SYNTHESIS OF SP² AND SP³ CARBON MATERIALS

A Dissertation in

Chemistry

by

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Abstract

Carbon is the backbone of hundreds of products ranging from conductors to insulators and lubricants to machining tools. Diamond is the hardest material known and graphite is one of the softest, but there is a need for materials in between these two extremes. By taking advantage of the different pressure-dependent thermodynamic stabilities of graphite and diamond, the degree of sp$^2$ and sp$^3$ bonding in amorphous carbon materials can be varied. This control over bonding opens avenues for tuning properties such as electrical conductivity, hardness, and optical transmission. Two approaches to controlling sp$^3$ and sp$^2$ carbon formation have been studied. The first investigates techniques to deposit carbon at elevated pressures by high-pressure chemical vapor deposition. The second group of experiments involves high pressure synthesis techniques using a diamond anvil cell and developing precursors that will react at lower temperatures and pressures to give materials with sought after properties. This report is an investigation of the effect of high-pressure on the formation of amorphous carbon materials deposited by high-pressure chemical vapor deposition, dielectric breakdown plasma enhanced chemical vapor deposition, and laser induced plasma enhanced chemical vapor deposition. This report describes novel deposition and growth techniques such as high-pressure CVD of sp$^2$ carbon wires in microcapillaries, with preliminary results showing increased sp$^3$ bonding with the formation of a hydrogenated carbon material via plasma enhanced depositions. The second method approaches the tuning of sp$^2$ and sp$^3$ hybridization of carbon from the other direction of taking high pressure synthesis techniques and develop initial precursors that react at lower pressures forming an sp$^3$ interconnected network. With pressure, amorphous carbons can also be made by compressing materials to the point where it is favorable for
atoms to form new bonds. My focus is on developing a precursor that will react at lower pressure and temperatures than current fabrication techniques for forming ultra-hard materials such as diamond and cubic boron nitride. We have investigated precursors with highly unsaturated groups like cyanides and acetylenes because they have the potential to form new bonds. We have characterized these compounds with in situ Raman, IR, and XRD to track structural changes. Three different precursors have been studied to understand the effect of the starting structure on the reactivity and sp²/sp³ nature. By lowering the reaction pressure, bulk high pressure synthesis techniques could be used for more commercial applications.
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I.D.    Inner diameter
O.D.    Outer diameter
DIC     Differential interference contrast
SEM     Scanning electron microscope
TEM     Transmission electron microscopy
EELS    Electron energy loss spectroscopy
IR      Inferred
UV      Ultra violet
MOF     Microstructured optical fiber
HV      High voltage
XRD     X-ray diffraction
FWHM    Full with half max
CVD     Chemical vapor deposition
HPCVD   High Pressure chemical vapor deposition
DBD     Dielectric breakdown
DFPT    Density functional perturbation theory
THz     Terahertz
KHz     Kilohertz
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Dedication

To my late father who couldn’t be here.
Chapter One
An Introduction to carbon based materials

1.1 Motivation

Ultra-hard materials are widely used as abrasives and for machining tools, as they are able to scratch, cut, and shape all other materials. Diamond is the ultimate ultra-hard material, having the greatest hardness of any naturally occurring material.\(^5\) The carbon atoms are arranged in a 3D network of sp\(^3\) bonded carbon, with a hardness of 60-120 GPa on the Vickers hardness scale and 10 on Moh’s hardness scale.\(^6\) Diamond also has one of the highest tensile strengths, predicted to be at 95 GPa.\(^5\) It is an insulator with a band gap of 5.5 eV, giving the material excellent optical transparency in the visible region.\(^7\) Diamond has several potential applications which are not feasible due to the limited geometries it can be grown in.

For example, if diamond could be synthesized into long wires, then optical waveguides become possible. Diamond has a high damage threshold, which would be perfect guiding high power light to be used in laser machining. The wire could also be robust with a high tensile strength of 95 GPa.\(^5\) In this application, light guided in diamond wires would allow devices to be produced based on weak effects since the electromagnetic field intensity could be very high and could interact with the structure over a long distance.\(^8\) Another application of diamond waveguides could be to provide the optical components for high power cascade Raman lasers, which have a widely tunable wavelength, but have been limited by the damage threshold of current optical fibers.\(^9\) Diamond has several highly desired properties to explore, but the focus in this dissertation is on the formation of sp\(^3\)
carbon which not limited to the diamond crystal structure. It is possible to obtain diamond like properties in a material without having 100% sp³ bonding. Amorphous materials with high amounts of sp³ bonding and some sp² bonding are opening avenues for cheaper synthetic methods.

Figure 1-1. (A) Ternary phase diagram of bonding in carbon and carbon hydrogen materials.¹ (B) Phase diagram of carbon.² [Robertson, J., Diamond-like amorphous carbon. Materials Science and Engineering: R: Reports 2002, 37, 129-281.] [Young, D. A., Phase diagrams of the elements; University of California Press, 1991.]

1.2 sp³ – sp² Amorphous Carbon Properties

Diamond’s properties are a result of the sp³ carbon-carbon bonds and not the crystal structure. This fact has led to interest in metastable carbon materials, an innovative new area of research. Current research focuses upon hybridization of carbon bonding to produce materials that have properties between graphite and diamond based on the composition of sp² and sp³ bonding carbons, despite the fact that they frequently have structural disorder.¹,¹⁰ Figure 1-1 A is a ternary phase diagram of different forms of carbon with varying
compositions of \( \text{sp}^2 \), \( \text{sp}^3 \), and hydrogen bonding, which emphasizes the continuum that exists between graphite and diamond.

Carbon materials composed of high \( \text{sp}^2/\text{sp}^3 \) carbon ratios are referred to as tetrahedral amorphous carbon (ta-C).\(^{11}\) When referring to the hybridization, it is important to keep in mind what the carbon is bonding to. Solid methane has 100% \( \text{sp}^3 \) carbon, yet no properties similar to diamond. Hydrogen only has one bond to one carbon atom and the molecules only interact by Van der Waals forces. This is because bonding to hydrogen is a terminal bond that does not contribute to forming a covalent network. Materials with large amounts of \( \text{sp}^3 \) carbon-carbon bonding, referred to as diamond-like carbon (DLC), have high hardness, low friction coefficients, and chemical inertness.\(^{11}\) As an example, Weiler et. al. have reported a tetrahedral amorphous carbon with 75% \( \text{sp}^3 \) carbon that has a hardness of 61 GPa.\(^{12}\)

Ta-C coatings only need to be only a few microns thick to provide mechanical rigor and chemical resistance, increasing service life by orders of magnitude.\(^{13}\) As a result, research has focused on films and not bulk material synthesis and so these amorphous \( \text{sp}^3 \) materials are usually produced using high energy, non-thermal deposition techniques, such as ion beam, sputtering, pulsed laser deposition, and plasma-enhanced chemical vapor deposition (PECVD).\(^{14-16}\) Some interesting uses of Diamond-like carbons include being deposited on shaving razor blades, on computer hard disk platters to protect the surface from crashes with the head, and are also used as a tool coating for machining alumina and plastic.

1.3 Diamond Analogue
In addition to ta-C, carbon nitride is another analog that has been predicted to have a hardness rivaling diamond due to its sp³ bonding and cubic carbon structure.¹⁷ This may present a material which can overcome diamond’s lower thermal stability and solubility in iron, which prevents it from being used as a metal cutting material.¹⁸ However, cubic carbon nitride which exhibits properties similar to those of diamond has yet to be made.

