PLASMA SYNTHESIS AND HPHT CONSOLIDATION OF BN NANOPARTICLES, NANOSPHERES, AND NANOTUBES TO PRODUCE NANOCRYSTALLINE CUBIC

BORON NITRIDE

by

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ABSTRACT OF THE DISSERTATION PLASMA SYNTHESIS AND HPHT CONSOLIDATION OF BN NANOPARTICLES, NANOSPHERES, AND NANOTUBES TO PRODUCE NANOCRYSTALLINE CUBIC

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Plasma methods offer a variety of advantages to nanomaterials synthesis. The process is robust, allowing varying particle sizes and phases to be generated simply by modifying key parameters. The work here demonstrates a novel approach to nanopowder synthesis using inductively-coupled plasma to decompose precursor, which are then quenched to produce a variety of boron nitride (BN)-phase nanoparticles, including cubic phase, along with short-range-order nanospheres (e.g., nano-onions) and BN nanotubes. Cubic BN (c-BN) powders can be generated through direct deposition onto a chilled substrate. The extremely-high pyrolysis temperatures afforded by the equilibrium plasma offer a unique particle growth environment, accommodating long deposition

times while exposing resulting powders to temperatures in excess of 5000K without any additional particle nucleation and growth. Such conditions can yield short-range ordered amorphous BN structures in the form of ~20nm diameter nanospheres. Finally, when introducing a rapid-quenching counter-flow gas against the plasma jet, high aspect ratio nanotubes are synthesized, which are collected on substrate situated radially. The benefits of these morphologies are also evident in high-pressure/high-temperature consolidation experiments, where nanoparticle phases can offer a favorable conversion route to super-hard c-BN while maintaining nanocrystallinity. Experiments using these morphologies are shown to begin to yield c-BN conversion at conditions as low as 2.0 GPa and 1500°C when using micron sized c-BN seeding to create localized regions of high pressures due to Hertzian forces acting on the nanoparticles.

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Chapter 1 Introduction

1.1 Motivation

The subject of super-hard ceramic materials research has been one of significant focus in recent times. This interest has been motivated by the various application areas, all of which can benefit greatly from the improvements afforded by super-hard ceramics. Whether it be hardened coatings for high-speed tool bits, ceramic armor, or penetrators, light-weight ceramics with superior hardness provide significant increases in overall capabilities. For example, high-speed tooling applications using low-cost super-hard powders for coatings enable longer life, faster machining times, and more flexible application of conventional manufacturing and machining methods to hardened materials. In armor plating, superhard ceramic powders provide high hardness-to-weight ratio, allowing ballistic protection greater than that of traditional hardened-steel armor plates, at a significantly lower weight.

One of these super-hard ceramics of interest is the cubic structured phase of boron nitride, or c-BN. The synthesis and utilization of this super-hard ceramic powder have become almost common practice in industry today; however, there is continued interest into means of alternative synthesis methods, especially for nanopowders, which lend themselves to scalability and overall increased cost effectiveness. The attributes of nanocrystalline c-BN in comparison to those of other BN phases, along with that of diamond, is given in Table 1.

Phase	Short-Range Order aBN	hBN	Micron cBN	Nano cBN	Diamond
Density (g/cm ³)	2.28	2.34	3.45	3.45	3.515
Bulk Modulus (GPa)	100	36.5	400	400	440
Hardness (GPa)	-	-	33-45	85	100

The method of plasma synthesis of c-BN is one which lends itself to both scalability and cost effectiveness compared to other synthesis routes. One of the most attractive aspects of plasma synthesis is the ability to perform direct synthesis and deposition of metastable c-BN. In addition to the cubic phase, there are also other interesting BN polymorphs that can be synthesized via ICP processing.



Figure 1-1: Comparison of Various BN Structures

These polymorphs such as hexagonal BN (h-BN), short-range order amorphous BN (a-BN), and turbostratic BN (t-BN) have multiple unique properties and applications of their own. Moreover, there are conversion routes from them to c-BN via high-pressure/high-temperature consolidation. Figure 1-1 [1] presents a comparison of the maximum packing density, showing c-BN's structure along with the sheet-like h-BN phase, which can be equated to graphene, as well as the nanotube morphology of BN. The turbostratic phase is a metastable phase of highly-strained

The cubic structured phases offers the most efficient packing density of the BN molecules. The hexagonal phase is a sheet-like phase equitable to graphene. BN nanotubes are an interesting structure where the extreme turbostratic lattice curvature from the hBN sheets self-terminate into cylindrical tubes.

h-BN planar sheets which can eventually roll themselves into nanotubes, as depicted. The work presented here offers an efficient and scalable means of synthesizing various polymorphs of BN which have unique properties. These desirable aforementioned characteristics obtained by their experimental processes are outlined in Figure 1-2.



Figure 1-2: Experimental Block Diagram with Key Discriminator Parameters & Powders Produced

1.2 Outline of this dissertation

An overview of the background of various forms of BN synthesis and characterization is outlined in Chapter 2. Chapter 3 then provides an overview of the ICP experimental system used for the research performed. A computational EM/CFD model developed specifically to aid in the execution of this research is described in Chapter 4 along with the results of a parametric study performed for a number of experimental conditions to characterize the plasma flow field. Chapter 5 explains the validation testing performed using a spectrometer to measure atomic emissions of the plasma to determine temperatures experimentally and compare them against Chapter 4's results. The initial experimental results and general characteristics of the plasma and the resulting powders are described in Chapter 6 Chapter 5. Chapter 7Chapter 6 then covers the specific results of the unique recirculation flow within the plasma which yields short-range ordered a-BN. In addition to the plasma synthesis of the results of the aBN, the high-pressure / high-temperature consolidation of these powders are discussed. Direct deposition of c-BN using the ICP system is characterized in Chapter 8. The synthesis of the turbostratic BN nanospheres, nanococoons and nanotubes are described in Chapter 9 along with their characterization. Finally Chapter 10 provides the final conclusions of the work presented here along with discussion of potential future expansions of the work enclosed.

Chapter 2 Background

Over the last two decades, there has been much focus by the research community on boron nitride, most notably its cubic phase. The sp³ hybridized bonding of the cubic phase makes it a highly desirable ceramic, offering superior stiffness over many other ceramics and hardness second only to diamond [2]. The sheet-like structure of the sp² bonded hBN consists of a 6 rings structure along the <110> plane with stacking sheets along the <002> direction as shown in the center image of Figure 1-1. The hexagonal rings have a uniform bond angle of 120° between each of the atoms as shown in Figure 2-1. The sp³ hybridization occurs when puckering compresses the atoms and reduces the overall bond angle resulting in armchair growth from the sp² to sp³. This growth results from the planar spacing along the <002> direction of the hBN particles being compressed to the point that the induced strain converts the sheets into a cubic structure with the resulting bond angle of 109.5° for the out of plane bond angles.



Figure 2-1: Comparison of hBN's sp² and cBN's sp³ bond geometry

One of the primary methods to synthesize cBN is though High-Pressure/High-Temperature (HPHT) processing. The elevated temperature enables molecular mobility, and the increased pressure allows the molecules to migrate into their most efficient packing density in the cubic structured phase. This cubic phase is a metastable phase, so once it is achieved under the high pressure conditions, the sample can be brought back down to ambient conditions with the cubic structure intact. Typically, a powder compact of micron-sized particles of sp² bonded h-BN is used as starting material. HPHT powder consolidation is often performed at 8-20 GPa at 1000-2400°C to convert hBN into cBN [3] [4]. The results of these experiments performed by Sumiya et al [4] saw successful cBN conversion however the particles saw fairly significant grain growth which yielded on the order of 100 - 300 nm particles. A general trend which was shown was that as temperature increases during consolidation, the required pressure to yield cBN begins to drop. For example at 1500 °C upwards of 20 GPa were required for conversion however when increasing above 2000 °C the required pressure can drop to as low as ~11 GPa. The increased temperature does promote greater mobility and thus easier phase conversion, however this reduction in pressure does come at an expense. Since the high pressure also helps mitigate particle growth, such reduction has shown grain sizes to grow from 30nm to upwards of 100nm at these reduced pressures. The drawback of this method is the challenge of scaling for industrial applications. As a very high consolidation pressure is necessary to ensure complete conversion to c-BN, while preserving a nanocrystalline structure, the size of the sample usually decreases with increasing pressure because the consolidation pressure is a function of compaction area for a given hydraulic press's axial load capacity. To overcome this limitation, activators or catalysts are often mixed with the h-BN starting powder to promote its conversion to c-BN at reduced pressures. For example, an addition of about 6 wt. % Mg powder [5], and other metallic catalysts [6], can reduce

the consolidation pressure from 20 GPa to 5GPa. It was shown though by Eko [6] that these lower consolidation pressures tend to yield higher cBN particle sizes after consolidation. The results seen in their work saw 20-50 micron sized grains as the end products. Also, as would be expected the consolidation pressure had a direct dependence on the percentage of BN converting to the cubic phase based on the availability of excess pressure at the point of equilibrium energy. Moreover, in the conversion of sheet-like h-BN or t-BN into c-BN, the characteristics of the starting powders become just as critical as the consolidation parameters. Balint and Petrescu showed that under fairly low consolidation and conversion conditions of 5.2 GPa and 1500°C, c-BN nucleation and growth rates are strongly dependent on particle size of the precursor h-N powder [7]. 100 to 250 micron sized hBN particles saw less than 20% cBN conversion however when fined powders were used, on the order of 38-54 microns cBN conversion increases quickly to 50%. Again though, these resulting cBN particles are on the order of 40-90 µm. On the other hand, under much higher pressures ranging from 12 to 25 GPa, a nanocrystalline structure is formed, which displays hardness greater than monolithic diamond [8], explained by the Hall-Petch relationship. In this case, Sumiya et al. saw began to see 100-300 nm particles resulting from the consolidation.

Methods for synthesizing c-BN by physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques have also been developed, although typically focused on cBN film growth rather than powder synthesis. Konyashin [9] provides an excellent review of the extensive literature on this subject. Typically, CVD and PVD methods result in nanocrystalline c-BN films, up to about 5 µm in thickness, as deposition products on a substrate [10]. Interestingly, a very thin film of h-BN forms first, which becomes the substrate for subsequent growth of c-BN [11] [12] [13]. The presence of an initial h-BN growth plane is a consistent feature of all such synthesis routes, but variations come in the type of BN that grows upon that film. Using plasma-assisted

CVD, not only c-BN but also other sp³-bonded phases with high hardness are synthesized, i.e., wurtzite [14], orthorhombic [15] [16], monoclinic [17] and BNNTs [18]. Plasma-enhanced CVD utilizes a focused laser beam to grow c-BN films [19] [20] [21]; however, because lasers have small focal points, scaling the technology is challenging. Conventional CVD in a controlled environment is also effective in growing BN films, but because of limitations in controlling the quenching rate after pyrolysis, h-BN is usually the final product [22]. In some cases, where film growth is performed in a high vacuum, the cubic phase is formed [23]. Effective heterogeneous particle growth was seen in the cubic phase due to the reduced energy barrier of heterogeneous growth over homogeneous. Nanocrystallinity is maintained however again in these film growth applications the overall thickness of the cBN is on the order of a few microns.

Inductively-coupled plasma (ICP) processing of precursor compounds is a promising method for the production of c-BN and related phases. The ICP method allows for a controlled-temperature plasma to be generated, where precursors can be injected axisymmetric with the plasma, thereby decomposing uniformly into their constituent elements. Desired particles are subsequently formed downstream in the presence of a steep declining temperature gradient. For thick-film growth of c-BN, ICP has been used by many researchers to yield high purity nanocrystalline c-BN films [24] which can result in a fine nanostructure on the order of 5nm for such films. Most often though, processing is carried out in high vacuum, with the formation of c-BN dependent on high voltage substrate biasing [25]. Similar to other synthesis methods, the presence of an initial h-BN film to promote the subsequent c-BN growth is observed by Chowdhury and Pal [26]. The characteristics of the c-BN growth quality, namely the percentage of c-BN compared to intermediate phases such as h-BN, t-HB and a-BN, as well as the average particle size, is a function of the experimental conditions. As would be expected, the temperature

time history of particles formed during precursor decomposition and subsequent film growth is strongly dependent on RF-plasma power during film growth [27]. In this case of thick film growth, a 13.56 MHz magnetron sputtering technique saw 90% cubic phase presence with the remaining 10% consisting of tBN and hBN. The RF power was shown to be the dominant factor in this study with experiments ran below 150 W seeing mixed results however when running 150W and 180W 90% cBN can be realized.

Although the cubic phase of BN remains to be the most highly sought-after phase because of its superior properties and broad applications, recently, there has been an increase in research into the intermediate BN phases such as short-range ordered amorphous BN and turbostratic BN, or t-BN, phase. The short range-order amorphous BN phase is one which as would be expected from its name, a lack of any periodicity of the structure for more than a few nanometers. The limited range order is one which typically consists of an sp³ bonded cubic-like structure with some eventual disorder in the structure in the form of a turbostratic transition layer which ultimately gives it its bulk amorphous structure. The tBN intermediate phase is especially interesting because it comes in a number of particle forms. Turbostratic is a fairly broad phase descriptor used to designate sheet-like phases, similar to h-BN, which have a fairly significant amount of disorder about the Z axis. This can be due to twisting of one sheet layer's <110> plane relative to another's in order to break the atomic alignment along the <002> plane. In PVD and CVD thin film applications [28], this has appeared to be the manner in which t-BN tends to present itself. More interestingly though, when ICP-CVD methods are used to deposit particles, the manner in which t-BN presents itself is a bit different. The significant lattice strain in the Z direction causes the sheet-like phases to curve so excessively that they reach a point of self-termination. When such curvature is happening about one direction, high aspect ratio BN nano-tubes, or BNNTs, are

formed [29] [30] [31]. These BNNTs are a favorable semiconductor material due to their wide bandgap of 5.5 eV. The dimensions of these high aspect ratio nanotubes are typically on the order of 20-40nm in dimeter and greater than 250nm in length, often times even on the micron scale [32]. These BNNTs tend to have a combination of sp^2 and sp^3 bonds present with a strong propensity to react with excess hydrogen and oxygen due to the residual dangling bonds and strong dipole moments. Wang [33] has shown that under atmospheric conditions and relatively low temperatures below 520°C, the used of microwave plasma enhanced CVD methods can promote BNNT growth when the proper templates are used. A porous anodic aluminum oxide template was used with pore sizes corresponding to the desired BNNT diameters in order to promote growth. Success of 30nm and 60nm BNNTs with respectively corresponding porous templates was demonstrated. As would be expected though, the plasma enhancement promotes somewhat of a disorder in the overall BNNT structure. Similar success using template growth in CVD applications has been shown to be possible using silica templates as well which again saw BNNT diameters consistent with the 7nm pore sizes [34]. When using arc-jet plasma methods in order to spray BNNTs onto a substrate rather than growth them on a substrate in a CVD manner, the resulting powders tend to be a more intertwined array of BNNTs which almost form a nanomesh. Lee has shown this to be the case for high temperature arc-plasma synthesis which yielded tube diameters in the range of 3-10 nm [35]. These BNNTs showed a predominantly sp² bonded structure based on the presence of the π bonds as indicated by the EELS analysis performed. A mixture of single and double walled tubes were seen which is typical of plasma processes which for BNNT growth tend to show a somewhat more dispersed range of resulting structures compared to other CVD growth techniques just do to the more stochastic nature of plasma jet synthesis.

When the turbostratic disorder is seen to happen about essentially every <xy0> plane, the end result after termination are what have been referred to as nanospheres or nanococoons. Nanospheres are typically defined as particles which are non-porous particles of continuous layers, similar to an onion-like structure [29] [32]. Nanococoon is used to describe similar onion-like layering when it is either hollow in the center of the spherical particle or there is non-t-BN material such as unreacted precursor trapped within the center, thus the term cocoon [33].

