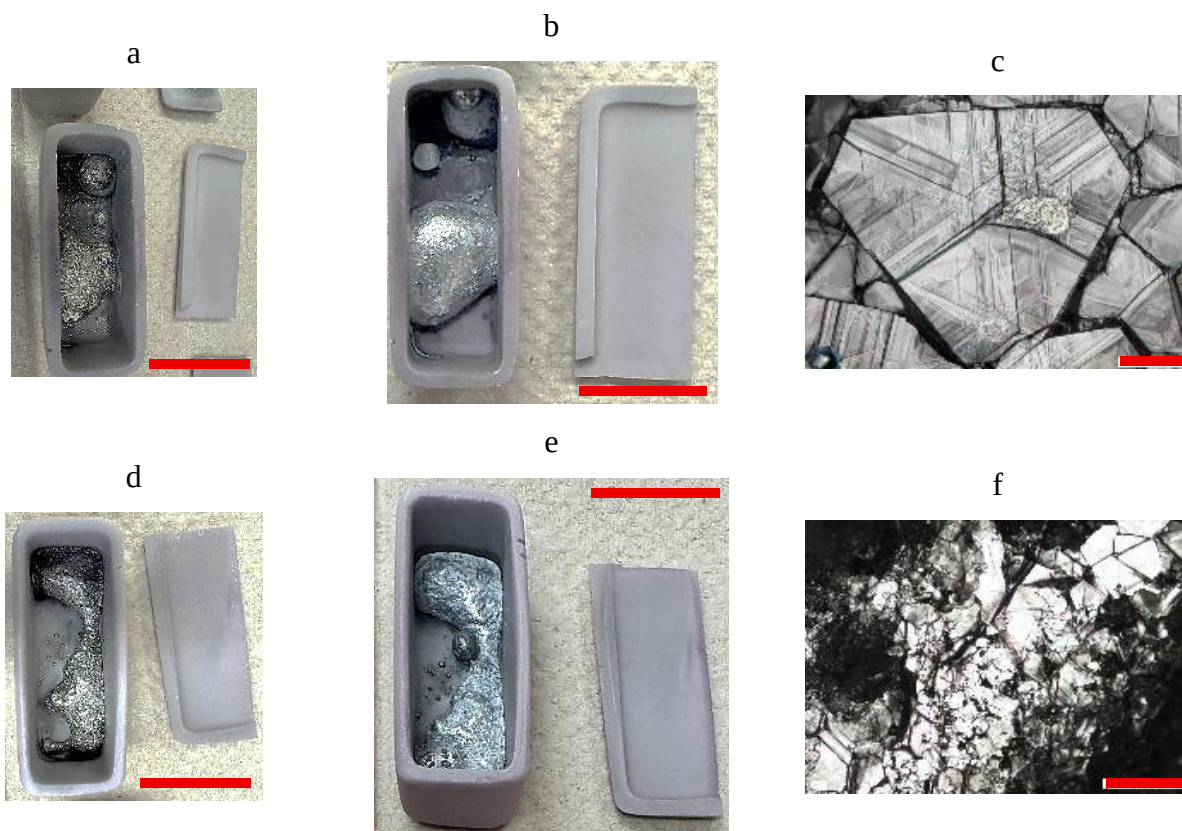


Figure 3.18 – key hBN experiments using Ga with flux. Ingot, crystal boule, and micrograph of crystals for (a-c) 10 wt. % Ga and (d-f) 15 wt. % Ga. Scale bars are (a, b, d, e) are 1 inch, (d) 200 and (f) 500 μm .

These crystals were grown using the same temperature schedules presented in Figure 3.10 using the Tilting CM furnace. Source materials were prepared in 1x2” alumina crucibles covered with slabs cut from other identical crucibles. Note that adding 10 wt. % Ga produced normal high-quality hBN crystals, but the metal solvent does not fully wet the crucible. With 15 wt. % Ga, wetting occurs and the solvent occupies more area. Another key observation is that the lids to the right of the ingot are deposit-free, implying that the vapor pressure significantly decreased. The downside is that the crystals are smaller, and gallium oxide (the white substance) forms. This gallium oxide prevents hBN nucleation via surface occupation and reduced nitrogen dissolution. Transition metals like chromium with higher gas solubilities tend to be nonselective of the gas

species if they have multiple oxidation and nitridation states. The Cr_xO_y then oxidizes the gallium further inhibiting hBN growth.

Optimization of APHT hBN single crystal area

Zr Getter

A typical growth experiment will take at least 6 days. To expedite the process, crystal growth was sought without ingot formation. Metal oxidation is the main competitor for hBN growth because boron will reduce metal oxides. Oxygen comes from metal powder surface oxidation or trapped air within the powder free space. Metal oxides are extremely stable in the absence of reductive reactants like H_2 . To minimize the amount of oxygen in addition to the vacuum and purge cycles, Zr, an oxygen getter, was used. Zr pellets were loaded closer to the furnace inlet than the hBN load. Initially only few pellets were used as a sacrificial getter (Figure 3.19).

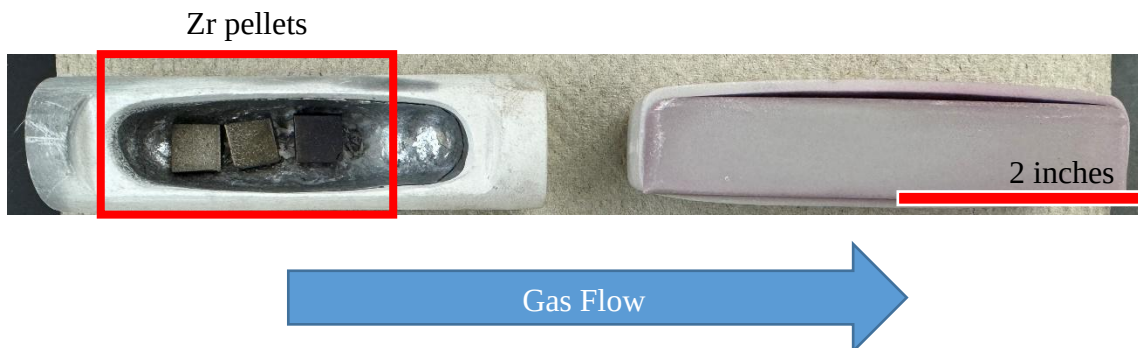


Figure 3.19. 3 Zr Pellets placed in a HPBN crucible upstream of hBN sample

Zr forms ZrH at temperatures of 100°C but decomposes above 600°C . Therefore, argon was flown until 800°C . H_2 was then flown into the furnace as well. After 15 hours in the dwell phase of crystal growth, nitrogen flowed in place of argon. After the slow cool around 1500°C , hydrogen was turned off to prevent the reduction of the Zr pellets.

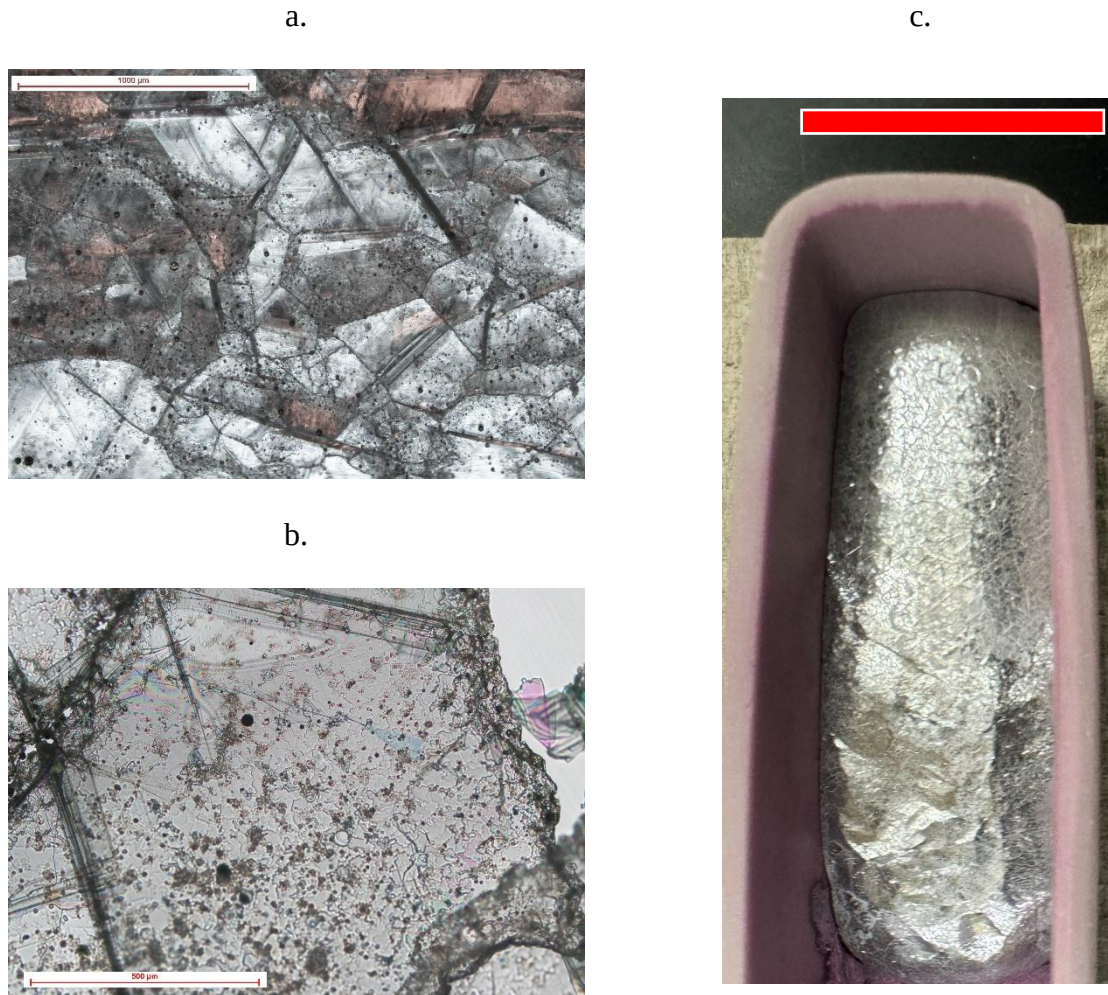


Figure 3.20. (a) Micrograph of crystals on ingot surface in reflection, (b) micrograph of exfoliated hBN crystal from ingot in transmission, (c) macro-photo of ingot with hBN crystals on surface. Scales are 1000 μm , 500 μm , and 1 inch, respectively.

After 3 of these similar experiments by varying the amount of Zr, the quality of the crystals did not improve. Therefore, it was concluded that there was no benefit for growing hBN by including zirconium in the furnace tube.

Boron gradients

Supersaturation is problematic in excess. At high concentrations of boron in the flux, hBN may nucleate at a higher rate than desired. Hence, concentration gradients were explored as a

means of controlling nucleation rates while keeping all other parameters of crystal growth constant. To that end, nine experiments were performed each varying the way in which boron was introduced to the final solvent.

First, four 25g ingots were made with different concentrations of boron in Ni-Cr: two low (0.25 and 1 wt.% B) and two higher concentrations (3.75 and 3 wt.% B). These ingots were placed abutted in pairs to sum to 4 wt.% B prior to crystal growth with the expectation that the high boron concentration would cause rapid diffusion to the less concentrated flux. This diffusion would create a gradient in crystal sizes as a result. Contradictory to expectations, this did not decrease nucleation on the dilute end. It did nucleate much more heavily on the concentrated end, however. An illustration of the hypothesis is presented in Figure 3.21.

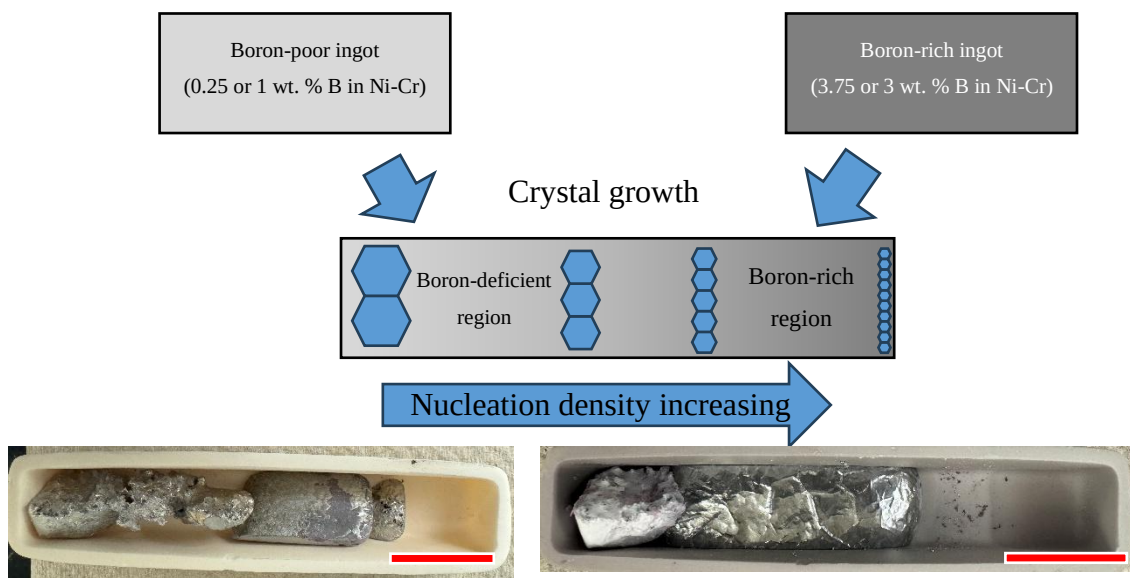


Figure 3.21 - Illustration of theory behind boron gradient experiment using pure boron sources. Two 25g ingots with 0.25 and 3.75 wt.% B in Ni-Cr are prepared with ingot formation in separate crucibles. They are then melted next to each other to induce a boron gradient for crystal growth. Below is the ingot formation step where the ingots are placed adjacent (*right*) and after running crystal growth (*left*). Scale bars are 1 inch.

In the second attempt to observe this mechanism, hBN powder was placed at the end of a crucible just beyond the solidified ingot. The intention was for slow dissolution of the powder and reprecipitating hBN as the concentration reached saturation. This experiment did not result in better crystals. This would be repeated later with a solid piece of HPBN to prevent separation of the solvent from the boron source.

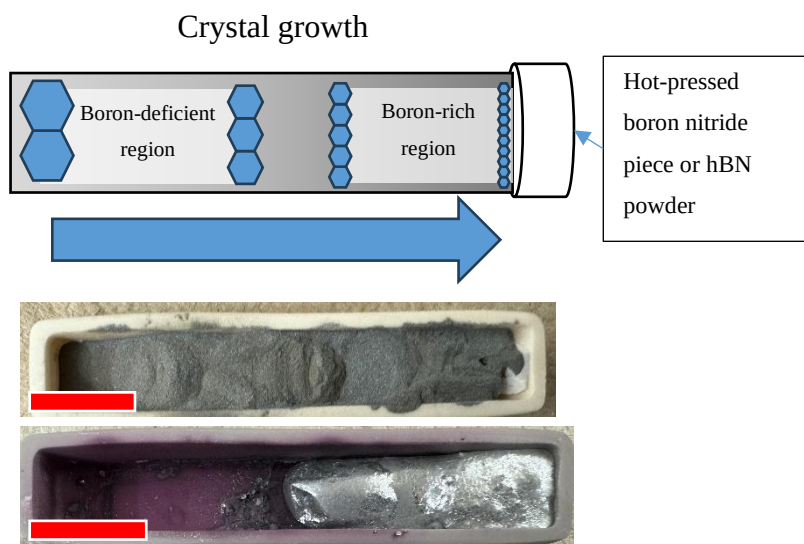


Figure 3.22 - Second boron-gradient experiment using HPBN solid as boron source for hBN growth. Ni-Cr powder mixture placed to the left of an HPBN piece. Below is the resulting crystal growth. Scale bars are 1-inch.

It was speculated that the buoyancy of the powder and particle size was limiting dissolution, therefore a hot-pressed piece of boron nitride and wedged it into the crucible so that it did not float atop the metal. This experiment resulted in larger crystals than the powder, but substantially smaller than normal growths. This would be repeated later for a similar result.

It was then hypothesized that maybe an isotopic gradient would work. Two ingots were prepared with Ni-Cr and $^{10}\text{B}/^{11}\text{B}$. These two were placed abutted in a larger crucible and subjected to crystal growth. The resulting ingot was a homogeneous mixture of both ^{10}B and ^{11}B determined

with Raman microscopy. In conclusion, the boron isotopes distributed randomly once the ingots melted thereby leading to hBN growth enriched equally in ^{10}B and ^{11}B .

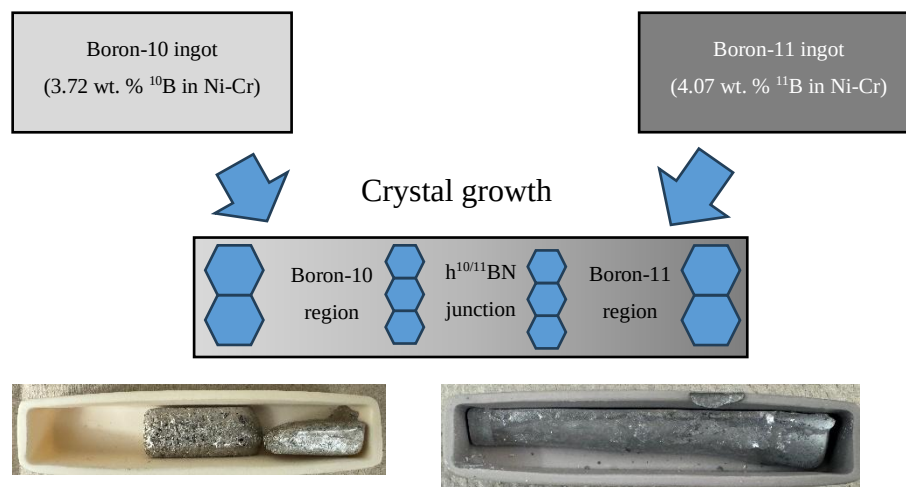


Figure 3.23 - Isotopic boron gradient growth experiment theory illustration. Image of ^{10}B (left) and ^{11}B (right) placed into alumina crucible. Resulting ingot with isotopic mixing as opposed to expected separation.

Isotopically enriched hBN and growth investigation

A key disadvantage of APHT as mentioned in Chapter 2 is the obscurity of the growth process. Isotopic enrichment was used to uncover nearly exactly what temperature hBN crystals began to form on the surface of the melt [95]. Isotopic enrichment of hBN crystals in boron-10 or -11 and nitrogen-14 or -15 can be achieved as shown by E. Janzen [147]. To do this, a series of ingots formed of ^{10}B enriched Ni-Cr were loaded for static $^{15}\text{N}_2$ growth where the SCM furnace chamber was backfilled to 850 torr (90% $^{15}\text{N}_2$, 10% H_2) and closed off from gas inlet and outlet. After reaching a predetermined temperature in the slow cool (green segment of Figure 3.10b) the system was opened and $^{14}\text{N}_2$ and H_2 were flowed continuously for the rest of the experiment. The intended mechanism is shown in Figure 3.24.

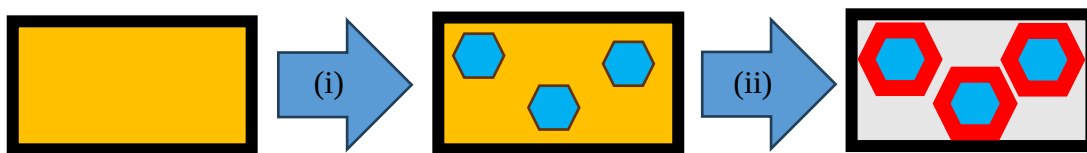


Figure 3.24 - Drawing of nitrogen switch experiments. Molten supersaturated flux of ^{10}B and ^{15}N (yellow background) is (i) cooled to precipitate $\text{h}^{10}\text{B}^{15}\text{N}$ crystals (blue hexagons) then while cooling and precipitating (ii) ^{14}N is introduced, creating distinct or transient regions of h^{10}BN (red outlines).

This distinguishable change in nitrogen isotope (from $\text{h}^{10}\text{B}^{15}\text{N}$ to $\text{h}^{10}\text{B}^{14}\text{N}$) permits the observation of when nucleation and growth occur. Understanding when the crystals nucleate will allow control of nucleation in future work. Understanding when growth occurs gives a temperature range over which other parameters like gas composition or time can be optimized to achieve continuous growth. Several temperatures from 1550 °C to 1500 °C were tested. Mixed nitrogen isotopes formed at 1520 °C in only one spot. At 1510 °C, more regions of isotopic mixtures formed. At 1500 °C, the crystals were only $\text{h}^{10}\text{B}^{15}\text{N}$. The final experiment from this set entailed a switch at 1508 °C. The results showed well defined junctions of $\text{h}^{10}\text{B}^{15}\text{N}$ and $\text{h}^{10}\text{B}^{14}\text{N}$ via mapping the area with Raman spectroscopy performed by Horiba, Ltd. shown below in Figure 3.25.

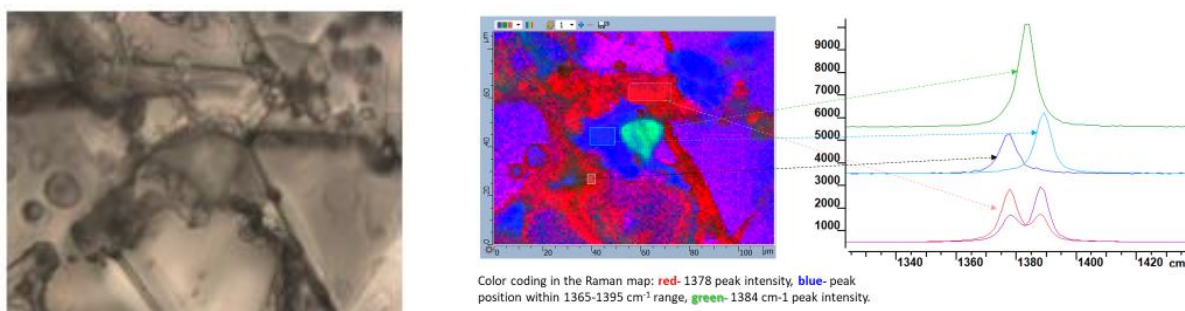


Figure 3.25 - Raman mapping of nitrogen switch experiment at 1508 °C with overlaid optical images at varying opacity. The red regions are $\text{h}^{10}\text{B}^{15}\text{N}$ and the blue regions are $\text{h}^{10}\text{B}^{14}\text{N}$. The green region in the center is a mix of the two nitrogen isotopes. Regional spectra are shown for each colored box in the Raman map. Green indicates homogeneous mixing of $^{14/15}\text{N}$ while the rest show separation of these isotopes.

One of the questions these experiments struggled to answer is whether there are isotope junctions in the c -direction (i.e., $\text{h}^{10}\text{B}^{14}\text{N}$ layer on top of $\text{h}^{10}\text{B}^{15}\text{N}$). Raman struggles to be sensitive beyond

confocal limits, but electron microscopy methods such as electron energy loss spectroscopy (EELS) are becoming more sensitive to distinguish isotopes [148]. This technique can be used to answer those questions with cross-sectional transmission electron microscopy (TEM). This kind of unnatural distribution of isotopes for both boron and nitrogen causes significant strain broadening the E_{2G} peak or presenting two separate peaks like those in Figure 3.25, indicative of inefficient mixing [149]. Fine tuning nucleation and axial growth will lead to the growth of square centimeter scale millimeter-thick single crystals of hBN and its isotopic variants.

Defect-controlled bulk single crystal hBN

As mentioned in Chapter 2, some defects create useful properties in hBN. In the case of hBN, two of these defects are the carbon substitution [136],[150]–[227] and the negatively charged boron vacancy (V_B^-) [174],[212],[228]–[324]. The former has been extensively investigated via first principles [150],[152],[169],[189],[191],[201],[202] and studied experimentally for its potential in optoelectronics as a single photon source. The V_B^- defect is of interest for quantum sensing [278],[281]. In the following chapter, V_B^- defects are controllably created experimentally and compared based on brightness and spectral signatures similar to Wu *et al* [311] where optical and mechanical properties were studied as functions of irradiation treatment.