Cubic boron nitride is another diamond analog which is chief in this class and is commonly used as an alternative to diamond. It shares the same crystal structure as diamond and the BN units are isoelectronic to carbon. The strong covalent structure has a hardness reported between 60-75 GPa with a bulk modulus of 367 GPa. Unfortunately, it has a yellow color and doesn’t have the same excellent optical transparence that diamond has. However, it is less reactive with iron-like metals. It is therefore used as a common coating for high performance graders and tooling. Due to the high hardness, tools coated with BN last 7-50 times longer than tungsten carbide.¹⁹

**1.4 Motivation**

My research presented in this dissertation will focus on synthesizing sp³ hybridized carbon materials, by using two different synthetic strategies. The first, used high pressures generated in a diamond anvil cell, to react small molecule building blocks to form extended network materials. The second technique involved developing novel synthetic strategies using high pressure reactants to control the thermodynamics of carbon deposition inside unique, high aspect ratio template geometries.

**1.5 Diamond Anvil Cell Synthesis**
The motivation of this work has been to use small molecule building blocks that will react
to form an extended network under an applied pressure. The reactions will take place under
pressures which will favor hard, dense products. This will lead to the development of 3D
designed, covalently bonded solids with diamond like properties. To make hard, dense
materials, covalent bonding is needed to hold the structure together in a tight lattice.
Mechanochemistry is a powerful technique to form new dense, covalent bonding. By
increasing the pressure, the distance between neighboring atoms can be reduced causing
unsaturated side groups to react, forming an extended covalent network.

Lithium dicyanamide LiN(CN)$_2$ was selected for study because it is a small molecule that
has carbon with a high degree of unsaturation and no hydrogen to prevent an extended
structure from forming. Additionally, it has two cyanide groups, each with a carbon
nitrogen triple bond, capable of reacting to form additional bonds. Dicyanamide is also
known to trimerize in the solid state when heated.$^{20-21}$ This work shows that dicyanamide
can be trimerized through a pressure induced reaction, showing that cyanide groups can
react in a controlled fashion with an applied pressure. The results from a few experiments
of cyanides reacting under pressure have led to a mostly sp$^2$ material.

Based on the results of lithium dicyanamide, tetracyanomethane C(CN)$_4$ was selected for
a new study because the central carbon atom already has sp$^3$ hybridization in addition to
the unsaturated side groups. The material was found to polymerize into an amorphous, air
stable solid at 15 GPa. The central carbon atom keeps its sp$^3$ hybridization after the cyanide
groups polymerize under pressure. Also, it is theorized that the central sp$^3$ carbon could act
as a seed, promoting the formation of more sp$^3$ carbon. This work lays the groundwork for
linking molecules together covalently with sp$^3$ hybridization using pressure induced
polymerization. Through optimization small molecules could be designed with a specific end structure in mind and linked together covalently by reacting side groups with pressure. The final crystal structure could then be controlled through strategic positioning of the side groups.

1.6 Plasma Enhanced Chemical Vapor Deposition Synthesis

An important consideration of chemical reactions is whether the desired product is a thermodynamically stable product or a kinetically favored product. The phase diagram (Fig. 1-1B) shows that near ambient conditions $sp^2$ will be the thermodynamically favored product. To access $sp^3$, either the kinetically favored product must be made, or the initial conditions must be changed. The latter was chosen, and modified plasma techniques, able to operate at higher pressures, were developed to change the thermal dynamics and kinetics of the reaction to deposit new carbon materials. By increasing the pressure, the formation of $sp^3$ carbon should become more thermodynamically favorable. Plasma’s success in this regard lies in the generation of highly reactive intermediates, such as ions and radicals, which will react quickly before the atoms can reorganize into a lower energy state.

Two different high pressure plasma reactors were developed. Both utilize a confined geometry to produce wire like structures. The first technique electrically generates the plasma inside hollow core silica capillaries. The plasma can be generated over several centimeters at pressures up to one atmosphere. This lead to the deposition of a hydrogenated, amorphous $sp^3$ carbon material. The second technique generates plasma with high energy laser pluses. At atmospheric pressure, this has also led to the deposition of a hydrogenated, amorphous $sp^3$ material. However, this technique shows greater promise
at generating plasma above atmospheric pressures and, therefore, may be more compatible with the higher pressure conditions needed for diamond to be thermodynamically favored.
Chapter Two

This work has been adapted from a publication format for this chapter.

Pressure-Induced Polymerization of LiN(CN)₂

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2.1 Abstract:

The high-pressure behavior of lithium dicyanamide (LiN(CN)₂) was studied with in-situ Raman and infrared (IR) spectroscopies, and synchrotron angle-dispersive powder X-ray diffraction (PXRD) in a diamond anvil cell (DAC) to 22 GPa. The fundamental vibrational modes associated with molecular units were assigned using a combination of experimental data and density functional perturbation theory. Some low-frequency modes were observed for the first time. Based on spectroscopic and diffraction data we suggest a polymorphic phase transformation at ~8 GPa, wherein dicyanamide ions remain as discrete molecular species. Above ca. 18 GPa, dicyanamide units polymerize forming a largely disordered network, and the extent of polymerization may be increased by annealing at elevated temperature. The polymerized product consists of tricyanomelaminate-like groups containing $sp^2$-hybridized carbon-nitrogen bonds and exhibits a visible absorption edge near 540 nm. The product is recoverable to ambient conditions, but is not stable in air / moisture.

2.2 Introduction

Carbon’s ability to possess variable orbital hybridization schemes gives it the properties of diamond, the hardest material known, and of graphite, one of the softest.\textsuperscript{22} Likewise, CN compounds can potentially exist with $sp^3$ hybridization and as graphitic-type materials, both analogous to diamond and graphite, respectively.\textsuperscript{17, 23} To date, only the formation of $sp^2$ carbon-nitrogen networks is well-established, and significant challenges remain in accessing novel, three-dimensional CN-based extended solids with computationally predicted energetic feasibility.\textsuperscript{17, 23-28} In addition to three-dimensional systems, fully $sp^2$ CN-rich materials are also of great interest from the standpoint of fundamental chemical
transformations as well as practical applications in catalysis and energy conversion.\textsuperscript{29-32} One strategy to synthesize novel CN-rich solids is to begin with highly unsaturated carbon-nitrogen building blocks, lacking hydrogen or amine functionalities, that will react into extended networks after modest pressures are applied with full atom economy (sans release of byproducts). By starting from metastable molecules (building blocks) in a high-energy state, subsequent rearrangement into a lower-energy extended network is thermodynamically favored and may be facilitated by topochemical considerations.\textsuperscript{33-36}

Dicyanamides represent one class of possible building blocks with a high concentration of CN units, and have been produced with a variety of alkali metals (Li, Na, K, Rb, Cs), alkaline earth metals (Mg, Ca, Sr, Ba), and rare earth metals (La, Ce, Pr, Nd, Sm, Eu, Gd).\textsuperscript{37-42} Rare earth metal CN networks have been used to make frameworks which are particularly interesting for studying molecular magnets and organic superconductors.\textsuperscript{43} Dicyanamides have seen commercial application as air-bag components.\textsuperscript{44} Studies on Metal(M)-dicyanamides have used heat as a perturbative variable, causing them to react and polymerize into extended structures.\textsuperscript{37,40}

It has been well established that dicyanamide anions can go through a trimerization process.\textsuperscript{20-21,45} This process involves three cyanide groups from different dicyanamide ions coming together to form a tricyanomelaminate ring. Jurgens \textit{et al.} reported that the trimerization process proceeds at ambient pressure and temperatures >613 K in the crystalline state with no observed intermediates or melting.\textsuperscript{20} Tricyanomelaminate is of interest because it contains a C₃N₃ triazine ring structure, which has been studied for understanding the formation of graphitic carbon nitrides.\textsuperscript{20,46-48}
The binary CN system (as well as other multicomponent analogues) has potential for similar structural flexibility to pure carbon, but precursor-based synthetic strategies have not been thoroughly explored under pressure. The unsaturated nitrile group has potential to form new bonds under pressure through cycloaddition-type reactions and could possibly result in the formation of extended network solids. A detailed analysis of the vibrational and structural evolution under pressure is of great importance in understanding the transformation from the highly unsaturated building-block to an interconnected network, providing fundamental information regarding the evolution of CN bonding and reaction mechanisms.