The reasoning for the increased attention in the t-BN phase ultimately stems from the underlying desire for more efficient and effective mechanisms for synthesizing cubic-phased BN. It has been shown in hot pressing [34] and ICP-CVD [35] applications that t-BN is a transition layer to c-BN, as evident by TEM imaging. In HPHT methods for converting powers to c-BN, t-BN is believed to be a good candidate as a source powder. As previously discussed, h-BN is typically the starting powder for such applications; however, given the transition layer characteristics that t-BN has been shown to possess, there is potential for t-BN to have a more efficient conversion mechanism to c-BN. What this ultimately means is that lower pressures may be used to possibly yield the same c-BN conversion characteristics, when compared to employing h-BN micron powders. Although Ref. [36] only reports the sensitivity to temperature, rather than to pressure, it was shown how using onion-like nested structures in the 30-150nm diameter particle size yielded effective c-BN conversion at 15 GPa and 1600°C. The benefits of such fine nanocrysallinity are also realized in this work with a combination of experimental and analytical work shown for the grain size dependence of bulk sample hardness. A fairly consistent hardness (H_v) of 50 GPa is shown for grains down to around 100nm in size. As grain size is reduced from there, there is almost an exponential increase in hardness. Experimental results, which concurred with analytical predictions for hardness growth with particle size reduction, saw almost 110 GPa

H_v for a 15nm grain size. A more focused sensitivity study into the pressure dependence of h-BN/t-BN/c-BN conversion trends is shown by Ref. [37], claiming c-BN transition at far lower pressures, in the MPa range. However, Nanocrystallinity is believed not to be maintained during the prolonged c-BN particle growth. Furthermore, the overall percentage of cubic phase conversion compared to the residual bulk t-BN source powder is quite low. Madhav [38] saw that by using disordered a-BCNO powder as the BN source in spray plasma applications cBN conversion was seen to occur at pressures in the 2-4 GPa range. The plasma spray process is different than traditional HPHT consolidation approaches and so the conversion pressures are estimated based on the Rankine-Hugoniot relationship of the particle impacting the substrate and other subsequent particles at supersonic velocities as they expect the plasma's jet. An interesting claim is made about the effectiveness of the disordered BN source having sp² bonds rather than sp³ bonds in promoting cBN conversion. It is suggested that the weaker sp^2 bonds convert easier to cBN than the stronger sp³ bonds which other disordered BN phases have been shown to have. Guo and Singh [43] showed that when using gas precursors for BNNT growth, the presence of a plasma to promote the nanotube growth is a critical parameter. The plasma's free ions and active electrons helped create localized regions of excess activation energy to promote BNNT growth. In this case the nanotubes were grown on thin Ni or Co coating on Si substrates. The localized plasma regions also promoted 3 dimensional BNNT growth rather than template oriented nanotubes growing orthogonal to the substrate. The increased temperature from the plasma assistance was also shown to increase the bundling of the BNNTs into meshes or larger arrays of tubes. In these cases, the BNNTs themselves maintained tube diameters of 5-20 nm with the tubes then bundling into clusters anywhere from 50 to 70nm across. Eventually, when growth temperatures were raised from 800°C to 950°C the nanotubes themselves cease to grow and larger low aspect ratio

nanoparticles are evident as shown by SEM imaging. Equally as dominant to the particle phase and size control as the temperature is the loading rate of the precursor vapor. At higher loading rates larger distinct low aspect ratio particles were shown to be fairly uniform. When reducing the loading rate by 50% BNNT growth begins to occur. Once reducing by another 50% limited BN growth off of the substrate is seen.

Chapter 3 Experimental Setup

The synthesis system employed here utilizes an inductively-coupled plasma torch in stagnationpoint flow as depicted in Figure 3-1 to generate desired BN powders. An argon plasma is generated by an RF power supply that inductively couples to the gas flowing through a quartz torch. The precursor vapors are introduced into the torch via a carrier gas at which point they decompose into their constituent elements upon reaching the plasma region and nucleate into the desired products downstream of the high temperature plasma region. The synthesis is done in a controlled nitrogen ambient at 1 atmosphere in order to minimize the amount of foreign contamination in the samples. The ability to run at atmospheric pressures provide significant flexibility to the scalability of this technique to larger industrial applications.



Figure 3-1: System Block Diagram



Figure 3-2: Experimental System – Inside Chamber

Inside the chamber the quartz torch and RF coil can be seen with the multiple gas feeds into it. The chilled substrate is shown below the torch at a ~ 2.5 '' gap with the counter-flow gas feed.

The synthesis experiments are performed in an enclosed chamber constructed of stainless steel, with various entry ports for gas delivery lines and a main door for easy access to the torch, matching network, and substrate as shown in Figure 3-2. As such, the system is accessible for modifying experimental parameters such as torch positioning and substrate height. The chamber is connected to a vacuum pump and exhaust, capable of bringing the chamber down to 8 Torr before backfilling with high purity nitrogen in order to create an oxygen-free environment. Less than 10 Torr is targeted as the desired purge pressure to ensure that any residual surface moisture in the system is eliminated and purged via the vacuum pump, with the atmosphere being below the vapor pressure of water. After the chamber is backfilled to atmospheric pressure, the nitrogen

feed remains open in order to maintain a positive pressure inside the chamber relative to the external environment.

The plasma gas of choice for this system is argon due to its inert characteristics which eliminate any propensity for reaction with the free boron atoms after precursor decomposition. Industrial grade argon of 99.995% purity is used for all of the experiments at a pressure of 15 psi. The flow rates for the argon are controlled by two separate volumetric flow control valves for the plasma and sheath gas, respectively. Depending on the desired experimental conditions, the ratio of these two is varied, but typically, the sheath gas flow rate is $5 \times$ to $10 \times$ that of the plasma volumetrically. The role of the sheath gas as depicted in Figure 3-3 is to cool the quartz torch being used to ensure that it doesn't melt from the prolonged exposure to the high temperature plasma, so the necessary flow rate to provide ample heat dissipation is a function of the RF power being coupled to the plasma.



Figure 3-3: Torch / Coil / Plasma Diagram

The Argon plasma gas is what primarily generates the plasma within the coil's cross section due to the inductive coupling. The Sheath gas, also argon, flows at a higher flow rate around the outside of the plasma region in the torch in order to provide adequate cooling to the torch as to not melt it due to the exposure to the high plasma temperatures.

The torch used in this system, shown in Figure 3-4 is an Agilent axial quartz torch with two radial inlets for the plasma and sheath gas, respectively. These torches are typically meant for mass spectrometry applications; however, given the similarities in the manner in which we are using the torch for precursor decomposition, the conditions for our applications and mass spectrometry align well and thus make these torches suitable for our needs. The radial inlets of the torch induce a radial circulation of the flow up-stream of the plasma region, ensuring uniform flow-field conditions once the gases reach the plasma domain.



Figure 3-4: Quartz torch w/ radial inlets

The plasma region is generated by the excitation and ionization of the argon shell electrons, but energy for this excitation comes from the inductive coupling of an RF power supply to the gas flow in the torch. A 1500W RF power supply operating at 40.68 MHz is the source for the incident energy to the torch. An impedance matching network and auto-tuner are used to match the impedance of the source with that of the load, in this case the plasma region, minimizing the reflected energy back to the power supply. This ensures maximum power transfer efficiency during the inductive coupling. The coupling of the incident RF energy is done through an RF coil attached to the matching network. The coil essentially serves as an antenna focusing the RF energy into the

The top inlet is the plasma gas and the lower one provides the sheath gas. Some residue and burning can be seen on the lower part of the torch from the precursor decomposition within the plasma.

center of the plasma torch, so it is critical to match the selected torch geometry to the specifics of the experimental system's RF power supply and candidate plasma gas. The region in which the RF coupling takes place is defined by the skin depth relationship of the signal, which in this case is the RF load [38]. The skin depth, δ , is defined by the equation below where ω is the frequency, in this case 40.68 MHz, μ is the permeability of free space, and σ is the conductivity of the medium, which in this case is ionized argon.

$$\delta = \sqrt{\frac{2}{\omega^* \mu * \vartheta}} \tag{1}$$

Once the tuner and matching network balance the source and load impedances such that the reflected RF energy back to the power supply is down to somewhere on the order of 2% of the incident energy, the high current RF power is carried by the coil's skin and transferred to the argon gas inductively, ionizing it. This describes the basic function of the steady state function of the plasma; however, an initial transient is necessary in order to initiate the plasma and "light the torch". This is because at ambient conditions, the inert argon gas has a very limited current carrying capacity. For this reason, an initial excitation is needed in the flow to initiate the RF coupling. In this case, a Tesla coil is clipped onto the plasma gas's feed into the torch in order to generate a high voltage arc throughout the plasma to the torch which acts as a ground. The torch itself is held in place by an insulated mounting; however, there is still a mean free path to ground. With the Tesla coil generating an initial transient environment of excited argon atoms as seen in Figure 3-5, once the RF power is initiated the energy has a path to couple to the gas flow. Once this occurs, the coupled atoms excite their nearest neighbors because of their increased temperature and excited shell electrons. After a short transient period, on the order of one second, a steady state EM field is generated within the flow field controlled by the RF coil's geometry and incident energy power levels.



Figure 3-5: Tesla Coil Arching within Plasma Region of Torch

The chemical of choice for producing the precursor vapors for this synthesis route is borazine. Borazine was chosen over other more traditional boron and nitrogen sources because it is a liquid at ambient conditions and has been shown by others to be successfully used for BN synthesis [39] [40]. Borazine has the proper stoichiometric B to N ratios desired for BN growth as well as being hydrogen rich in order to aid in the termination of dangling bonds. Additionally, being a liquid at ambient conditions allows for it to be easily used in a bubbler with a carrier gas in order to introduce the precursor vapors into the system. Nitrogen is used as the carrier gas so that (I) the amount of additional elements introduced into the experiment are limited and (2) to limit the reaction of the residual borazine liquid between experiments. Borazine is highly reactive with water, so it is critical to ensure it remains in a controlled environment. For this reason, the bubbler is continually kept at a positive pressure of 15 to 20 psi. Gross on/off control of the precursor delivery is controlled by 2 ball valves, with fine control performed by a needle valve with micrometer control. Overall flow rate is monitored by a flow meter to verify the carrier gas's flow rate compared to settings for a given micrometer position. Conservation of mass and partial pressure calculations are then used to determine the precursor loading rate. Modification of the precursor loading rate can be performed by chilling the bubbler in order to reduce the vapor pressure of the borazine, as predicted by the Clausius–Clapeyron relation. Since heating of the borazine can be dangerous, the preferred method of increasing the precursor loading rate is to reduce the carrier gas pressure. Then for a given temperature and associated vapor pressure, the partial pressure ratio increases and thus so does the mass flow rate of the precursor vapor relative to the carrier gas. Examples of these relations can be seen below in Figure 3-6.



Figure 3-6: Precursor vapor's partial volumetric flow rate as a function of temperature for a series of total volumetric flow rates of precursor vapor & carrier gas.

The precursor delivery line, once introduced into the experimental chamber, is mixed with the plasma gas up-stream of the torch. Traditionally the centerline tube in the torch is what is used for precursor delivery for these torches, but again those are for mass spectrometry application. In those cases, a very small amount of precursor is being introduced into the plasma for analysis, so the centerline feed is logical. For the application of ICP synthesis of nanoparticle powders, a number of problems arise from this approach. The area of the center feed is far smaller than that of the plasma region in the torch so velocity matching of the two flows becomes very challenging, In order to maintain a stable plasma, the precursor loading rate needs to be well below the required rate for the desired deposition for a given experimental run time. If the needle valve was opened enough to provide this desired precursor loading rate, the incident velocity of the precursor vapor and carrier gas would be so great that it would destabilize the plasma and ultimately extinguish the torch. The contour plot in Figure 3-7 shows an example of what this flow field would look like for a matched flow rate for the precursor gas. You can see the axial velocity in the center tube is almost an order of magnitude greater than the average axial velocity of the plasma gas. The large disturbance from the velocity mismatch can be seen in the center of the torch where the highest area of RF energy is coupled to the flow. Although the model isn't capable of predicting how the RF coupling is occurring exactly, it is an effective first order prediction of what is occurring in the flow field to help infer the impacts on the EM environment.



Figure 3-7: Axial Velocity of plasma flow field in m/s with precursor feed

The high velocity of the center-line inlet is due to the necessary volumetric flow rate for the precursor required coupled with the small cross-section of the center feed. It can be seen how the precursor / carrier gas injecting into the plasma region at such a rate can become destabilizing to the plasma.

For this reason, the precursor is mixed with the plasma gas in order to be able to adequately load the system with the amount of precursor vapor desired. The radial ports of the torch ensure that by the time the flow reaches the plasma region, the precursor is homogenously dispersed in the plasma gas so that the localized destabilizations are minimized and averaged out throughout the plasma. This approach does not create the concern about variation on particle growth environments due to the radial distribution of the temperature because it is theorized that the greatest temperatures are in the areas of largest gradients. This ensures that whenever a gradient is present, the temperature experienced is so great that the variation in particle growth characteristics is negligible. Once the particle flows down-stream, the temperature gradients converge to a nearly constant temperature, allowing for a uniform growth environment.



Figure 3-8: Plasma Stagnation Flow - (a) Argon Only; (b) With precursor vapor

Image (a) shows the plasma only existing slightly below the end of the torch. The expansion of the sheath gas along with the radial variation in RF energy are what cause the cone like shape of the plasma. Once the flow gets far enough from the coil there isn't enough RF energy to maintain the plasma and so the argon atoms no longer become excited. Image (b) now shows the precursor introduced into the plasma and decomposing. Now even though the plasma conditions are the same as in image (a) the free B+ atoms are still forming BN molecules downstream. The free B+ is what causes the green color of the flow. The stagnation flow an also bee see at the bottom of the flow field as it approaches the substrate.

The method of controlled particle growth and powder deposition is one based on traditional stagnation flow with some additional unique design features. An aluminum substrate is used for the deposition which is cooled by two chillers in series to promote powder deposition by thermophoretic forces resulting from the significant temperature gradient between the chilled substrate and the flow-field exiting the plasma torch. The substantial temperature gradient is what also preserves the metastable phases by quenching the BN particles at rates on the order of 10¹² K/s upon their contact with the chilled substrate. The unique design feature of the substrate which aids in maintaining the low substrate temperature as well as increasing the overall quench rate is a multiple ported counter-flow which is concentrically aligned with the plasma torch's flow.



Figure 3-9: Drawing of Substrate w/ Counter-Flow Ports

The counter-flow consists of 5 ports as shown in Figure 3-9 equal to a total equivalent area of 9.12 mm². The counter-flow gas used is nitrogen in order to preserve the desired experimental inert environment, while still serving the purpose of rapidly quenching the post-plasma gases downstream. Although diatomic nitrogen is able to ionize, it is not nearly as easy to as monatomic argon because of the difference in energies of the outer shell electrons (e.g. triple bond for molecular nitrogen). Furthermore, the impedance matching of the RF system is tuned to the argon flow which makes coupling to the nitrogen difficult under these conditions. The result is that the nitrogen counter-flow can be used to control where the plasma is "extinguished" downstream of the torch as well as to quench the particles in the flow field. Since this is not actually a combustion problem the reaction is not being truly extinguished; however, it is essentially fully de-coupling the source power supply's RF energy from the force and subsequent ionic heating which serves the same role as extinguishing in classical combustion problems. Given that the counter-flow's primary role is to act as a heat sink, there certainly are more optimal gases to use, however it was found that the benefits of maintaining the nitrogen environment outweighed the improved

quenching from other gases. Experiments were performed with hydrogen as an alternative counterflow gas; however, the results saw larger oxide contaminations in the sample from $B(OH)_3$ which is believed to be promoted by the excess hydrogen induced into the plasma interacting with boron radicals.