Conclusion and Contribution

In conclusion, hBN crystal flakes of groundbreaking thickness and size have been grown. Extremely thick >80 microns hBN was grown using 50 wt% Ni and 50 wt% Cr 200 gram alloy melted in HPBN and dwelling at 1550°C for 3 days and slow cooling to 1500°C at 1°C/hour in the Thermal Technologies furnace without hydrogen. Additionally, these flakes were composed of large area single crystal grains of >3 mm² in size. The longer dwell with high vacuum (~10 μ Torr) allowed minimal crystal nucleation and maximized growth. The HPBN ceramics contain boron oxide or calcium carbonate as typical binders. These interfere much less than the impurities of alumina such as silicon. Silicon was briefly investigated as a method of controlling hBN nucleation

in iron, however, it had the opposite effect even in as low concentrations as 0.03 wt%. Hence, while HPBN does not permit isotopic control, it does facilitate larger crystal flakes.

Large area single crystals of $h^{10}\text{BN}$ were synthesized using the Small CM furnace initially with standard ingot formation under Ar/H_2 in an alumina crucible. The initial crystal growth was performed with 60 sccm of H_2 rather than the standard 20 sccm. This resulted in relatively lower quality crystals with several visible defects. However, upon reusing this same boule under the standard growth controls and gas (20 sccm H_2 , 250 sccm N_2) the resulting crystals were an order of magnitude larger than typical crystals. This is likely due to the oxide reduction from the tripled H_2 on the original growth cycle. The thorough reduction of oxides in the initial growth followed by the barrier of the new (albeit poor quality) $h^{10}\text{BN}$ coated surface prevent ambient oxidation from moisture leading to a lower concentration of oxygen in the boule for the next growth.

Chapter 4 - Optimized boron vacancy creation in hBN

In this chapter, the production of negatively charged boron vacancies via neutron irradiation fluence is optimized. The results of most irradiation treatments are characterized by Raman spectroscopy or photoluminescence.

Background

Boron vacancies can be charge neutral (V_B^0) or have electrons trapped within the vacancy (V_B^-) and be negatively charged, as depicted in Figure 4.1. The latter is of more interest due to its magnetic sensitivity. These vacancies have a spectroscopic signature in Raman, photoluminescence, and cathodoluminescence [325]–[327] that can be used to identify and quantify them [233]. The most desirable of these defects is that which contains 2 unpaired electrons [328] as shown in Figure 4.1b.

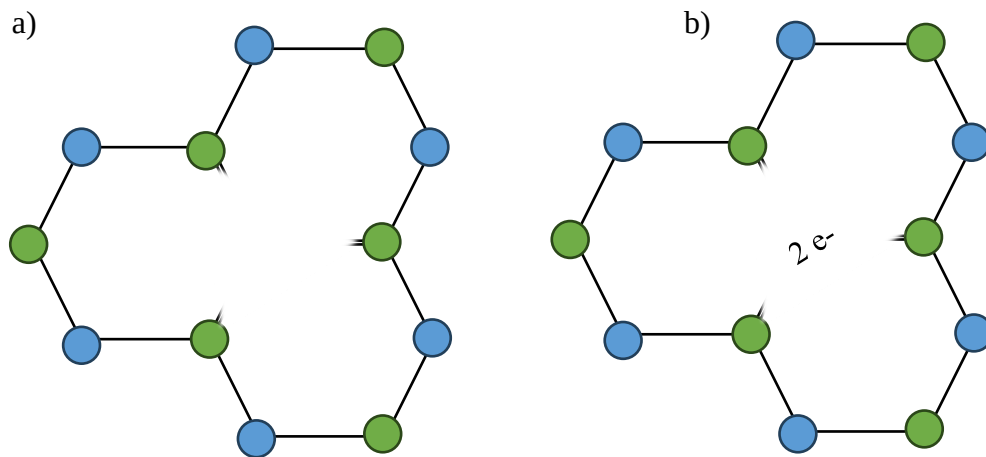


Figure 4.1 - Illustration of (a) neutral boron vacancy and (b) negative boron vacancy. Blue and green circles represent boron and nitrogen atoms, respectively.

V_B^- defects can be created via ion implantation or neutron irradiation as tabulated by Carbone et al [233](Table III). Their resulting properties vary depending on the method used.

In ion implantation, ionized elements are propelled into materials at high energies ~80-200 keV [329]. Depending on the implant species and target composition, the depth of penetration

varies though typically it is limited to several hundred nanometers. Some ions get trapped in the lattice, some pass through, and some collide with lattice constituents (B, N). For ion implantation, collisions are indiscriminate and will disrupt the lattice significantly. When boron is displaced, either neutral or negative boron vacancies are formed. The advantages of ion implantation are the localized targeting, fine fluence control, and ease of use relative to neutron irradiation. The cons of ion implantation are that it is indiscriminate and has low stopping power.

In comparison, neutron irradiation is highly selective to boron-10 due to its high cross-capture area of 3840 barns [330]. Neutrons are also capable of passing through the material with ease marginalizing depth as a variable [331]. The entire crystal is subjected to irradiation making localized dosing impossible. Fluence in most irradiation reactions is calculated based on probabilities, power, and time with no instantaneous cut-off. Additionally, while neutron irradiation is highly selective, the daughter products are not. An energized lithium and helium produced from the transmutation of boron-10 are dispersed into the lattice displacing more atoms, causing dislocations and further disrupting the lattice. The most troublesome aspect with neutron irradiation is accessibility to a neutron reactor. Neither neutron irradiation or ion implantation have any control of the resulting charge state of the boron vacancies; however, the starting material can be engineered to optimize the resulting properties such as isotopic enrichment to reduce hyperfine interactions [238].

Hyperfine interactions are the result of non-zero nuclear spins of neighboring atoms [332]. The nuclear spin is governed by the number of neutrons/protons in an atom's nucleus [333],[334], thus the lower the surrounding nuclear spins, the fewer the interactions with V_B^- . Reducing hyperfine interactions is important for increasing optically detected magnetic resonance (ODMR) signal lifetimes. ODMR spectra shows electronic transitions between V_B^- spin states and hyperfine interactions create convolutions thus limiting sensitivity. ODMR is a key measurement of the V_B^- signature centered at 3.4 GHz under 532 nm excitation [229].

V_B^- optical signatures can be used to roughly gauge their concentration [233]. The V_B^- electrons exhibit a magnetically sensitive spin that is traceable by ODMR. These spin transitions are a powerful sensor for magnetic fields with sensitivities of up to $\sim 45 \frac{\mu T}{\sqrt{Hz}}$ [335]. Such sensitivity competes with the current standard, the diamond nitrogen-vacancy center (VN^-). Another benefit of V_B^- in hBN is its greater stability than the VN^- center in diamond [244],[302],[313] and higher

spatial resolution due to inverse cube relationship (Equation 4.1) regarding magnetic dipoles [336],[337].

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{1}{r^3} [3(\mathbf{m} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{m}] \quad 4.1$$

Since hBN is a 2D material it can exist in a single layer allowing direct contact of the V_B^- to the measured surface maximizing the measurement accuracy and allowing spatial resolution. Though this defect has unique properties of its own, it comes at a cost. As discussed in Chapter 3, defects degrade the pristine material's properties. For instance, thermal conductivity of hBN exponentially decays with V_B density, as well as optical emission strength and crystallinity. Defects create asymmetry and lead to vibrational losses due to phonon dispersion [338]. The optical emission strength decreases because the defect concentration overwhelms the lattice significantly detracting from the intrinsic photon emission due to increased non-radiative transfer [339].

Applications

The V_B^- can be used for magnetometry [340] or the detection of magnetic fields [278] with high precision. Magnetometry is highly useful for a plethora of applications [341]. Another possible application of the V_B^- is to serve as a precursor for introducing other defects. The process of neutron irradiation is not gentle and creates clusters of defects. While these are unintentional deformities, they can serve as a space for new elements that could be useful defects proposed by theory [342].

Investigation of V_B^- densities and effects on structural properties of $h^{10}B^{15}N$

See publication: “Structural characterization of neutron irradiated hexagonal boron-10 nitrogen-15 single crystals” [343].

To optimize the V_B^- for ODMR magnetometry and maximizing coherence times samples of $h^{10}B^{15}N$ were irradiated by thermal neutrons. Each sample received a different thermal neutron fluence to vary the V_B^- defect density. Thermal neutrons (energy is less than 0.5 eV) cause the boron-10 to undergo transmutation to lithium-7. Reports in the literature on methods to generate boron vacancies are presented below in **Error! Reference source not found..**

Table 4.1 - Power, irradiation time, and thermal neutron fluence from literature for comparison			
Power (kW)	Time (hours)	Fluence ($\times 10^{15}$ neutrons/cm²)	From Reference
100	0.75	3.6	[343]
150	1	7.2	This work
300	0.75	11	This work
300	1	14	[343]
300	1.5	22	This work
	2.5	26	[324],[344]
		26	[345]
300	2	29	This work
300	2.5	36	This work
300	3	43	This work
300	4	58	This work
300	5	72	This work
300	10	140	[343]
		270	[345]
300	60	840	[343]
	15	2300	[255]

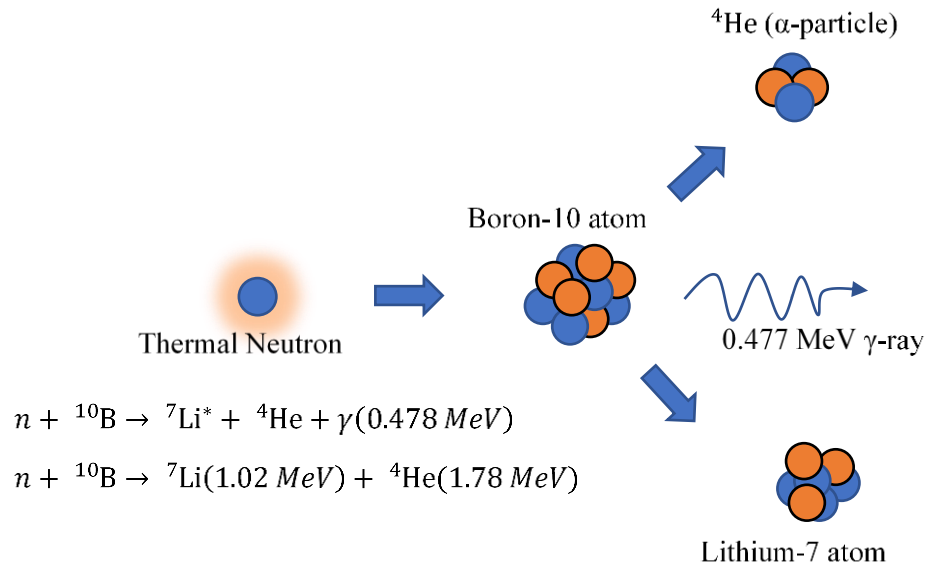


Figure 4.2 – Thermal neutron irradiation induced transmutation of ${}^{10}\text{B}$ into ${}^7\text{Li} + {}^4\text{He}$
 With neutron irradiation for little as 1 hour, the color of the crystals changed. This change in color increases with fluence as shown in Figure 4.3.

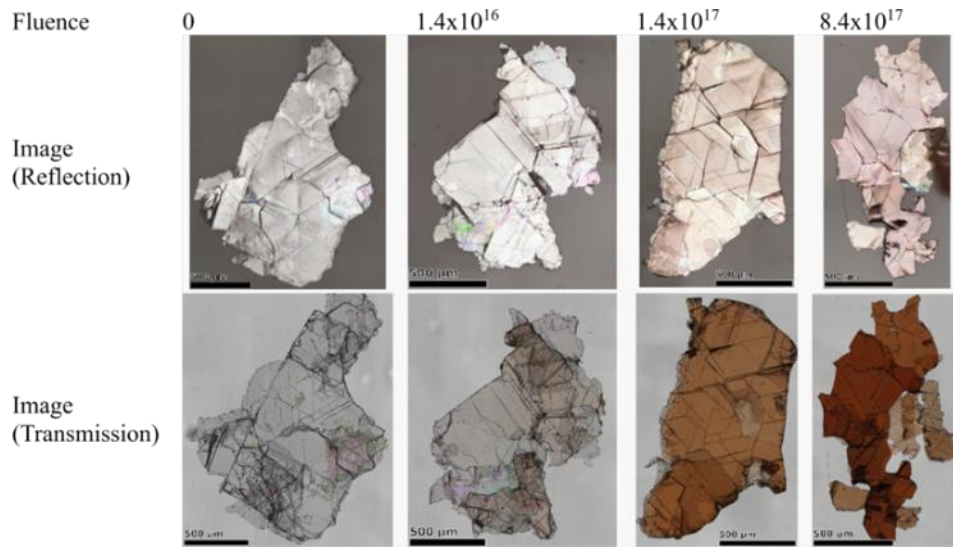


Figure 4.3 - Optical microscope images at 50x magnification. Increasing color saturation is indicative of V_B^- density.

It is important to retain the hBN crystal quality as much as possible to maximize coherence time [346] and photoluminescence (PL) intensity [347]. To measure the quality as a function of neutron

fluence, XRD, Raman, Brillouin spectroscopy, selected area electron diffraction (SAED) via TEM, and secondary ion mass spectroscopy (SIMS) were employed. XRD and Raman spectroscopy reveal crystal lattice parameter changes like interlayer spacing and vibrational modes influenced by defects, respectively. Lattice expansion previously reported is correlated to interlayer swelling due to helium (a byproduct of transmutation) accumulation [348]. High resolution XRD provided by Oak Ridge National Laboratory Center for Nanophase Materials Sciences (CNMS) revealed exactly that in fluence (Figure 4.4).

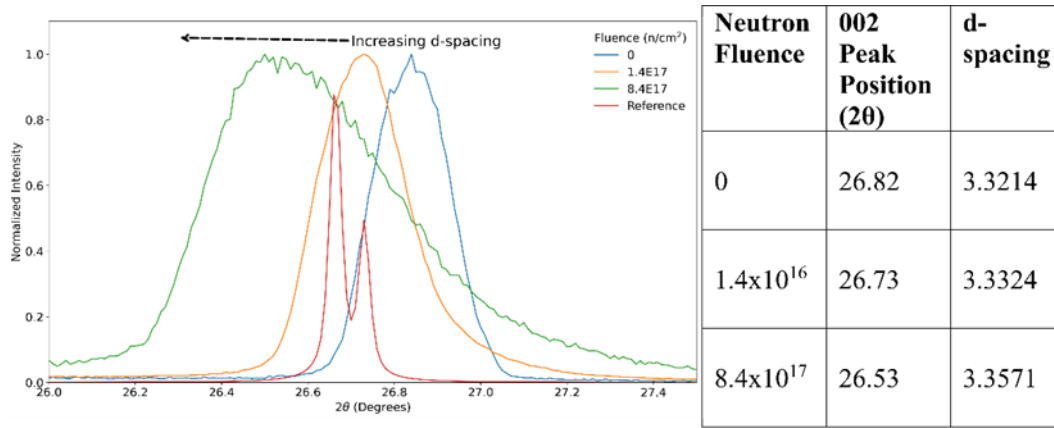


Figure 4.4 - XRD Pattern of irradiated $h^{10}B^{15}N$ crystals. Reference data from ICDD JCPDS hBN_00-045-0894 [349].

Increasing d-spacing (i.e., the interlayer distance) is due to helium accumulation. In Figure 4.4, an increase of 0.03 nm is induced from helium swelling after $8.4 \times 10^{17} \text{ n/cm}^2$; minor changes for lesser fluences are apparent in the shift from the blue curve to the orange curve. The leftward shift in the 002 peak XRD pattern is clear as fluence increases, indicating minor expansion. In addition, the defect vibrations create a new peak in the Raman spectra of hBN at 1320 cm^{-1} which increases in intensity with fluence. The peak width of the characteristic E_{2G} peak of hBN also increases with fluence shown in Figure 4.5.

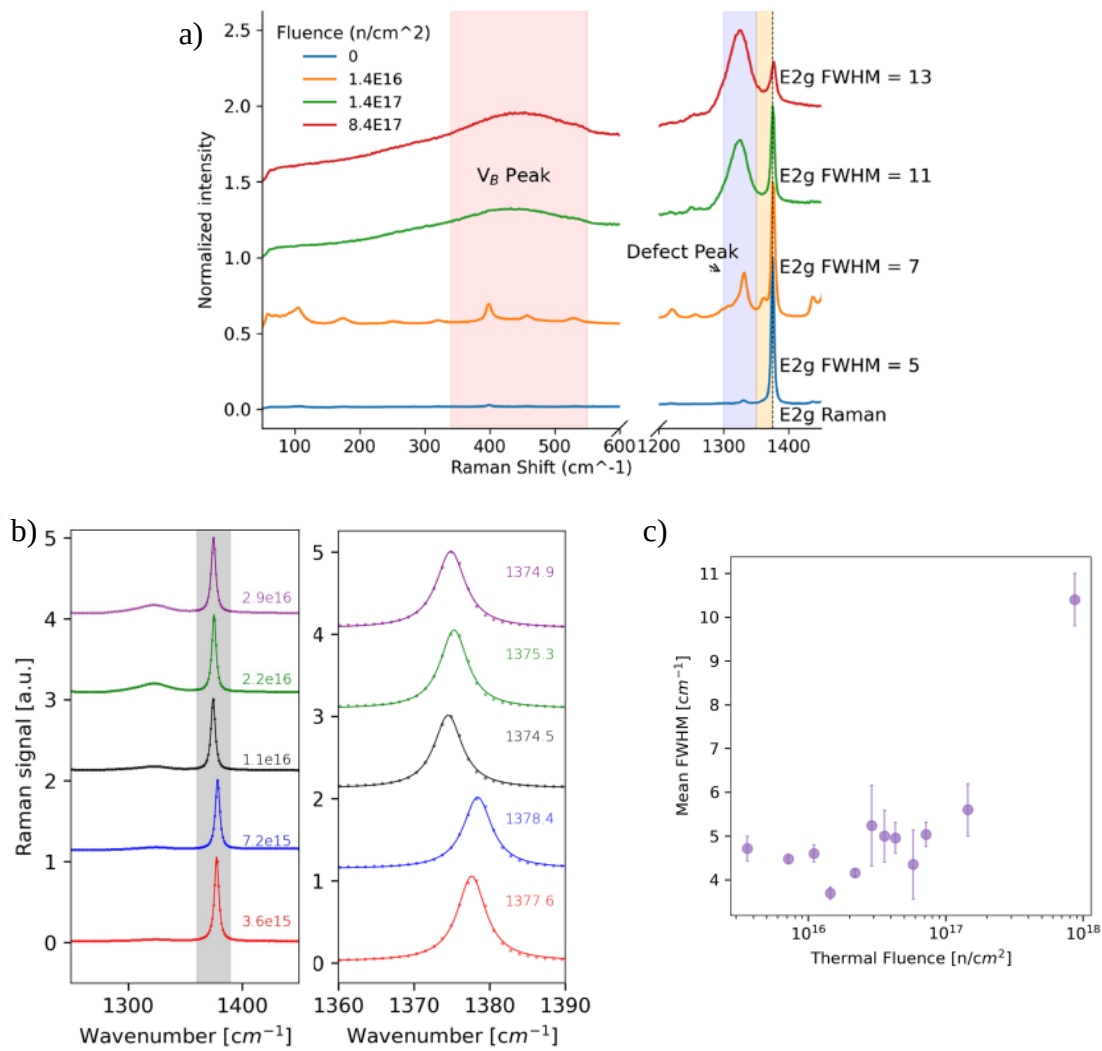


Figure 4.5 - Raman spectra of thermal neutron irradiated $h^{10}B^{15}N$ crystals (a, b) for different fluences indicated either in the legend (a) or on the curve (b). (b) E_{2G} position indicated in the top right of magnified plots. (c) FWHM of E_{2G} plotted as function of fluence. In (a) the red, blue, and yellow shaded regions correspond to Raman signatures that increase with fluence. While the red and blue are correlated with boron vacancies and other defects, respectively, the yellow region defect is unclear but convolutes with the E_{2G} and defect peaks at the highest fluence.

Brillion spectroscopy reveals the mechanical properties (elastic coefficients) along each lattice direction and interlayer shearing resistance [350]. The elastic coefficients decreased as the fluence increased (Figure 4.6).

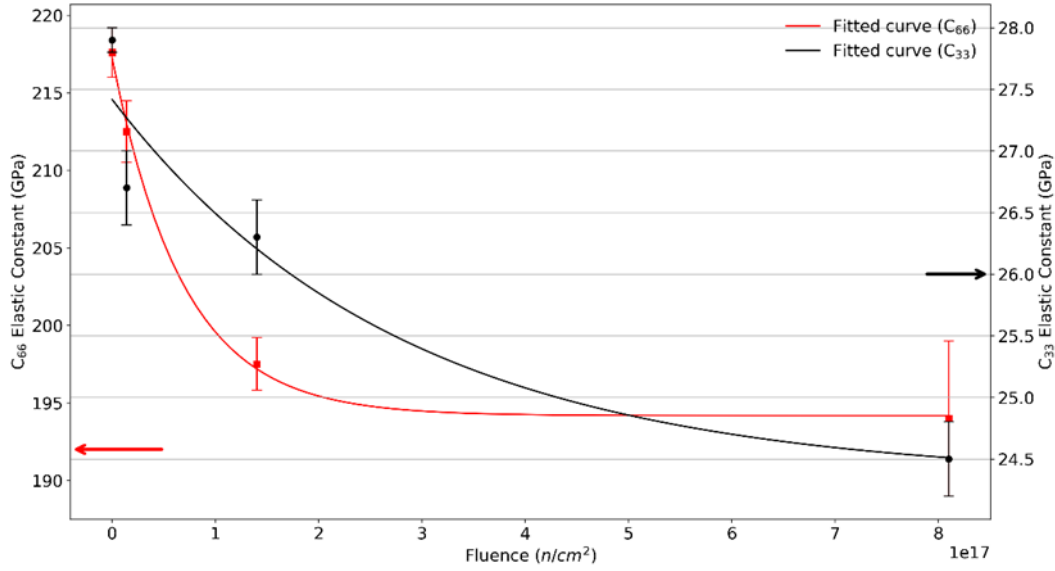


Figure 4.6 - Elastic stiffness coefficients as a function of fluence in $h^{10}B^{15}N$

Brillion scattering shows that both compressive and shear (C_{66} and C_{33}) resistance decay exponentially with fluence reaching as low as 192 GPa and 24.5 GPa respectively. This is likely due to the perforation of the crystal illustrated in Figure 4.8. SAED is parallel to XRD, describing lattice spacing and crystallinity. Blurring or spreading in SAED patterns correlate to lattice defects such as dislocations and stacking faults [351]. Such patterns were uncovered in cross-sectional TEM alongside SAED presented in Figure 4.7

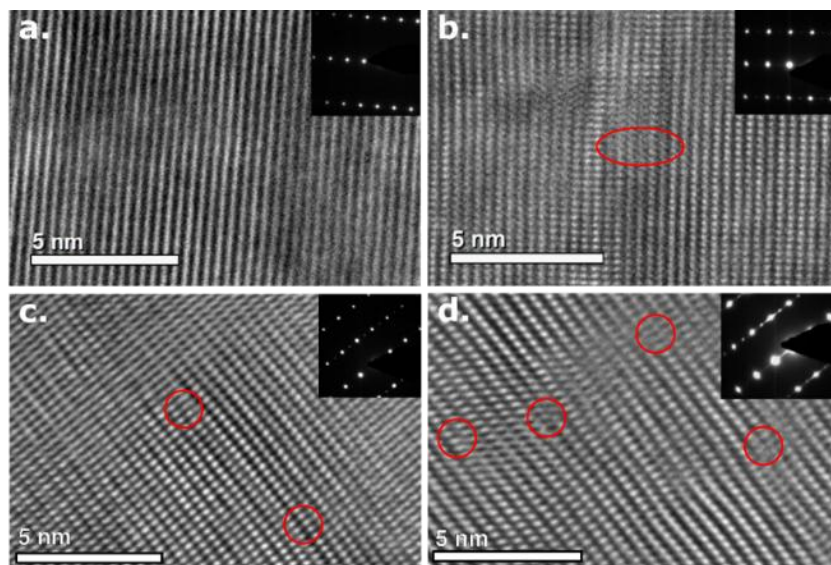


Figure 4.7 - Cross-sectional TEM images of $h^{10}B^{15}N$ (a) before and after (b) 1.4×10^{16} (c) 1.4×10^{17} (d) and 8.4×10^{17} neutrons/cm² irradiation fluence with SAED pattern insets. Red circles highlight visible deviations from pristine $h^{10}B^{15}N$.