In this study, we present in situ, high-pressure spectroscopic and structural results for LiN(CN)\(_2\) compressed to 22 GPa. Raman and IR spectroscopies were used to probe the evolution of CN bonding, while synchrotron PXRD was used to obtain structural information. Utilizing these methodologies, a partially amorphous network comprising tricyanomelaminate-like groups was successfully synthesized through the polymerization of lithium dicyanamide.

2.3 Methods

2.3.1 Synthesis

Anhydrous LiN(CN)\(_2\) was prepared in a very similar manner to a previous report. The as-purchased NaN(CN)\(_2\) (Alfa-Aesar) was recrystallized from water and dried under vacuum. Anhydrous LiCl (4.53 g, 107 mmol) was stirred under argon with a slight excess of NaN(CN)\(_2\) (10.00 g, 112 mmol) in dry THF (33 g) at 100 °C in a closed H-tube for 3 days and filtered. After solvent removal under vacuum, the crude LiN(CN)\(_2\) was
dissolved in boiling dry MeCN and allowed to cool. The liquid was decanted and the crystals pumped dry with mild heating to afford anhydrous LiN(CN)$_2$ (7.17 g, 87%), which was handled only in a drybox.

**2.3.2 DFPT Calculations**

Raman Intensity calculations were performed using density functional perturbation theory$^{51}$ implemented in the Quantum Espresso software.$^{52}$ For exchange and correlation functional, Perdew-Burke-Ernzerhof parametrization of the Generalized Gradient Approximation was used.$^{53}$ For electronic structure calculations and DFPT calculations, a uniform 6x6x4 grids of kpoints mesh used with a cut-off energy of 1100 eV for the plane wave expansion of wavefunctions.

**2.3.3 Sample Preparation**

Samples of LiN(CN)$_2$ were ground in an agate mortar to a fine powder (~5 micron) under an inert argon atmosphere (O$_2$ < 0.5 ppm, H$_2$O < 0.5 ppm). This powder and a ruby sphere were loaded into DACs with culet sizes ranging between 300-500 µm. The DAC was prepared by pre-indenting a rhenium gasket to a thickness between 50-70 µm. The sample chamber was prepared by drilling a ~150-190 µm hole into the center of the indentation. Pressure was determined by measuring the florescence of a ruby sphere.$^{54}$ In most cases a pressure medium was not used to avoid any potential sample contamination, but for some of the IR scans the sample was diluted with dry potassium bromide. All samples were sealed to a starting pressure of ~0.1 GPa within the inert argon atmosphere before removing from the glove box.
2.3.4 Raman

Samples were excited with a 532 nm diode laser, focused through a 20× long working distance objective (NA=0.40) and Raman light was collected in the back-scatter geometry through a 50 μm confocal pinhole and two narrow-band notch filters (Ondax). The Raman Signal was collected using a Princeton Instrument spectrograph SP2750 (Trenton, NJ) and dispersed off an 1800 or 300 gr/mm grating on to a liquid nitrogen cooled CCD, providing a maximum spectral resolution of <2 cm\(^{-1}\). The spectrometer was calibrated with the emission lines from Neon assuring a wavelength accuracy of <1 cm\(^{-1}\). Laser-induced damage was avoided by keeping the beam power at ~1 mW with exposure times less than 300 s. As a result of these measurement conditions, no change was observed in the reaction pressure, suggesting that photo-induced chemistry was not important in this energy / laser power range. The Raman spectrum of Li\(_3\)C\(_6\)N\(_6\) was acquired on a Renishaw inVia Raman microscope with 785 nm excitation due to high fluorescence at shorter excitation wavelengths.

2.3.5 IR

A Varian 670-IR spectrometer was used to collect mid-IR absorption from ~600-4000 cm\(^{-1}\). IR light was generated by a globar source and collected by a liquid nitrogen-cooled HgCdTe detector after passing through the sample with a pair of reflecting objectives. Reference spectra were obtained using the same DAC after the cell was decompressed and the diamonds were cleaned.
2.3.6 X-ray Diffraction

Powder X-ray diffraction (PXRD) was collected at the High Pressure Collaborative Access Team (HPCAT), beamline 16-IDB, of the Advanced Photon Source (APS), Argonne National Laboratory. A monochromatic beam with a wavelength of 0.4066 Å was focused to a spot size of ~5x7 μm². Diffraction data were recorded using a MAR image plate and the images were processed using the fit2d(v12.077) data analysis program. Lattice parameters were obtained through full profile refinement using the Le Bail method, as implemented in GSAS with EXPGUI. Rietveld refinement was attempted, but judged unacceptable due to inadequacies in powder averaging statistics.

2.3.7 Sample Annealing

In one run, the high-pressure sample was annealed to increase the extent of reaction before measuring Raman spectra and visible absorption. The DAC with the LiN(CN)₂ at 20 GPa was placed in an oven at 373 K for 14 h. It was then allowed to cool to room temperature before Raman and visible absorption data were collected.

2.4 Results

2.4.1 Diffraction
Figure 1. Structure of LiN(CN)$_2$. (A) Tetrahedral coordination of lithium by four dicyanamide groups. (B) Octahedral coordination of lithium by six dicyanamide groups. (C) View perpendicular to the $c$-axis consisting of alternating chains of edge-sharing tetrahedral and octahedral lithium atoms that are parallel to the $c$-axis. (D) View of 4 unit cells along the $c$-axis where each dicyanamide ion bridges three different chains of Li polyhedra. The colored lines highlight the bonding of individual dicyanamide groups.

The crystal structure of lithium dicyanamide was previously reported as monoclinic with space group $P2/c$ (no.13).$^{41}$ We confirm this result and obtained ambient-pressure lattice parameters of $a = 5.3169(13)$ Å, $b = 5.2964(13)$ Å, $c = 11.6454(11)$ Å and $\beta = 101.245(12)^o$, which closely match the previously reported results.$^{41}$ We note that the calculated lattice parameters obtained after relaxation using DFT ($a = 5.3079$ Å, $b = 5.2489$ Å, $c = 11.4977$ Å and $\beta = 101.551^o$) are in good agreement with this result. Within this
structure, there are chains of lithium atoms that occupy alternating tetrahedral and octahedral sites and propagate down the $c$-axis (Fig. 1.). The dicyanamide molecules act as bridging units in the $a$-$b$ plane between Li polyhedral, of which nitrogen atoms form the vertices.

As pressure is increased from 0.1 to 3.6 GPa, $a$ expands slightly from its starting value, $b$ and $c$ decrease monotonically, and $\beta$ increases. We note that the error bars are relatively large due to pressure-induced peak broadening, but the observed increase in $a$ might be related with an anisotropic compression mechanism (discussed below). As the pressure is further increased to 9.5 GPa, $b$ and $c$ continue to decrease, and $\beta$’s rate of increase slows. Between 3-9.5 GPa, $a$ decreases almost linearly, and after 9.5 GPa the XRD patterns could no longer be reliably described using the starting $P2/\overline{1}c$ structure, indicating a transition to another crystalline phase.