Chapter 4

Computational Characterization of Plasma Flow Field Using Coupled EM/CFD Simulation Environment

To better determine the critical synthesis parameters, it is important to understand the roles of the experimental parameters. It has been previously shown that the critical drivers are the temperature field and associated pyrolysis times, along with the velocity downstream of the plasma. Direct measurement of these characteristics can be difficult because of the excessive temperatures within the plasma. At certain points in the experiment, measurements can be made, but an overall understanding of the flow field characteristics is required to fully understand the synthesis parameters' impact on the resulting powders formed. This understanding is especially important in order to be able to take lab scale results and scale them up to more industrially representative applications. A strategic manner to achieve this understanding of the flow field and what is happening within the plasma is through computational simulation.

The modeling package selected for this work is ANSYS's HFSS and Fluent simulation environments. The two are used together in ANSYS Workbench in order to calculate the electromagnetic fields generated in inductively-coupled plasma torches by an RF coil along with the subsequent heating of the plasma and precursor carrier gas because of their flow conditions based upon the electromagnetic energy mapping. ANSYS's High Frequency Structural Simulator (HFSS) is an electromagnetic solver capable of computing E fields generated in an RF environment. The detailed 3D geometry of the coil carrying the RF power, quartz torch, and plasma gas domain can be imported into the 3D simulation thus allowing for the prediction of E fields, even in the case of complex torch geometries. The analysis then permits for the field sensitivities to coil positioning, power levels, and RF frequencies to be parameterized and understood. With
the plasma region's sensitivities to these physical condition now determined, the driving functions which promote the synthesis of nanopowders can be better understood.

For various plasma applications, others have generated similar models to capture the magneto-hydrodynamics of their experimental systems. There are two types of system which are typically modeled in this manner, i.e., DC arc plasma and RF inductively-coupled plasma. Levouvier [41] was able to model the 3-dimensional laminar flow of a DC arc jet plasma, whereas Deng [42] captured 2-dimensional flow fields while also looking into the effects of both laminar and turbulent plasma gas flow. Much work has been done on the 2-dimensional modeling of ICP systems [43] [44] [45] [46] [47] [48] [49], with only one example of 3-dimensional ICP modeling found in the literature [50], which was similar to the proposed modeling methods here, albeit with some key differences. The specifics characteristics of each of these modeling approaches will be discussed later in conjunction with the assumptions made in the modeling approach proposed here.

There are two main elements of the modeling of an RF inductively-coupled plasma torch: the electrodynamics which captures the inductive heating, and the fluid dynamics of the plasma gas through the torch which captures the plasma gas's flow to the substrate. The fluid flow is governed by the Navier-Stokes equation:

Conservation of Mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho V) = 0 \tag{2}$$

Conservation of Momentum, for incompressible laminar flow including viscosity induced shear tensors within the fluid flow as well as gravitational affects:

$$\frac{\partial \rho V}{\partial t} + \nabla \cdot (\rho V \times V) = \nabla p + \nu \rho \nabla^2 V + J \times B + \rho g$$
(3)

And Conservation of Energy:

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho h V) - \nabla \frac{\lambda}{c_p} \nabla h = \mathbf{J} * \mathbf{E} - S_{radiation}$$
(4)

J*E becomes equal to the resulting resistive heating energy with $S_{radiation}$ being the heat flux energy lost due to the radiation of the plasma to the ambient surroundings. J, B and E are the electrodynamic elements of the system: current flow, magnetic field, and electric field respectively. J and E are related by Ohm's law where σ is the electrical conductivity of the plasma domain:

$$J = \sigma E \tag{5}$$

The Electric and Magnetic fields are related to the Vector Potential, A by:

$$E = -i\omega A, \quad B = \nabla \times A \tag{6}$$

The total current through the plasma is then defined by the Maxwell-Ampere relationship

$$\Delta A = -\mu_0 J \tag{7}$$

The entire system can then be defined using the Maxwell equation where J^{coil} defines the current through the RF coil and thus relates it to the Potential and induced fields within the plasma

$$\nabla^2 A - i\omega\mu_0 \sigma A + \mu_0 J^{coil} = 0 \tag{8}$$

The advantages provided by a robust three-dimensional coupled CFD / EM solver is apparent from the complex mathematical relationships between the induced resistive heating and the fluid flow. Figure 4-1 shows an example of the 3D geometry created and imported into the simulation environment. One of the advantages of using a commercial modeling environment such as ANSYS is the ability to analyze more complex geometries by utilizing the robust meshers and solvers embedded in the ANSYS products. This allows for not only the validation of this modeling approach with this specific application but also the ability to first model scale up and other applications in order to ensure the desired flow field environment is being established. This ultimately can allow for iterative design optimization to be conducted before constructing any elaborate synthesis apparatus.



Figure 4-1: Torch Geometry w/ RF Coil & Plasma Domain

Certain assumptions are made about the plasma's environment in order to determine the system's governing equations. The most critical assumption is that the plasma is optically thin with local thermodynamic equilibrium, which has been validated by Lebouvier [41]and Holik [50] in previous ICP modeling work. In the EM model, the plasma region is modeled as a solid with the electromagnetic properties of argon gas for the density and electrical conductivity. The temperature dependent electrical conductivity is estimated by using the relationship to the electron density, n_e, and mean free path, λ_{e} , which was verified with empirical and experimental results for argon plasma in the literature [51]. The electrical conductivity has been defined by Olsen [52] to be:

$$\vartheta = \frac{e^2 n_e \lambda_e}{\sqrt{3m_e kT}} \tag{9}$$

The electron density within the plasma is calculated using Frost's [53] solution to the Saha equation:

$$n_e = (K_1 N_a)^{1/2} \left[\left(1 + \frac{K_1}{4N_a} \right)^{1/2} - \left(\frac{K_1}{4N_a} \right)^{1/2} \right]$$
(10)

where

$$K_{1} = \left(\frac{2g_{i}}{g_{o}}\right) \left(\frac{(2\pi m_{e}kT)^{3/2}}{h^{3}}\right) e^{-\frac{eV_{i}}{kT}}$$
(11)

The statistical weights of the ions to neutral atoms, g_i / g_0 is assumed to be 0.5 by Frost [53] and for this particular application the first ionization energy, eV_i , is 15.759 eV for Argon ions. The mean free path for noble gas molecules is calculated by:

$$\lambda_e = \frac{RT}{\sqrt{2\pi}d^2 N_a P} \tag{12}$$

where d is the diameter of the argon molecules being ionized and P is the operating pressure, in this case 1 atm.

It is assumed that only the electrons from the ionization contribute to the plasma's conductivity. Any residual neutral Argon atoms or positively charged ions have a mobility which are at least two orders of magnitude less than that of the free electrons, so their contribution to overall electrical conductivity is ignored [54].

HFSS is unable to model a moving domain so its ability to truly capture a fluid's response is somewhat limited; however, it is adequate for this application. The rate at which the coupling takes place is driven by the RF frequency, resulting in orders of magnitude difference between the coupling time and the actual dwell time because of the speed with which the gas is flowing through the torch. Furthermore the characteristic frequency of an argon plasma operating at atmospheric conditions is orders of magnitude greater than the MHz range of ICP operations [50] [38]. This provides ample time for the plasma to equilibrate effectively instantly after each RF cycle. This essentially results in a standing field through which the argon gas flows and creates the plasma, making the assumption that the EM field's motion is not captured in the model valid. Once the EM results are coupled with Fluent, the associated heating will be captured, but for the purposes of determining local field strengths. The discrete argon atom motion can be ignored. This is because at the flow velocities in question, the actual displacement through the plasma domain of a given atom for the time step of these high RF frequencies would be well below the mesh discretizing size of the model. This quasi-static characteristic is what allows for the modeling of the plasma domain as stationary from an electromagnetic standpoint to be valid. The mechanism by which the field is induced is by the power oscillating at the operating frequency through the coil. The coil is included in the model as a solid copper wire with a source current on the end. The current is correlated with experimental power levels by using Ohm's Law relationship of $P=I^2R$ where R is estimated to be the complex impedance of the coil because of its geometry and operating frequency of 40.68 MHz [55]. The power is known from the RF power supply's ranges and setting in the experimental setup so the direct calculation of the current load at the operating frequency is straightforward given the known incident RF power and calculated equivalent resistance. The coupling efficiency between the incident RF power and the plasma domain is assumed to be perfect given the optimization of the characteristic skin depth and physical design of the system which has been shown to be a valid assumption [38] [43]. In this system's case, with the 40.68 MHz operating frequency and an Argon plasma with a 50 1/(Ohms*m) conductivity, using Equation 1 the skin depth is estimated to be 1.12cm. This is the penetration depth of the RF field radially from the coil so a total diameter of 2.24cm is effectively coupled which is just slight larger than the diameter of the quartz torch being used. Experimentally it has been seen with the experimental system being modeled here for the coupling to be between 97 and 99% efficient. This is based on comparing the

incident energy from the RF power supply to the reflected energy back out of the matching network. Anything not reflected is assumed to be fully coupled to the plasma.

The work here utilizes preprocessing and solver version of HFSS 16 in ANSYS Workbench v15. These first results shown are an example of the E-field solved for within the plasma domain and the field's sensitivity on source power. Figure 4-2 and 4 show the E field for a 625 W and 800 W cases, respectively, demonstrating the power level impacts on E field intensity. In Figure 4-1 the quartz tube is also included to aid in visualizing the results in reference to real application. Because of the large variations in field strength within the region, the contours are plotted as logarithmic contours to aid in visualizing and interpreting the results more effectively. Although helpful, these plots and results do not provide much interpretation of the impact on the flow field without coupling these results with a CFD solver.



Figure 4-2: 625W HFSS Results for E Field

Figure 4-3: 800W HFSS Results for E Field

The HFSS results show the increase in the E field strength within the plasma domain for the 800W RF power case compared to the 625W RF power case. On their own, these results aren't very telling however the following section will show how these field results will be used to map the energy source into the CFD solver in order to determine flow field temperatures.

With the E field defined by the HFSS solver as shown by Figure 4-2, these results can be mapped into Fluent to determine the heating induced in the plasma gas region. Again, utilizing a 3D simulation environment for solving the gas flow provides multiple benefits. Since plasma torches typically have multiple gas inlets for the purposes of providing the plasma gas, sheath cooling gas, and precursor carrier gas, the variation of the torch's flow field can be captured based on these differences in pressures, velocities, etc. These inlets are also typically radial inlets, so the 3D solver allows for the radial velocity components to be captured in the results. Furthermore, these models can be expanded to look at substrate positioning to predict boundary layer thicknesses and stagnation flow characteristics. These flow field characteristics are difficult to measure in situ

during plasma synthesis, so the simulation's characterization of what is occurring in the plasma region.is used to correlate the structure and size of experimentally collected nanopowders.

Using the Fluent v15 beta features, the volumetric heating from the EM source in HFSS is mapped onto the fluid domain in Fluent. At this point of the coupling, a checksum is performed to verify that the total power mapped into the fluid domain is equal to that of the experiment setting. Recall earlier it was discussed how HFSS results are determined based on the current load applied to the coil in the model which is calculated based on the estimated impedance of the coil. This step verifies that the EM field modeled in HFSS appropriately represents the experimental condition attempting to be simulated in Fluent. The fluid domain is modeled as a laminar incompressible flow using the coupled steady state solver. For plasma systems, it has been shown that laminar flow yields the optimal RF coupling and resulting thermal heating results compared to turbulent plasma gas flow [42]. For given incident power levels and radial positions with a torch, turbulent flow sees a 20% reduction in resulting temperature. Figure 4-4 shows an example of the results from the simulation environment being developed here. A cross sectional view of the torch/plasma region is shown to visualize the radial variation in temperature in the flow field. The larger domain downstream of the torch is modeled as an ambient pressure and temperature outflow, with the bottom of the domain being modeled as a wall to capture the stagnation point. Figure 4-4 shows an example of this stagnation point flow field.



Figure 4-4: 625W Case - Temperature (K)

The contours are helpful for an overall visualization of the results; however, they do not provide the critical information necessary for correlating the plasma conditions with the quality of powders produced experimentally. As previously mentioned, it is believed that the key driver is the time integrated temperature gradient exposure during pyrolysis and deposition. For this reason, it is imperative to be able to predict the temperature and velocities as a function of position within the torch. Figure 4-6 shows an example of this temperature profile for the 625W case along the centerline of the torch. These temperature profiles are captured using iso-surfaces with very small widths so that they are essentially axial vectors of an individual radial point; however, because of mesh variations, this is not exactly the case. Later, the importance and benefit of these thin isosurfaces for evaluating radial asymmetries will be discussed. The coordinate system used for all of these simulations defines the (0,0,0) point as the downstream exit of torch, with the positive

Figure 4-5: 625W Case - Stagnation Point Velocity (m/s)

The highest temperature in the plasma is seen right in the center of the plasma region in the center of the RF coil. The field isn't perfectly axisymmetric due to the slight pitch in the RF coil which is captured by the 3D solver. Also there is the radial swirling of the gas flow due to the side inlets of the sheath and plasma gas. The right image shows the velocity decay at the stagnation point in the center of the substrate.

axial or Z direction being downstream outside of the torch from the origin. Figure 4-6 shows the highest temperature seen to be within the torch, then decaying as the flow exits as seen in the temperature contours of Figure 4-4.



Figure 4-6: Temperature Profile Along the Torch Centerline for 625W case

To further characterize the plasma flow field environment, a parametric study is performed to understand how each of the critical experimental factors contribute to the key characteristic parameters of the flow field. Again, the focus of the modeling results are on the temperature and velocity profiles to resolve the temperature history. The various parameter combinations modeled, as shown in Table 2, examines different RF power levels which are the key drivers in the temperatures. Then within the 1000W and 1200W RF power levels, the plasma and sheath flow rates are modified again to have two results to compare, where only one independent variable is modified. With these results, side by side comparisons of how modifying the sheath velocity solely impacts the flow field, as well as with the RF power changes in the same inlet conditions to the sheath and plasma gas rates.

The 0 position in the plot is the bottom end of the torch. It can be seen that the plasma gas starts at ambient conditions and then begins to heat up as it reaches the plasma and peaks at the center of the coil. The centerline temperature begins to decay as it flows away from the peak E field strength and then rapidly decay as it exits the torch and plasma region completely.

RF Power	Plasma Mass Flow Rate	Sheath Mass Flow Rate	
600 W	0.6 LPM	6 LPM	
	0.8 LPM		
	1.2 LPM		
800 W	0.8 LPM		
	1.2 LPM	8 LPM	
	1.6 LPM		
1000 W	0.8 LPM		
	1.2 LPM	10 LPM	
	1.6 LPM		
	0.8 LPM		
	1.2 LPM	14 LPM	
	1.6 LPM		
1200 W	0.8 LPM		
	1.2 LPM	12 LPM	
	1.6 LPM		
	0.8 LPM		
	1.2 LPM	14 LPM	
	1.6 LPM		

Table 2: M&S Parametric Study Configurations

Starting with the 1000W cases, it can be seen how just the variation of the sheath gas flow rate affects the flow field. For each case, a contour plot of the total temperature, in Kelvin, and axial velocity, in m/s, is shown. In addition to the contour plots, a spatial profile along the torch centerline is shown for the total temperature and axial velocity. For the velocities, positive Z flow is flowing down through the torch. Anything negative is back-flowing and recirculating. There are

a few trends, independent of the conditions which should be noted. Firstly, given the fact that the simulation uses a 3-dimensional model, there are a number of asymmetries in the flow. The pitch of the coil induces an electromagnetic field within the domain that is not axisymmetric, and the radial inlets produce a swirling effect which further induces asymmetric temperatures and velocities once the flow reaches the plasma region within the coil near the end of the torch. As seen in the centerline flow profiles, a periodic rise and fall in temperature can be seen which for the higher energy cases corresponds to the alignment with the coils at the point of greatest RF power coupling. Once the end of the torch is reached, the temperature of the flow decays fairly quickly as the flow gets further from the coil and then reaches close to a steady temperature before reaching the substrate. It is believed that within this constant temperature region, downstream of the highly ionized plasma region, is where the free B^+ & N^- radicals bond and particle growth initiates.