Not only do the layers become visibly more disordered as fluence increases, but SAED patterns present more points with spreading/blurring. The damage to the structure is evident in Figure 4.8. Pristine $h^{10}B^{15}N$ shows perfect continuous honeycomb structure, but after neutron irradiation, bulk defects like large gaps or voids formed.

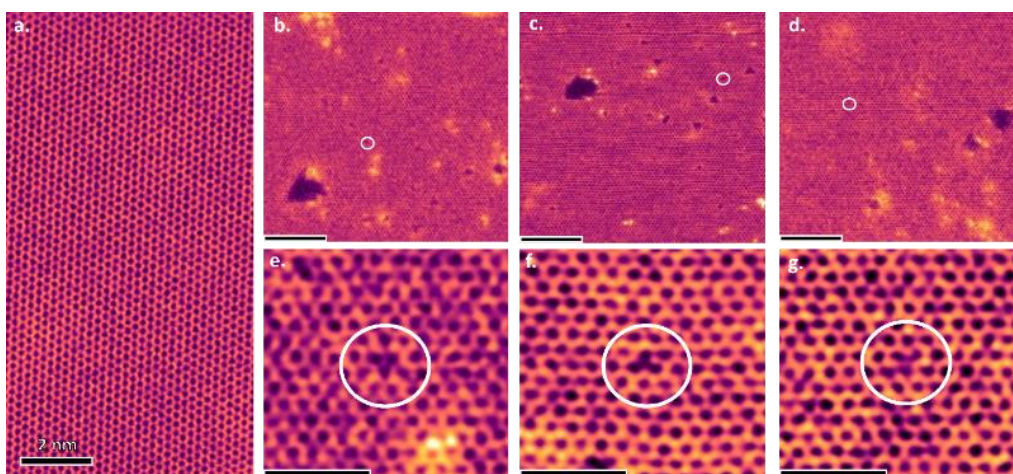


Figure 4.8 - False-colored plan-view STEM Images of (a) pristine $h^{10}B^{15}N$, and irradiated $h^{10}B^{15}N$ (1.4×10^{17} neutrons/cm²). Low magnification defects in (b-d) are circled and further magnified in (e-g) respectively. Scale bars in (b-d) are 4nm and (e-g) 1nm.

The ^7Li concentration in $h^{10}\text{B}^{15}\text{N}$ due to the transmutation of ^{10}B to ^7Li was measured by dynamic secondary ion mass spectrometry (SIMS) (Figure 4.9). This provides a rough estimate of the irradiation fluence efficiency using the conversion $\left(X = \frac{[^7\text{Li}]}{[^{10}\text{B}]}\right)$.

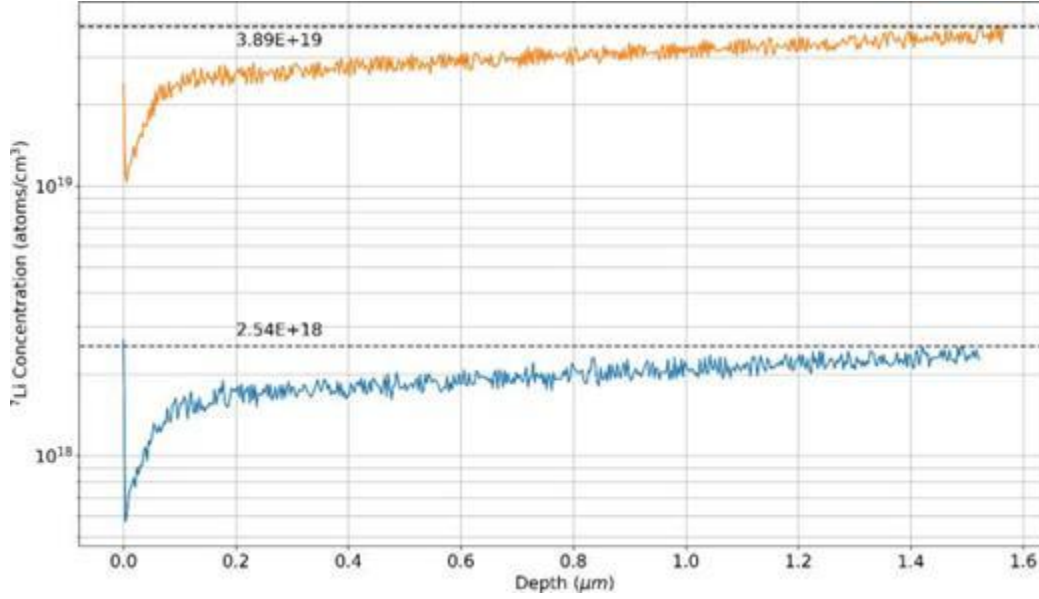


Figure 4.9 - SIMS Measurement of ^7Li in irradiated $h^{10}\text{B}^{15}\text{N}$ crystals with (a) 5.8×10^{16} neutrons/cm² after 4 hours (blue) and (b) 8.4×10^{17} neutrons/cm² after 60 hours (orange). The maximum value is reported adjacent to their respective fluence profile.

The PL intensity is proportional to ODMR contrast and decreases drastically beyond an hour of irradiation as shown in Figure 4.10b where 2.2×10^{16} (1.5 hours) and 1.4×10^{17} neutrons/cm² (10 hours) produce the brightest emissions. Additional studies on this decrease have revealed it is due to the increasingly significant losses through a non-radiative transfer mechanism [339].

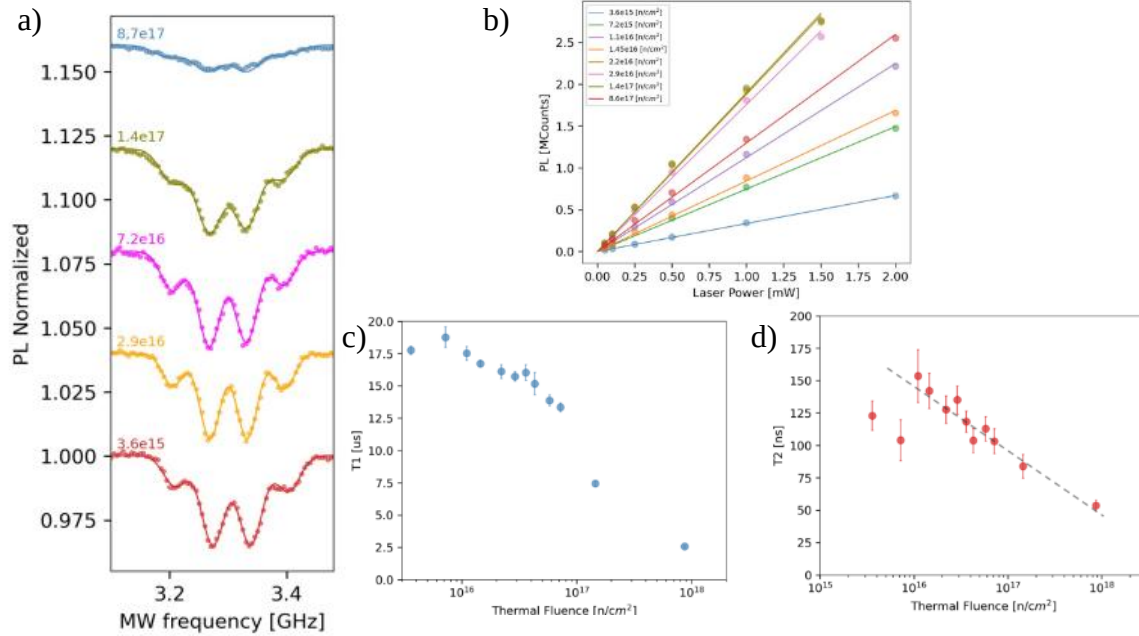


Figure 4.10 - (a) ODMR spectra (b) PL Intensity with laser power (c) T1 relaxation time (d) T2 spin decoherence time for select fluences.

As shown, despite a higher concentration of vacancies at $1.4 \times 10^{17} \text{ n/cm}^2$, this same defect density forces shorter decoherence times due to interactions between the vacancies and other defects. However, irradiation is necessary for the conversion of ^{10}B to V_B^- .

Annealing V_B^- experiments

In general, annealing at high temperatures repairs some defects [352],[300] and allow lithium to migrate out of the lattice [353], improving crystal quality. To test whether thermal annealing improves ODMR signal, 3 different fluences of irradiated $\text{h}^{10}\text{B}^{15}\text{N}$ crystals were heated to 500 or 600°C under different cover gases (N_2 or air), and for 5 mins and 30 mins. The defect peaks originally seen in the Raman and PL spectra were reduced significantly for the higher temperature anneals for both times and gases, but the annealing also healed the vacancies and reduced the characteristic Raman at 1320 cm^{-1} and 1.54 eV PL peaks discussed earlier.

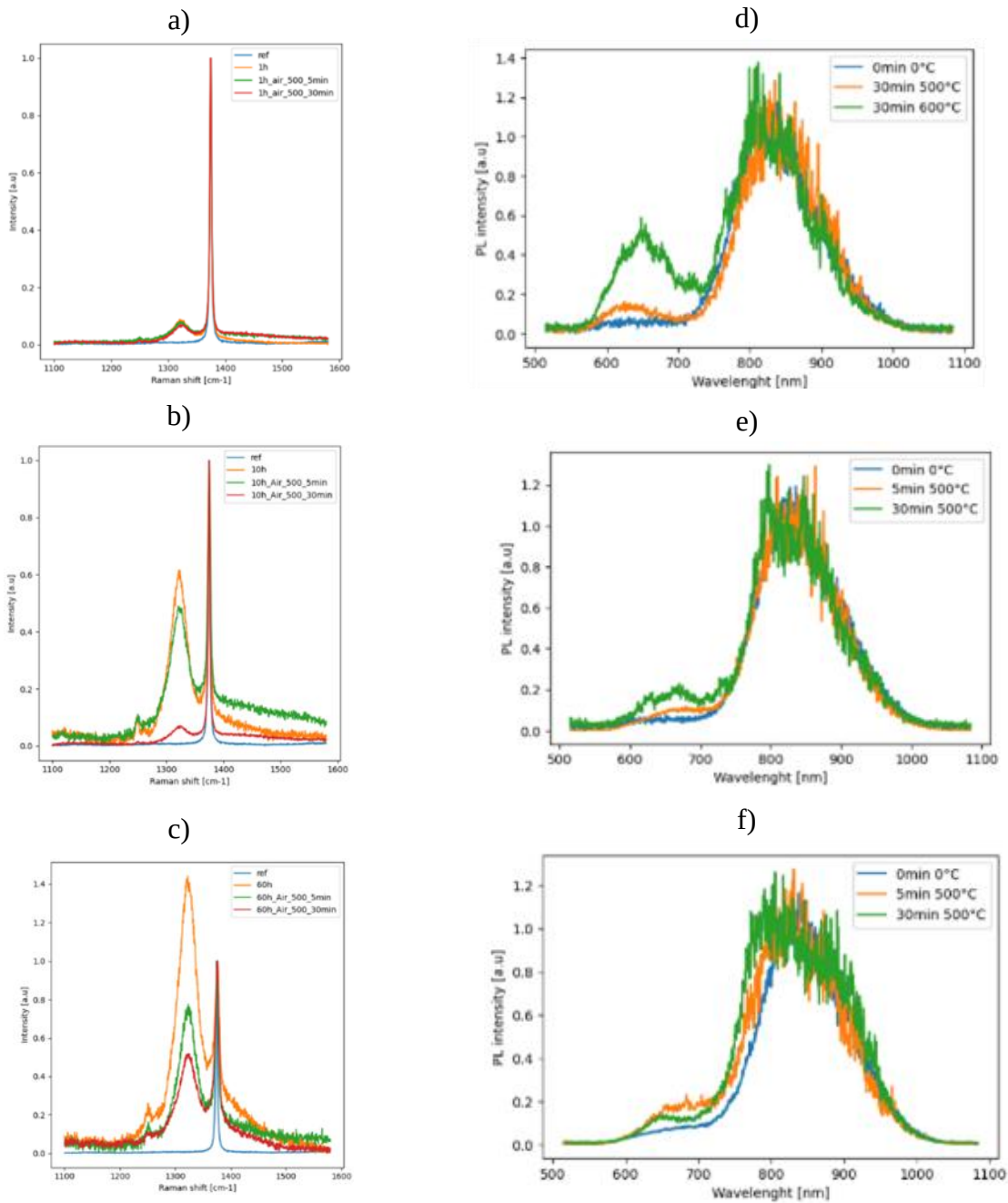


Figure 4.11 - Raman (a-c) and PL (d-f) spectra from irradiated and annealed $h^{10}B^{15}N$ crystals. (a, d) Irradiated for 1.4×10^{16} , (b, e) 1.4×10^{17} , and (c, f) 8.4×10^{17} n/cm^2 .

Despite the decrease in emission intensity, the contrast improved slightly, which is an important parameter for detection sensitivity; however, the coherence time of the electron spins did not significantly improve as shown in Figure 4.12.

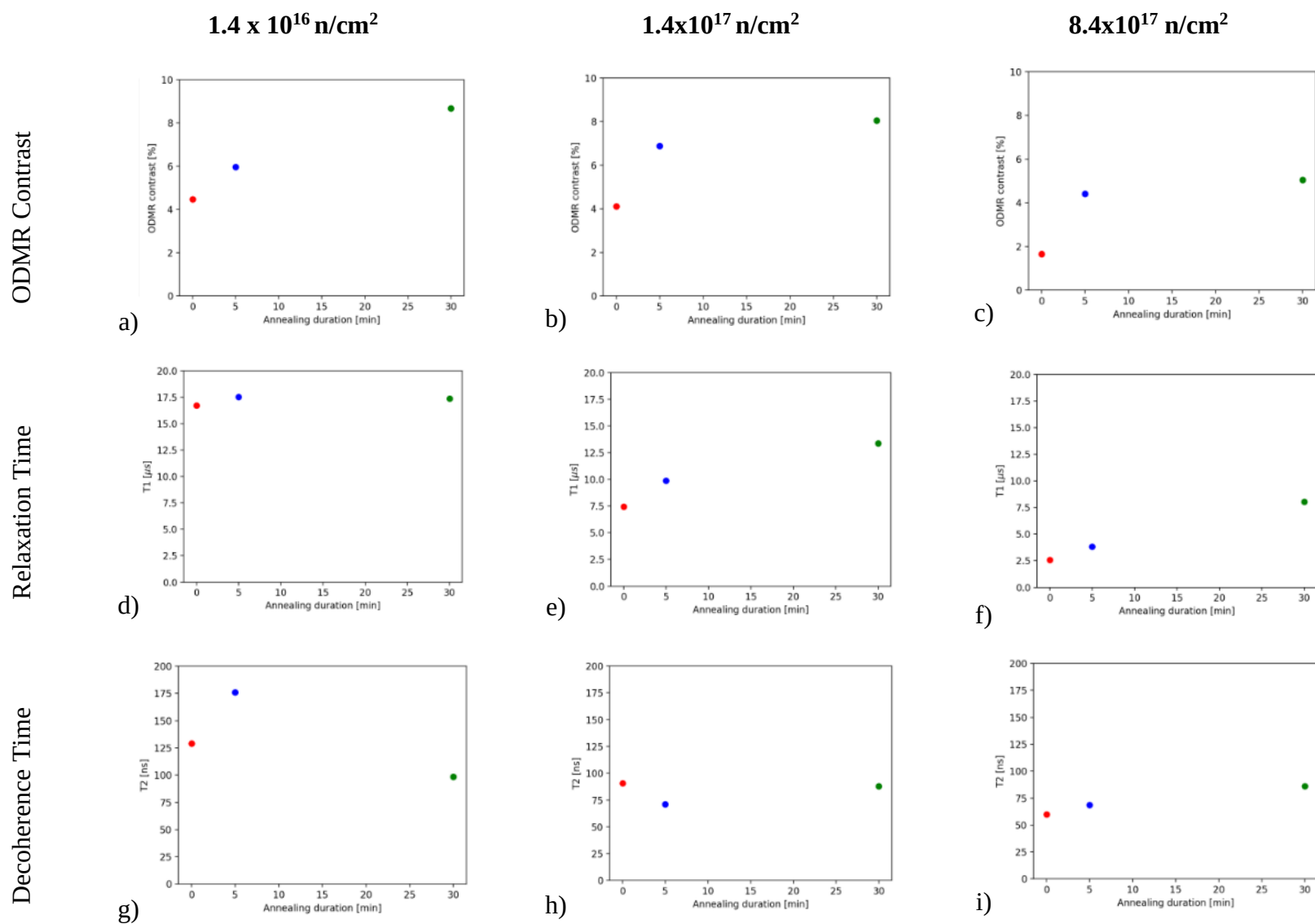


Figure 4.12 - Key parameters of V_B^- : (a-c) contrast, (d-f) relaxation time (T_1), and (g-i) decoherence time (T_2) as functions of annealing time at 500°C under air.

Small increases in relaxation time were not encouraging. The overall decoherence times remained within 30% of the unannealed values. Hence, the annealing was trivially successful but not practical for the minute improvements. Note that the appearance of the crystals became less red orange, likely correlated with the decrease in defect density shown in Figure 4.13.

Conclusion and Contribution

In conclusion, several experiments were performed to make the $h^{10}B^{15}N$ crystals necessary for this investigation. The negatively charged boron vacancy was created to varying densities in $h^{10}B^{15}N$ to serve as a quantum sensor. Due to the limiting factors (contrast, T_1 , T_2) of these sensors, several considerations were accounted for in the creation of these V_B^- defects. These sensitivity parameters were studied in parallel with the structural properties of the host crystals revealing an optimal fluence between 7.2×10^{16} and $1.4 \times 10^{17} \text{ n/cm}^2$ to get both the best contrast, T_1 , and T_2 . Additionally, when exposed to higher or nonoptimal fluences, contrast and T_1 can be recovered with brief annealing at 500 °C under air; however, T_2 remains unaffected. When annealing is conducted at ~1800 °C, these defects are almost completely removed, recovering the crystal.

Chapter 5 - Optimization of controlled carbon doping of hBN

Background

Common impurities in hBN are usually elements of similar size to B and N. The most suitable element is that which lies between them on the periodic table: carbon. Carbon can be substitutional or vacancy adjacent. A variety of such defects is presented below in Figure 5.1 [189].

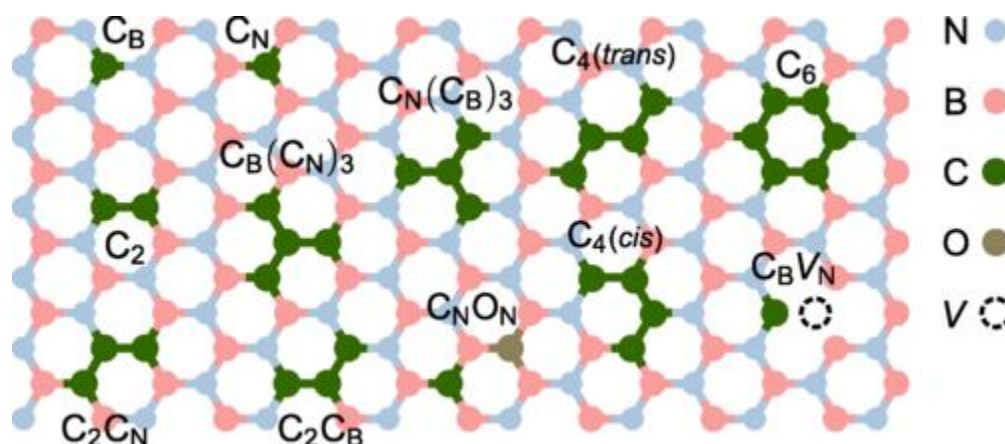


Figure 5.1. Possible carbon defects in hBN. Varying degrees of substitutions from single site to sextuple sites are shown in addition to co-substitution with oxygen or vacancies [189].

Each of these defects has its own unique properties. The defects themselves negligibly impact the structural integrity of carbon-doped hBN (hBN:C). Some properties these defects introduce are new inter-bandgap emissions [354] at energies from 1.54 to 4.1 eV measured with photoluminescence spectroscopy

[155],[157],[163],[166],[175],[176],[184],[196],[199],[206],[207],[209],[220],[221],[227],[355].

It remains a challenge to assign specific emissions calculated from theory to experimentally engineered samples because experimental samples include multiple defects. The most common defects are the $C_B C_N$, ‘B-center’, and donor acceptor pairs (DAPs) where two non-adjacent carbons interact electronically [356]. To differentiate between these defects, techniques in conjunction to PL like ODMR [215] and single photon emission are used [215],[216]. With sufficient spatial and

spectral resolution, individual isolated emissions can be assigned depending on emission energy and magnetic sensitivity; however, there is still some uncertainty even after narrowing the field of view to $<1\ \mu\text{m}$.

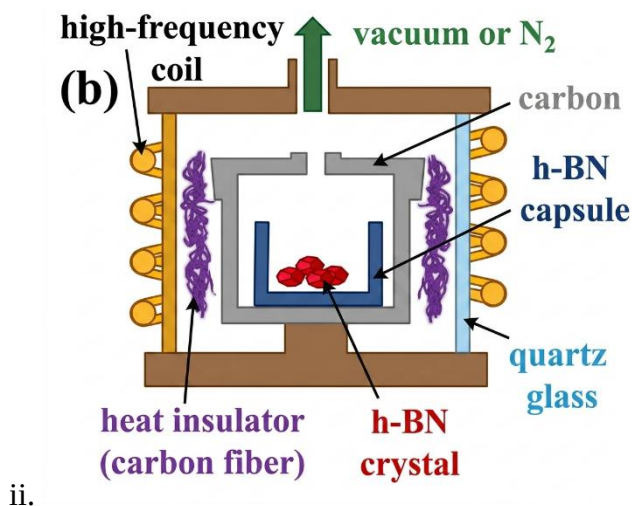
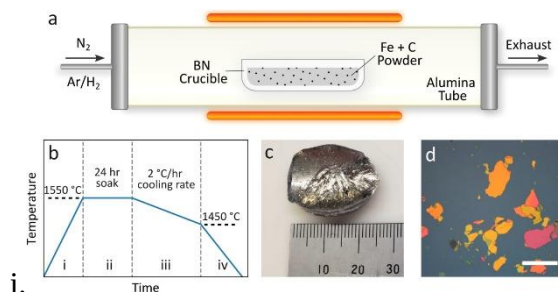
Applications

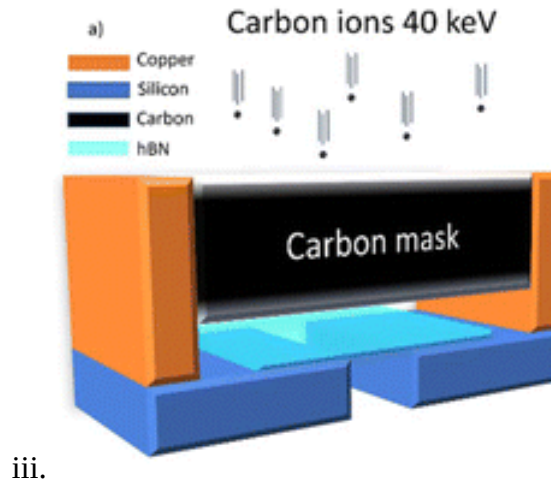
hBN:C with single photon emitters can be used in quantum photonics and cryptography using the individual photons as on/off switches [357]. Individual photons of the same wavelength permit quantum key distribution quantum photonics [358]. Carbon defect sites are also more reactive, and have been used in catalysis [359],[360] and hBN photovoltaics [361]. Other uses include strengthened dielectric properties [362] and enhanced thermal conductivity of more than $800\ \text{W/m}^2\text{K}$ [363]. Expanding these defects to single crystals allows them to be incorporated into heterostructures for high-performance electronics.