At 13.5 GPa we observed a peak at 9.28° that continued to shift to higher angles as pressure was applied up to 22.2 GPa, and some crystalline features were observed to the highest pressure measured. As shown in Fig. 2, these features indicate that, while most crystalline diffraction is undetectable above ca. 15 GPa, the sample is not completely amorphous.
2.4.2 Raman

The isolated dicyanamide ion has $C_{2v}$ symmetry and possesses nine fundamental vibrational modes. According to group-theory analysis, solid lithium dicyanamide has 72 vibrational modes. The irreducible representation of all zone-center modes is given as $M = 16A_g + 19A_u + 17B_g + 20B_u$, of which 33 ($A_g, B_g$) are Raman active and 39 ($A_u, B_u$) are IR active. Table 1 shows assignments for observed Raman and IR modes of LiN(CN)$_2$ compared with calculation results from DFPT calculations. Given the large number of vibrational modes possible in the crystalline state and the lower number of modes observed, we report mode numbers following fundamental assignments in the context of the isolated dicyanamide ion, knowing that some of these modes will be split in the solid by crystal-field effects. The peaks in the Raman and IR were fit using Lorentzian peak shapes.
The highest-frequency Raman mode observed at 2234 cm\(^{-1}\) is assigned to the C≡N symmetric stretch (\(\nu_1\)). This assignment is in agreement with our calculations (2235 cm\(^{-1}\)) and comparable with the symmetric stretch of Na dicyanamide of 2225 cm\(^{-1}\) reported by Perkins.\(^{58}\) The shift observed between Li and Na dicyanamides can be explained by differences in cations and through crystal structure effects. Our assignment is in contrast with Reckeweg \textit{et al.}, who reported the symmetric C≡N stretch at 2305 cm\(^{-1}\); the mode observed by Reckeweg \textit{et al.} at 2236 cm\(^{-1}\) was assigned to a combination of C-N symmetric and asymmetric stretching modes.\(^{41}\) The assignment by Reckeweg \textit{et al.} is likely related to a typographical error as the combination band at 2236 cm\(^{-1}\) was reported to have strong intensity, whereas the \(\nu_1\) fundamental was reported as having very weak intensity. Since the fundamental symmetric mode should have very strong Raman intensity, this discrepancy can be resolved by simply switching the reported assignments in their table entry (which are consecutive). The C≡N asymmetric stretching mode (\(\nu_7\)) was observed at 2166 cm\(^{-1}\) and is in reasonable agreement with our calculated value of 2180 cm\(^{-1}\). Reckeweg \textit{et al.}\(^{41}\) reported the C≡N asymmetric stretching mode at 2168 cm\(^{-1}\), which is in agreement with this work, whereas this mode was observed at 2174 cm\(^{-1}\) for the Na analogue (Perkins).\(^{58}\) For the isolated C\(_{2v}\) molecule, the symmetric (A\(_1\)) and asymmetric (B\(_2\)) C≡N stretching modes are active in both the Raman and IR. In the solid state, these modes are split into A\(_g\), A\(_u\), B\(_g\) and B\(_u\) components, but the Raman and IR frequencies remain nearly coincident. Unfortunately, we were unable to observe these stretching modes in the IR due to the strong absorption of the diamond anvils used in our experiments (between ca. 2000-2400 cm\(^{-1}\)).
Table 1. Experimental Raman and IR modes for LiN(CN)$_2$ at 0.1 GPa. DFPT calculations for this study were conducted at 1 atm.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Mode Character</th>
<th>Experimental observations (cm$^{-1}$)</th>
<th>Theory (cm$^{-1}$)</th>
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<tr>
<td>$v_1$</td>
<td>R (s)</td>
<td>$v_2$ (N≡C)</td>
<td>2243</td>
</tr>
<tr>
<td>$v_2$</td>
<td>IR (m)</td>
<td>$v_1$ (N-C)</td>
<td>944</td>
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<td>$v_3$</td>
<td>R (w)</td>
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<tr>
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<td>R (s)</td>
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<td>671</td>
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<tr>
<td>$v_{4a}$</td>
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<td>$\gamma_5$ bend</td>
<td>227</td>
</tr>
<tr>
<td>$v_{4b}$</td>
<td>R (w)</td>
<td>$\gamma_5$ bend</td>
<td>206</td>
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<tr>
<td>$v_5$</td>
<td>R (w)</td>
<td>$\gamma_3$ bend</td>
<td>240</td>
</tr>
<tr>
<td>$v_6$</td>
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<td>549</td>
</tr>
<tr>
<td>$v_7$</td>
<td>R (s)</td>
<td>$\gamma_3$ bend</td>
<td>554</td>
</tr>
<tr>
<td>$v_8$</td>
<td>IR (s)</td>
<td>$\gamma_3$ bend</td>
<td>2166</td>
</tr>
<tr>
<td>$v_9$</td>
<td>R (m)</td>
<td>$\gamma_2$, bend</td>
<td>-</td>
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<td>Lattice</td>
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<td>R (w)</td>
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<td>Lattice</td>
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$^*$DFPT gives a large number of discrete modes with this character due to crystal field splitting. For simplicity, the range of these modes has been compared with experimental data in the context of the fundamentals of the isolated ion.

The C-N symmetric stretching mode ($v_2$) was observed in the IR and the Raman at 944 cm$^{-1}$ and 943 cm$^{-1}$, respectively, and is in general agreement with our calculations and the previous study by Reckeweg et al.$^{41}$ For the Na salt, the C-N symmetric stretch was observed at 937 cm$^{-1}$ (Raman) and 931 cm$^{-1}$ (IR).$^{58}$ The C-N asymmetric stretch ($v_8$) was observed in the IR at 1346 cm$^{-1}$, but not observed in the Raman where it could possibly be obscured by the strong T$_{2g}$ diamond phonon near 1333 cm$^{-1}$. The calculated frequency of the C-N asymmetric stretching mode at 1422 cm$^{-1}$ is significantly shifted from the observed position and the origin of this discrepancy is presently unclear. However, the observation

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of this mode at 1339 cm\(^{-1}\) in the IR by Reckeweg \textit{et al.} is in good agreement with in the present study (no Raman frequency was reported previously).\(^{41}\)

The symmetric bending (\(\nu_3\)) mode was observed in the Raman at 671 cm\(^{-1}\) and is shifted from our calculated value of 650 cm\(^{-1}\). Reckeweg \textit{et al.} reported this mode at 682 cm\(^{-1}\), whereas Perkins observed this mode at 671 cm\(^{-1}\) for the Na salt.\(^{41, 58}\) We tentatively assign the \(\nu_4\) symmetric bending mode at 227 cm\(^{-1}\) based on comparison of Raman intensity with our calculations. However, two additional bands are observed at 206 cm\(^{-1}\) and 240 cm\(^{-1}\), and calculations reveal that they both have similar character to \(\nu_4\) (symmetric bending).

The asymmetric bending modes (\(\nu_5, \nu_6\) and \(\nu_9\)) are difficult to discern based on similarities in character and frequency. Perkins was unable to make definitive assignments for the Na salt, but from a detailed analysis of the combination modes he was able to reach the tentative assignment of \(\nu_5 (A_2)\) at 544 cm\(^{-1}\), \(\nu_6 (B_1)\) at 526 cm\(^{-1}\) and \(\nu_9 (B_2)\) at 517 cm\(^{-1}\).\(^{58}\) Based on our DFPT calculations, we suggest assignments of \(\nu_5\) at 549 cm\(^{-1}\) and \(\nu_6\) 554 cm\(^{-1}\) and \(\nu_9\) is unobserved experimentally, but occurs at 530 cm\(^{-1}\) in calculations.