For the first comparison, the sheath velocities are varied for the 1000W / 0.8 LPM plasma gas flow rate condition. Firstly, the temperature variation from the 10 LPM sheath gas to 14 LPM sheath gas are shown in Figure 4-7; and the axial velocity changes in Figure 4-9. As expected, with the reduced sheath gas volumetric flow rate comes less total mass flow through the system, resulting in an increased overall temperature trend due to the energy balance.

Total Temperature Contour Plots



Figure 4-7: 1000W, 0.8 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Temperature Profile Comparison

Comparing the two different sheath cooling gas conditions, as would be expected the overall temperate profile for the higher sheath gas condition on the right is lower. The finer mesh in these conditions capture the slight axial variations in temperature as the flow gets closer to each part of the coil in the given cross section. The temperature contour plots show how the sheath gas shapes the conical plume of the plasma downstream of the torch's end. The swirling flow for this quasi-static condition shows the slight radial variation in the flow's substrate termination

In the previous section, the importance of velocity matching for the sheath and plasma gas was discussed. The criticality of this can be seen in the model's velocity predictions shown in Figure 4-9. Once the end of the internal quartz cylinder in the torch is reached, the flow fields of the sheath and plasma gas meet one another and begin to mix. Because of the large mismatch in both of these cases, a fairly sizable recirculation zone can be seen in the center of the torch. The plots on the right-hand side show the increased "squeezing" of the plasma gas's flow because of the increased flow rates and temperature gradients inducing baroclinic pressure variations as evident by the contour plots shown in Figure 4-8. When the plasma gas flow rate gets too low and that is coupled with high rate sheath gases, the plasma gas doesn't have enough momentum to overcome the baroclinic forces. This ultimately results in the large region of recirculation to occur within the torch. It should be noted that the exact flow within these recirculation zones is not well characterized given the simplicity of the turbulence model used in this simulation. There is much uncertainty of just how to accurately model the turbulence parameters of the highlighted ionized plasma region, so for that reason, the inaccuracies of the solutions within these subsets of the domain are accepted. For the purposes of this model though, simply understanding where and when the recirculation are beginning is adequate and accurate enough based on the laminar solvers. The majority of the flow-field is laminar, so the predicted temperatures based on the laminar mass flow rates are within the acceptable predictive errors.



Figure 4-8: Dynamic Pressure gradients inducing baroclinc forces - (Left) 800 Watt / 12 LPM Sheath Gas / 0.8 LPM Plasma Gas condition, (Right) 800 Watt / 8 LPM Sheath / 1.6 LPM Plasma Gas condition.

Axial Velocity Contour Plots



Figure 4-9:1000W, 0.8 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Axial Velocity Profile Comparison –

The velocity profiles shown in the two contour plots show how the velocity mismatch between the sheath and plasma gas start to create a small region of recirculating flow in the center of the plasma region. As would be expected, the higher sheath rate pinches the plasma gas flow inward earlier upstream and more severely. The plots of the centerline velocity show how for the 14 LPM sheath on the right the total velocity peaks out at a higher velocity and also has a greater recirculation velocity. Both of them then decay to zero as the end of the flow field is reached at the 0.05m positon where the substrate is positioned.

As the plasma gas's flow rate is increased, the overall temperature begins to drop because

of the higher flow rates and shortened exposer time to the RF energy as the argon flows through

the coupled RF field. Overall though, the temperature variation and velocity trends appear to match the initial case.



Total Temperature Contour Plots

Figure 4-10: 1000W, 1.2 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Temperature Profile Comparison

Increasing the total plasma gas flow rate compared to the previous runs shows the overall reduction in the total temperature. The different sheath gas rates then further shapes the difference in the temperature contours seen within the plasma region.

As the plasma gas flow rate is increased, the velocities of the two inlets get closer to matching, and the recirculation zone begins to shrink, as seen in Figure 4-11.

Axial Velocity Contour Plots



Figure 4-11: 1000W, 1.2 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Axial Velocity Profile Comparison

Lastly, for the 1000W cases, the plasma gas is increased even more in order to capture the trends in temperature and velocity profile changes with increased plasma flow rate, as evident in Figure 4-12 and Figure 4-13.

Total Temperature Contour Plots



Figure 4-12: 1000W, 1.6 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Temperature Profile Comparison

Axial Velocity Contour Plots



Figure 4-13: 1000W, 1.6 LPM Plasma, 10 LPM Sheath (Left) / 14 LPM Sheath (Right) Axial Velocity Profile Comparison

The first part of the 1200W cases focused on varying only the RF power to compare against the 1000W results for the 14 LPM sheath rates and 0.8/1.2/1.6 LPM plasma gas rates. Figure 4-14, Figure 4-15, and Figure 4-16 show the side-by-side results of the temperature and velocity profiles for the 0.8, 1.2, and 1.4 LPM plasma conditions, respectively. Overall, when comparing back to the 14 LPM sheath results shown in Figure 4-7 to Figure 4-13, the increased RF power gives an overall temperature increase across the entire flow field in almost a vertical shifting manner. Overall, some recirculation is still present, as expected given the no change in the flow field conditions.



Figure 4-14: 1200W, 0.8 LPM Plasma, 14 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-15: 1200W, 1.2 LPM Plasma, 14 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-16: 1200W, 1.6 LPM Plasma, 14 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles

The next section of the 1200W cases shown in Figure 4-17 thru Figure 4-19 reduce the sheath gas down to 12 LPM, while again examine the 3 plasma rates of interest. As expected, the

reduced total mass flow rate in the system results in an increase in the overall temperature;

however, the flow trends remain fairly consistent.



Total Temperature (Left) & Axial Velocity (Right) Contour Plot

Figure 4-17: 1200W, 0.8 LPM Plasma, 12 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-18: 1200W, 1.2 LPM Plasma, 12 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-19: 1200W, 1.6 LPM Plasma, 12 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles

Moving on to the 800W cases, the sheath gas rates modeled are far lower in order to match up with what is typically run experimentally. Higher sheath rates would begin to significantly reduce the overall temperature in the system and ultimately result in unstable plasma regions experimentally. Once the 1.6 LPM plasma / 8 LPM sheath case is reached, the benefits of the velocity matching can be seen, with the recirculation zone downstream at the end

of the torch (Z=0) completely gone. As the recirculation of the flow is reduced, the spatial temperature decay profile also becomes more stable, as shown in Figure 4-22.



Total Temperature (Left) & Axial Velocity (Right) Contour Plot

Figure 4-20: 800W, 0.8 LPM Plasma, 8 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-21: 800W, 1.2 LPM Plasma, 8 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-22: 800W, 1.6 LPM Plasma, 8 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-23: 600W, 0.6 LPM Plasma, 6 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-24: 600W, 0.8 LPM Plasma, 6 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles



Figure 4-25: 600W, 1.2 LPM Plasma, 6 LPM Sheath Temperature (Left) Axial Velocity (Right) Profiles

Finally, the axial temperature histories for the iso-surfaces at fixed radial positions within the flow are examined. Figure 4-26 shows how moving out of the centerline, the maximum temperature and the overall decay profiles axially vary pretty significantly. This is not only due to the obvious variations in the flow from the sheath domain to the plasma domain, but also due to the radial dependency of the RF field intensity.



Figure 4-26: 1000W, 0.8 LPM Plasma, 10 LPM Sheath Radial Position Temperature Sensitivity - Center Line (Left), 2mm radius (Middle), 5mm radius (Right)

Chapter 5

Experimental Validation of Coupled Simulations via Atomic Emission Measurements

In order to have confidence in the model predictions, it is critical to be able to validate the simulation results with some empirical data. Direct measurement of plasma temperatures are difficult because the temperatures far exceed the limits of thermocouple materials. Measurements of the electric field within the plasma using Langmuir probes is a possibility; however, it is difficult to do so in many circumstances since it must be physically introduced into the plasma and still requires calculations to relate the electric field measurements to plasma temperature [56]. An alternative method to determining plasma temperature is by measuring the atomic emissions from the argon ions and using those intensities to determine the temperature [57] [58]. A triple spectrometer is used with a fiber optic detector to collect the atomic emission signals during the experiments [59]. The fiber optic detector is mounted with a focusing lens in order to focus the collected emission onto the smallest area possible within the plasma. A pin-hole filter is used to limit the depth of field to maximize the local resolution of the measurements taken. The entire focusing apparatus is mounted on a translation stage which is in turn mounted onto a scissor jack as shown in Figure 5-1. This allows for precise manipulation of the measurement point both axially along the plasma torch and radially. It is assumed that the temperature gradient through the flow field is axisymmetric and so radial measurements along one plane shall suffice for adequate characterization. The uniformity of the measurements taken on either side of the centerline for the plane measured validates this assumption.



Figure 5-1: Optics for Spectrometer Measurement

The fiber optic mount for the spectrometer used is shown here along with the vertical and radial translation stages used to move the optics focal point around the plasma.

For each collection point in the flow field, multiple collections are made in order to obtain a statisitcal average of the intensitities and determine the confidence in the calculated temperature based on the standard deviation between measurements. Overall, the measurments are more accurate closer to the plasma compared to down stream and radially outward. This is to be expeted since the signals are greatest closest to the plasma region. The plasma is assumed to be in local thermodynamic equalibrium and so the intensity measurments of the emissions are linearized using equation 13 in order to determine the temperature of the ionized argon atoms [58].

$$\ln(\frac{I\lambda}{Ag}) = -\frac{E_j}{kT} + \ln(\frac{hcN_0}{4\pi Z})$$
(13)

Linear Relation of Intensities to Determine Temperature

The plotting of this linearization shows the extraction of the temperature estimation based on the slope shown in Figure 5-2.



Figure 5-2: Emissions from 800W Experimental Case

Curve fitting the intensities for each of the wavelengths detected allows for the temperature at the measured point to be determined. Using the curve fit to the plot along with equation 13 allows for the temperature to be solved. Data collection performed with the help of Dr. Gang Xiong

Measurements are taken for multiple experiments under the conditions shown in Table 3 at various positions downstream of the torch's exit. The measurements are collected at varying increments, but there is clearly a consistent linear trend of the fairly slow decay of temperature, as measurements are taken downstream as indicated in Figure 5-3.

Parameter	Case 2	Case 3	Case 4	Case 5
RF Power	800 W	800 W	800 W	1000 W
Sheath Gas				
VFR	10 LPM	10 LPM	8 LPM	12 LPM
Plasma	1.0	0.8	1.0	1.2
Gas VFR	LPM	LPM	LPM	LPM

Table 3: Experimental Conditions for Temperature Profile Measurements



Figure 5-3: Plasma Temperature Based on Spectrometer Measurements

The significantly higher temperature at the end of the torch for the 1000W case can be seen to be almost 2.5x that of the 800W cases. Interesting through the temperature decay downstream of the plasma becomes fairly uniform once it gets further away from the torch. As the emissions become less as the flow gets further from the torch and the RF source, the uncertainty in the temperature estimates based on the emission measurements begins to grow excessively. For the 25mm position adequate measurements were only able to be achieved for cases 3 and 5.

As the temperature measurements are taken further downstream, the significant increase in the uncertainty becomes apparent from the growing standard deviation in the measurements. As previously mentioned, this is to be expected since the further the measurements are taken from the plasma region within the torch, the closer the signal gets to the noise floor of the measurements. Since the temperature is being calculated from atomic emissions, far enough from the torch the argon flow no longer has any emission despite the fact that the flow field's temperature is still quite hot until it impinges on the chilled substrate.

Comparing the initial measurement results with the temperature predictions for the EM/CFD model simulating the same experimental conditions, the results are within roughly 10% of one
Chapter 6 Experimental Results - Plasma Flow Field Stabilization & Particle Growth Control Characteristics

In order to perform effective experiments, is critical to ensure a stable plasma is generated. With the simulation and experimental measurement tools at our disposal, it is possible to tailor the plasma flow field using specific parameters, but there are limitations to the range in the experimental conditions. As previously mentioned, the simulations assume a quasi-static E&M environment, along with teady-state flow. The same is true for the experimental conditions for which we can properly analyze atomic emissions with the spectrometer, along with assuming local thermodynamic equilibrium (LTE). In order to get through the transient phase of torch initiation, there are a number of parameters which need to be considered.

The first parameter is the critical substrate gap which is the distance from the bottom of the coil to the substrate. This distance is a critical parameter because the plasma is a large energy sink once the ionization of the plasma is established. Prior to that, it is not a desired free path for the energy source to couple to, so, if the potential between the current carrying RF coil and the substrate, for their spacing distance, is great enough, the coil will arc to the substrate. Once this occurs, it is nearly impossible for the plasma to be established. Along with the substrate gap's criticality is that of the counter-flow rate. As the counter-flow's rate increases, the stagnation plane with the plasma flow gets closer and closer to the bottom of the torch as seen in Figure 6-1. If that plane enters the torch, the turbulence of the flow can disturb the ion distribution enough to cause the RF coupling to be interrupted, extinguishing the plasma. Note that the nitrogen counter-flow gas is far more difficult to ionize than the argon plasma gas.





Figure 6-1: Plasma without counter-flow

Figure 6-2: Plasma with maximum counter-flow

The counter-flow, when implemented in a manner that does not adversely affect the plasma, provides a very effective means of maximizing the quenching rate. Overall, the key is to maximize the pyrolysis residence time inside the plasma while then also minimizing the particle growth time outside of the plasma. This minimization is done by maximizing the quenching rate of the flow downstream of the plasma which yields the best control of particle growth. The XRD plots below show an example of synthesis results, which although have an excessive level of oxide particle shells as evident by the strong B(OH)₃ peak, do help depict this sensitivity well. Sample 1-65 is a baseline experiment which experienced fairly excessive particle growth caused by excessive temporal exposure within the plasma followed by suboptimal quenching rate during deposition. 1-72 not only implemented a higher plasma flow rate in order to reduce the dwell time within the plasma but also implemented a counter flow to maximize the quenching rate. Using the peak broadening of the XRD patterns for the two samples in Figure 6-3, the average particle size is predicted to reduce from 176nm down to 31nm by controlling the time integrated temperature exposure of the particles to inhibit particle growth.

Table 4: Experimental Condition & Results Comparison

Experiment	Sheath (LPM)	Plasma (LPM)	Run Time (Min)	Particle Size (nm)
1-72	8	1.2	2.5	31
1-65	8	0.8	2.5	176.8

The benefits of the counter-flow on particle growth is shown based on the peak broadening estimates in the XRD.





Figure 6-3: Stagnation Flow Condition's XRD Pattern

Figure 6-4: Counterflow Condition's XRD Pattern

Another parameter directly related to the plasma's sensitivity to nitrogen is the maximum critical precursor loading rate the system can tolerate without destabilizing the plasma. It was previously discussed how the bubbler / precursor vapor / carrier gas system works, and there is a proportional relationship between the precursor loading rate and carrier gas flow rate. This can be controlled somewhat by varying the liquid precursor temperature to reduce the vapor pressure or alter the carrier gas pressure in order to adjust the partial pressure ratios. However, again this is limited by the volatility of the borazine precursor. For these experiments the typical precursor loading rate is on the order of 0.05 mg/s to 0.65 mg/s; however, plasma stability becomes very challenging for conditions greater than ~0.25 mg/s.