Single crystal hBN:C is particularly useful in these applications. Single crystallinity maximizes device sensitivity because there are minimal grain boundaries at which scattering occurs. Carbon-doping of hBN by flux method has only been controllably demonstrated in reference [335] using carbon powder with the source materials. These defects are activated by electron irradiation. Despite being consistent, their investigation is limited to the formation of the B-center defect: an out-of-plane substitution dimer (two-carbon atoms on adjacent lattice sites oriented perpendicular to the a -direction). A large benefit for the carbon defect variety is the potential of different wavelengths for single photon emitters. Tuning for different wavelengths is not possible with just one defect type apart from slight shifts due to mechanically induced strain [364]; therefore, other methods must be considered.

To create other defect types, two additional methods were explored: diffusive doping and ion implantation. Flux or in-situ doping involves changing the amount of carbon included with the

source materials. Diffusive doping mimics the work of Onodera et al [196] with high temperature (2000°C) annealing in a carbon-rich environment. In this investigation lower temperatures (1700-1900°C) were used and compensated for by using longer dwell times (3-18 hours). Ion implantation has been explored slightly [173], but the effect of implant species on the resulting defect chemistries are further investigated in this work. In Figure 5.2, a schematic of each of these methods is shown.





iii.

Figure 5.2. Doping mechanisms and experimental procedures for (i) flux doped [224] and its (a) experimental apparatus, (b) temperature schedule, (c) resulting boule, and (d) hBN:C exfoliated from the boule onto SiO₂; (ii) diffusion doped [195], and (iii) ion-implanted hBN:C [173]

Carbon doping via flux method

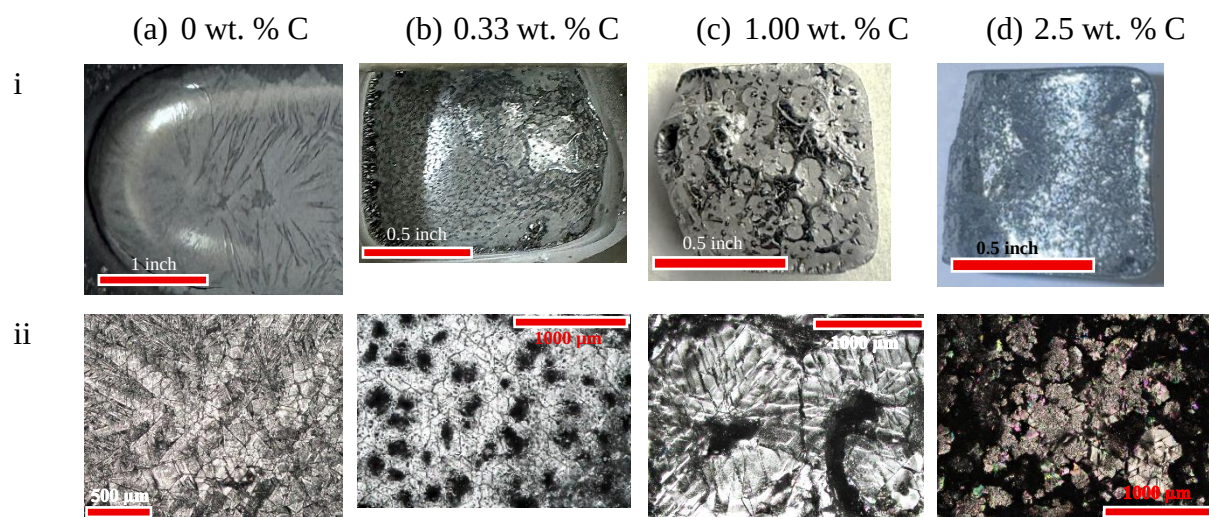
Previously carbon doping was attempted with some success using CO gas [198]. It produced only small crystal grain sizes ($\sim 200 \mu\text{m}$) and resulting in other hBN polytypes. The most straightforward doping method is to include carbon (graphite powder) in the initial source materials for APHT grown hBN. Carbon, iron, and boron were mixed in an alumina crucible identical to those discussed in Chapter 3 and subjected to the same temperature control schedules. In another study, including 1.8 wt. % C in the source materials was reported to increase the hBN crystal grain size ($> 40,000 \mu\text{m}^2$) without evidence of doping [226]. No PL was provided to show the 4.1 eV peak indicative of the carbon dimer. However, this induced more macrostructural ($\sim 100 \mu\text{m}$) cracks, due to nucleation competition with graphite, where the smooth surface of hBN was interrupted by faults. The crystal quality improved slightly because carbon acted as an oxygen getter forming CO_x byproducts. The crack density was reduced with the addition of gold [157] because of the improved dispersion of carbon minimizing graphite co-nucleation.

Here, compositions with crushed graphitic (or ^{13}C powder) carbon range from 0.33 to 2.58 wt. % C (or 1.01 wt% ^{13}C) (above which graphite was precipitated instead of hBN) with 2.32 wt. % B powder in low-carbon (14 ppm) iron mixed in an alumina crucible before being subjected to ingot formation (Figure 3.10a) under forming gas followed by crystal growth (Figure 3.10b) under nitrogen and forming gas. The flux doping was performed using the TCM furnace (Figure 3.7) for natural graphite and the SCM (Figure 3.6) for carbon-13. Iron was chosen to maximize both carbon and boron solubility simultaneously and to simplify the solvent system despite it being a non-ideal solvent.

Parameters studied as functions of carbon incorporation are visual and structural changes via XRD and Raman spectroscopy, spectral changes via PL, and magnetic changes using ODMR. Additionally, doping with carbon-13 distinguished dimer defect responsible for the 4.1 eV emission. Some samples exhibited transient single photon emission from exfoliated flakes.

Visual and Structural Characterization

In a majority of hBN:C growths, a shell formed on the surface of the ingot during the crystal growth. Very small grains $\sim 10\text{-}20\text{ }\mu\text{m}$ laterally, formed between clusters of very large single crystals ($\sim 500\text{ }\mu\text{m}$). Select examples are provided below in Figure 5.3.



iii

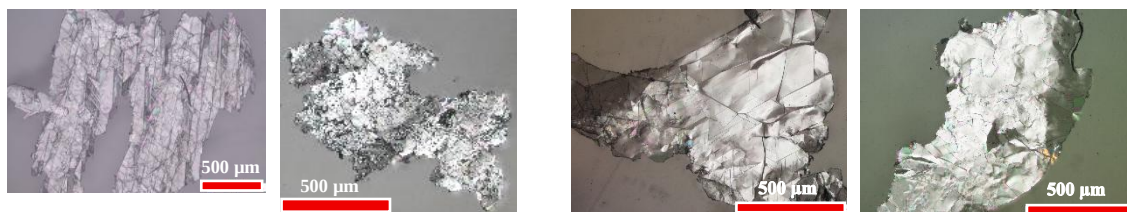


Figure 5.3. hBN on iron ingot surface with varying grain sizes. Small pillars formed when carbon was introduced.

Reducing the complexity of the solvent comes at the cost of worse crystals. Those shown in Figure 5.3 are not representative of typical crystals like those shown in Chapter 3. The shells formed with or without carbon; therefore, they are unrelated, but likely due to the flux (iron). A feature that appeared when carbon was introduced was the black regions shown in (b-d, ii). These pillar or column-like structures protrude orthogonal to the ingot surface. As more carbon was introduced these pillars increased from 100 microns in diameter to 200 microns in (c, ii) but no larger. Also, as more carbon was included, there was no clear trend in grain size change apart from two conditions: (1) the co-precipitation of graphite or (2) very sparse hBN:C growth like (c, ii) resulting in smaller free-standing flakes (c, iii). The crystals themselves did not change in appearance as observed with other methods.

XRD and Raman measurements were taken on the carbon-doped hBN samples to assess their structural integrity of the crystal lattice. Such measurements were taken as functions of the same four hBN:C growths as presented in Figure 5.3. The results are presented in Figure 5.4 and Figure 5.5.

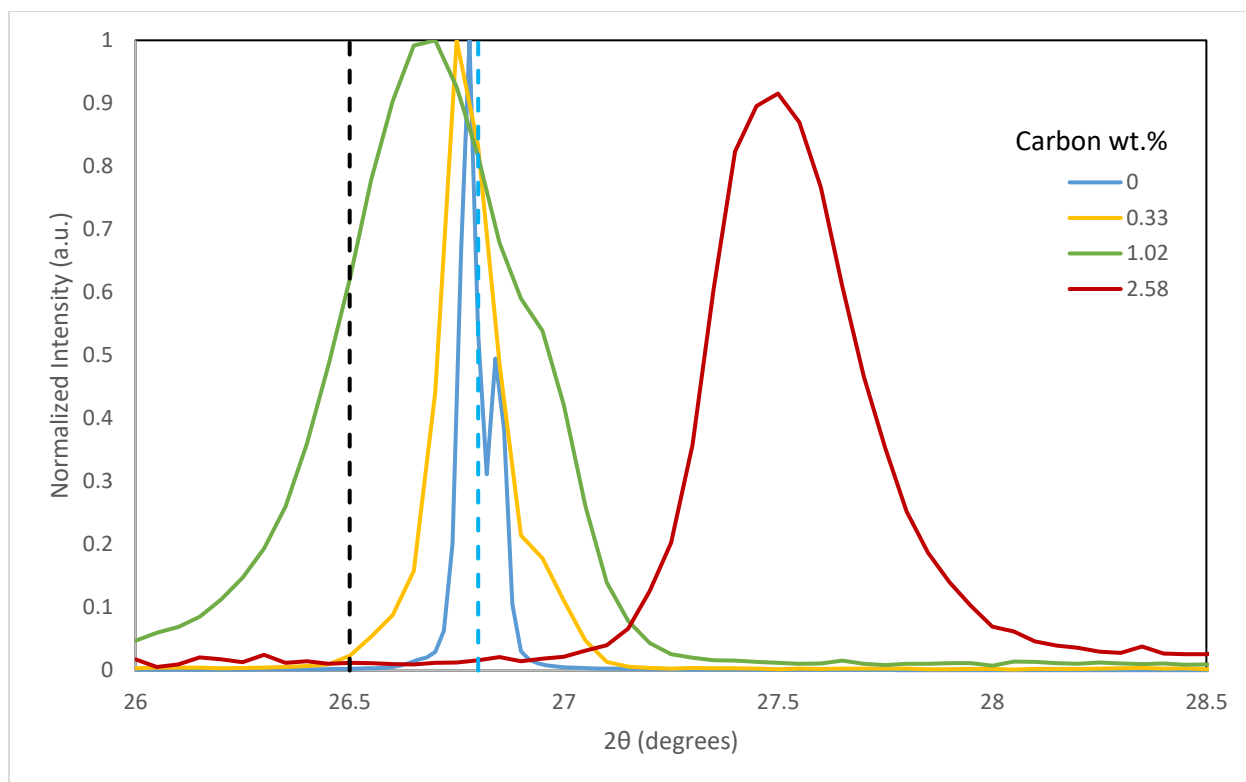


Figure 5.4. XRD Pattern of hBN:C with varying amounts of carbon included with the source materials. Graphite and hBN $\langle 002 \rangle$ peaks are shown with black and blue dashed lines, respectively.

XRD patterns show that there was significant change in the layer spacing or the crystal structure due to the inclusion of carbon. As more carbon is included there is a shift to lower then to higher diffraction angles implying that small amounts of carbon cause minor expansion in the d-spacing, but with abundant carbon the d-spacing decreases. It is expected that as more carbon is introduced, there should be more evidence of graphite. Figure 5.4 contradicts that expectation because the $\langle 002 \rangle$ position of graphite (black dashed line) is at lower degrees than that of hBN (blue dashed line). The disorder caused by carbon doping may be causing The quality is consistent with exfoliated flake size in that it decreases with more carbon.

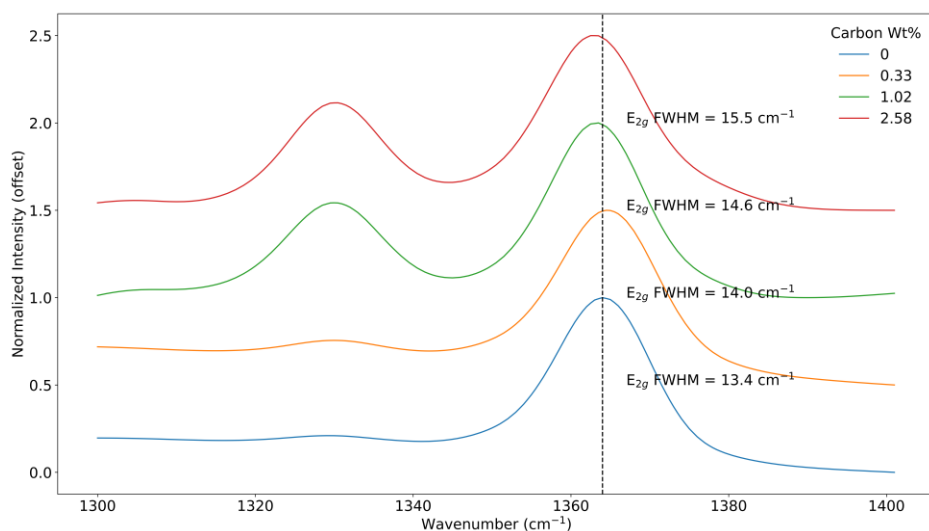


Figure 5.5. Room temperature Raman spectra of flux-doped hBN:C with varying carbon included in the source materials. Spectra are linearly background subtracted and normalized over 1310 to 1390 cm^{-1} . Offset is 0.5.

The changes are much more evident in the Raman spectra than XRD. In Figure 5.5, the germination of a new peak begins at 1.02 wt. % C, just left of the intrinsic E_{2G} peaks, at 1330 cm^{-1} . In graphitic and diamond analysis a peak at this position indicates sp^3 carbon. Despite the lack of a graphitic peak formed in these crystals, they've formed a defect peak meaning they've created a variety of potential defects such as sp^3 bonds to carbon or vacancies. Additionally, the resulting strain from the carbon defects is shown by the increasing FWHM of the E_{2G} peak from 13.4 to 15.5 cm^{-1} . The positions shift slightly higher then lower at 0.33 and 2.58 wt. % C, respectively. Though the changes are minor, they are consistent indicating progressively more defective hBN:C crystal. The peak positions are at 1364 cm^{-1} which differs from other experiments indicating substantial strain in even the pristine iron-solvent hBN, likely due to irregular bonding.

Spectral Characterization

Given the wide range of possible emissions, luminescence is a critical analytical technique for observing spectral signatures of carbon defects in hBN:C. One such technique is cathodoluminescence (CL) where an electron beam is used to excite the material rather than light. For flux hBN:C, samples were exfoliated to $>100 \text{ nm}$ onto SiO_2 using the tape press method. Since hBN is an insulator, it suffers from charge buildup under electron irradiation. Using very thin hBN layers (prepared by cleaving) helps to avoid this problem. This was followed by an anneal at 500

°C for one hour in forming gas and concluded with a 5-minute etch under O₂ plasma at 50 sccm and 50 W power. To confirm this did not impact the spectral properties of the hBN:C, spectra were recorded before annealing, after annealing, and after plasma etching. These results are shown in Figure 5.6.

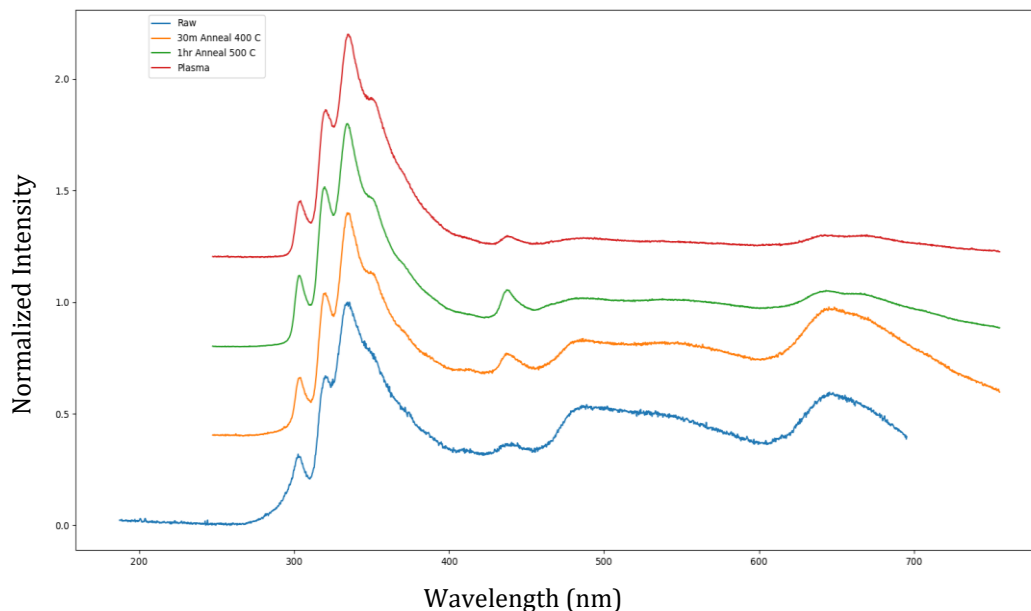


Figure 5.6. CL Spectra of identical hBN:C flake as exfoliated (blue), after annealing (orange/green), and after oxygen plasma (red).

Disappearing peaks at >450 nm imply that some residues were emitting and were removed by the cleaning procedures as their intensity decreases. This same process was repeated for 3 other samples with the same compositions as those presented previously. The post-treatment spectral signatures are very similar despite their visual appearances. A comparison of the different carbon concentrations is provided in Figure 5.7

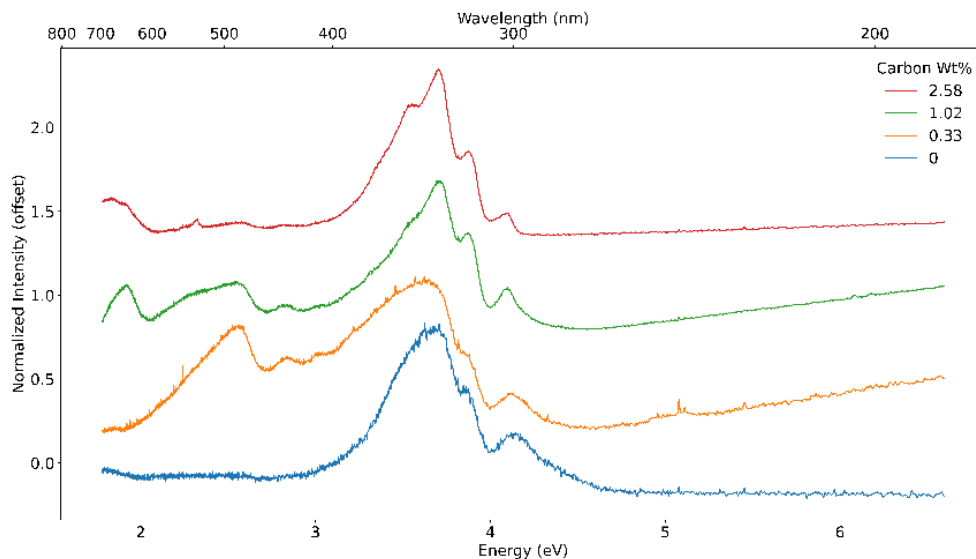


Figure 5.7. CL spectra for hBN:C with varying carbon content in the source materials.

In the 3 to 4 eV energy range, there are several peaks in the CL spectra that may be associated with a variety of point defects. The pristine hBN sample has two main peaks at 3.7 and 4.1 eV. In contrast, in the lower energies, between 2 and 3 eV, the absence of peaks in the pristine sample indicates that the peaks seen in the other 3 correspond to carbon-related defects. Possible contenders discussed in theoretical studies are C_4 or $C_B C_N V_B V_N$ [152] for 2.94 or 3.07 eV respectively. At 2.5 eV, C_3 , $C_3 V_B$, $C_N V_B$, C_N are possibilities with predicted emissions from 2.49 to 2.45 eV. A table of carbon defects and their emissions are presented in Appendix D for further speculation.

Another spectroscopic technique discussed in the previous chapter is PL. PL is useful for the same reasons as CL but does not require an SEM. PL uses a fixed wavelength laser to excite contrary to CL's electron beam. It is a widely employed technique to identify carbon defects in hBN:C. Flux doping always produced a PL peak at 4.1 eV using a high energy cryogenic PL laser on unexfoliated flakes. Collaborators at Montpellier University measured the following spectra (Figure 5.8).

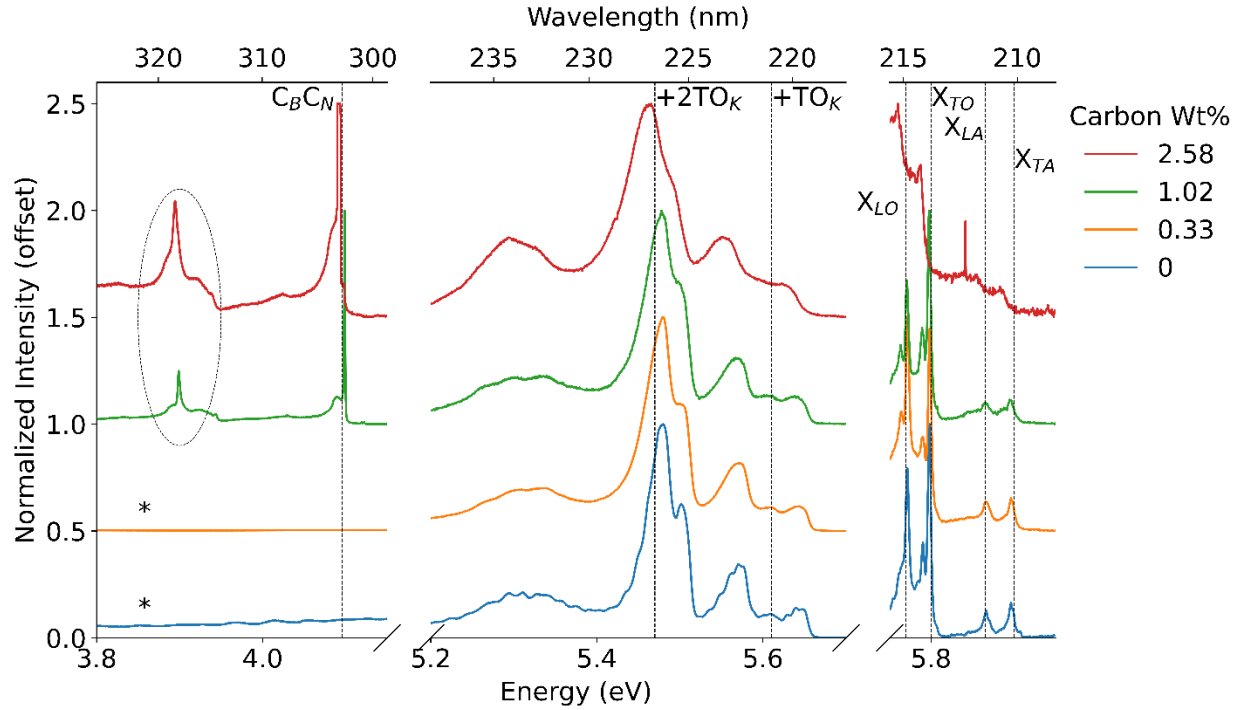


Figure 5.8. PL Spectra of hBN:C with varying carbon in source materials. Intrinsic hBN peaks are labeled as X and TO_K. The carbon dimer's spectral signature is also identified at 4.09 eV. An additional defect (dashed ellipse) also appears at 3.9 eV. The asterisks denote un-normalized sections of data due to noise.

The peaks expected of intrinsic hBN appear at near band gap energies ~6.0 eV (Figure 5.8). As the source carbon content increases these peaks get relatively weaker and noisier, especially at 2.58 wt. % C. An additional feature appears at the two higher carbon concentrations at 3.9 eV as well. These were predicted to be SW defects stabilized by the carbon dimers [153]. The B-center fabricated in [224],[365],[366], is also a carbon dimer, but is oriented out of the plane in recent studies [194]. This is supporting evidence that the dimer is the most stable form of carbon incorporation in hBN.