We report seven low-frequency lattice mode vibrations, which are observed with Raman for the first time. The lattice modes are sensitive to any increase in pressure, and quickly broaden. The last seven peaks are lattice vibrations located at 145, 138 121, 106, 91, 78 cm\(^{-1}\). All seven modes agree well with our calculated values (145, 140, 117, 104, 89, 77 cm\(^{-1}\)).

\subsection*{2.4.3 Raman Under Pressure}

With this understanding of the vibrational spectroscopy of the starting material, we now turn our attention to the behavior during compression. As pressure is increased, the
frequencies of the carbon nitrogen triple bond stretching modes ($\nu_1$, $\nu_7$) increase until 6.6 GPa. At 7.6 GPa the $\nu_1$ mode splits into two components separated by 5 cm$^{-1}$. **Fig. 3** shows these two peaks continuing to increase in frequency with increasing pressure as they slowly diverge from each other. The asymmetric mode becomes too weak to be accurately fitted beyond 18 GPa.

The frequency of the symmetric bending mode ($\nu_3$) at 671 cm$^{-1}$ increases linearly with increasing pressure, but a new shoulder appears on the high-frequency side at 7.6 GPa. Both of these peaks are visible until 14.8 GPa. The peak at 554 cm$^{-1}$ that has been tentatively assigned as $\nu_6$ has almost no change in frequency versus pressure. At 7.6 GPa a peak forms on the high-frequency side and is separated by +24 cm$^{-1}$. The mode at 549 cm$^{-1}$, tentatively assigned as $\nu_5$, has little change in position with increasing pressure. At 8.6 GPa a shoulder appears on the low-frequency side of $\nu_5$ and is separated by -11 cm$^{-1}$. At 7.6 GPa, however, a new peak does form on the low-frequency side of $\nu_5$, at -35 cm$^{-1}$. These five peaks have little change in frequency versus pressure and beyond 14.8 GPa no Raman peak were observed between 400-750 cm$^{-1}$.

The frequency of the $\nu_4$ mode at 227 cm$^{-1}$ gradually increases with increasing pressure up to 16 GPa, which is similar to the peak at 240 cm$^{-1}$. At 7.6 GPa the peak at 240 cm$^{-1}$ gradually splits into two and both peaks continue to higher frequency with increasing pressure. The peak at 206 cm$^{-1}$ also shifts with increasing pressure and crosses the $\nu_4$ position near 4.3 GPa. After 5 GPa the rate of frequency increase with pressure decreases. The lattice modes 145, 138 and 121 cm$^{-1}$ follow the same trends of increasing frequency with increasing pressure.
Figure 3. (A) Raman spectra of LiN(CN)$_2$ with pressure at room temperature. Spectra have been normalized to the most intense peak in each panel for clarity. Each spectral range has been scaled by the value at the bottom of each panel. (B) Pressure dependence of the observed Raman modes of LiN(CN)$_2$.

2.4.4 IR Under Pressure

The IR frequency of the $\nu_2$ near mode 944 cm$^{-1}$ increases with increasing pressure until 9.3 GPa, however there is a notable change in the slope of the pressure dependence near 4.4 GPa (Fig 2). Above ~9 GPa the frequency of this mode appears to decrease with additional pressure increase. A new peak appears at 5.7 GPa on the high frequency side of
$v_2$ that is shifted by $+47$ cm$^{-1}$ and shows positive frequency correlation with increasing pressure.

![Figure 4](image-url)

**Figure 4.** (A) IR spectra of LiN(CN)$_2$ with pressure at room temperature. Unaltered IR spectra have been offset for clarity. The spectra on the right were obtained with potassium bromide dilution due to strong absorbance. One tick mark on the vertical axis equals one absorbance unit (A.U.) (B) Pressure dependence of the observed IR modes of LiN(CN)$_2$.

The asymmetric N-C stretching mode near $1348$ cm$^{-1}$ ($v_8$), which was only observed in the IR, has a linear frequency increase with increasing pressure until $6.9$ GPa, at which point a new peak emerges on the low-frequency side (Fig. 4). The new peak has a slight frequency decrease with increasing pressure. The original $v_8$ peak continues to increase in frequency until $8$ GPa, where it splits into two components separated by $\sim 13$ cm$^{-1}$. 
Figure 5. (A) Optical transmitted image of LiN(CN)$_2$ in a DAC at 15.8 GPa before polymerization. A ruby sphere is used to measure the pressure and is located at the top of each image. (B) LiN(CN)$_2$ just after polymerization. (C) LiN(CN)$_2$ after annealing at 373 K for 14 hours. (D) The visible transmittance of annealed LiN(CN)$_2$. (E) Raman of lithium dicyaminide at 13 GPa before polymerization, at 18 GPa before annealing and 20 GPa after annealing. For comparison, the Raman spectrum of lithium tricyanomelamine on a glass substrate at 1 atm has also been plotted.

2.4.5 High-pressure annealing

Pristine LiN(CN)$_2$ at ambient conditions is translucent and colorless, owing to its ionic and molecular nature. As pressure was increased from 0 GPa to 15 GPa, the material’s color remained unchanged when inspected under visible light illumination. When the pressure was increased past 15 GPa, the material began to transition from colorless to a translucent red color, which became darker as the pressure was increased to 20 GPa. This absorption behavior is similar to a previous reported C$_3$N$_4$ carbon nitride material, which is indicative of similar structural motifs in both compounds. In order to accelerate this transition and ensure more complete reaction, the sample was annealed at 373 K and 20 GPa for 14 hours.
After annealing, the material exhibited a brilliant red color, with a visible absorption edge near 540 nm (2.3±0.1 eV) (Fig. 5).60

The Raman spectrum of the sample above ~15 GPa has only one remaining feature from the starting molecule (the symmetric C≡N stretch, $\nu_1$), and four new broad bands appear with features similar to amorphous carbons.61 These new features become significantly stronger after annealing but no new modes that might arise from subsequent crystallization were observed. After annealing, $\nu_1$ completely disappears, which indicates that heating provides thermal energy to accelerate the extent of polymerization, or possibly activates an additional reaction mechanism. For the annealed sample, the so-called “D” and “G”-like bands can be observed between 1400-1600 cm$^{-1}$, but the D peak is partially obscured by the Raman scattering from the diamond anvils. The G band is located at 1598 cm$^{-1}$ and the D band is located at 1392 cm$^{-1}$. Two ring vibrational modes are observed at 745 cm$^{-1}$ and 1021 cm$^{-1}$, which are shifted to higher frequency than previous observations due to the high-pressure conditions. Koglin et. al. identified similar peaks in melamine, which might be a suitable analog for polymerized LiN(CN)$_2$.62-63

2.5 Discussion

At low pressure our results agree with previous reports on LiN(CN)$_2$ and other dicyanamides using Raman / IR spectroscopies and PXRD. The unit cell dimensions were similar to the previously reported values and the IR and Raman data at the starting pressures show quantitative agreement with previously studies.37, 41, 58 As the material is compressed to 7.6 GPa most of the peaks in the Raman and IR have a monotonic trend of increasing frequency with increasing pressure. This agrees with our diffraction data that show the unit cell volume is decreasing, and thus the bond lengths get shorter which causes them to shift.
to higher frequencies. Both lattice parameters $b$ and $c$ decrease monotonically over the entire pressure interval. However, between 0-3 GPa, $a$ appears to increase slightly with pressure. This effect might be related to negative linear compressibility and has been observed in many other systems including some cyanide-based compounds.\textsuperscript{64-66} The monoclinic structure necessitates that the $a$-direction is not a principal compression axis, however analysis of the compressibility tensor using the PASCaL Software does indeed show linear expansion along the lattice vector $[0.9526, 0, -0.3043]$.\textsuperscript{67} By examining the crystal structure, it seems reasonable that LiN(CN)$_2$ could exhibit mild linear negative compressibility over a limited pressure range. Baughman et. al. reported several similarities that materials with linear negative compressibility share, one of them being “hinge-like” structures.\textsuperscript{68} The dicyanamide molecules do indeed form “hinges” where each nitrogen is associated with a different chain of alternating tetrahedral and octahedral lithium ions, thereby allowing for stretch densification. This behavior could potentially explain the observed increase in $a$ and should be investigated in more detail in future studies.