The last critical parameter for maintaining a stable plasma is the sheath and plasma gas total flow rates, as well as their ratios to one another. The sheath gas's critical velocity is directly related to the RF power incident to the system. As the power increases so does the plasma temperature within the torch's plasma region. For this reason, it is critical to maintain adequate sheath gas mass flow through the system in order to cool the quartz torch effectively to prevent melting. This relationship is proportionally related to the energy balance shown in equation 14, but not exactly as was shown by the HFSS and Fluent models previously. This relationship assumes a uniform power distribution; however, as seen from the RF coupling model, this may not be the case. The energy distribution is instead related to classical helical antenna theory within the diametric volume of the RF coil [60], with the resulting temperatures being a function of this distribution, as seen in the simulation results and spectroscopy measurements. Depending on the gas, the specific heat of the gas may be a function of temperature, $c_p(T)$. However, since argon is a monatomic gas, its specific heat can be assumed to be constant, which can be found from the previously tabulated data of Appendix B of [50].

$$\dot{E} = \dot{m}c_{p}\Delta T \tag{14}$$

Equation 14 effectively predicts the overall average temperature within the plasma based on the incident power and total mass flow rate of the combined sheath and plasma gas flowing through the torch. This total average temperature is a good mechanism for ensuring the plasma torch doesn't melt when changing either the incident RF power or sheath gas parameters. This relation is effective for making sure the overall temperature doesn't change drastically from experiment to experiment which can melt the quartz torch, however as shown previously by the CFD modeling and spectrometer measurements doesn't capture the maximum temperatures seen within the bulk of the plasma domain.

The plasma gas mass flow rate is also critical, even more so during the initiation of the torch. It is important to have enough argon atoms within the torch's domain for the initial RF

energy to couple to in order to generate the plasma. Below a critical energy, there are not enough collisions to establish the plasma. After initiation though, reduction of the plasma gas flow rate is far more tolerable down to whatever level necessary to create the desired flow field and synthesis environment. For this reason, typically, the torch will be initiated at one condition and then quickly adjusted to the desired experimental condition. The plasma gas flow rate criticality during experiments is more tied to the sheath gas rate ratio rather than its absolute rate. This criticality is derived from the characteristics of the concentric volumetric flow domains for the sheath and plasma gas within the torch. As shown in the earlier M&S section, when there is a large plasma to sheath gas velocity mismatch, rather than the typical flow field as shown by Figure 6-5 a recirculation zone as shown in Figure 6-6 can form within the torch which can alter the overall pyrolysis time. In some conditions it can help increase the pyrolysis time as desired however it can also begin to deposit with the torch as shown in Figure 6-6 and yield aBN rather than the desired BN substrate deposition.



Figure 6-5: Plasma & Sheath Gas Flow Rate Ranges

The cross-sectional-area ratio of the sheath to the plasma domains is ~ 6.5 , so there is already a significant velocity mismatch between the two. If the plasma gas flow rate becomes too low relative to the sheath gas, the expansion of the sheath gas creates a throttling point in the plasma region. Such recirculation zone trends for the flow fields are outlined in the velocity contour plots of Chapter 4. These situations can be problematic because it is optimal for them to maintain a fairly constant velocity through the flow field to ensure uniform precursor decomposition and nanoparticle deposition downstream onto the substrate. If the sheath gas is too fast relative to the plasma gas, a small recirculation zone can be created in the torch. The problem then arises where the torch itself is being cooled by the sheath gas and thus presents a source for thermophoretic forces to draw the constituents from the decomposed precursor vapors to the surfaces of the torch. Since the recirculation significantly reduces the momentum of these constituents and newly formed BN particles, the thermophoretic forces induced by the ΔT between the flow & the torch are great enough to promote deposition onto the torch. Once this occurs, a preferential growth surface is presented to subsequent particles introduced into the recirculation zone. This will ultimately result in nearly complete deposition within the torch, with limited particle deposition downstream onto the substrate.





Figure 6-6: Torch Diagram w/ Two Flow Conditions Depicted

Figure 6-7: Torch Deposition of aBN

Chapter 7

Experimental Results on Short-Range Order Structured Amorphous BN (a-BN) Phases

7.1 Short-Range Order Structured Amorphous BN (a-BN) ICP Synthesis

The recirculation zone phenomenon, although not a typically desirable trait of plasma torches, plasma synthesis, or stagnation flow, does provide some interestingly unique characteristics. With the critical characteristics understood, the method of torch deposition is one which is quite repeatable. The resulting products from this deposition method is an interestingly amorphous structured BN phase. The powders are described as interesting because they result from experimental parameters which are largely different from that of typical plasma and CVD synthesis. Most notably, the largest deviation from the norm is that of the dwell time within the plasma. Thus far, the discussion has been focused on controlling the dwell time to limit the particle growth; however, in the recirculation zone, this is far from the case. Instead the exposure time of the precursor vapors and subsequently formed particles is essentially on the order of the experimental run times, which are anywhere from 2 to 10 minutes. As the vapors recirculate and as deposition within the torch is promoted, the deposited particles loosely agglomerate and situate on top of the plasma region within the torch. See Figure 7-1.



Figure 7-1: Torch Diagram of Recirculation Zone & Conditions Causing It

After the completion of deposition within the torch, the agglomerated samples are collected and crushed back into powder form for analysis purposes. The overall trend of these results are a primarily amorphous structure with a limited amount of turbostratic structured phase present, as shown by the X-ray diffraction plots Figure 7-4 and Figure 7-5. The peaks show a significant amount of broadening around the h-BN peaks, indicative of the sheets being skewed into a t-BN phase; however, given the amount of amorphous structure present, the particle size predictions because of the broadening may be skewed. Figure 7-2 and Figure 7-3 show SEM images of the resulting powders after crushing of the a-BN material deposited within the plasma torch. There is a fairly consistent particle size with limited distribution, as seen in Figure 7-2. The ultra-fine details of the spherical shells can been seen on the edge of Figure 7-3, where some contrast can be seen against the background of the SEM holder.



Figure 7-2: SEM Imaging of aBN Torch Deposition after crushing up agglomerated powders. SEM Images collected with the help of Zhizhong Dong.



Figure 7-3: Magnified SEM Imaging of aBN Torch Deposition

Zooming in with higher magnification shows the fine nano-structure within the powder. Images collected with the help of Zhizhong Dong



Figure 7-4: XRD Scan of aBN

The XRD scan of the amorphous powders are shown here with the hBN peaks overlaid. The short-range order can be seen with little structure shown with the exception of the two wide peaks around 26 and 41 degrees.

An interesting trend is that the results are largely independent of the critical parameters for substrate deposition, such as incident RF power to the plasma and the gas flow rates. Regardless of the overall plasma temperature based on the incident RF power and flow rates, or the overall exposure time due to the experiment's length, the overall trend of resulting agglomerates of a-BN / t-BN mixtures is impacted minimally as evident by Figure 7-5. This is believed to be due to the fact that the environment which the particles are exposed to, just above the plasma region, is well above any critical crystallization temperatures [22] [61] and so any perturbations in the specifics of the flow conditions are essentially irrelevant since the temperatures continually remain in excess of 5000K. The primary mechanism believed to be contributing to the continued annealing of the

deposited material is the radiative heating of the samples based on their proximity and almost intimate contact with the ionized plasma field.



Figure 7-5: XRD Scan of aBN Samples - 625W & 1000W

Another favorable trend of the recirculation zone is that it also serves to essentially eliminate any oxygen contamination within the sample. Everything upstream of the plasma is sealed off and kept at a positive pressure solely fed by the argon gas cylinders and the bubbler carrier gas / precursor vapor mixture. Thus, the oxygen contamination is essentially zero there. The plasma is then generated between the deposition region for the sample and the torch exit to the rest of the chamber. Although the chamber is double purged and backfilled with high purity nitrogen for all experiments, a certain amount of oxygen contamination will ultimately leak into the chamber at atmospheric pressure. A positive pressure is maintained at all times within the chamber, but still oxygen appears able to diffuse in at low levels based on the initial results from the substrate deposition. For the amorphous samples though, there are no $B_xO_yH_z$ contaminants seen in any of the XRD scans performed. The increased velocity and temperature of the plasma region prevent oxygen from diffusing upstream against the plasma gas flow, so a nearly perfectly inert control volume is generated within the torch.

The results of the low and high RF power see fairly similar results in terms of the overall short-range ordered structure of the powders deposited within in the torch. The overall temperature within the plasma doesn't appear to have much impact of the resulting powders.

Imaging of the powders via TEM is performed to better understand the specifics of the broadly amorphous structure, determine visually whether there are any signs of crystallinity, and gather better insight into the growth mechanisms. Figure 7-6 shows an example of the particles of one of the analysis sites at two different magnification levels. Image (a) confirms the agglomeration of multiple nanoparticles within the sample. Because of the agglomeration, the thickness of region of the sample being imaged varies relatively significantly. This results in the large contour of darkness/brightness to the images caused by layers being out of focus. The SAED pattern of this region is shown as well with 3 rings matching the reflections from the planes (002), (101), and (112) of h-BN (PDF#97-016-2870). The continuous nature of the rings are indicative of the polycrystalline nature of the sample, as can be seen in the image. Image (b)'s higher magnification gives better insight into the average particle size of roughly 23nm for this area of interest. The imaging also confirms that the composition of hexagonal phase within the sample is limited and difficult to find at the higher magnification levels. Image (b) shows the predominantly amorphous structure of each of the particles visible.



Figure 7-6: TEM Imaging of aBN Agglomerated Powders

Further analysis of the short-range order powders via TEM show the fine nano particles generated. Overall particles around 20nm in diameter can be seen. TEM Images collected with the help of Zhizhong Dong.

Although direct synthesis of the cubic phase of boron nitride is an ultimate goal, these results yielding a-BN do pose some unique benefits. Amorphously-structured boron nitride is an sp³ bonded phase, same as that of the super-hard phases of cubic and wurtzite. As discussed in the background, many alternate routes to producing c-BN, such as high pressure – high temperature (HPHT) pressing, utilize h-BN as a starting powder. H-BN is an sp² bonded phase and theoretically requires more energy to transition into the cubic phase. These nano sized a-BN powders may prove to be a more efficient initial source of boron and nitrogen for HPHT synthesis routes. Sumiya et al [62] demonstrated the use of micron size a-BN for consolidation and conversion to other BN phases at pressures and temperatures of 7-10 GPa and 500-2000°C, respectively. Zhu's work [63] focused on the use of h-BN as an HPHT consolidation starting powder. They looked at the transition phases of h-BN to c-BN via the intermediate phase routes of h-BN to t-BN to a-BN to

c-BN, claiming that an amorphous BN phase as a starting point may be a more efficient conversion route to c-BN. The evidence in the literature shows the potential benefits in consolidation from the use of a fine nano-scale amorphous / short-range order BN phase as a starting point for consolidation. Furthermore, it has been shown that the synthesis process of a-BN, via recirculating plasma flow, is highly robust to variations in flow conditions. By determining the fundamental growth parameters, other flow configurations with the appropriate experimental parameters can be determined that may be scalable to larger industrial applications for producing nano-scale amorphous BN.

It is especially interesting that given the high temperature conditions which exist within the plasma, along with the prolonged exposure times, that the short-range order is maintained. Moore [64] claims that BN will fully sublimate at temperatures above 3000K; however, based on the analyses and spectroscopic measurements performed, the BN deposited within the plasma region are exposed to temperatures far above these limits. Furthermore, the cooling sheath gas is downstream of the powder deposition, which would bring into question just how much cooling it can provide to the agglomerated BN deposited within the torch. One would expect that in line with typical annealing characteristics, such exposure would promote crystallization and particle growth. It has been shown that maintaining a nanostructure after annealing can be a challenge because of the further nucleation crystallization and growth promoted by the increased mobility at higher temperatures [65]. For h-BN nano-fibers, temperatures above 500°C will begin to promote crystallization [66]. This general characteristics, and may offer further benefits to nanopowder synthesis.

7.2 High Pressure / High Temperature Consolidation of aBN to yield cBN 8 GPa / 1000° C / 15 minutes

In order to determine just how well the nanoscale a-BN powders would serve as a BN source for other applications, initial HPHT experiments are performed to evaluate their consolidation and conversion to c-BN. Powders shown in Figure 7-7 with a ~ 20nm short-range order "amorphous" [67] particle size are used as the initial powders for this first experiment in a manner similar to h-BN HPHT consolidation and conversion [4] [7] [8].



Figure 7-7: XRD Scan of aBN Powders Used for HPHT Consolidation

In collaboration with Diamond Materials, Incorporated (DMI, a High Pressure High Temperature press [68] is used to consolidate the powders at the condition of 8 GPa and 1000°C for 15 minutes. Density calculations based on measurements of the consolidated sample yields results slightly above the theoretical density of 2.1g/cm³ for h-BN. Figure 7-8 shows calculations for measurements taken at multiple points during the consolidation phase. These results seem to indicate that some conversion to c-BN has occurred, although quite limited, given that the calculated density is far from that of c-BN's theoretical 3.45 g/cm³, based on maximum packing density of the cubic phase [67].



Figure 7-8: Estimated Bulk Density of Consolidated Powders at Each Consolidation Step

As the load is increased the pellet density begins to exceed the theoretical maximum density of hBN, indicating some cBN conversion although not a significant amount.

After consolidation, the pellet is crushed back into powder for further analysis. XRD scans in Figure 7-9 show that the majority of the sample is h-BN, based on the primary peaks. The nanocrystalline size is maintained, based on the peak broadening estimation of 11.6 nm particle size. Given that the density of the sample is not much greater than theoretical, it is likely that the percentage transitioned to c-BN is minimal and lost in the noise of the XRD scan.



Figure 7-9: XRD of Consolidated aBN Powder

Figure 7-10: XRD of Consolidated aBN Powder w/ Particle Sizes

7.3 High Pressure / High Temperature Consolidation of 50% a-BN Seeded with 50% Micron Sized c-BN to yield nano c-BN 8 GPa / 1000°C / 15 minutes

The lack of transition to c-BN can be attributed to the observations that at 8 GPa and 1000°C without a catalyst, it is difficult to get h-BN to transition to c-BN based on the work of others [4] [5]. Micron-sized c-BN is selected as a candidate catalyst for the next set of experiments. c-BN is selected as the catalyst because of its high hardness and to promote the further growth of cubic phase BN by providing a possible preferential growth plane similar to CVD methods. The micron scale cBN's stiffness and hardness under the 8 GPa pressing load provides localized regions of far greater contact pressures when acting on the initially amorphous nanoscale BN powders, similar to a series of diamond-BN presses "squeezing" the amorphous powders in-between them, also resulting in effective consolidation. A mixture of 50/50 % by weight of micron-sized c-BN and coarsely milled a-BN powders is used to test the a-BN's ability to transition to c-BN seeded with c-BN. For a given area under one of the larger micron size c-BN particles, a maximum packing density of the spherical nano particles is assumed to exist which equates to the localized consolidation pressures being increased by 1.698x of the bulk consolidation pressure at

each of the nano particles. Consolidation is performed under the same conditions as the previous 100% a-BN sample, 8 GPa / 1000 °C / 15 min, with the resulting products showing more promise than the pure a-BN sample. The consolidated pellet is crushed into powder to perform further characterization on the sample. The XRD plot shown in Figure 7-11 now shows the presence of both h-BN & c-BN with a limited amount of amorphous remaining. Based on the comparison of the h-BN and c-BN primary peak intensity ratios, the c-BN content is estimated to be between 67% and 73% by weight, compared to the 50% initial ratio. The a-BN, which converts to h-BN, maintains a favorable particle size of 28nm, calculated by the peak broadening; however, it can be seen that some of the initial catalytic seeding c-BN did not consolidate into a nano structure, maintaining its large micron grain size.