To explore the PL spectra from the carbon-doped hBN at lower energies (<2.3 eV), a 532nm wavelength laser PL was employed. This measurement reveals color centers that are defects in the visible wavelength range. At room temperature the same hBN:C crystals from the same experiments were examined yet again. The results of which are much less clear but present a well-defined emission that could be correlated (Figure 5.9).

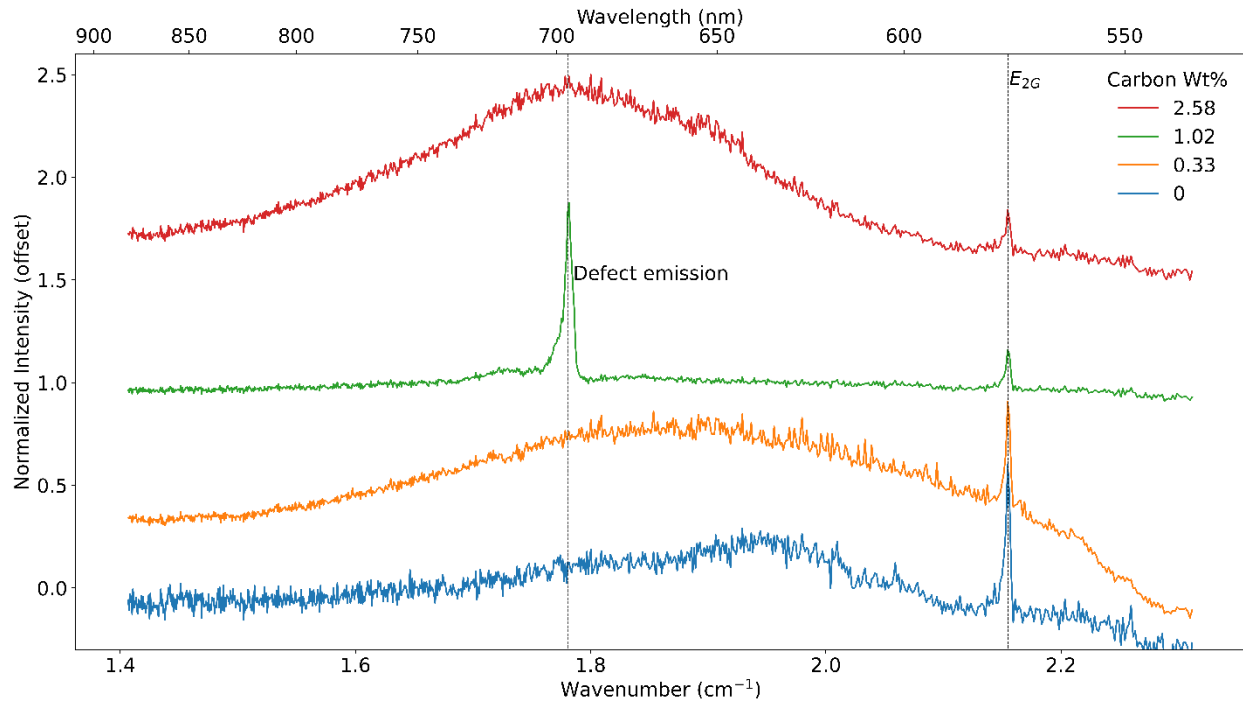


Figure 5.9. 532nm PL Spectra of hBN:C with varying carbon in source materials. Intrinsic Raman modes of hBN are labeled at 575nm. A sharp and bright emission appears at 690 nm.

The bright emission at 1.78 eV in Figure 5.9 from the 1.02 wt. % C sample is possibly a donor acceptor pair (DAP) as mentioned earlier. Theory estimates the $C_B C_N$ -DAP-2⁺ is responsible for this emission [152]. Which entails two monomer substitutions that are two bond lengths away. To further illustrate, the proposed defect is presented in Figure 5.10a.

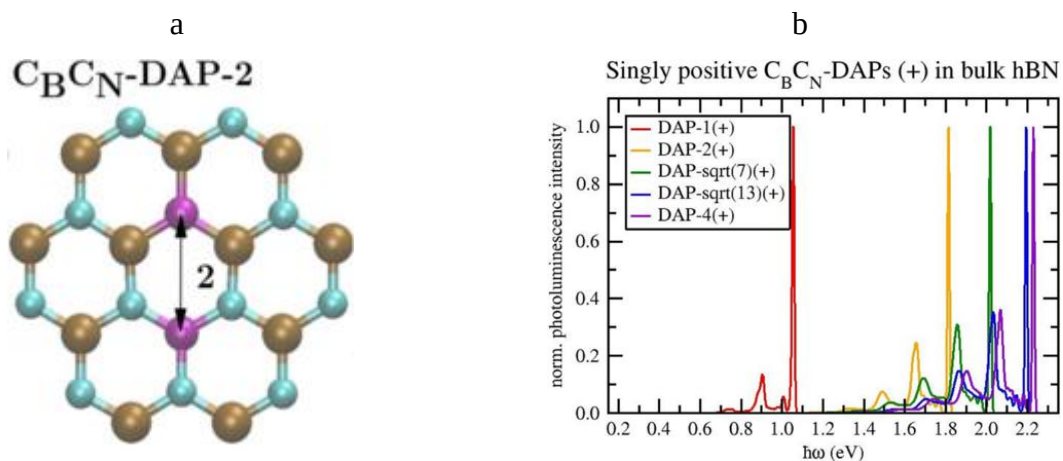


Figure 5.10. (a) $C_B C_N$ -2 donor acceptor pair (DAP) [152]. Cyan spheres are boron, brown spheres are nitrogen, and purple spheres are carbon atoms. (b) PL spectra for positively charged DAP-2 defects [152]. The yellow spectrum corresponds to the proposed defect for 1.02 wt. % hBN:C.

Despite not being directly adjacent to each other, the carbon substitutions introduce new charge states within the band gap lower than that of intrinsic boron nitride. These new states are a result of electrons with different spins coupling over bond lengths greater than 1.45 Å permitting emission in less than UV wavelengths.

For more insights into the nature of carbon in hBN, this set of hBN. The splitting of the excited state electrons provides insight into the electronic structure of the defect if it is magnetically sensitive. Several carbon-related defects have shown magnetic sensitivity in the literature [215],[168],[356]. Therefore, ODMR will narrow the range of possible defects. More than 300 spectra revealed only the 1.02 wt. % hBN:C sample showed any splitting or detectible contrast under 120 Gauss. The data recorded is presented in Figure 5.11 at varying microwave gains. The microwave gain is proportional to the duration of the initial laser pulse [367] and helps to increase contrast at the expense of peak width.

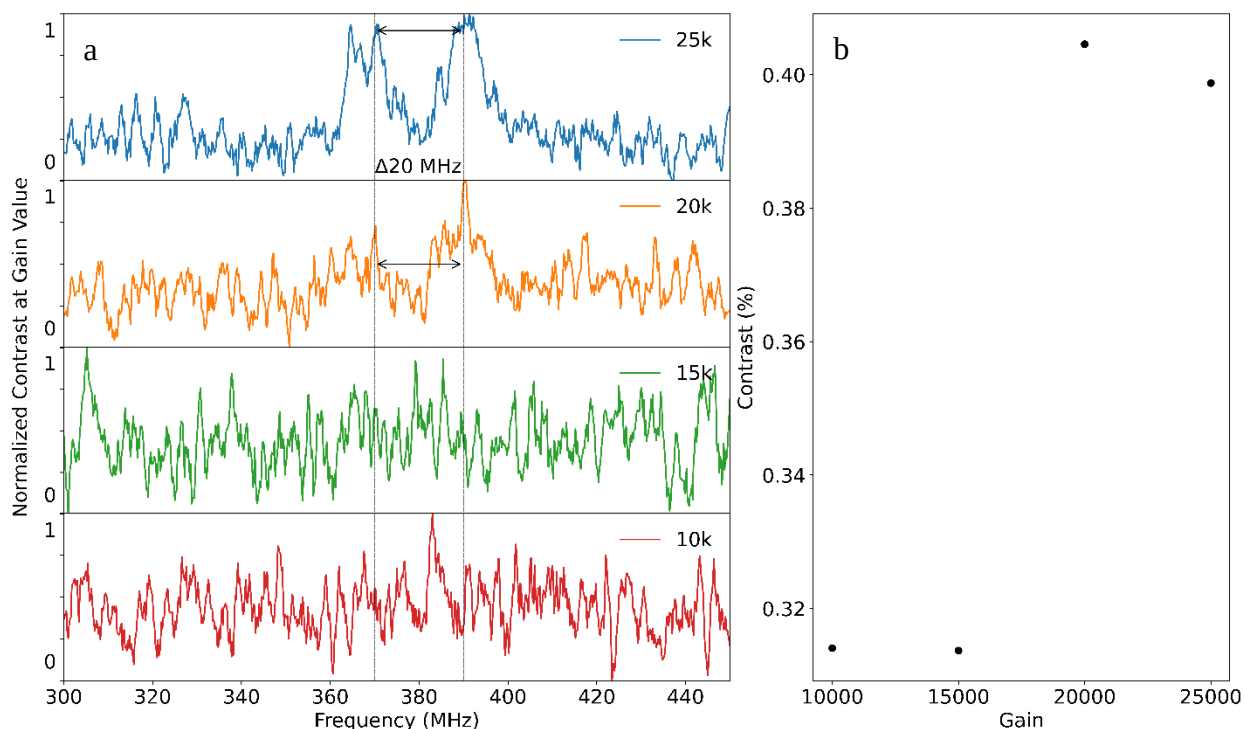


Figure 5.11. (a) ODMR Spectra of 1.02 wt. % hBN:C at varying microwave gains under an external field of 120 Gauss. A 20 MHz splitting is indicated with 2 dashed lines. (b) ODMR contrast plotted as a function of gain.

At low microwave gain, the peaks are indistinguishable from the noise; however, as gain increases, the peak becomes much more evident at 20 and 25000 gain with a maximum contrast of 0.41%. Despite being detectable in ODMR, the low frequency is insufficient to identify the defect type.

Due to the large number of possible defects that carbon can introduce and the wide range of identifying characteristics, it is difficult to assign spectral peaks to specific defects apart from the signature for the $C_B C_N$ dimer in the DUV PL at 4.1 eV (Figure 5.8). Lower energy PL spectra also suffer from the peaks convoluting with one another: they contribute to each other's luminescence resulting in broad peaks like the one at 700nm in Figure 5.9. This resulted in some consistent carbon dimer control at low carbon concentrations, but as more carbon is introduced, the metal surface is covered in pillar-like structures, and the exfoliated flakes tend to be much smaller overall.

Carbon doping via diffusion

Carbon doping can be achieved through high temperature diffusion [195] into hBN in a carbon-rich environment. With high quality hBN crystals or powders, different defects were introduced using diffusive doping. Using the furnace from Chapter 2 (Webb), yellowing like Onodera et al [195] occurred in the materials grown at KSU as well as in 50 μm powders. High temperature annealing was done at temperatures from 1600 °C to 1900 °C for 3 to 18 hours in nitrogen. hBN is commonly annealed at 1700 °C [368], therefore, introducing defects likely requires higher temperatures to make the lattice more susceptible to incorporation following an transport model (equation 5.1) [369].

$$C_{defects}(z, t) = C_0 \left[1 - \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) \right] \quad (5.1)$$

Where z is depth through the thickness of the crystal, t is time, and D is the temperature dependent diffusion coefficient which likely follow Arrhenius model. These diffusion doping experiments entailed whole crystal flakes being set directly on a graphite crucible alongside hBN powder as an indicator. Because of the powders high surface area, they more clearly change color in the process than the single crystal flakes (Figure 5.12).

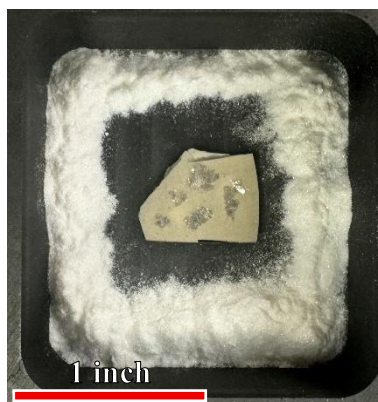
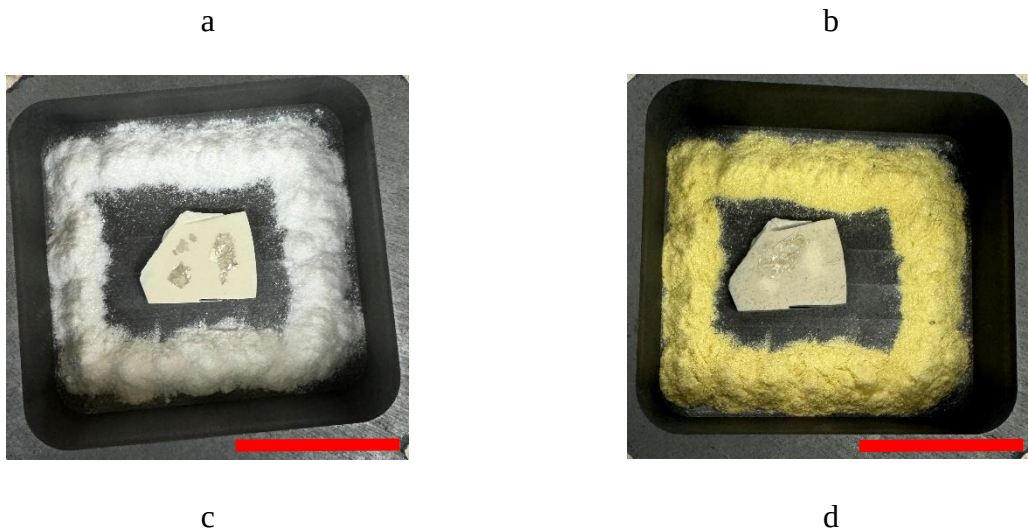


Figure 5.12. hBN powder surrounding hBN crystal set on a pBN wafer chip in a graphite crucible before annealing.

Visual and Structural Characterization

Like *in-situ* hBN:C, there are visual indications of carbon-doping for diffusive doping [196],[198], the latter were samples grown at KSU. This yellow was evident with the hBN powders, but less so with most hBN crystals even when placed in direct contact with the graphite crucible. Figure 5.13 shows a before and after comparison of hBN powder and hBN crystal of the same experiment that was annealed at 1917 °C for 3 hours.



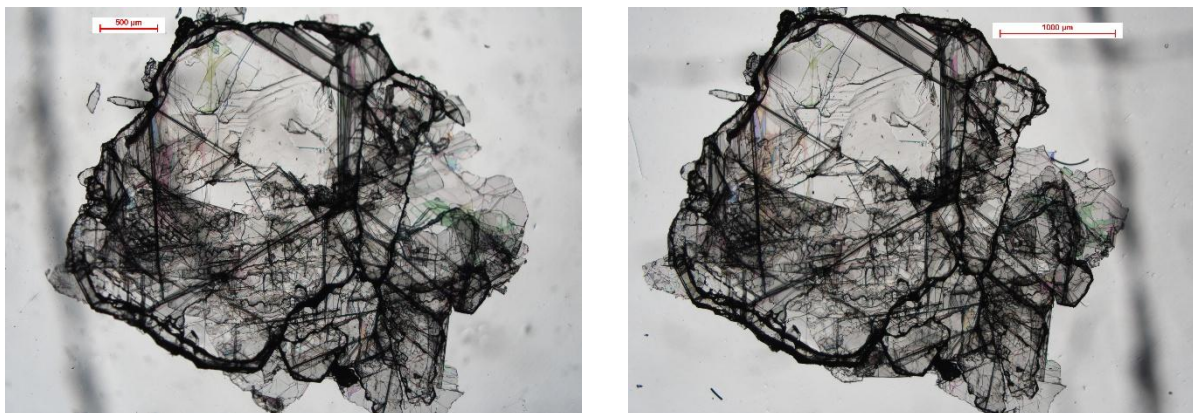


Figure 5.13. hBN powder surrounding hBN crystals on a pyrolytic BN (pBN) wafer chip set in a graphite crucible (a) before and (b) after 3h at 1917 °C annealing. (c) hBN crystal set atop pBN before and (d) after same annealing conditions. Scale bars are (a, b) 1 inch, (c) 500 μm , and (d) 1000 μm .

There is clear yellowing of the hBN powders, but the crystals are less obvious. Even in transmission micrographs (Figure 5.13c, d) the color difference is barely noticeable in the crystals. There is no evidence that the crystals were doped in either Raman or XRD (Figure 5.14).

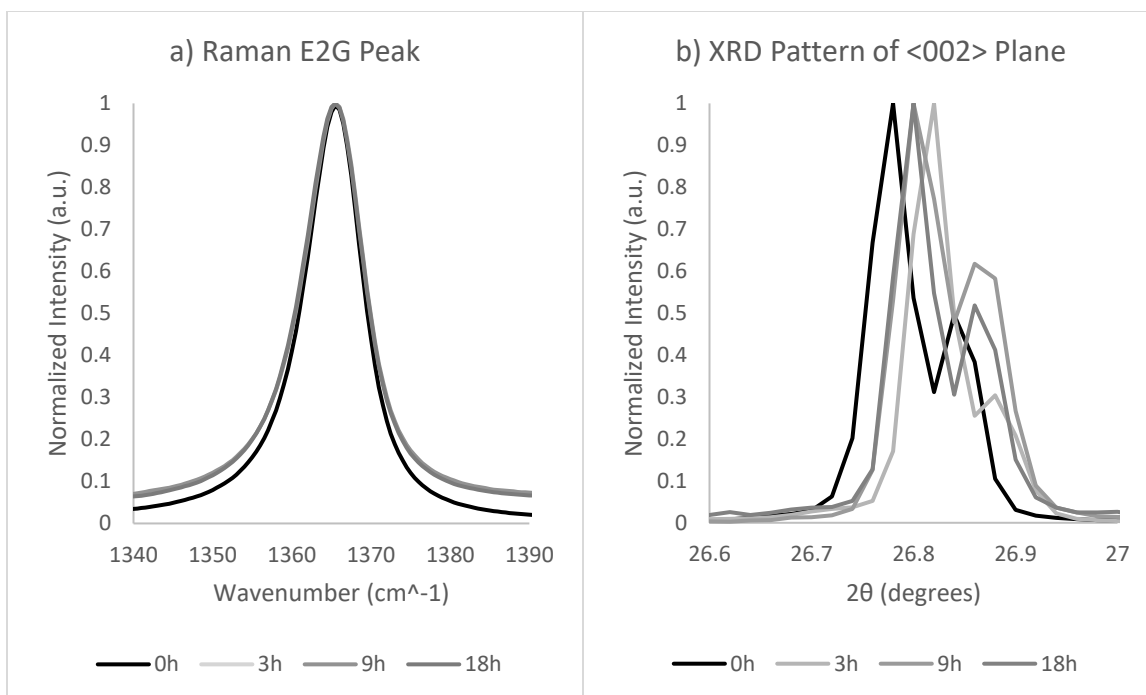


Figure 5.14. (a) Raman spectra and (b) XRD patterns of hBN:C crystals via diffusion for different annealing times.

The Raman spectra for the hBN:C crystals did not change, perhaps the annealing process improved intrinsic defects while incorporating carbon. Contrary to the flux doped samples, there is no new peaks at 1330 cm⁻¹, which may imply the presence of different defects or retention of high-quality crystal structure. The XRD patterns show a slight decrease (-0.02°) in layer spacing from the pristine sample indicating that the crystal underwent minor change. However; with increasing annealing time, the peaks did not change correlatively. This was similar in the case of the surrounding hBN powders used as an indicator however, the XRD showed significant differences from the pristine powder.

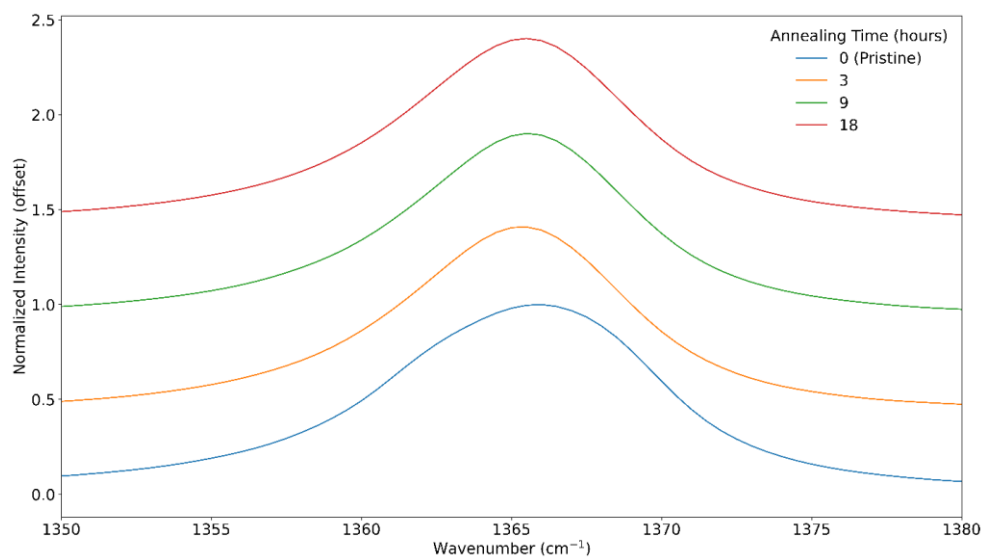


Figure 5.15. Raman spectra of hBN:C powders with varying annealing times at 1700 °C.

There isn't much change in the Raman spectra for the powders. There's some change in symmetry of the E_{2G} peak from annealing, likely due to recrystallization at such high temperatures.

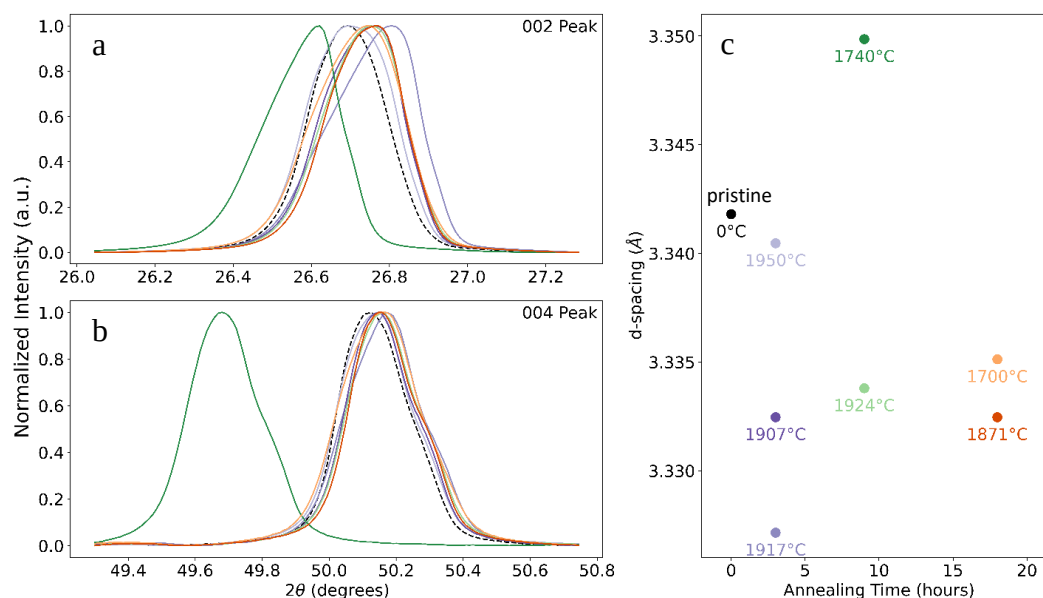


Figure 5.16. (a) $\langle 002 \rangle$ and (b) $\langle 004 \rangle$ XRD patterns of hBN:C powders with varying annealing times. (c) Colors correspond to annealing duration (purple, green, and orange are 3, 9, and 18 hours, respectively) and tones correspond to temperatures (lighter tones are higher temperatures).