Based upon spectroscopic and PXRD observations, a polymorphic phase transition occurs around 9 GPa. The first signs of this transition begin at $\sim$ 7.5 GPa where we observe seven new peaks in the Raman and two new peaks in the IR, as well as slope changes in the pressure-dependence of their frequencies. It is important to note that the original peaks which are associated with the molecular crystal are still present and did not change remarkably in frequency and intensity. This indicates that the overall nature of bonding remains largely unchanged after the transition, i.e., the crystal remains molecular and is a new polymorph of LiN(CN)$_2$. These new peaks arrive just before the XRD patterns change near 9 GPa and the diffraction data can no longer be fitted using the starting $P2/c$ structural
model. All of these observations are consistent with a first-order phase transition in crystalline LiN(CN)$_2$, likely due to a lower-symmetry form based on the increased number of vibrational modes observed.

Above ~18 GPa, the spectroscopic data point towards a more dramatic chemical (polymeric) transformation involving the formation of new covalent bonds. All of the molecular Raman peaks except $\nu_1$ were no longer detectible above ~16 GPa. There are also drastic changes in the IR near 1550 cm$^{-1}$, with the onset of broad absorption bands above 17 GPa. Above 19 GPa, IR transmission associated with these broad bands decreased drastically until the signal was saturated beyond the detectable limit, and all IR features of the starting material are lost beyond 19-20 GPa. These changes in the Raman and IR spectra suggest a pressure-induced reaction between cyanide units and concomitant bond order changes from $sp$ to $sp^2$.

It has been established that certain cyanide-based molecules can undergo pressure-induced polymerization.$^{33, 69-76}$ For dicyanamides specifically, it has been reported that when heated at ambient pressure they will undergo a trimerization reaction to form tricyanomelaminate ($C_6N_9^{3-}$). A possible mechanism for the pressure-induced reaction observed here is a similar scheme to the previously-reported, thermally-induced trimerization reaction at atmospheric pressure.$^{20-21, 45}$ This trimerization reaction would involve three dicyanamides, each contributing a nitrile group, resulting in the formation of triazine rings and comparable to the tricyanomelaminate product. The broad IR feature observed here above 17 GPa (Fig. 4) is likely composed of two peaks at 1450 cm$^{-1}$ and 1550 cm$^{-1}$. Li$_3$C$_6$N$_9$ exhibits similar features showing a large amount of absorbance across the same spectral region,$^{21}$ and the position of these bands are generally consistent with the
formation of triazine rings.\textsuperscript{77-78} The Raman spectra above 15 GPa also share three prominent features with Li$_3$C$_6$N$_9$: C≡N stretching, ring rotation modes and a broad band central band in the region of sp$^2$ C≡N/C≡C stretching. We note that the central band observed for Li$_3$C$_6$N$_9$ (\textbf{Fig. 5e}) is more pronounced near 1400 cm$^{-1}$ due to contributions from a glass substrate.

Above 18 GPa most of the X-ray diffraction signal is very broad and essentially undetectable, indicating a significant loss of long-range correlations and tendency towards amorphization. Nevertheless, PXRD patterns still exhibit some crystalline features beyond 20 GPa indicating that the material is not completely amorphous after the initial polymerization event.

While the pressure-induced material shows spectroscopic similarities with thermally trimerized LiN(CN)$_2$, this material changes again after high-pressure thermal annealing at 373 K. After heating, all evidence for C≡N stretching vanishes, indicating an increased extent of polymerization and possibly a new, thermally-activated reaction mechanism. As with the material obtained before annealing, the presence of the D/G peaks and the peaks at 743 cm$^{-1}$ and 1024 cm$^{-1}$ are evidence of ring formation in the final product.\textsuperscript{62, 79} The Raman data show that these modes become more intense after annealing, which is potentially associated with the rings being in strained conformations immediately after reaction, which are unable to relax until the annealing process occurs.

Unlike other cyanide-based materials that have been observed to turn opaque after pressure-induced polymerization, the final LiN(CN)$_2$ product remains transparent. It is likely that other systems graphitize to a much larger extent, but in the case of LiN(CN)$_2$, the remaining Li atoms present in the structure prevent polymerization over longer length
scales and, thus, an optical gap remains in the polymerized material exhibiting an absorption edge near 540 nm. This absorption edge is slightly more transparent than the C₃N₄ carbon nitride material prepared by Purdy et. al.⁵⁹ For the trimerized structure presented by Jurgens et. al. the C₆N₉₃⁻ anions are approximately planer and are surrounded by six sodium ions.²⁰ The sodium ions are isolating the C₆N₉₃⁻ anions from each other, preventing reaction into a more extended network. If the trimerized material is heated further it will decompose instead of reacting further.²⁰ It is likely that this situation is analogous to the lithium dicyanamide case presented here where Li ions prevent longer-range polymerization in a similar fashion, although the extent of polymerization is greater than in pure Li₃C₆N₉ based on the absence of detectable nitrile groups in the Raman spectrum.

Further characterization on the resulting material was not possible since the material is not air stable and reacts violently when exposed to atmosphere, which prevents further characterization after recovery, such as TEM. Possible explanations for the air sensitivity include lithium reacting with oxygen or moisture in air, as well as the formation of unstable rings with carbon-carbon or nitrogen-nitrogen bonds. It is our speculation that through disruption, the lithium ions are preventing more organized and/or larger extended networks from forming. In future studies, it would be of interest to recover the material under inert conditions to further examine the extent of polymerization.

2.6 Conclusion

Using a DAC we studied LiN(CN)₂ with Raman and IR spectroscopy and synchrotron x-ray diffraction data to understand how its chemical nature changes with increasing pressure
and to determine a new pathway for polymerization of CN networks. We have characterized the structure and vibrational properties at low pressure with results in correspondence with previous reports. Upon compression, our results suggest that LiN(CN)$_2$ exhibits negative linear compressibility up to ~3 GPa. At ~8 GPa we observe a polymorphic phase transition by the emergence new peaks in the Raman and IR, as well as structural changes via PXRD. Above 15 GPa the material begins to react, and spectroscopic signatures of aromatic carbon-nitrogen bonds are observed, with strong similarities to the thermal trimerization product of LiN(CN)$_2$ at atmospheric pressure. The final product is recoverable to atmospheric pressure, but is highly reactive and not stable in air.

2.7 Acknowledgment

We thank J. Smith and R. Hrubiak for assistance with XRD measurements. This work was supported by DARPA under ARO Contract No. 31P4Q- 3-I-0005. Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775, with partial instrumentation funding by NSF. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357. D.Y.K. acknowledges the Texas Advanced Computing Center (TACC) at the University of Texas at Austin and Argonne Leadership Computing Facility (ALCF) which is a DOE Office of Science User Facility supported under Contract No. DEAC02-06CH11357 for providing high performance computing resources and the support of NSAF Grant No. U1530402.
Chapter Three

This work has been adapted from a publication format for this chapter.