Figure 7-11: XRD of cBN Seeded HPHT Consolidated aBN

The conversion was primarily into hBN however it did maintain its nanostructure with a 28nm particle size. The intensity ratio of the cBN to hBN peak indicates some conversion of the aBN to cBN in addition to the 50% cBN seeding. The particle size measurements from the peak broadening however are dominated by the cBN seeding indicating a small percentage of actual cBN conversion from the aBN.

The less than ideal conversion to nano-scale c-BN is likely caused by the pressing conditions used. Previous work has shown that under an 8 GPa load, consolidation at only 1000°C

results in less than complete conversion, even in the presence of a catalyst. TEM imaging of the sample shown in Figure 7-12 confirms the results inferred from the XRD results. Figure 7-12 on the left shows a boundary region of the catalyst c-BN still maintaining its well-structured phase and large particle size. On the right, a region of conversion is shown where some of the amorphous regions can be seen with boundaries starting to consolidate into a high aspect ratio cubic order. The polycrystalline mixture of hexagonal and cubic in this region is confirmed by the d-spacing in the SAED pattern shown in the insert of Figure 7-13.



 Figure 7-12: TEM of Unconverted aBN at cBN catalyst boundary
 Figure 7-13: TEM of hBN / cBN mixture

 TEM Images collected with the help of Zhizhong Dong

Overall the plasma synthesized a-BN appears to be a favorable initial powder for consolidation using HPHT, with significant benefits over other starting powders such as h-BN (due to its starting nano size) or ammonia borane (which has temperature limits due to hydrogen evolution during heating that presents safety issues).

7.4 High Pressure / High Temperature Consolidation of 50% a-BN Seeded with 50% Micron Sized c-BN to yield nano c-BN 2 GPa / 1500°C / 15 minutes

A second series of consolidation experiments are performed using the a-BN powders as the initial BN source; however, a different High Pressure High Temperature consolidation system is employed. The new consolidation system is the QuickPress Apparatus from Depths of the Earth® [69] at Rutgers University (Figure 7-14), which is capable of consolidating at up to 4.0 GPa and 2000°C. For safety reasons, the system in these experiments is limited to 2.0 GPa and 1500°C. Although the consolidation pressure is less than desirable, this new system does allow for consolidation temperatures greater than the previous 1000°C, which as previously discussed, has limitations in terms of c-BN conversion [3] [4].



Figure 7-14: QuickPress HPHT Consolidation System

The system uses a hydraulic 100 ton ram and a high current inductive heating system to apply pressure and temperature, respectively, to the sample assembly being consolidated. The sample assembly itself consists of multiple parts. The powders are first loaded and green pressed into a capsule. Given the desired consolidation pressures, a 10mm diameter capsule is used to minimize the area (maximize the pressure). Because of the temperatures being in excess of 1000°C, a tantalum capsule is utilized for the experiments. Alternatively, titanium capsules of larger diameters can be used; however, at the higher temperatures, BN samples tends to react with the titanium and contaminate the samples. An example of these capsules is shown in Figure 7-15 with an MgO sleeve around it, used for centering in the furnace assembly.



Figure 7-15: Tantalum Capsule with MgO Sleeve

The capsule is then loaded into a graphite furnace, which is encased by a glass insulator as well as a salt sleeve. High current is run through the graphite furnace to resistively heat it and in turn inductively heat the sample. The insulators ensure that the current path flows only through the graphite furnace to maintain a constant resistance path and thus temperature. Thermocouple wires are welded together and embedded within the furnace assembly to monitor the temperature and allow the power supply to be adjusted to ramp up to the desired consolidation temperature. The entire furnace assembly sits on an insulator plate and bottom block to ensure temperature is maintained for the sample area. The rest of the system is cooled by a closed loop chilled water system. The salt sleeve with the graphite furnace in it sitting on top of the base plug insulator blocks and disks can been seen in Figure 7-16, along with the thermocouple wires coming out of the bottom of the assembly.



Figure 7-16: Furnace Assembly

Once ready for consolidation, the samples are brought up to 2.0 GPa and held there, while the temperature is gradually increased to 1500° C. Once the desired temperature and pressure are reached, the sample is held at those conditions for 15 minutes, after which the sample is brought back to ambient conditions in 1 minute. This is done by terminating the resistive heating and allowing the chiller to run at its maximum volumetric throughput. The quenching is done to ensure that any metastable phases achieved under the 2.0 GPa / 1500° C are quenched and maintained. A gradual reduction in either the heat or the temperature may result in undesirable particle migration.



Figure 7-17: Sample After Consolidation and Quenching

During this quenching procedure, there is a possibility that the tantalum sample holder may crack because of thermal shock from rapid cooling. As seen in Figure 7-17, the sample is intact within the salt sleeve assembly; however, once removed from the salt sleeve, the capsule breaks up into fairly consistently thick disks along the height of the capsule, as shown in Figure 7-18. The salt sleeve and graphite furnace are easily chipped away from the sample, and the consolidated sample with a tantalum ring around it remains.



Figure 7-18: Fractured Capsule After Quenching

To achieve the desired pressures, the capsule is of fairly small diameter. As such, the amount of powder used and resulting consolidated sample size are quite small. To best characterize the samples, they are left in the tantalum capsule rings. Removing them would risk the fracture of the consolidated sample and loss of the limited powders, so characterization is done with the tantalum rings included. The analyses were focused on the BN fracture surfaces of each of the disks as shown in Figure 7-19.



Figure 7-19: SEM Image of BN Fracture Surface. SEM images collected with the help of Zhizhong Dong

As shown previously, the a-BN samples require either a catalyst as shown in the literature review or c-BN seeding to promote c-BN phase transitions. The consolidation experiment here uses the same 50% micron sized c-BN / 50% a-BN ratio as previously; however, the applied condition is now 2.0 GPa and 1500°C. In this case of c-BN seeding, the c-BN is not acting in a catalytic manner but rather providing localized regions of high contract pressures to promote the

conversion of the nano particles into c-BN. The pre-consolidation XRD scan of the powder mixture is shown in Figure 7-20.



Figure 7-20: Seeded aBN Powders for Consolidation - 50% aBN / 50%cBN

In the XRD, the tantalum ring around the samples produces a strong peak, but since the purpose of this characterization is to get an initial assessment of the BN phase ratios and particle sizes, its inclusion does not cause any problem. For these characterizations, all of the sample disks, as seen in Figure 7-18, are placed onto a zero background holder on a spinner stage to ensure proper representation of the entire sample. The diffractometer handles the summation statistical averaging of the reflected x-rays as it scans the entire sample. Looking at the intensity of the peaks, the primary (111) peak of c-BN is significantly stronger than the (002) peak of h-BN, indicating a majority of the sample conversion to c-BN.



Figure 7-21: XRD of 50% cBN / 50% aBN at 2.0 GPa & 1500 C

The XRD scan of the samples are shown in Figure 7-21 with the broadening of the (111) cBN peak shown in Figure 7-22, indicating that a rather fine particle size of 93nm is maintained. The fine short-range order amorphous BN powder is credited with the conversion to c-BN and maintaining of a nano structure. The c-BN seeding is believe to generate localized pressures from Hertzian-like forces on the a-BN particles, so that they reach local pressures that are far greater than the bulk 2.0 GPa externally-applied pressure. Such local pressures can be very high, allowing for cubic phase conversion, while overall externally-applied pressure is relatively low. The temperature at 1500°C allows for the necessary mobility to promote such conversion.



Figure 7-22: cBN Particle Sizing of 50% cBN / 50% aBN at 2.0 GPa & 1500C

A disk from the consolidated sample is also examined by XPS to compare the bond types present in the sample. For these XPS scans, the boron scans are increased to go out to 202 eV in order to catch the π bond satellite of the B1s peak associated with sp² bonds located out around 200 eV [70]. This information can be used to distinguish better between sp² and sp³ B-N bonds. Since the XPS is a localized scan of the surface over a 30 micron diameter region, it is possible to isolate areas of the conversions throughout the sample. The scan region below shows an area containing both sp² h-BN and sp³ c-BN. An etching procedure is performed at 1000 eV for 80 seconds to remove a few nanometers of material in order to gain some insight into the fracture surface characteristics verses that of the bulk consolidated sample. Overall there is not much change in the sp² to sp³ ratios when comparing the surface results of Figure 7-23 and

Figure 7-24. The surface oxide is still present at the 193 eV peak, but there are sp^2 and sp^3 bonds distinctly present in both scans.



Figure 7-23: Surface XPS of of 50% cBN / 50% aBN at 2.0 GPa & 1500C

Figure 7-24: Etched XPS

7.5 High Pressure / High Temperature Consolidation of 80% a-BN Seeded with 20% Micron Sized c-BN to yield nano c-BN 2 GPa / 1500°C / 15 minutes

Given the success of this consolidation, the next experiment investigates reducing the amount of c-BN seeding to gauge its criticality. The weight ratio of the seeding is reduced to 20% micron sized c-BN / 80% a-BN with the consolidation conditions of 2.0 GPa / 1500° C remaining the same. Since the seeding is providing localized increases in consolidation pressures, it is actually the volume ratio of the seeding which is the critical parameter. However to ensure

consistency from experiment to experiment, weight ratios were used to compare the samples. Again for baselining, the pre-consolidation powder mixture's XRD scan is shown in Figure 7-25.



Figure 7-25: Seeded aBN Powders for Consolidation - 80% aBN / 20%cBN

The large reduction in the amount of c-BN in the initial powder has a negative effect on c-BN conversion, as evident in the XRD results shown in Figure 7-26.



Figure 7-26: 20% cBN / 80% aBN at 2.0 GPa / 1500 C

Compared to the 50/50 c-BN/a-BN mixture, only a very small amount of c-BN is present in the final sample, based on the weak intensity of the (111) peak of c-BN. It is likely that the seeding is actually all that is contributing to this characterization. Using peak broadening to estimate the particle size, Figure 7-27 shows the small amount of c-BN present is greater than 100 nm, indicative that only the initial micron sized c-BN is present, with negligible conversion of a-BN.



Figure 7-27: 20% cBN / 80% aBN at 2.0 GPa / 1500 C w Particle Sizing

XPS is performed on the surface of one of the capsule disks to better characterize the fracture surface of the sample. While the XRD is an aggregate average of all of the disks of the capsule, the XPS scans focus on a 30 μ m diameter area of one of the sample disks. Consistent with the XRD results, Figure 7-28 shows that the sp³ boron bond for the cubic phase of BN of 190 eV is quite low in intensity compared to that of the other binding energies. Comparing the intensity ratios, the ratio of atomic percentages can be determined; and for this surface scan, the sp² to sp³ ratio is roughly 12:1. Assuming that the sp² is completely hBN and sp³ is the c-BN seeding, based on the density ratio of ~1.5x this means that this scan is showing roughly 8:1 sp² to sp³. This is less than the bulk initial weight ratio of 20/80 which indicates this particular region scanned was possibly under-seeded and thus mostly unconverted to c-BN. Instead the a-BN converts solely to

 sp^2 h-BN. There is also a strong intensity peak at 193 eV, suggesting B₂O₃, which is not unexpected since an exterior oxide layer is expected to be on the BN particles, presumably introduced during handling prior to consolidation.



Figure 7-28: Surface XPS Scan - 20% cBN / 80% aBN at 2.0 GPa / 1500 C

In addition to the surface scan, an ion bombardment step is performed at 1000 eV for 80 seconds to mill away the fracture surface in order to profile the depth of the sample. For BN samples, 1000 eV for 80 seconds equates to roughly 4 nm of material removed. After the 4nm surface milling, the sp² to sp³ ratio has changed to 9:1, based on the intensity ratios of Figure 7-29. This is likely because the fracture planes induced by the thermal stresses during the quenching process are likely to occur at the locations of predominantly h-BN particle planes. As the milling

gets down further into the core of the sample, more c-BN becomes present. Also the second sp² peak around 199 eV nearly vanishes; and all that is left is the typical sp² peak at 200 eV



Figure 7-29: Etched XPS Scan - 20% cBN / 80% aBN at 2.0 GPa / 1500 C

Looking at the fracture planes of the consolidated capsules under a field emission scanning electron microscope, further insight into the microstructure of the resulting consolidated sample can be gathered. Consistent with the XRD and XPS results, the lower magnification imaging in Figure 7-30 shows a large area with a number of unreacted micron-size c-BN seeding particles located throughout the plane. The remainder of the sample displays an agglomerate of sheet like BN particles. In this case with inadequate seeding to achieve the necessary localized pressures for c-BN conversion, the 1500°C temperature effect is expected to promote sheet-like h-BN phase formation from a-BN phases.



Figure 7-30: FESEM of 20% cBN / 80% aBN at 2.0 GPa / 1500 C. SEM images collected with the help of Zhizhong Dong

Increasing the magnification of the FESEM, a better look at the sheet-like high aspect ratio particles can be seen in Figure 7-31, with the micron c-BN seeding around them. The sheet morphologies are noticeably large in size. In the (002) direction, they are fairly thin; however, in the other planes, there is significant particle growth. Without adequate local consolidation pressures, the elevated temperatures promote the particle growth seen here. Zooming in further on section (a) of Figure 7-31, a closer look at some of the small particles of c-BN conversion can be seen in Figure 7-32. Compared to the micron-sized initial particles, they are much smaller, i.e, around 180 nm in size, though still not quite technically in the nanoscale regime (i.e., < 100nm).


Figure 7-31: Magnified FESEM - 20% cBN / 80% aBN at 2.0 GPa / 1500 C. SEM images collected with the help of Zhizhong Dong



Figure 7-32: Inset (a) of Magnified FESEM - 20% cBN / 80% aBN at 2.0 GPa / 1500 C. SEM images collected with the help of Zhizhong Dong

Chapter 8 Experimental Results – cBN Direct Deposition

8.1 XRD Characterization of ICP Synthesis of c-BN powders

With the appropriate ratios of sheath and plasma gas providing the proper axial velocity matching between the two, plasma synthesis can be performed such that the precursor vapors flow through the plasma and decomposes via pyrolysis, resulting in BN particles nucleating downstream of the plasma and powder products depositing onto the chilled substrate. Under these operating conditions, the amount of amorphous powders deposited within the torch are insignificant (as previously discussed in Chapter 7 on the recirculating plasma flow case).

The experimental results for the direct substrate deposition produced results which differed from what was initially expected. Seemingly regardless of the RF power levels, precursor dwell times, or experimental deposition run times, a significant presence of oxide contamination in the samples is observed. Figure 8-1 shows an example of the stagnation flow deposition surrounding the counter-flow jets in the substrate.



Figure 8-1: Substrate Deposition of Oxide Contaminated Powders

The mostly white deposition is a good visual indicator of possible powder composition, since c-BN powders are typically a dark gray. Hexagonal BN is known to be white in color; however, the initial characterization work shows an almost negligible amount present. Looking at the XRD pattern shown in Figure 8-2, the diffraction patterns indicate the powder to be primarily B(OH)₃.