In Figure 5.16, there is significant change in both shape and position of the 002 peak. After 3 hours of annealing the shape skews right and the d-spacing changes by 0.017 Å. Further annealing seems not as effective suggesting that there is a maximum amount of change the powders undergo at these conditions. The XRD 002 peaks become very asymmetric with higher

temperatures annealing indicating a structural change. This shift corresponds to the changes in d -spacing further illustrated in Figure 5.16c. The d -spacing calculated shows an overall decrease with annealing which indicates significant change crystallinity. Graphite and hBN are homologous, but their $\langle 002 \rangle$ d -spacing is slightly different: 3.35 Å for graphite and 3.34 Å for hBN. With annealing hBN:C powders exhibit transitions to lower d -spacing which suggests these carbon dopants are reducing the interlayer spacing like what was observed in graphite doped with Si.

Furthermore, it is of interest to learn how the annealing changed the composition of these powders, hence inert gas fusion (IGF) measured the carbon and oxygen content of the powders. The results of the IGF are in Figure 5.17.

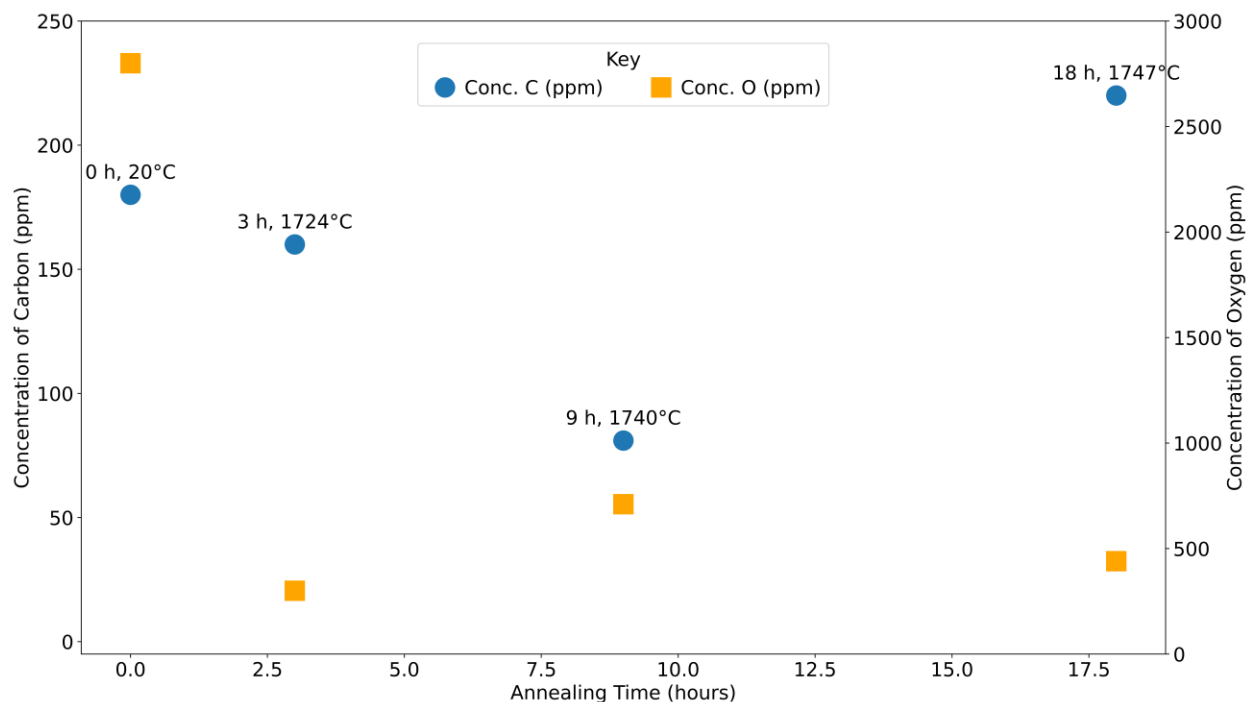


Figure 5.17. Inert gas fusion analysis on hBN:C powders annealed in a carbon-rich environment for carbon (blue) and oxygen (orange).

The reason oxygen is measured is to understand if there is co-doping of both oxygen and carbon seen in previous experiments [198]. The pristine powders showed the highest oxygen concentration and a relatively high carbon concentration. The oxygen concentration decreased significantly with annealing. The carbon concentration in the hBN powder increased with the annealing time. The high concentrations of carbon and oxygen were suspected to be surface

adsorbates. Therefore, Brunauer-Emmett-Teller (BET) surface analysis was performed after vacuum annealing for 4 hours at 300°C (Figure 5.18).

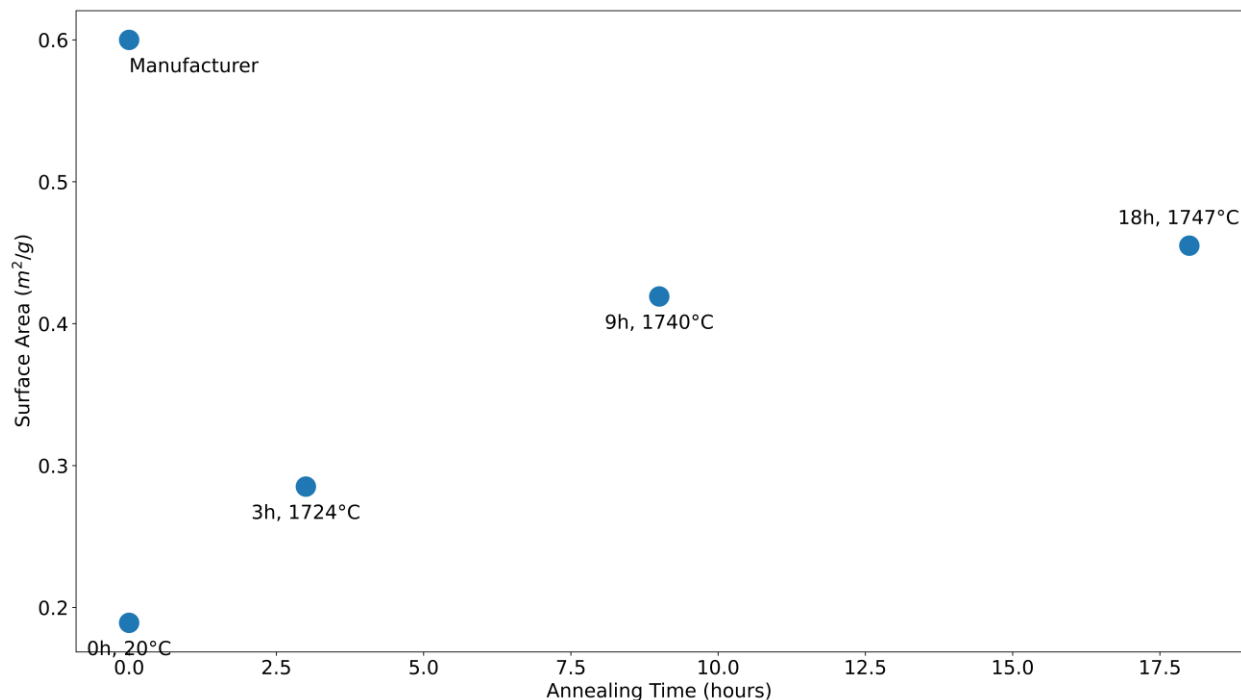


Figure 5.18. BET analysis of hBN:C powders with annealing temperatures and time annotated. The hBN powder manufacturer reports a surface area of 0.6 m²/g, while the measured value is a third of that. This may be due to the storage conditions of the hBN powder. However, this may account for the high concentrations of C and O in the pristine powder. There is slight increase in surface area with annealing time with more carbon incorporated on the surface. As the surface area increases with up to 9 hours of annealing, there may be a chemical passivation of the hBN powder surface reducing the amount of atmospheric oxygen physisorbed, explaining the lower oxygen concentrations.

Spectral Characterization

hBN:C powders were shared with collaborators for cryogenic micro-PL using 196nm excitation. The results of which are in Figure 5.19.

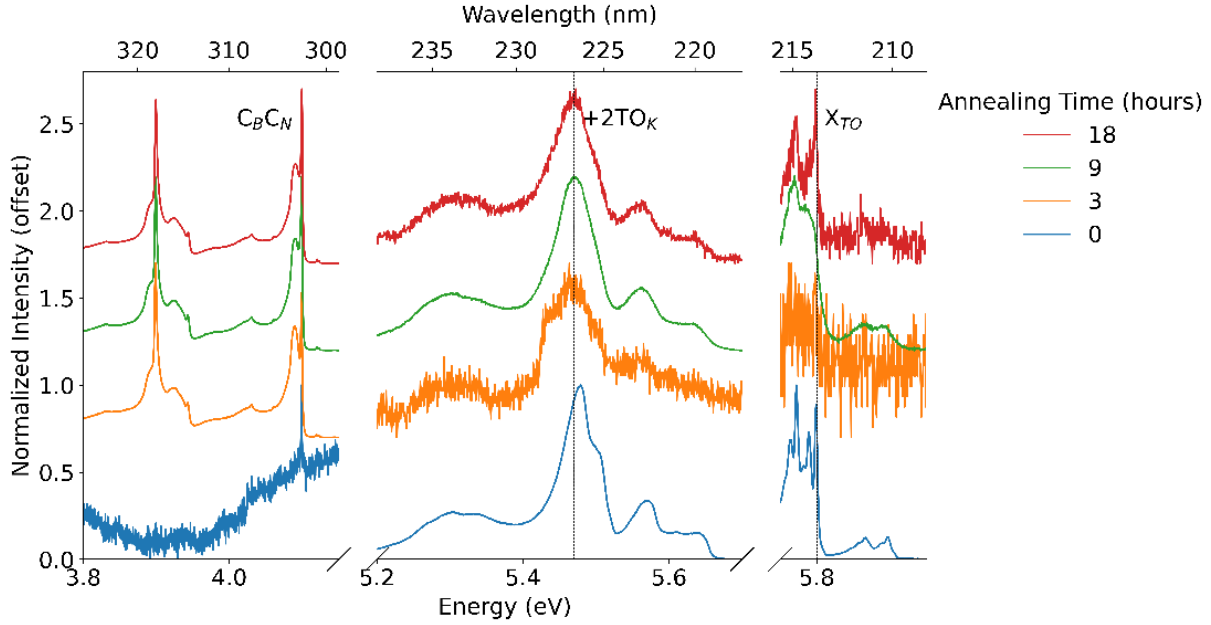


Figure 5.19. 8K 196nm excitation PL spectra of diffusively doped hBN:C powders for varying annealing times.

Again, the familiar intrinsic peaks appear at energies greater than 5 eV with a lower intensity than the hBN crystals. After annealing in a carbon-rich environment, the 4.1 eV peak associated with the carbon dimer appears once more as well as the 3.9 eV. Note that neither of these peaks are present in the pristine powder. Grain boundaries result in SW defects like those shown in Figure 3.4f. The hBN powders consist of 50 μm diameter ellipsoidal particles with small crystallite sizes. These crystallites are terminated around their perimeter with edges of dangling bonds. When annealed these dangling bonds at the edges result in irregular bonding behavior such as SW defects. Carbon defects further stabilize these SW defects resulting in a higher density of them leading to the PL signature at 3.85 eV [153]. These defects appear with as low as 3 hours of annealing, indicating a more time efficient way of creating hBN:C than flux doping, but no new defects appeared.

Carbon doping via ion implantation

Ion implantation is a common method of producing useful defects in silicon [370], diamond [371] and other materials [372]. With the abundance of elements that can be delivered via ion implantation, carbon among them, hBN was postulated to host similar defect states within its wide bandgap. A common problem with carbon doping via flux is carbon clustering, limiting what

defects can be made with thermodynamically governed doping processes. Carbon will typically cluster in dimers [189] or other chains with each other more favorably as observed in flux and diffusion. Therefore, ion implantation overcomes the solubility limit of carbon in hBN inducing substitutions with the appropriate acceleration or implant species. The single carbon substitution on either a boron (C_B) or nitrogen (C_N) site can create *n*-type or *p*-type doping in boron nitride, respectively. Both are considered extremely challenging [373],[374] while retaining high quality crystal. Hence it is highly desirable.

To investigate *n*-type doping via C_B defects, $h^{10}BN$ flakes (~5 microns thick) pressed onto a silicon wafer were sent to Los Alamos National Lab for ion implantation using a ZEISS 200 kV Ion beam implanter. The resulting flakes were then characterized using Raman, XRD, and PL.

Visual and Structural Characterization

Contrary to the previous doping methods, the flakes did not change in appearance. This was anticipated because the implantation process was predicted to only penetrate the top 50 nm which would likely not cause a change in the bulk appearance. Microscope images are provided in Figure 5.20.

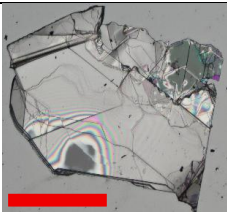
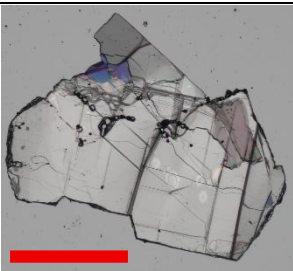
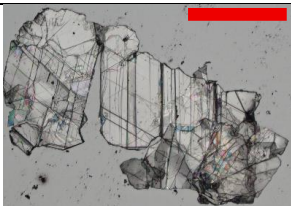
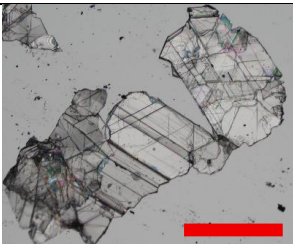
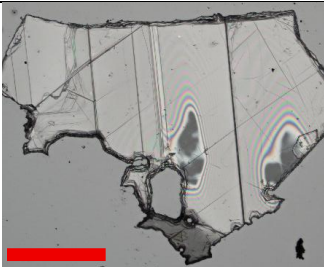
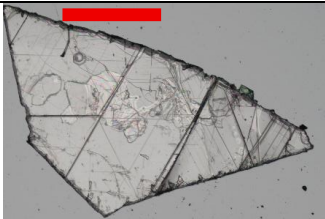
Before Implantation	After Implantation	Implant Species
		$^{12}\text{C}^+$
		$^{12}\text{C}^+ \text{}^{11}\text{B}^+$
		$^{12}\text{C}^+ \text{}^{14}\text{N}^+$

Figure 5.20. h^{10}BN flakes before (left) and after (right) implantation with the specie(s) listed. Scale bars are 500 μm .

Structurally speaking, the ion implantation did not induce significant damage to the lattice. This is reflected in the Raman spectra and XRD diffractions patterns presented in Figure 5.21.

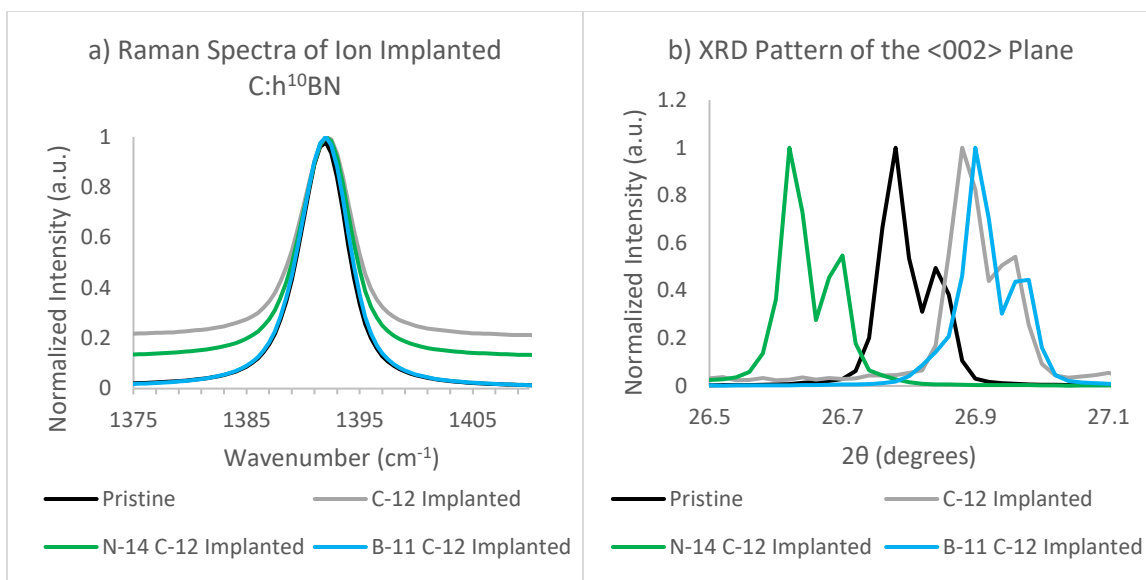


Figure 5.21. Raman spectra and XRD patterns of hBN:C via implantation for different implant species.

After ion-implantation, the h¹⁰BN retained the same peak position (1394 cm⁻¹) and did not develop any new peaks in Raman. Interestingly, the XRD pattern shifts to lower angles in the nitrogen plus carbon implanted sample and to higher angles in both the carbon and carbon plus boron samples. This would indicate a form of swelling similar to that seen in the irradiated section (Figure 4.4). This implies that the nitrogen co-implantation induced different structural defects, but not necessarily different spectral defects. The opposite can be said for the remaining implanted crystals. This could imply that the nitrogen species are more likely to be stopped in between planes whereas those without nitrogen cause the layers to compress. Whether this is due to the newly created defects or general damage due to the atomic size remains unclear.

Spectral Characterization

After ion implantation, 5 flakes of h¹⁰BN:C were examined under room temperature 532nm laser photoluminescence. The results of which are shown in Figure 5.22.

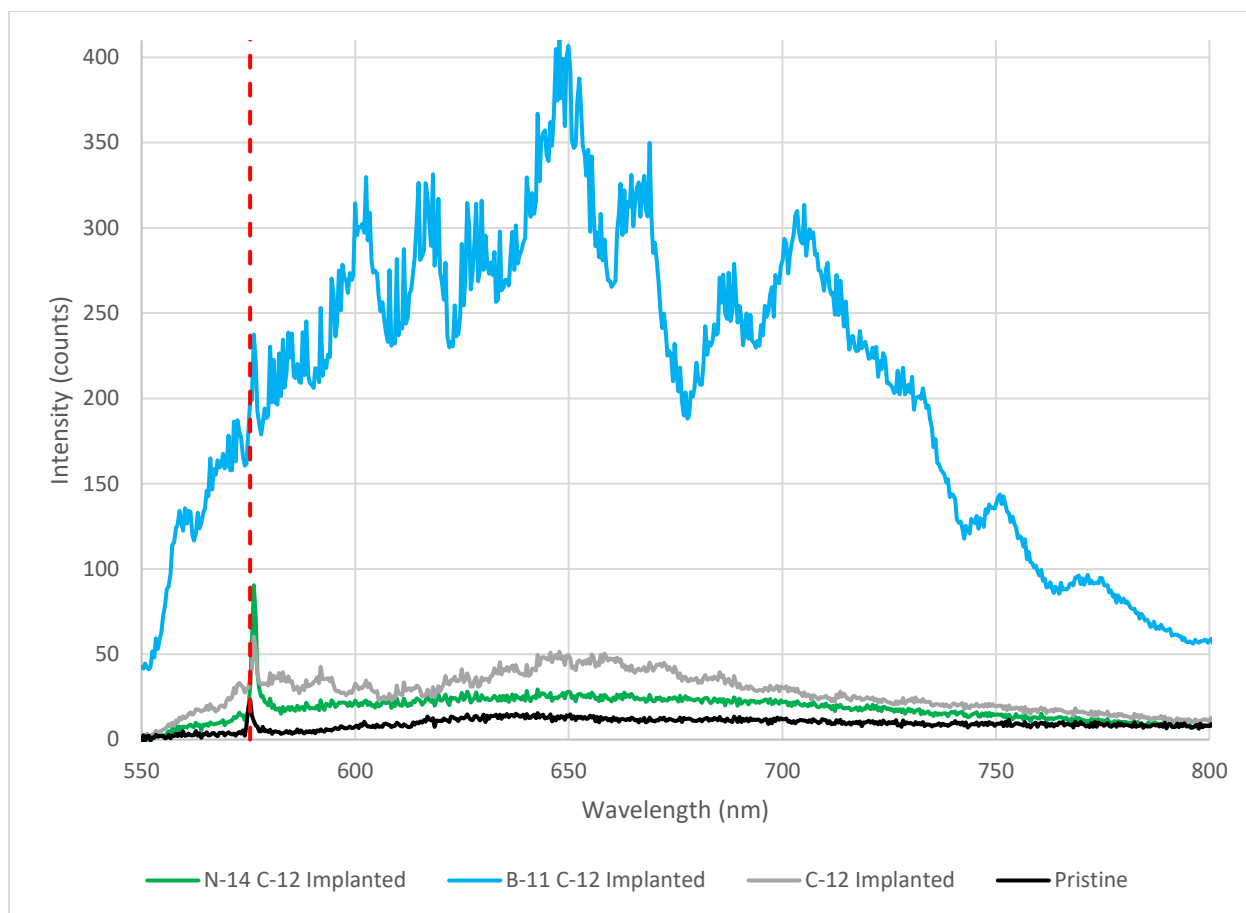


Figure 5.22. 532nm Excitation Room temperature PL spectra of pristine (black), carbon implanted (gray), nitrogen plus carbon co-implanted (green), and boron plus carbon co-implanted (blue) $h^{10}BN$. The red line indicates the intrinsic emission of hBN at 575 nm (E_{2G} vibration).

Several peaks appear in the implanted samples indicating that there are many defects absent in the pristine sample. Despite the similarity in oscillations in these spectra, they are very dim relative to the boron implanted sample. This means that boron ions are causing displacements with higher photonic activity. Appendix Table C.1 cannot be used to assign these individual peaks due to convolution and overlapping emission wavelengths for more than one defect. However; ion implantation can lead to several defects that are different from those produced with flux or diffusion doping.

Conclusion and Contribution

In conclusion, carbon defects in $hBN:C$ were explored with variety of techniques. Through low temperature deep UV PL, the primary and most stable defect formed in both flux and diffusive doping was the carbon dimer ($C_B C_N$). To repeatably make this dimer in the lowest amount of time

and without hindering the crystal growth process, it is recommended to use the diffusion method. In as little time as 3 hours, hBN begins to dope with this dimer. If defects beyond the dimer are desired, more energetically involved processes are required. Ion implantation resulted in much more diverse carbon-related defects than thermodynamically governed doping processes. If the fluence can be more spatially controlled in the future, this method would prove the most effective. This dissertation demonstrated that the dimer also stabilized SW grain boundary defects. With increasing presence of these dimers, the PL signature at 3.9 eV became more evident. This suggests that carbon dimers may tend to localize themselves near grain boundaries which is apparent in room temperature PL mapping. However, there is still potential for other defects that are both single photon emitters and magnetically sensitive due to the doping demonstrated here.

Chapter 6 - Suggestions for future investigations

Graphite dopants

As mentioned in Chapter 2, there are other dopants of interest that could be attempted in graphite such as Zr or Ti. These are fairly temperature resistant metal dopants that may be as facile as adding them to the flux like boron doped graphite. There is also the investigation of doping graphite with nitrogen and silicon. While the more bulk characterization methods did not explicitly conclude on the incorporation of silicon into graphite crystals, other analytical techniques such as SIMS or glow discharge mass spectroscopy (GDMS) may provide that answer.

Allotropes of hBN

Many researchers have expressed interest in rhombohedral boron nitride (rBN) which is layers of hBN in a 3-layer period (ABC) stacking structure. While attempts using solvents to mimic the foil used by Qi *et al* [375] using Fe and Ni in tandem with solid-state diffusion of boron or hBN powder, there was little evidence in XRD or the lower Raman modes. Additionally, it has been shown recently that our method can produce rBN in small quantities [376] and somewhat uncontrollably. It was also a possible result of the hBN:C flux method [377], but not observed.

Similarly, Bernal BN (bBN) is sought for its potential role in single harmonic generation (SHG) [378]. SHG is the conversion of low frequency waves to higher frequency at the expense of reduced intensity. SHG is a fundamental technique employed in most laser sources hence if bulk bBN can be produced, UV lasers can become more compact and enhance on-chip SHG photonics. Preliminary studies have shown that rBN growth can be done with APHT, however, the consistency and distribution remain to be investigated.