**Tetracyanomethane Under Pressure: Extended CN Polymers with Built-in sp³ Centers**

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Key Words: Tetracyanomethane, Diamond anvil cell, High pressure, Amorphous-carbon, Raman-spectra, TEM, EELS
3.1 Abstract

Tetracyanomethane C(CN)$_4$ is a tetrahedral molecule containing a central sp$^3$ carbon that is coordinated by potentially reactive nitrile groups are predicted to react to form extended CN networks with high sp3 content by design. C(CN)$_4$ was studied with in-situ synchrotron angle-dispersive powder X-ray diffraction (PXRD) and Raman and Infrared (IR) spectroscopies in a diamond anvil cell (DAC) to 21 GPa. The pressure dependence of the fundamental vibrational modes associated with the molecular solid were determined and some low-frequency Raman modes are reported for the first time. Based on the collected spectroscopic and diffraction data, C(CN)$_4$ starts to polymerize at 9.8 GPa. Above 13.8 GPa the material formed an interconnected amorphous network, which is recoverable to ambient conditions.

3.2 Introduction

The carbon-nitrogen (CN) system has many similarities with pure carbon systems. Both systems have a sheet allotrope, graphite and graphitic carbon nitride, and each has a cubic allotrope, diamond and cubic carbon nitride, for example. The hybridization of these elements determines the material’s properties. For carbon nitrogen materials, there are several successful techniques to synthesize sp$^2$ materials, however, for sp$^3$ CN materials, significant challenges remain to produce three-dimensional extended materials.

Tetracyanomethane was originally characterized in the early 1970’s. The molecule’s tetrahedral symmetry drew the attention of a few researchers who studied its vibrational states. Its simple tetrahedral symmetry makes it an ideal building block for pressure induced polymerization, leading to an extended, three-dimensional carbon-nitride structure. It contains four cyanide groups which have been well established to undergo
pressure induced polymerization. The tetracyanomethane building block is also hydrogen free, which allows for the possibility of unterminated growth of the structure. Tetracyanomethane also starts with 20% sp³ carbon-carbon bonding which has the potential to act as a three-dimensional link between reacted cyanide groups. The starting sp³ carbon might also serve as a seed, promoting the development more sp³ carbon-carbon bonds.

In this study we present Raman and IR spectroscopic data and PXRD structural data on tetracyanomethane as it evolves under pressures up to 20 GPa. Raman and IR spectroscopy provide information on how the bonding developments, while synchrotron PXRD was used to monitor how the structure progresses.

### 3.3 Experimental Methods

The tetracyanomethane was synthesized by Dr. Purdy and Dr. Epshteyn.

**3.3.1 Sample Preparation**

In an argon glove box (O₂<0.5 ppm, H₂O<0.5 ppm), samples of tetracyanomethane were ground to a fine powder of <1 microns in an agate mortar. This powder, with the addition of a ruby sphere, was placed into DACs with culet sizes between 300-500 µm. A rhenium gasket was prepared by pre-indention to a thickness between 50-70 µm. A ~150-190 µm hole was drilled into the center of the indentation, creating the sample chamber. By measuring the florescence of the ruby sphere, the pressure inside the sample chamber could be determined. Normally a pressure medium was not used, but dry potassium bromide was used to dilute samples for some of the IR runs. To prevent reaction/contamination with air, all samples were sealed inside the glove box at a minimum pressure of 0.1 GPa.
3.3.2 Raman

Raman was collected in the back scatter geometry with excitation from a 532 nm diode laser. The light was focused through a 20× long working distance objective (NA=0.40) and collected through a 50 µm confocal pinhole and two narrow-band notch filters (Ondax). A Princeton Instrument spectrograph SP2750 (Trenton, NJ) with 1800 or 300 gr/mm grating and a liquid nitrogen cooled CCD was used to collect data with a spectral resolution of <2 cm⁻¹. Neon emission lines were used to calibrate the spectrometer to an accuracy of <1 cm⁻¹. To avoid damaging the sample, laser power was kept below 5 mW of power and exposure times were varied up to 300s. It was observed that the laser could help promote reaction progress at high pressure.

3.3.3 IR

Mid-IR absorption from 500-4000 cm⁻¹ was collected on a Varian 670-IR spectrometer. A Globar source was used to generate IR light which was then focused through a pair of reflecting objectives. The signal was measured on a liquid nitrogen-cooled HgCdTe detector. After the data were collected, the same DAC was decompressed and the diamonds were cleaned and references were collected.

3.3.4 ADXRD

Powder X-ray diffraction (ADXRD), took place at the High Pressure Collaborative Access Team (HPCAT), beamline 16-IDB, of the Advanced Photon Source (APS), Argonne National Laboratory. Data were collected with a monochromatic beam with a wavelength of 0.4066 Å and was focused to ~5×7 µm² spot. Diffraction data were recorded using a MARCCD and the images were processed using the fit2d(v12.077) data analysis program.
Lattice parameters were obtained through full profile fitting using the Le Bail method, as implemented in GSAS with EXPGUI.\textsuperscript{56-57}

3.4 Results

3.4.1 ADXRD

Tetracyanomethane has previously been reported as a hexagonal lattice with the R3c space group.\textsuperscript{81} We confirmed this result and obtained ambient-pressure lattice parameters of $a = 8.951(2)$ Å and $c = 11.54(4)$ Å, which closely matches the previously reported results.\textsuperscript{81}

The molecule has been shown to have the expected $T_d$ symmetry.\textsuperscript{81} The tetrahedral centers are stacked on top of each other along the $c$ axis. Each nitrogen points directly at a carbon atom in the neighboring molecule with a distance between 3.00 - 3.05 Å.\textsuperscript{81} Figure 1 shows the trends in the XRD patterns as the material compresses. We are able to fit this unit cell to up to a pressure of 15.9 GPa. Lattice parameters $a$ and $c$ both decrease in a manner that is typical for a decreasing unit cell, indicating that there is no phase transition before C(CN)$_4$ polymerizes. By 17.4 GPa, the material no longer has any clear diffraction peaks and appears X-ray amorphous.
3.4.2 Raman and IR Assignments

The isolated tetracyanomethane molecule has 21 vibrational modes. As a crystalline solid, group theory analysis predicts tetracyanomethane to have 36 vibrational modes. The irreproducible representation of all zone-center modes are given as $M = 9A_1 + 9A_2 + 18E$, of which 23 ($A_1, E$) and are both Raman and IR active. For comparison purposes, we report mode numbers following fundamental assignments for the isolated ion, knowing that some of these modes will be split in the solid owing to crystal effects. Table 1 shows assignments for observed Raman and IR modes based on previous results from the literature.
Table 1. Experimental Raman and IR modes for Tetracyanomethane at 0.1 GPa