Figure 8-2: XRD Scan of Deposited Powders w/ Oxide

The deposited powders are a favorably small particle size, with an average size of 59 nm for Figure 8-2 and 25.6 nm for Figure 8-3, based on the broadening of the primary peaks in the scans. The XRD indicates that the samples deposited are solely B(OH)₃; however using XRD only for characterization may be somewhat misleading. As previously discussed, given that the experiments are performed at ambient pressure, it is expected that some oxygen contamination may be present within the chamber. This oxygen will react with the free hydrogen produced by the borazine decomposition and the dangling bonds from the BN particles, forming oxide shells around the BN particles. Given the XRD's inability to probe more than a few nanometers into the sample, coupled with the small size of the particles, even after crushing up the powders for

characterization, it is nearly impossible to isolate a significant number the BN molecules of the particles.



Figure 8-3: XRD Scan of Direct Deposition

A very small peak can be seen in Figure 8-3 corresponding to the (100) plane of c-BN, centered around 43 degrees. The estimated particle size for the cubic phase is very close to that of the B(OH)₃, which supports the theory that the two peaks correspond to BN particles that have an oxide shell around them.

8.2 XPS Characterization of c-BN Powders Produced via ICP

To confirm the presence of BN phases in the powders deposited on the substrate, X-ray Photoelectron Spectroscopy (XPS) is performed. XPS not only provides information on individual elemental presence but also molecular and phase information can be inferred based on the binding energies identified for each element.



Figure 8-4: XPS Results for Deposition Containing Oxide

Looking at the XPS results in Figure 8-4, there is a significant amount of boron associated with a B_2O_3 bond, based on the strong peaks in the oxygen and boron scans at 533 and 193 eV, respectively [71]. The peak intensities are determined by the atomic percentage of each element's scan, so the 2:1 ratio for B_2O_3 compared to BN make the plots visually somewhat misleading since each B_2O_3 molecule has twice the number of Boron atoms in it compared to BN. Overall though the sample is contains a significant amount of oxide contamination with a 5:1 molecular ratio with the BN in the sample . The second small oxygen peak is assumed to correspond to residual moisture

in the sample from water vapor, but because XPS cannot resolve hydrogen bonds, it cannot be confirmed. The sp³ bond peaks for B is 191eV [10], and the 188 eV peak is associated with the B-B bonds of unreacted free boron in the sample. The corresponding peaks can be seen in the nitrogen scans confirming the small amount of the two phases of BN present.

8.3 TEM Imaging of c-BN Powders Produced via ICP

TEM is used to further evaluate this phenomenon of conflicting information coming from the two X-ray characterization methods. The imaging from the TEM provides visual indicators of the structure, especially for intermediate phases that would not be well captured by XRD. Another advantage of TEM is that since the powders are dissolved in an isopropyl solution before being deposited onto lacey carbon grids, the alcohol washing of the samples removes residual boric acid on the particle surfaces because of the solubility of boric acid in alcohol. TEM Imaging and SAED patterning of multiple samples confirms the existence of small c-BN particles. Figure 8-5 (a) shows an average particle size of 12nm, and insert (b) confirms the presence of c-BN based on the diffraction rings corresponding to the (111) and (220) planes of c-BN (PDF# 97-002-7879). Figure 8-6 shows another sample that, after washing, confirms c-BN presence. The imaging shows agglomeration in this particular sample; nevertheless, the SAED patterns confirm the (111) and (220) planes of c-BN. The rings of Figure 8-6 (b) are slightly less discrete than the spots in the rings of Figure 8-5 (b) because the particles in sample 1-121 are much smaller, thereby showing the polycrystalline structure of the sample. As the particle size gets smaller and smaller, the discretization of the points in the SAED pattern begin to blur together into what would almost be expected of a short-range order amorphous structure [67]. Sample 1-89, as shown in Figure 8-7,

corresponds to direct c-BN growth, as confirmed by SAED; however, this case is characterized by fairly excessive particle growth as visualized in the TEM.



Figure 8-5: (a) TEM of cBN nano particles; (b) SAED pattern of region – Sample 1-79. TEM images collected with the help of Zhizhong Dong



Figure 8-6: (a) *TEM of cBN nano particles;* (b) *SAED pattern of region – Sample 1-121. TEM images collected with the help of Zhizhong Dong*



Figure 8-7: (a) TEM of cBN nano particles; (b) SAED pattern of region - Sample 1-89. TEM images collected with the help of Zhizhong Dong

8.4 Modifications to ICP System to Improve c-BN Production

It was shown with the case of the recirculation region in the torch that if the decomposition and particle growth region, in that case upstream of the plasma, is kept free of oxygen, the deposited BN particles will terminate on themselves; and a minimal amount of oxide will be present in the system. In the case of the direct deposition onto the substrate, this is a bit more challenging. Two approaches are taken to better control the amount of oxide contamination introduced into the deposition. The first is to increase the sheath gas velocity to better shield the control volume downstream of the plasma in which particle formation and growth are occurring. Any oxide which makes its way into this control volume must diffuse in through the sheath region and is assumed to do so at nearly a constant rate. The characteristic time for the oxygen diffusion into the plasma can be defined by equation 15 where d is the characteristic length, the torch's radius in this case and D is the mass diffusivity of oxygen into argon.

$$t_{diffusion} = \frac{d^2}{D_{Oxegyn-Argon}}$$
(15)

Simplifying the problem and assuming that the diffusion is a one dimensional problem for the axisymmetric sheath region, it can be seen how the rate and thus time for oxygen to diffuse through the thickness of the sheath is essentially constant. It becomes critical then to ensure that the time it takes for anything within the sheath gas region to travel from the end of the torch down to the chilled substrate be less than this critical diffusion time through the sheath region. The mass transfer Peclet number is dimensionless parameter which can be used to characterize the sheath gas velocity's dependency. It is defined by equation 16 where the characteristic length, L, is again the torch diameter and u is the flow velocity. With a sheath volumetric flow rate of 6 LPM, the flow has an oxygen diffusion based Peclet Number of 46 which increases to 107 with a sheath rate

of 14 LPM. These high Peclet numbers rationalize the simplification of the oxygen diffusion problem into a one way 1D radial diffusion problem as proposed.

$$PE_L = \frac{L_{characteristic} * u}{D_{Oxygen-Argon}}$$
(16)

So as the axial velocity of the sheath is increased and superimposed with the diffusion velocity, the point within the particle growth region where oxygen is first introduced moves further and further downstream, as shown by Figure 8-8. What this allows for is ample time for B - N collisions to occur and form the BN particles before the oxygen is able interact with a significant number of free B^+ radicals.



Figure 8-8: Diagram of Oxygen Diffusion into Particle Growth Region

The second modification to the experimental procedure is to increase the overall precursor loading rate. What this provides is a higher number of boron atoms introduced into the plasma and particle growth region from the precursor compared to the essentially "fixed" amount of oxygen which diffuses into the region. It was previously discussed how the plasma can only tolerate a limited amount of foreign matter into it before it is destabilized so the flow rate of the precursor vapor and carrier gas cannot simply be increased indiscriminately. Instead, the operating pressure of the bubbler is reduced from 20 PSI to 15 PSI, such that the ratio of borazine vapor to carrier gas is increased since the vapor pressure of the borazine remains unchanged. Additionally, the carrier gas for the precursor is changed to argon so that the percentage of carrier gas in the precursor delivery would not contribute to the plasma destabilization, just the precursor vapor itself. Under these conditions, the total flow rate of borazine vapor and carrier gas can be increased slightly, likely because the highly volatile borazine vapor decomposes from the radiative heating of the plasma far easier than the N_2 carrier gas ionizes within the plasma, so the result is less destabilization per unit volume of the carrier gas / precursor vapor mixture.



Figure 8-9: Plasma with Moderate Counter-flow

The rapid quenching of the counterflow which is shown in Figure 8-9 not only allows for phase conversion control, but also improves the particle growth control. SEM Imaging of the

agglomerated powders is performed, and a side-by-side comparison is displayed in Figure 8-10. The image on the left shows a 1000W case where the counter-flow quenching nitrogen is limited. Compared to the image on the right, with the same experimental conditions, the particles are visibly far coarser. Note the significant difference in the magnification and associated scale between the two images.



Figure 8-10: SEM Imaging of Counter-flow Quench Rate Sensitivity. SEM images collected with the help of Zhizhong Dong

Zooming in on the left case of Figure 8-10, very few nanoparticles of 28nm in diameter can be seen in Figure 8-11, with the background being the primarily micron sized particles.



Figure 8-11: High Magnification SEM image of Low Quench Rate Condition. SEM images collected with the help of Zhizhong Dong



Figure 8-12: Substrate Deposition for Improved Experimental Conditions

Figure 8-12 shows the results of the changes to the experimental set up. The substantially darker deposition is clearly seen on the substrate, indicative of BN presence with an off-white ring surrounding the deposit. Also shown is a close up of the deposition around the counter-flow ports in the substrate. The presence of the white ring on the outer perimeter of the deposition, as seen in

Figure 8-12, supports the theory that oxygen diffuses from outside inward through the sheath region, as any B_xO_y formed in these outer most radial regions of the plasma would subsequently be carried the furthest outward radially by the stagnation flow-field geometry. Upon collection, these powders have a tendency to "roll up" as very fine sheets into loosely agglomerate tubes as shown in Figure 8-13.



Figure 8-13: Agglomerate Tubes of 1-143

Interestingly though, even after annealing the powders, as shown in Figure 8-14, the resulting XRD still shows the presence of what appears to be $B(OH)_3$, as seen in Figure 8-15. Annealing takes place at 600°C in a nitrogen environment for 6 hours, after which essentially no particle growth is seen based on the peak broadening of the XRD. A fairly significant amount of amorphous counts can be seen underneath the primary peaks. In case 1-143, we also began to see the presence of some h-BN in the sample, as well at the 26.6 degree primary 20 peak.



Figure 8-14: cBN Deposition Sample – Post Annealing



Figure 8-15: XRD for Sample 1-143, Pre & Post Annealing

Further characterization of these samples are performed with XPS to obtain better insight into the bond types and atomic ratios of each bond. Recall from the previous XPS analyses done, sp^2 and sp^3 BN bonds are found, but primarily the samples are B_2O_3 . After implementing the experimental changes discussed, the XPS in Figure 8-16 now shows the primary boron peak to be at BN's sp^3 191 eV peak. The B-B peak of 188 eV has also increased. Nonetheless, there is still some oxide present.



Figure 8-16: XPS of 1-143

Comparing the corrected intensity ratios, the atomic percentages for each element's peak can be determined. The sp³ BN polymorph present here is now $4.6 \times$ that of B₂O₃ on a molecular ratio. The increased loading rate for the precursor, coupled with the elimination of the nitrogen carrier gas, is the likely cause for the increased presence of unreacted free boron, as indicated by the 188 eV B-B peak. The experimental modifications have increased the BN peaks; however, there may also be unreacted Boron.

8.5 TEM Imaging of Improve c-BN Powders

Again TEM is used to gain further insight into the nanostructure of the as-deposited powders. With the TEM, not only is the highest resolution into the atomic structure capable of being seen, but also because of the high vacuum processing, the oxide shells are eliminated after alcohol washing during preparation of the lacey carbon TEM grids. Looking at the highest magnification images at various locations throughout multiple samples, a fairly consistent trend is seen, as depicted in the left half of Figure 8-17. Prior to imaging, the plasma synthesized powders are ground and sonicated in order to break up the agglomerates as best as possible prior to deposition onto TEM grids. Even

after this treatment, the resulting particles deposited onto the grids possess a significantly shortrange order to them. The right half of Figure 8-17 shows an FFT of the imaged area to determine the phases present based on d spacing of the particles in the image in the same manner as a diffraction image. Measuring the diameters of the points in the diffraction pattern, the presence of cubic phase is confirmed in this sample based on the presence of the (1 1 1) plane at 0.20871 nm, (2 0 0) plane at 0.18075 nm, (2 2 0) plane at 0.12781 nm, and (3 1 1) plane at 0.10900 nm.



Figure 8-17: TEM Image of Short-Range Ordered cBN Nano Particles

Additional characterization is done on the deposited BN powder samples from various high-quench rate experiments. Again, the trend of very short-range ordered samples with a mixture of c-BN, a-BN and h-BN can be seen. Figure 8-18 shows a good example of this blended mixture of periodic phase presence with the average length of the ordered regions being on the order of 10 to 15 nm.



Figure 8-18: High Resolution Image of Additional Short-Range Order Region

Looking at another location of the same powders as Figure 8-18, Figure 8-19 now shows regions of greater amorphous content, as evident by the non-discrete lattice points in the diffraction image generated by the FFT of the imaged region.



Figure 8-19: Additional High Resolution TEM Imaging of Short-Range Order Region

Increasing the quenching counter-flow gas from 8 LPM to 12 LPM yields what appears to be more clear regions of the c-BN metastable phase being maintained during deposition as seen in Figure 8-20 and Figure 8-21. A large number of fine particles are shown in Figure 8-20's diffraction pattern, with the smaller analysis area for the FFT in Figure 8-21 showing the single (111) plane of nanostructured c-BN. The trend of 10-20 nm phase periodicity appears to remain consistent throughout these various experimental condition runs and imaging locations through the samples.



Figure 8-20: Additional High Resolution TEM Image of Short-Range Order Region with Fine Particle Sizing



Figure 8-21: TEM Image of cBN Region with Diffraction Pattern Insert

Although there are regions through the various samples which show evidence of cubic phase presence based on the TEM imaging and diffraction patterns of the finer areas, the bulk sample analyses such as the XRD and SEM show differing results. This is due to the fact that the overall percentage of c-BN present is still lower than desirable. Looking at other regions throughout the sample, a more consistent trend appears to be present when looking at the larger bulk particles. A number of regions display what appears to be a sheet-like structured phase, similar to hexagonal phase, but with significant lattice strain. An example of these phenomena is shown in Figure 8-22 with some of the spherical particles shown to be loosely agglomerated of the left side with a higher resolution insert of the high curvature region focused in on the right. The curved lattice region is roughly 20nm thick consisting of about 20 atomic layers. This highly unique structure is likely an artifact of the high energy synthesis characteristics of the synthesis and particle growth region coupled with chilled deposition of the powders allow for such metastable phases to be maintained. The nomenclature turbostratic is used to describe such BN phases with high lattice strain and curvature which typically result in nanospheres or BNNTs as described in Chapter 2.



Figure 8-22: TEM of region with region of high lattice curvature. TEM images collected with the help of Zhizhong Dong

Chapter 9 Experimental Results – Turbostratic BN Direct Deposition

9.1 XRD, TEM & SEM Characterization of t-BN Powders Produced via ICP

With the increased precursor loading rate, increased sheath rate, and prolonged pyrolysis / nucleation times downstream of the plasma coupled with a steady counter-flow quenching gas rate, the t-BN phase is the dominant phase. RF power levels in the 800W to 1000W range appear to be necessary for t-BN to form, along with the counter-flow being lowered to around 4 LPM which yields an axial velocity of 7.3 m/s. As shown in Figure 8-9, this reduced counter-flow rate results in only the quenching the particles just prior to impacting the substrate, rather than affecting things further upstream within the plasma. This elongated nucleation time is believed to allow for the increase in BN phases to form after the plasma pyrolysis.

Further investigation into these polymorphs is done via TEM to get better insight into the individual particle sizing and diffraction patterning. In the regions imaged, a little amount of true amorphous material is found, with a majority of the sample being differently-oriented structured polymorphs. In Figure 9-1 insert (a), the agglomerates can be seen with an estimated average particle size of under 8 nm. Insert (b) shows the higher magnification imaging of Region A shown in (a), where sheet-like t-BN polymorphs can be seen. Insert (c) shows the SAED patterns where the (111) plane and (220) planes of c-BN can be seen.