Doping hBN

As mentioned in Chapter 5, *p*-type doping of hBN has rarely been observed without sacrificing crystal quality [379]–[384]. Therefore, it is something to further investigate with different forms of magnesium to minimize vapor pressure and keep it in the flux. Additionally, there are other defects of interest for SPEs proposed by theory [342] giving a diverse set of experimental directions for creating these defects in bulk hBN. Since a large portion of the potential impurities are significantly larger than the B and N constituents of hBN, large spaces must be made to accommodate them. Performing this kind of structural change in flux growth hBN is thermodynamically unfavorable. Therefore, using the neutron irradiated $h^{10}\text{B}^{15}\text{N}$ from higher neutron fluences may serve as an acceptable platform to incorporate these impurities. Annealing at higher temperatures will help form the bonds necessary to incorporate these larger elements.

Junctions for devices

Compositional junctions are necessary for modern electronic devices. Since hBN is difficult to *p*-dope, it would be beneficial to create heterojunctions with conductive materials. In many heterostructures hBN can be a tunneling medium for electrons [385],[386]. Some in-plane junctions of hBN and graphene have been fabricated as well [387]–[389]. Depicted in Figure 6.1 is an example of such devices fabricated in 2012. Some of these films are stacked while aligned and others perpendicular (cross-junction in Figure 6.1b, yellow) to observe the through plane electron transport.

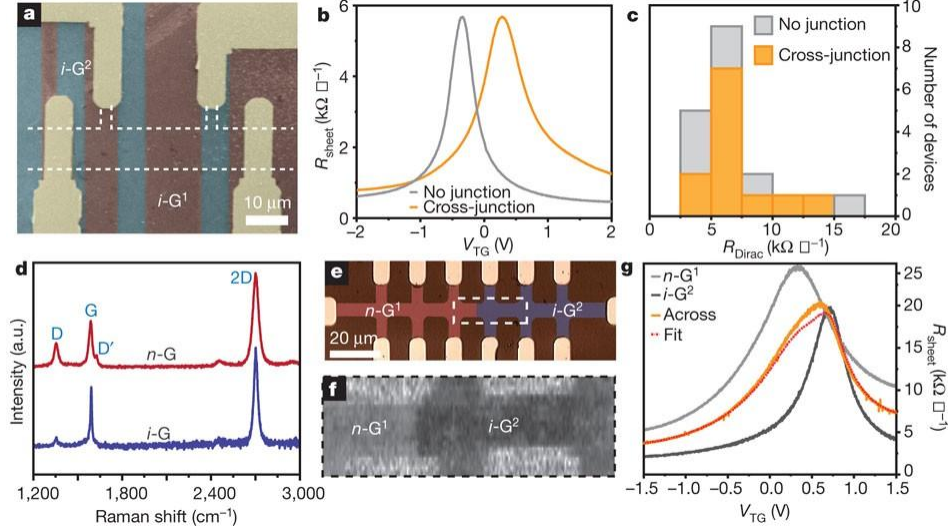


Figure 6.1. (a) SEM image with false-color overlay of an $i\text{-G}^1$ (red)/ $i\text{-G}^2$ (blue) cross-junction device before patterning. The final device area is indicated by the dashed lines. Cross-junction devices contained 1–4 junction regions. (b) Four-terminal top gate (TG) dependence for devices without (grey) and with (orange) $i\text{-G}^1/i\text{-G}^2$ junctions, showing very similar peak resistances. (c) Histograms of Dirac-point sheet resistance (R_{Dirac}) for devices with and without junction regions. (d) Raman spectroscopy of n -doped ($n\text{-G}$) and $i\text{-G}$ growths (both synthesized in second step in order to allow direct comparison). (e) Optical image with false-color overlay of a heterojunction device. (f) Two-dimensional Raman mapping of the ratio of the integrated D' and G peaks for the boxed area in (e). (g) Gate dependence of the junction region shows good agreement with an area-weighted average of the homogenous regions (red line, $\Delta R_{\text{junction}} \approx 0.15 \text{ k}\Omega \mu\text{m}$) [387].

These devices permit the free flow of electrons confined to the graphene lattice or deep UV emitting films for sterilization. If bulk materials could be synthesized with these junctions, it would greatly expedite device production and with isotope enrichment, could further diversify their applications. Additionally, doping these films (Figure 6.1d, e) expands their applications.

Apart from heterojunctions, hBN HPhPs permit strong optical anisotropy [390] and total internal reflection at certain face angles [391]. Its large bandgap allows coupling over a large spectral range with lattice vibrations minimizing losses. The manipulation of the isotopic composition can be used to geometrically control light at sub-diffraction level [44]. For instance, h^{11}BN interacts with light differently than h^{10}BN . If a structure of these two isotopically enriched materials can be made in alternating atomic layers, it would permit high control of light through

the c -plane of the $h^{10}\text{BN}$ layer [392]. Similarly, changing the nitrogen isotope allows the same in-plane control creating in-plane waveguides for certain wavelengths. Investigations measuring this phenomenon through s-SNOM show that such control is possible.

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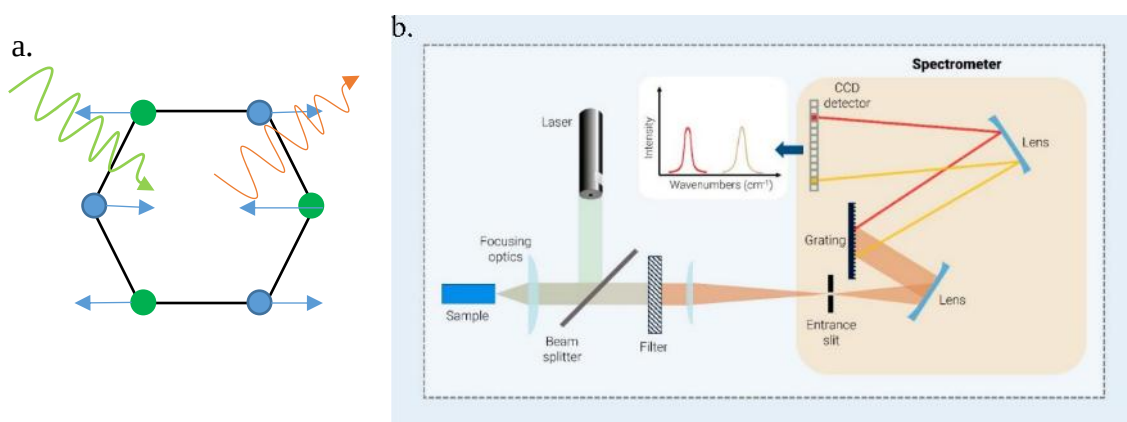
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Appendix A - Analysis Techniques

In this section, the characterizing and analytical techniques brought up in this document are further explained for convenience of the reader. Informational graphics illustrate the mechanism of the measurement and a typical setup for the instrument performing the measurement are also supplied.

Raman Spectroscopy

Raman spectroscopy detects bond type, sp^2 or sp^3 , concentration of specific isotopes, ^{10}B or ^{11}B , and extended defects such as dislocations and grain boundaries of a material (by using the FWHM of the characteristic peaks). Raman spectroscopy is an optical characterization technique by way permeating a material's surface with photons. These photons induce vibrations in the material's bonds detracting from their incident energies. The resulting photons are reemitted back into the optical collection and separated by their wavenumber. The wavenumber is a vibrational frequency used to identify materials, and the uniformity of these vibrations corresponds to the quality of the material. A limitation of Raman spectroscopy is that it does not assess impurity concentrations. A cartoon to illustrate the process is presented below in Appendix Figure A.1.

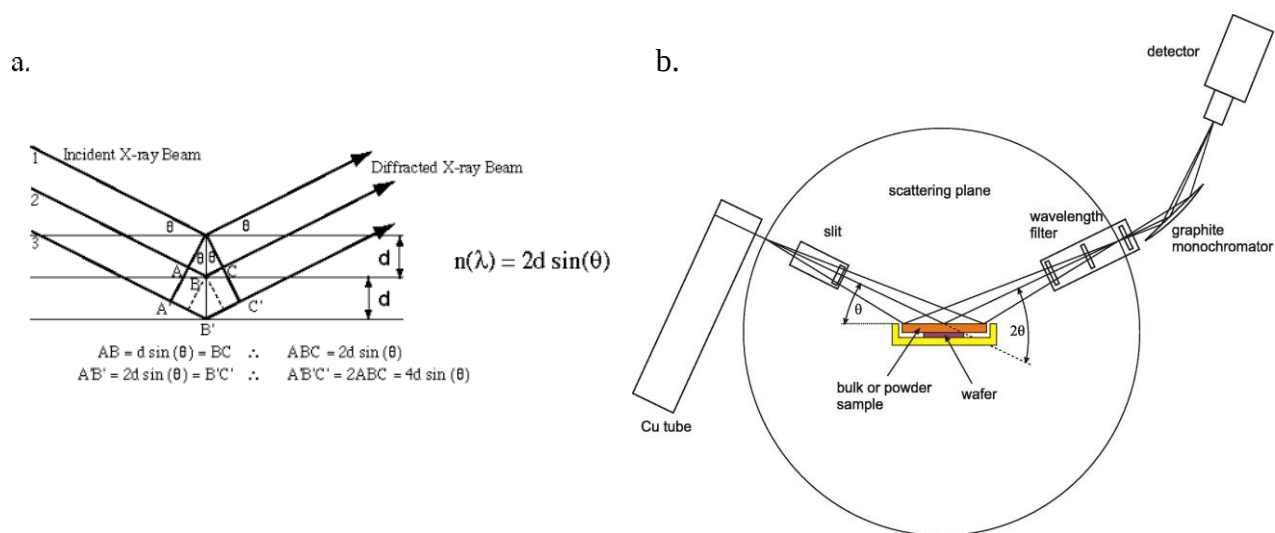


Appendix Figure A.1. (a) Schematic of Raman Scattering in hBN with green incident laser and directional vibrations corresponding to the E_{2G} motion producing an detectable wave (orange) that is passed through the (b) Raman spectrometer [393]

In this dissertation, Raman spectroscopy was used to measure the phase purity of graphite (whether there is sp^3 bonded carbon) and the relative concentration of carbon, boron, and nitrogen isotopes. It was also used to measure the quality of the crystals using the FWHM of the characteristic peaks (G-peak and E_{2g} for graphite and hBN, respectively).

X-Ray Diffraction

X-Ray diffraction is an optical characterization technique in which x-ray wavelength light travels through a sample. Some of the light is diffracted by the constituent atoms at certain angles relative to the x-ray source and detector. As the light is diffracted, a rotating detector collects the diffracted light strongly at certain angles where the x-rays strongly reflect off of crystal planes. Depending on the crystal structure, the angles of high intensity diffraction occur at predictable locations. Below in Appendix Figure A.2a is an example of using Bragg's law (Eqn. 2.1) to approximate interlayer spacing in a crystal structure. The Bragg-Brentano XRD configuration is also shown.

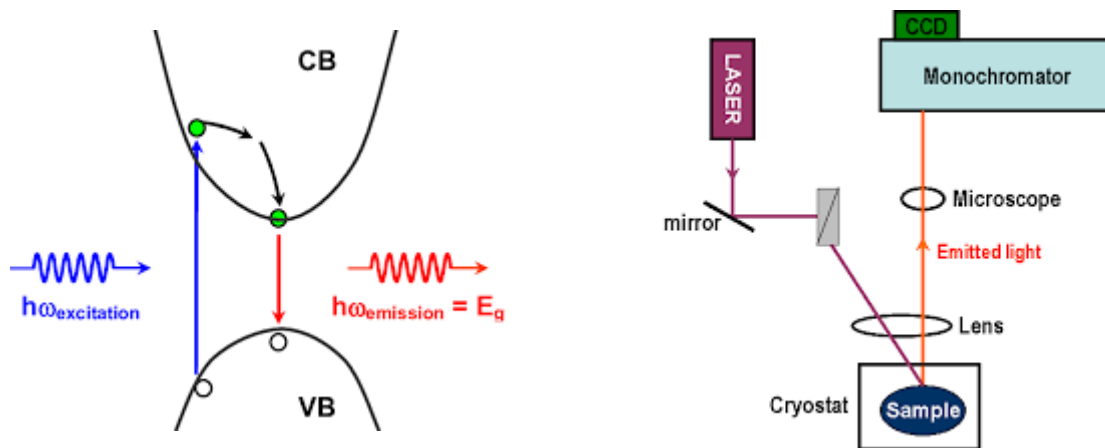


Appendix Figure A.2. (a) Schematic of x-ray diffraction measurement mechanism [394] (b) X-ray diffractometer design [395] where the source (copper tube) producing 1.54 Å x-ray waves is rotated synchronously with the detector around the sample resulting in a 2θ motion.

XRD was used to characterize the crystal quality of the materials studied. Since both crystals (graphite and hBN) are hexagonal, the diffraction pattern consists of strong peaks for the 002, 004, and 006 planes. The 002 plane was the primary plane considered for large crystals due to its intensity. XRD verifies the phase purity of these materials with the detection of stacking order and other allotropes of carbon or boron nitride.

Photoluminescence

Photoluminescence is the emission of photons that have been excited by high energy incident photons that are *typically* above the band gap of the material. The material redistributes the incident energy; the emission is at lower energy than the incident light. This allows the detection of key properties of the sample such as: band gap, excitation lifetime, and electron relaxation time [396]. These properties are vital to understanding the potential roles that the material can play in larger assemblies.



Appendix Figure A.3. Mechanism of photoluminescence [397] with incident blue light exciting an electron from the valence band (VB) to the conduction band (CB) where it will lose some energy and fall to the lowest energy level of the CB before emitting the remainder of its energy as a red photon. Typical PL equipment setup [398] consisting of a source laser, mirror, and monochromated coupled-charge detector (CCD).

In this dissertation, deep ultraviolet photoluminescence was performed by our collaborators at Montpellier University in France. They used an incident laser wavelength of 196nm, and the spectra were taken at temperatures of 8 Kelvin. New features appeared due to carbon-related impurities in hBN:C at ~4.0 eV revealed by these measurements.

Optically Detected Magnetic Resonance

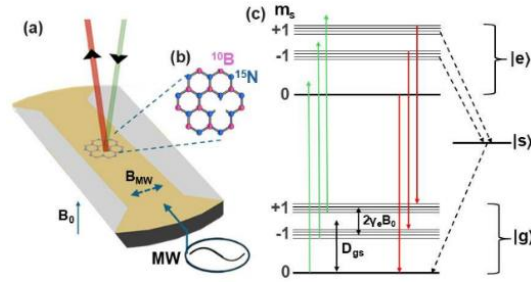
Optically detected magnetic resonance (ODMR) is used to detect magnetic sensitivity in materials using light. First PL lasers excite electrons to one single state also known as population inversion. Then, an external magnetic field is applied to the material with another magnet or a coil. This causes the excited electrons to have non-degenerate excited energies. ODMR uses microwaves to cause the excited electrons excited to oscillate between nondegenerate energy levels split via the Zeeman effect and further exacerbated by the external magnetic fields. The difference between the photoluminescence emitted with and without the microwaves (reference) active and normalized by the reference signal is known as contrast. This is provided in the formula below:

$$\frac{I_{MW}[\text{counts}] - I_{REF}[\text{counts}]}{I_{REF} [\text{counts}]} * 100 = \text{Contrast} [\%]; \quad (\text{A.1})$$

I_{MW} – photoluminescence with microwaves on

I_{REF} – photoluminescence with microwaves off

Using the same microscope as PL, microwave transmission is added in the form of an antenna or co-planar waveguide.

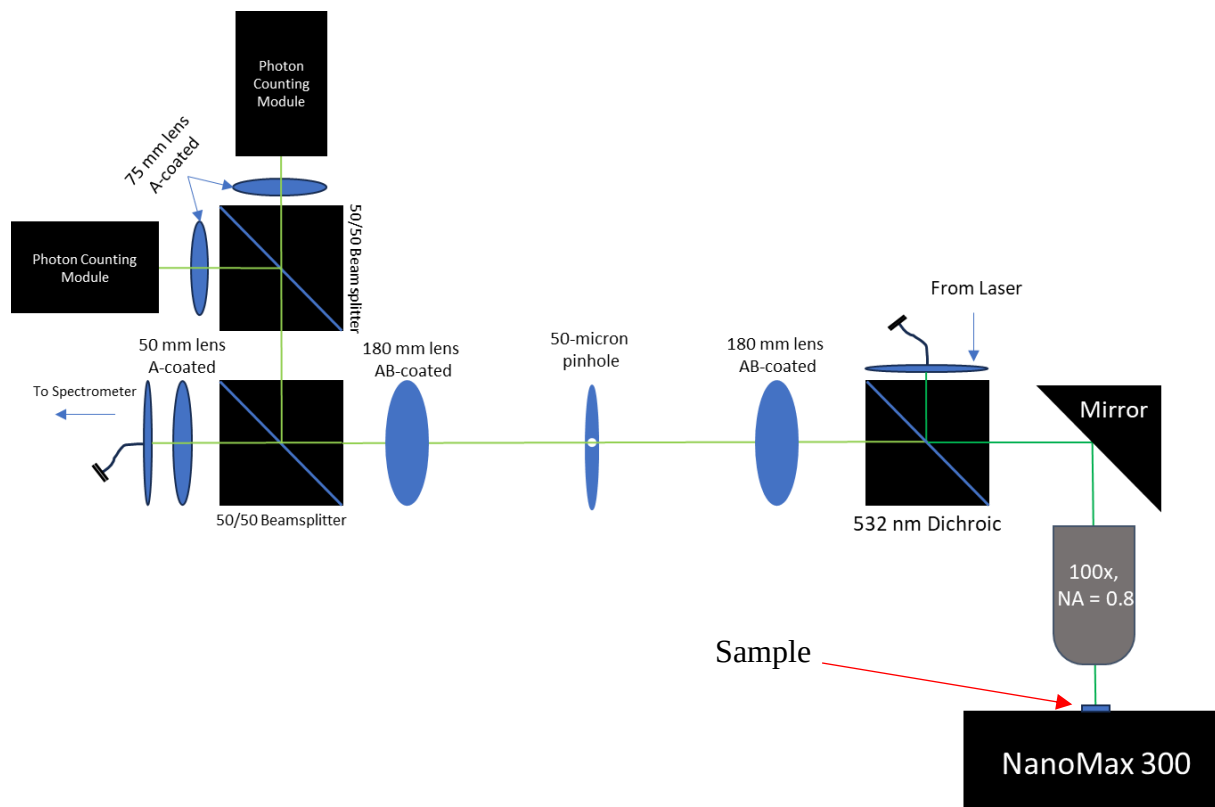


Appendix Figure A.4. Diagram of ODMR measurement setup and mechanism of optically detected magnetic resonance and typical PL equipment setup [367],[399]. (a) An incident green laser shines onto a negatively charged boron vacancy (V_B^-) and emits a red light. An external field (B_0) perpendicular to the V_B^- . Microwaves (MW) are supplied through the gold waveguide that cause oscillations between the $\pm 1 \rightarrow 0$ excited states. (b) A diagram of the V_B^- structure in $h^{10}B^{15}N$. (c) Energy diagram of the V_B^- where green arrows indicate the excited (e) transitions and red arrows indicate the emission de-excitation transitions to the ground state (g).

These singlet states are electron spin transitions from the $-\frac{1}{2}$ to the $+\frac{1}{2}$ spin state indicated by a single peak in contrast. Triplets see two peaks in ODMR due to the 0 to ± 1 spin states. Sometimes there is a combination of the two due to excitation areas encompassing more than one defect. In this dissertation, ODMR was used to detect the magnetic sensitivity and the duration of the population inversion of the negatively charged boron vacancy (V_B^-).

Single Photon Emission (Hanbury Brown Twiss)

To resolve emissions on the scale of single photons, normal PL methods are employed for excitation; however, the emitted photons are collected in a particular way. After excitation, the excitation source (laser) is closed, and the emitted photons are collected along a light path consisting of several filters to only permit photons of the energy/wavelength of interest.



Appendix Figure A.5 – Confocal PL microscope setup with single photon counting capabilities. From emission source atop the NanoMax 300 piezo sample stage to the detectors: a laser is passed through a notch filter for its wavelength followed by a corresponding short-pass dichroic. The beam is reflected through a 100x 0.8 NA microscope lens. The emission is sent back through the lens and reflected through an AB coated lens and reduced through a 50 μm diameter pinhole onto another AB coated lens. The emission is then split through a 50 mm A-coated lens to a spectrometer to record its wavelength. The other half of the emission is sent through another beam splitter to two avalanche photodiodes (APDs) each through a 75 mm A-coated lens. The filters result in an operating spectral range of 532-700 nm [400].

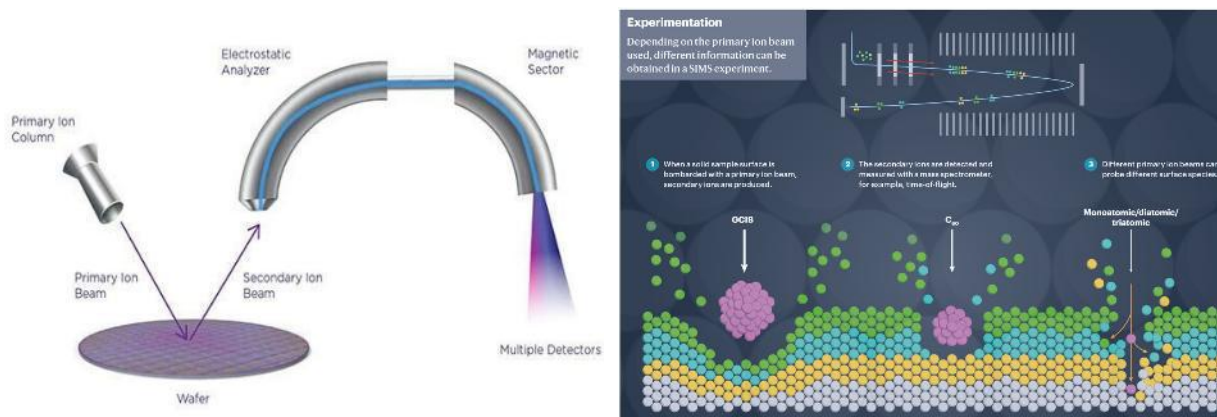
In Appendix Figure A.5, light emitted from the sample passes through several apparatuses reducing its intensity greatly. This is to make the time tagging for higher order photon correlation (g^2) compatible with the processing speed of the APDs. The Hanbury Brown Twiss method

involves measuring photons that are nearly isochronous being split between the two APDs. For single photon emissions, the time difference will drop to almost zero, indicating a single photon emitter.

In this dissertation, single photon emission was measured on both bulk and exfoliated to <100 nm hBN flakes to located single photon emitters. Bulk flakes proved too intense for the APDs, hence they needed to be exfoliated to reduce intensity. To take such measurements, PL maps were recorded across 20+ exfoliated flakes. Then, the collection radius was narrowed to the focal center of the 100x magnification objective. Lastly, photons were counted for 2 hours to assure the photostability of the emitter.

Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) destructively measures the composition of a material. SIMS involves sputtering the surface of a material with high energy ions [401]. As the surface is ablated, the particles are scattered and filtered into a detector for concentration approximation. Time of Flight (ToF) is based on how long the secondary ions take to reach the detector.



Appendix Figure A.6. Diagram of SIMS measurement setup [402] and mechanism of SIMS [401].