Figure 9-1: Sample 1-143 TEM - (a) 7.67nm particle size; (b) high magnification region A; (c) SAED pattern of region A. TEM images collected with the help of Zhizhong Dong

Another interesting nanocrystalline polymorph is found, as shown in Figure 9-2. In this location the particles appear to have a core-shell structure, with the outer ring being something similar to h-BN sheets, and with a different polymorph within the ring. It is difficult to discern if lattice fringes are seen or if, rather, a short-range ordered amorphous structure is present. The shell structure is likely a turbostratic BN polymorph based on the significant lattice curvature with either unreacted boron or an alternative polymorph present in the core. These types of t-BN structures typically lead to the formation BNNTs or BN nanococoons [72].



Figure 9-2: 1-143 Region B. TEM images collected with the help of Zhizhong Dong

Looking further into other locations where the high curvature of t-BN can be seen, there are some trends that are noticed. Firstly, the linear planar sections are only 5 to 7 nm long before rchanging in direction change. The curvature of the nanospheres are not constant, but rather consist of these short linear sections, which appear to be spherical when zoomed out at lower magnification. Another consistent trend is that the shell walls are only 7 to 8 atomic layers thick, which is especially noticeable in the multiple overlapping particles in the right image of Figure 9-3. The final consistently noticeable trend is that for the nanospheres, which appear to self-terminate creating small nanococoons, typically contain what appears to be unreacted boron, as seen in the left image of Figure 9-3. The t-BN nanococoons images containing the unreacted boron are consistent with the XPS results showing an increased presence of B-B 188 eV peaks.



Figure 9-3: Additional tBN Sample with Multiple Locations Imaged. TEM images collected with the help of Zhizhong Dong

Examining the diffraction patterns of the bulk t-BN powders generated by a 12 LPM sheath /1.2 LPM plasma gas / 1000W plasma with 4 LPM counter-flow under XRD, a significant increase in the <002> plane's intensity is seen around 26°. Typically for t-BN, this is the only strong peak observed under XRD caused by high lattice strain. The other typically detected peaks for orthogonally-stacked h-BN planes are now skewed because of the significant curvature breaking the order of these planes, throughout the particle relative to the diffraction x-ray source. This results in the majority of the other planes appearing as an amorphous background with no distinctly strong peak. Note that the pattern shown in Figure 9-4 has the background removed along with the K α . There is, however, still a strong oxide shell peak visible around 27°, however, the ratios of the oxide to the <002> plane have been drastically reduced. This is evidence that the increased precursor loading rate and sheath gas velocities can reduce the overall oxide content.



Figure 9-4: Typical tBN XRD Pattern with Increased <002> Plane Intensity

Comparing the peak broadening of the <002> peak to the oxide shells, there is a noticeable difference in the predicted particle sizes. The <002> peaks are 73 nm in size, whereas the oxide shells are 26 nm. As seen in in the previous SEM images, the smaller oxide shells are likely the nanospheres whereas the larger particles are BNNTs with fairly high aspect ratios. The estimated particle sizing from the peak broadening and measurements from the imaging are both in the 20 nm range for the nanospheres. Since these nanospheres and nanotubes have a tendency to self-terminate in structure, the overall amount of dangling bonds is reduced and thus the oxide contamination along with it. This is a beneficial trait as, in general, for a variety of BN applications such as semiconductors or powders for consolidation, the presence of dangling bonds reduces the overall quality [73].



Figure 9-5: XRD Comparison of <002> plane and oxide shells for 1000W plasma

Imaging of a 12 LPM sheath gas/ 1.2 LPM plasma gas / 1000W plasma synthesis condition with an increased counter-flow rate of 12 LPM shows very fine nanoparticles scattered throughout the bulk sample.



Figure 9-6: SEM Imaging of tBN Nanospheres . SEM images collected with the help of Zhizhong Dong

Increasing the sheath to plasma gas ratio further, to even better control the particle growth environment, the resulting powders appear even finer, as seen in Figure 9-7. This experimental condition again uses a 12 LPM sheath gas, but with reduced plasma gas of 0.8 LPM, to increase the dwell time within the particle growth region. The RF power is reduced to 800W to match the temperature in the particle growth environment to previous 1000W conditions. The counter-flow is also reduced to 4 LPM so that the quenching region begins right at the bottom of the plasma region, rather than further upstream where it could disrupt the plasma. The resulting nanospheres are in the 25 to 65 nm range in diameter, as seen in Figure 9-7.



Figure 9-7: SEM Imaging of tBN Nanospheres with Longer Synthesis Dwell Time. SEM images collected with the help of Zhizhong Dong

Reducing the sheath gas to 8 LPM, while maintaining the 0.8 LPM / 800W / 4 LPM conditions for the plasma / RF / counter-flow, respectively, results in forming powders composed of BNNTs rather than nanospheres. With all other parameters kept the same, the reduced sheath gas increases the overall temperature in the plasma, which might be expect to result in increased particle growth rates. Using the M&S tool developed here, a comparison is made of the computed flow fields. It can be seen in Figure 9-8 that the temperature within the plasma region, the negative values for position, on average are about 3000 K to 4000 K less for the 12 LPM case shown on the left compared to the 8 LPM case on the right of Figure 9-8. Additionally, the temperature seen downstream of the torch decays far more quickly as the flow moves downstream axially.



Figure 9-8: Centerline Axial Temperature Profile Comparison for 12 LPM Sheath (Left) / 8 LPM Sheath (Right) with 0.8 LPM Plasma & 800W RF Power

The temperature history is just as critical to particle formation and nucleation trends, so the axial velocities of the flow field need to be examined as well. The overall axial velocity contours for the two cases can be seen side-by-side in Figure 9-9; however, it is easier to examine the axial velocity profile down the centerline of the plasma domain, as shown in Figure 9-10 for comparison.

It can be seen that the higher sheath gas rate increases the counter-flow region as expected as indicated by the increased negative velocity at the negative axial positions. The increased sheath gas mass flow does increase the overall flow rate downstream of the torch, as would be expected from the laminar subsonic flow's conservation of mass. Overall what this means for a particle exposed to these flow fields is that with the sheath gas reduced down to 8 LPM, the resulting residence time to the elevated nucleation temperatures is drastically increased because of the far slower velocities of the plasma gas downstream of the torch.

Axial Velocity Contour Plots



Figure 9-9: Axial Velocity Comparison for 12 LPM Sheath (Left) / 8 LPM Sheath (Right) with 0.8 LPM Plasma & 800W RF Power



Figure 9-10: Centerline Axial Velocity Profile Comparison for 12 LPM Sheath (Left) / 8 LPM Sheath (Right) with 0.8 LPM Plasma & 800W RF Power

Without the BN particles being able to self-terminate into the nanospheres, the BN particles appear to grow into high aspect ratio BNNTs that form into what others have called a nanomesh

[74]. The nanomesh is essentially an agglomeration of BNNTs of roughly 70 nm in diameter, consistent with the peak broadening estimates from the XRD analyses previously discussed.



Figure 9-11: SEM Imaging of tBN Nanomesh with Longer Synthesis Dwell Time and Reduced Sheath Gas. SEM images collected with the help of Zhizhong Dong

Overall, the ability for the ICP process to yield t-BN nanospheres and BNNTs is quite efficient compared to produce cBN (by direct deposition), which is characterized by fairly low yield rates. The ICP process also appears to be able to control t-BN structure type and overall particle size through the use of RF power controls and counter-flow quenching techniques.

9.2 High Pressure / High Temperature Consolidation of 80% t-BN Seeded with 20% Micron Sized c-BN to yield nano c-BN 2 GPa / 1500°C / 15 minutes

To compare against the successful results of the high pressure high temperature consolidation of the a-BN powders made via the ICP process, consolidation experiments are performed with the t-BN powders as the source powders. As discussed in Chapter 2, other researches have shown the benefits of using t-BN in consolidation experiments given its more efficient conversion to c-BN [3] [63]. The nanostructure of these powders are also likely to aid in conversion via HPHT because, in general, finer powders yield more efficient conversion characteristics [7]. Viewing the lattice strain of the t-BN as a defect in the crystallinity, it can be understood how they would aid in the mitigation of grain growth. Recently studies into t-BN's contribution to grain growth during field-assisted sintering (FAS) observes the absence of t-BN resulting in 2-5x crystallite growth in size [75]. The tBN powders were used as synthesized from the ICP process for these experiments. No annealing, washing or any other preparation processes were performed on the powders. This thus leaves the residual oxide layers on the nanoparticles however this was deemed as favorable given the previous work done by [76] which showed that small amounts of water addition to aBN powders, on the order of 8%, saw cBN conversion increase from only 20% to nearly 100%.

The first t-BN consolidation experiment matched the conditions of the previously conducted a-BN consolidation conditions. Again, in order to promote cubic phase conversion, micron sized c-BN seeding is used at a 20% mass ratio. The 80% t-BN / 20% c-BN mixture is consolidated at $2 \text{ GPa} / 1500^{\circ}\text{C} / 15 \text{ min}$ using the Depths of the Earth® system used in Chapter 7.



Figure 9-12: HPHT Source Powder - 80% tBN / 20% cBN

After consolidation, the results of the capsules are similar to the results in Chapter 7. The powders consolidate into pellets which thermally fracture upon rapid quenching after consolidation. The sample disks aree again collected and placed in the XRD using a zero background holder. Contrary to the results of the 80/20 ratio a-BN mixture, the t-BN mixture shows far more conversion to the cubic phase, as evidenced by the significant increase in the intensity ratio of the c-BN <111> peak at 43.6° , as compared to the h-BN / t-BN / BNNT <002> peaks shown in Figure 9-13. Again, as seen with the a-BN samples, the tantalum capsule leaves a ring of material attached to the consolidated disks, which results in strong peaks in the diffraction patterns, as shown in Figure 9-14.



Figure 9-13: XRD Pattern for 80% tBN / 20% micron cBN After Consolidation at 2 GPa / 1500C / 15 min


Figure 9-14: XRD Pattern with Phase Identification for 80% tBN / 20% micron cBN After Consolidation at 2 GPa / 1500C / 15 min

The peak broadening of the <111> plane of c-BN in Figure 9-15 shows an average particle size of only 35nm, which strongly indicates the conversion of the t-BN powders to the cubic phase, since the seeding c-BN powders are much larger in overall particle size. Comparing these results to Figure 7-27, which had the same seeding ratio and consolidation conditions but no cubic phase conversion, the efficiency of t-BN as a BN powder source for c-BN synthesis via HPHT techniques is evinced.



Figure 9-15: XRD Pattern with cBN Particle Size for 80% tBN / 20% micron cBN After Consolidation at 2 GPa / 1500C / 15 min

FESEM images (Figure 9-16) of the t-BN / c-BN interface are obtained on one of the fracture planes of the consolidation capsule. As would be expected, the thermal stresses induced during the quenching process after consolidation result in fractures along planes with high ratios of t-BN remaining. The image shows the random orientation in almost a fiber like fashion of the high-aspect-ratio t-BN nanotubes, with the darker c-BN phases below the BNNT plane. On the right side of Figure 9-16, fine c-BN particles can be seen mixed in with the coarser micron c-BN seeding particles. Figure 9-17 shows a higher magnification image of the interface plane on the left side where the BNNTs begin to collapse to the nanospheres at the c-BN interface. The right image of Figure 9-17 shows the magnified details of the BNNTs, with 114nm diameters and micronmeter lengths.



Figure 9-16: SEM of Fracture Plane with BNNT and cBN Interface. SEM images collected with the help of Zhizhong Dong



Figure 9-17: SEM Image of BNNT / cBN Boundary (Left) and Magnified BNNTs (Right). SEM images collected with the help of Zhizhong Dong

9.3 High Pressure / High Temperature Consolidation of 100% t-BN to yield nano c-BN 2 GPa / 1500°C / 15 minutes

To better understand the behavior of t-BN powders under consolidation conditions, a final HPHT experiment is performed using only the t-BN powders without any seeding. Additional powders made under the same parameters as the seeded t-BN consolidation are used for this experiment at 2.0 GPa / 1500° C / 15 min. It can be seen for this sample in Figure 9-18 that the oxide presence is quite low compared to the <002> BNNT peak.



Figure 9-18: tBN Source Powder for HPHT Consolidation

Interestingly, after consolidation, there is a significant c-BN <111> peak present in Figure 9-19, despite no c-BN seeding with the t-BN source powders. For this case the particle size

estimated in Figure 9-20 is estimated to be slightly larger, now at 55nm, yet still quite fine by nano-BN standards. This trend is consistent with the other t-BN HPHT experiments discussed in Chapter 2. t-BN has a more favorable transition to c-BN compared to other BN source powders such as h-BN due to the disorder and high lattice strain in the starting powders. The thermodynamic phase transition comparison of h-BN and t-BN's conversion routes to c-BN is well discussed and depicted in Figure 6 of [67]. It is shown there how t-BN's conversion route becomes more temperature dependent than pressure dependent. At a lower consolidation pressure, the increased temperature provides the necessary mobility to convert to c-BN compared to the higher pressure and temperature needed to achieve c-BN conversion. There does appear to be slightly more residual t-BN remaining, as indicated by the slightly stronger <002> peak intensity; however it is still less than 10% of the primary c-BN peak's intensity. It is believed that the significant disorder in the t-BN helps aid in mitigating particle growth by breaking up any order along the grain boundaries where growth would occur.



Figure 9-19: XRD Pattern with Phase Identification for 100% tBN After Consolidation at 2 GPa / 1500C / 15 min



Figure 9-20: XRD Pattern with Particle Size for 100% tBN After Consolidation at 2 GPa / 1500C / 15 min

Chapter 10 Conclusions & Future Work

A novel method of synthesizing sp³ amorphous nano-BN with a short-range order structure has been demonstrated resulting from recirculating flow and deposition within a plasma torch. The growth characteristics of the BN particles under these conditions are unique, where the extreme temperature and prolonged exposure time have seemingly no effect on crystallization or particle growth. Despite the 6000+ K environment, the as-synthesized nanospheres maintain a fine ~20nm diameter in their loosely agglomerated state. This short-range ordered BN polymorph seems to be a favorable starting powder for HPHT consolidation for conversion to nanocrystalline c-BN. A significant advantage over alternative starting materials, such as ammonia borane, is that the a-BN is already hydrogen deprived, with no safety limitations on the consolidation temperature due to 'explosive' hydrogen evolution. The degree of the conversion has been shown to depend on amount of micron-sized c-BN seeding ion the starting powder. For example, efficient conversion to c-BN from a-BN (with moderate c-BN seeding) is observed at 2.0 GPa and 1500°C consolidation conditions. Temperature dependent mobility can be a limiting factor, as when consolidating at 1000°C (at 8.0 GPa), far less c-BN conversion occurs. Nonetheless, regardless of the consolidation conditions, conversion from a-BN needs c-BN seeding in the starting powder. At sub-critical seeding amounts, the amount of c-BN conversion from short-range ordered amorphous BN powders is essentially zero, as exemplified with the 0% and 20% seeding cases. Overall though, when compared to micron-sized h-BN powders, these ICP- produced a-BN powders seem to be more advantageous in HPHT consolidation, with at worst, comparable limitations in certain aspects but far greater efficiencies elsewhere.

Direct synthesis of c-BN has also been demonstrated using the RF-ICP when implemented with a rapidly-quenching inert counter-flow. The effectiveness of the rapid quenching in the modified stagnation flow not only maintains the metastable cubic phase, but also limits particle growth, resulting in a fine nano-scale polycrystalline powder deposition. By varying experimental parameters for the substrate deposition, formation of an intermediate phase t-BN is demonstrated. The t-BN particles can be produced in the form of both nanospheres (nano-onions) and nanotubes, depending on the plasma conditions. These novel shell and nested structured BN phases are shown to be favorable as BN starting powder for HPHT consolidation and conversion into nanocrystalline c-BN. Compared to starting with a-BN nanoparticles, employing t-BN is more efficient in terms of needing far less initial c-BN seeding to produce final c-BN.

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