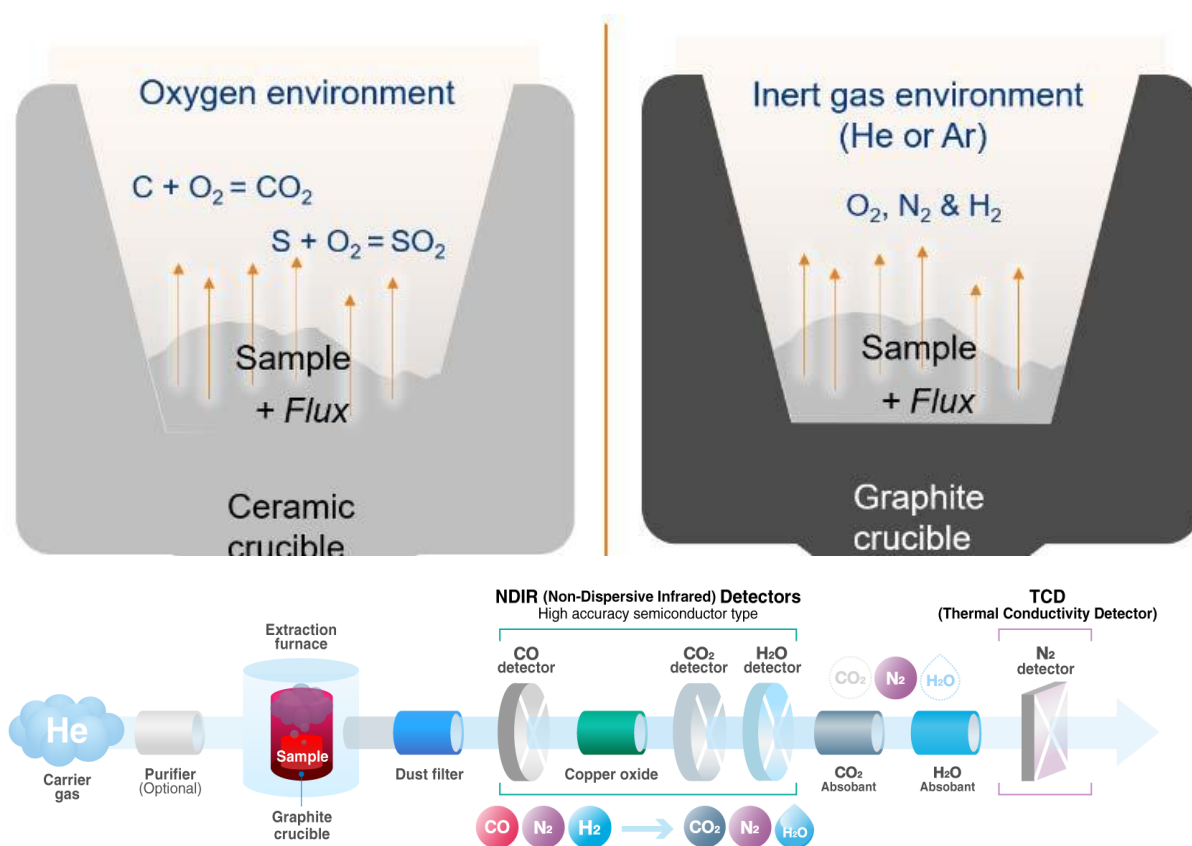
In Appendix Figure A.6, energetic ions impact a material causing ablation of the constituent atoms. These are then sent to a mass spectrometer. In the case of ToF, it is time based, where heavier ions are detected at longer times than smaller species and collects information in batches of sputtered materials. In dynamic SIMS, the ion beam is continuous and detects primarily lighter ions due to

the destructive nature of the technique reducing the information to only elements and their concentrations. ToF is also limited to relative abundance, but dynamic SIMS can measure exact concentrations with appropriate calibration.

In this dissertation, this technique was used to measure the concentration of lithium-7 in neutron irradiated $h^{10}B^{15}N$.

Inert Gas Fusion

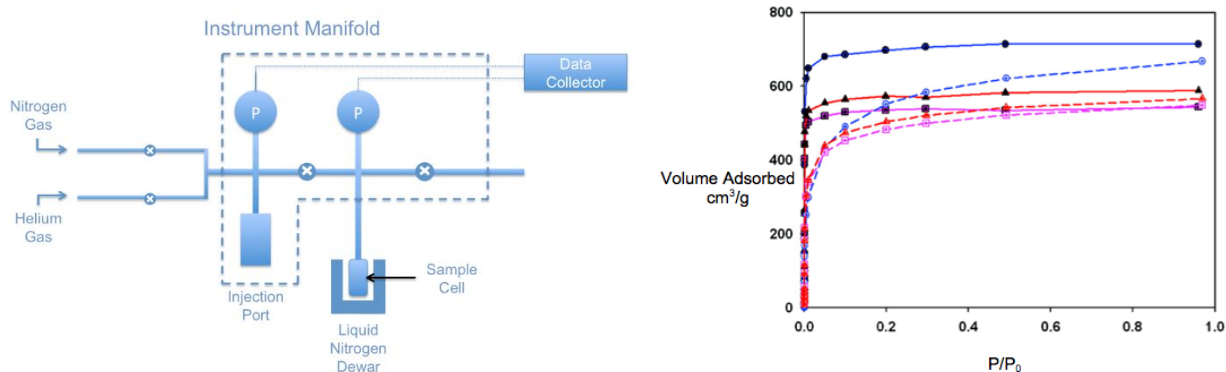
Inert gas fusion (IGF) is a compositional analysis technique used to measure the concentration of light organic elements such as sulfur, carbon, or oxygen. A mass of sample material is set inside a ceramic or graphitic crucible and heated under an oxygen or argon atmosphere. Under oxygen, sulfur or carbon react to form SO_2 and CO_x respectively. These gaseous products are sent through a series of detectors, and their concentration is measured over time. Once the sample is completely evaporated, the concentration is integrated over time to get the total concentration. A schematic for the measurement is provided in Appendix Figure A.7



Appendix Figure A.7 – Non-dispersive infrared detected inert gas fusion reaction schematic for carbon/sulfur and oxygen [403]. Measurement flow diagram for concentrations of resulting molecules [404].

Brunauer-Emmett-Teller Analysis

Brunauer-Emmett Teller analysis (BET) is often used to measure the active surface area and pore structure in catalytic materials. An inert gas (He, Kr, or N₂) is physisorbed onto the surface and diffuses into the pores of a sample. The gas molecules will absorb and occupy the available surface area with a preference for catalytically active sites. Samples are put under vacuum and heated to remove any currently adsorbed gases. After outgassing for 3-24 hours, the samples are loaded into the adsorption chamber under vacuum. Then the analytical gas is slowly introduced into the sample chamber. Gas that is absorbed will not leave the chamber, while the rest is exhausted to a waste vacuum chamber. A sensitive flow meter measures the outlet flow, and the difference is what is absorbed by the sample. Using an equation of state for the analytical gas, the volume adsorbed is converted to a monolayer area using a Langmuir adsorption isotherm plot giving an equivalent area for the gas adsorbed. An illustration of the instrument flow as well as the Langmuir isotherm is provided in Appendix Figure A.8.



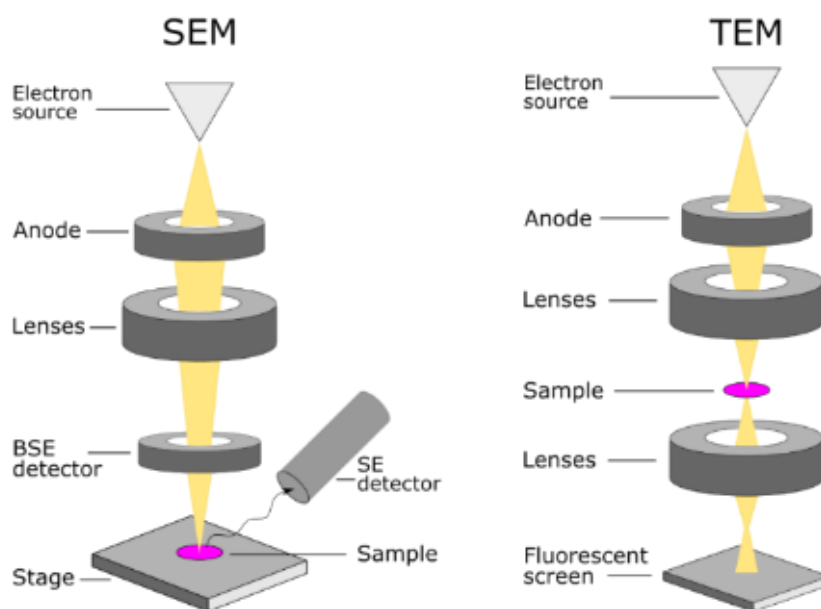
Appendix Figure A.8 - BET Mechanism and Langmuir adsorption isotherm plot.

The pressure ratio is only considered until saturation. The monolayer capacity is calculated from this curve. Then the reciprocal of the monolayer capacity is used to calculate the active surface area of the sample [405].

In this dissertation BET, was used to measure the active surface area of hBN powders as a function of annealing time.

Scanning/Transmission Electron Microscopy

Microscopes and optical systems are diffraction limited; therefore, to get resolution beyond this limit, electrons are used to visualize surfaces. Electrons are accelerated and focused to a point on the sample surface. In scanning electron microscopy (SEM), the electrons are deflected to both a backscattering (reflection) detector (BSE) and a secondary detector (SE). The BSE detects electrons that penetrate the material whereas SE detects lower energy electrons deflected from the topography of the material. Transmission electron microscopy (TEM) is similar except the sample is thin and mounted over the detector. The sample thickness is sufficiently low such that most electrons pass through to another detector below the sample.

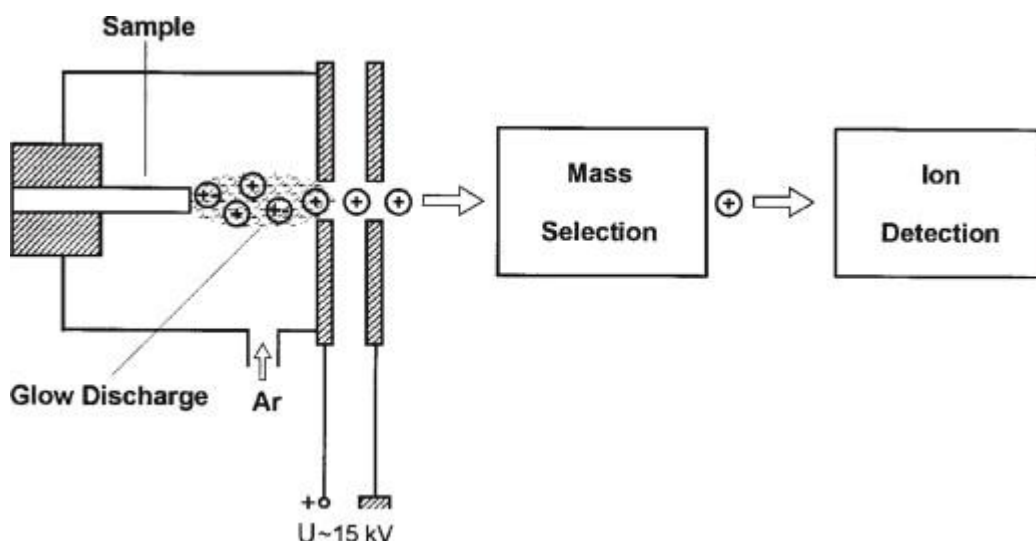


Appendix Figure A.9. Diagram of S/TEM measurement setup [406].

In this dissertation, SEM was used to visualize small features in greater detail possible than in optical microscopy. These features include the etch pits shown in Chapter 2. TEM was used to visualize crystal structures of $h^{10}B^{15}N$ after neutron irradiation both in-plane and in cross-section.

Glow Discharge Mass Spectroscopy

Glow Discharge Mass Spectroscopy (GDMS) is a destructive compositional analytical technique in which a sample is sputtered with argon ion plasma. Contrary to SIMS, instead of gallium or cesium ions, argon plasma is generated over the sample surface. This reactive plasma breaks material down into the gas phase and they are fed to a mass spectrometer that separates ablated elements based on their mass. An advantage of GDMS is that it can measure concentrations of multiple elements as once, whereas SIMS and IGF are limited. The disadvantage of GDMS is that it has no spatial resolution, only overall concentration.



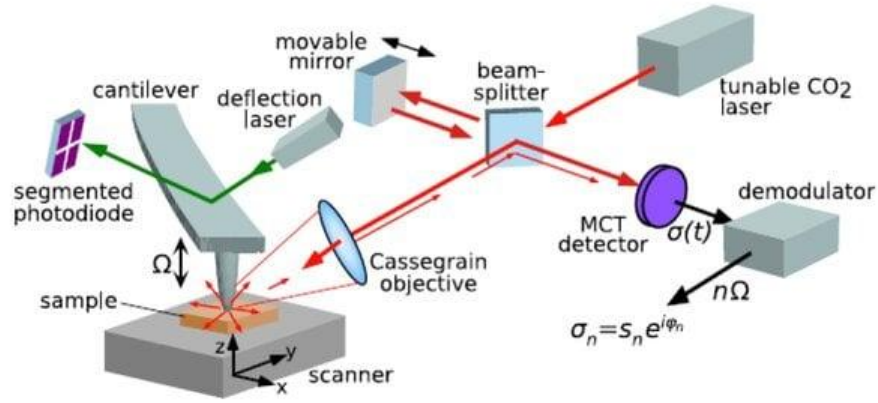
Appendix Figure A.10 Diagram of GDMS measurement setup [407]

In this dissertation, GDMS was used to measure the amounts of various elements in hBN boules to understand the sources of impurities interfering with crystal growth such as Silicon, Magnesium, and other metals that originate from source materials.

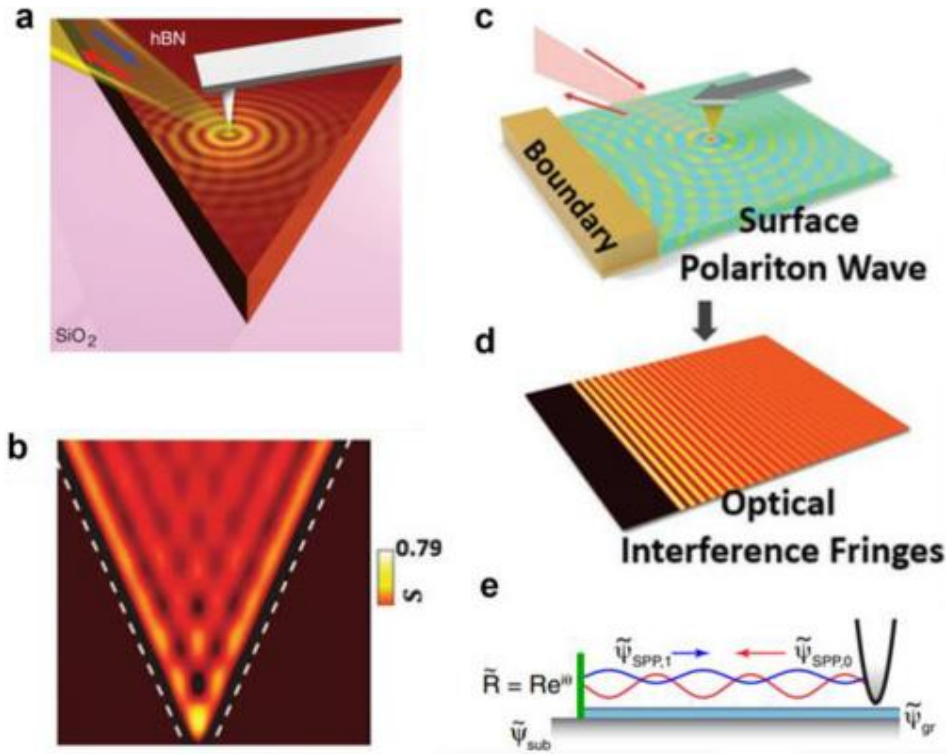
Scattering Scanning Near-field Optical Microscopy

Scattering scanning near-field optical microscopy (s-SNOM) is an analytical technique that couples light with atomic force microscopy. In addition to the laser used to measure the surface topography, a second laser (typically infrared) is focused on the sample surface. This laser is reflected from the surface to an interferometer that measures how the incident light was changed from interacting with the sample. The change in the laser corresponds to bond vibrations similar to Raman spectroscopy indicative of the material analyzed [408]. A diagram of such a setup is provided in Appendix Figure A.11 as well as the mechanism of light interaction with a sample.

i.



ii.



Appendix Figure A.11 – (i) s-SNOM experimental set up [409] and (ii) (a) illustration of interference pattern produced by interaction with hBN (b) c-axis view of interference pattern measurement. (c) Measurement illustration ascribing the interference patterns to surface polariton interactions. (d) Hypothetical interference pattern of (c). (e) Depiction of interference from source (wave) to the AFM probe (right) resulting in a different wave (red). [410]

Appendix B - Glossary

Defect – impurity or structural deviation from a material's standard structure

Exfoliation – the removal of the surface materials from a solid metal's surface

Dwell – time during which an equipment is kept at a constant temperature

Isotope – a chemical element whose atoms have a number of neutrons different from its protons

Enrichment – increasing an element's specific isotope greater than its naturally occurring concentration

Etching – the mechanical or chemical process of removing atoms from a material

Flux – liquid phase mixture of metals

Irradiation – exposure of a material to high energy particles intentionally damaging material

- In this work, thermal or slow neutrons are used intentionally for irradiation

Transmute – the conversion of one element to another

Lattice – material or crystal network of order bonded atoms with repeated unit cells

Vacancy – an empty space in a crystal lattice, normally occupied

Substitution – a lattice space in which an element is replaced with a different element

Diffusive – by way of diffusion

Annealing – materials at high temperature for atoms to rearrange within the lattice

Implantation – particles accelerated to high speeds ejected towards a surface to incorporate the particles

Dimer – a defect composed of two adjacent defects

Magnetometry – measuring magnetic field and its directionality

Photon – energy transported as a packet of light

Phonon – energy transported as a lattice vibration

Anisotropic – properties vary dramatically between parallel and perpendicular to a material surface

Photovoltaic – conversion of sunlight to electricity

Ballistic – transporting without obstruction

Spectroscopic – optical measurement

Epitaxial – process by which material is grown on the surface of another material

Functionalization – process of chemically modifying the surface of a material

Physisorption – process of a molecule adhering to a surface through physical trapping

Plasmon – a surface charge formed by electron oscillations

Refractive Index – the degree by which light bends when passing through a material relative to air

Transduction – conversion of physical phenomena to measurable signal

Bandgap – energy required to excite electrons from the valence band to the conduction band

Hyper lensing – propagation of light waves produced from changes in refractive index, to far-field detectors

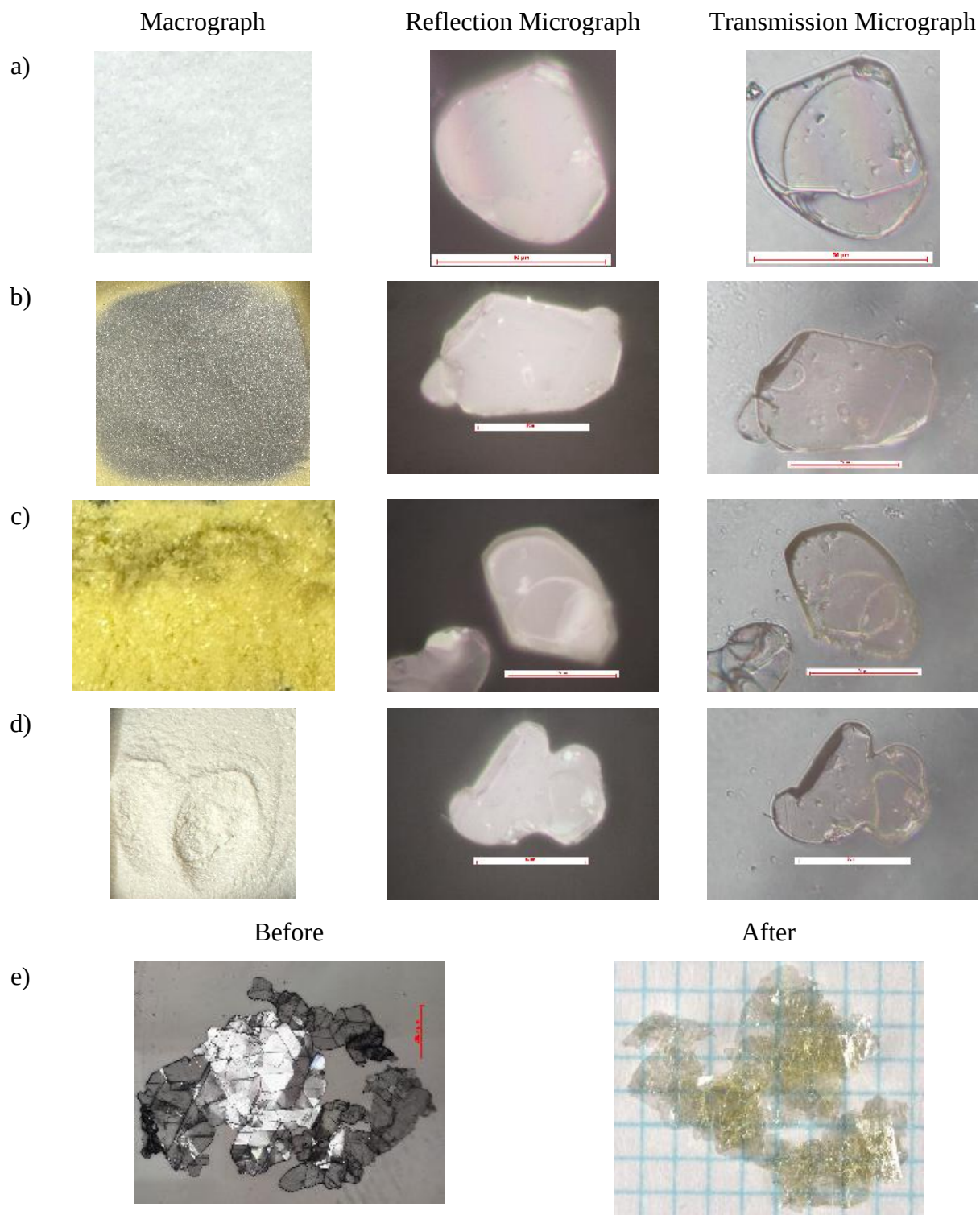
Monochromated – reduced from multiple wavelengths to a single wavelength. Used to separate mixed wavelengths of light into their constituents

Appendix C - Supplementary Figures

DEFECT(s)		ZPL (eV)	ZPL (nm)
Key	Single site defect		
	Dimer		
	Trimer		
	Quatramer		
	Donor-Acceptor Pairs (DAPs) +/-0		
C_N^*		5.47	226
$C_B C_N$ -DAP-1		4.1	302
$C_B C_N V_B V_N$		3.07	403
$C_B C_N C_B C_N - trans$		2.94	422
$C_B C_N C_B C_N - connect$		2.94	422
$C_B V_N$		2.67	464
$C_B C_N C_B V_B^*$		2.59	478
$C_B C_N C_N (II)$		2.49	498
$C_N V_B^{**}$		2.49	498
C_N^{**}		2.45	506
$C_N V_N$		2.43	510
$C_B C_N$ -DAP-2		2.4	516
$C_B C_N C_B V_B$		2.28	544
$C_B C_N$ -DAP-4+		2.2	563
$C_2 C_2 - 3$		2.2	564
C_N		2.17	571
$C_B C_N C_N V_N$		2.16	574
$C_B C_N$ -DAP-sqrt(13)+		2.15	576
$C_N V_B^*$		2.13	582
$C_B C_N V_N$		2.09	593
$C_B V_B$		2.06	602
$C_N V_B$		2.03	609

$C_B C_N$ -DAP-sqrt(7)+	2	619
$C_B C_N$ -DAP-sqrt(7)-	2	619
$C_B C_N V_B$	1.93	641
$C_B V_N^*$	1.92	645
$C_B C_N C_N$	1.82	681
$C_B C_N C_N V_B$	1.97	682
$C_B C_N$ -DAP-2+	1.8	688
C_B	1.71	725
$C_B C_N C_B$	1.61	768
$C_B C_N C_N$	1.6	774
$C_B C_N$ -DAP-sqrt(13)	1.6	774
$C_B C_N C_B V_N$	1.59	780
$C_B C_N$ -DAP-4	1.55	799
$C_B C_N$ -DAP-4-	1.55	799
$C_B C_N$ -DAP-sqrt(13)-	1.45	854
$C_B C_N C_B$	1.3	953
$C_B C_N$ -DAP-sqrt(7)-	1.25	991
$C_B C_N$ -DAP-2-	1.15	1077
$C_B C_N$ -DAP-1+	1.05	1180
$C_B C_N$ -DAP-1-	0.45	2753

Appendix Table C.1. Zero-phonon emission lines (ZPL) of various carbon defects in hBN predicted by density functional theory calculations.



Appendix Figure C.1 Macrographs, reflection, and transmission micrographs of hBN powders with (a) no annealing, (b) 3h annealing, (c) 9h annealing, (d) 18h annealing, and (e) a hBN crystal after 9h annealing (same experiment as (c)).