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Observed in</th>
<th>Mode Character</th>
<th>Experimental observations (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This study</td>
<td>Literature</td>
</tr>
<tr>
<td><strong>First Order</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v_1)</td>
<td>(v_s) (N≡C)</td>
<td>R</td>
<td>2285 (80) 2288 (82)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IR</td>
<td>2289 (80) 2276 (82)</td>
</tr>
<tr>
<td>(v_2)</td>
<td>(v_s) (C-C)</td>
<td>R</td>
<td>561 (80) 560 (82)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>562 (80)</td>
<td>563 (80) 560 (82)</td>
</tr>
<tr>
<td>(v_3)</td>
<td>(\delta) (C-C-N)</td>
<td>R</td>
<td>572 (80) 575 (82) 573 (82)</td>
</tr>
<tr>
<td>(v_4)</td>
<td>(\delta) (C-C-C)</td>
<td>R</td>
<td>117 (80) 113 (80) 115 (82)</td>
</tr>
<tr>
<td>(v_5)</td>
<td>(\delta) (C-C-C)</td>
<td>R</td>
<td>133 (82) 136 (80)</td>
</tr>
<tr>
<td>(v_6)</td>
<td>(\nu_{as}) (N≡C)</td>
<td>R</td>
<td>2281 (80) 2273 (80)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IR</td>
<td>2281 (80) 2276 (82)</td>
</tr>
<tr>
<td>(v_7)</td>
<td>(\nu_{as}) (C-C)</td>
<td>R</td>
<td>1063 (80) 1056 (82)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1059 (80)</td>
<td>1056 (82)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IR</td>
<td>1058 (80) 1058 (82)</td>
</tr>
<tr>
<td>(v_8)</td>
<td>(\delta) (C-C-N)</td>
<td>-</td>
<td>- (80)</td>
</tr>
<tr>
<td>(v_9)</td>
<td>(\delta) (C-C-N)</td>
<td>-</td>
<td>- (80)</td>
</tr>
<tr>
<td>Lattice</td>
<td>R</td>
<td>192 (80)</td>
<td>190 (82)</td>
</tr>
<tr>
<td>Lattice</td>
<td>R</td>
<td>176 (82)</td>
<td>178 (82)</td>
</tr>
<tr>
<td>Lattice</td>
<td>R</td>
<td>156 (82)</td>
<td>154 (82)</td>
</tr>
<tr>
<td>Lattice</td>
<td>R</td>
<td>43 (82)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Combination modes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2v_2)</td>
<td>IR</td>
<td>1129 (82)</td>
<td>1123 (82)</td>
</tr>
<tr>
<td>(892+\nu_5)</td>
<td>IR</td>
<td>1031 (82)</td>
<td>1025 (82)</td>
</tr>
<tr>
<td>(\nu_7+) Lattice</td>
<td>IR</td>
<td>1097 (82)</td>
<td>1095 (82)</td>
</tr>
<tr>
<td>(v_2+2\times Lattice),</td>
<td>IR</td>
<td>890 (82)</td>
<td>876 (82)</td>
</tr>
<tr>
<td>(v_2+\nu_5+) Lattice</td>
<td>IR</td>
<td>887 (82)</td>
<td>889 (82)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>878 (82)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(v_8\) demined from the combination mode

We observe the C≡N symmetric stretch (\(v_1\)) at 2285 cm\(^{-1}\) and 2289 cm\(^{-1}\) in the Raman (figure 2) and IR (figure 3) respectively. This assignment is in excellent agreement with Gardiner *et. al.* (Raman 2288 cm\(^{-1}\)) and Hester *et. al.* (Raman 2288 cm\(^{-1}\)).\(^{80,82}\) The C≡N
asymmetric stretching mode ($\nu_6$) is observed at 2280 cm$^{-1}$ in the Raman and 2281 cm$^{-1}$ in the IR. The position is slightly higher than Gardiner et. al. (Raman 2273 cm$^{-1}$) and Hester et. al. (IR 2276 cm$^{-1}$). We agree with Gardiner et. al. in assigning this mode as $\nu_6$.\textsuperscript{80} We believe that Hester et. al. accidentally skipped (T$_1$) which is $\nu_5$ when making their assignment for $\nu_{as}$ N≡C and $\nu_{as}$ C-C and both should be one number greater.

We observe the C-C symmetric stretch only in the Raman and it has split into three peaks 561, 562, 563 cm$^{-1}$ due to crystal field effects from being in a solid. Gardiner et. al. and Hester et. al. only report one peak for $\nu_2$, 560 cm$^{-1}$ and 562 cm$^{-1}$ respectively, locations which agree with the average of our values.\textsuperscript{80,82} We observe the C-C asymmetric stretching $\nu_7$ in the Raman and IR and that it has been split by the crystal field effects of being in a solid. In the Raman we observe two peaks at 1059 and 1063 cm$^{-1}$ and two peaks in the IR at 1058 and 1062 cm$^{-1}$. The average of our values agrees with Gardiner et. al. (1061 cm$^{-1}$) and Hester et. al. (1061 cm$^{-1}$).\textsuperscript{80,82}

In the Raman, the peak at 572 cm$^{-1}$ has been assigned as the C-C-N bending mode $\nu_3$. This is in close agreement with Gardiner et. al. (573 cm$^{-1}$) and Hester et. al. (573 cm$^{-1}$).\textsuperscript{80,82} The peak at 117 cm$^{-1}$ in the Raman has been assigned as $\nu_4$ C-C-C bending. Gardiner et. al. reports this at 115 cm$^{-1}$ and Hester et. al. reports at 116 cm$^{-1}$.\textsuperscript{80,82} We are the first to report the presence of a second C-C-C bending mode $\nu_5$ at 133 cm$^{-1}$. This mode is unobserved by Gardiner et. al. and Hester et. al. but Gardiner’s et. al. calculation predicts this mode to be at 136 cm$^{-1}$ which is close to our reported value.\textsuperscript{80,82} We do not observe $\nu_8$ and $\nu_9$ but Gardiner reports their positions at 540 cm$^{-1}$ and 478 cm$^{-1}$ respectfully.\textsuperscript{80} We report four lattice modes 192, 176, 156, 43 cm$^{-1}$. Hester et. al. observed three of these modes 190, 178, 154 cm$^{-1}$. 

3.4.3 Combination Modes

In figure 3 several combination modes are observed. The combination of $2\nu_2$ at 1128 cm$^{-1}$, the combination of $\nu_7 + \text{lattice}$ at 1097 cm$^{-1}$ and $\nu_7 - \text{lattice}$ at 1031 cm$^{-1}$. At 890, 887 and 878 cm$^{-1}$ is likely to be the combination of $\nu_2 + \nu_5 + \text{lattice}$ or $\nu_2 + 2 \times \text{lattice}$.

3.4.4 Vibrational Modes with Increasing Pressure
Figure 2. (Top) 532 nm excitation Raman of C(CN)$_4$ with pressure. The relative intensities between each region are reported below each group. (Bottom) The position of each fitted peak plotted with pressure.

Both $\nu_1$ and $\nu_6$ increase in frequency with increasing pressure, with $\nu_1$ increasing slightly faster. At 11.8 GPa the intensity of both modes decreases sharply, indicating that the triple bond has begun to react. After 13.8 GPa both of these modes become inseparable and weak in intensity. In the IR, $\nu_1$ and $\nu_6$ increase in frequency with increasing pressure, but after 7.8 GPa these peaks begin to overlap with the CO$_2$ peak, which is present, preventing further deconvolution.

As pressure is increased, the three peaks of $\nu_2$ respond to pressure differently. One of them begins to separate immediately at 0.5 GPa by increasing in frequency faster than the other two. At 8.7 GPa another peak splits off. All three of these peaks disappear at 12.9 GPa.

Figure 3. (Top) IR spectra of C(CN)$_4$ plotted with pressure. (Bottom) The pressure dependence of fitted IR modes with pressure.
The C-C asymmetric stretching mode ($\nu_7$) increases in frequency with increasing pressure both in the Raman and IR. Each mode shifts at a different rate, causing the pair to separate as pressure is increased. In the Raman at 11.8 GPa, these peaks lose all of their intensity. However, in the IR these peaks persist longer, disappearing after 14.8 GPa.

The bending modes $\nu_3$, $\nu_4$, and $\nu_5$ all increase in frequency with increasing pressure and are no longer present after 13.8 GPa. For the lattice modes they all increase in frequency with increasing pressure. Just like all of the other Raman modes, they disappear after 13.8 GPa.

Figure 4. 532 nm excitation Raman of C(CN)$_4$ with pressures up to 21 GPa.

At 5.5 GPa we begin to see the formation of D and G peaks, which are normally observed in amorphous carbon materials. These peaks have almost no change in position with increasing pressure. They do, however, have an increase in intensity as pressure increases, with a peak in intensity at 14.9 GPa.
Table 2. Raman peak positions on polymerized C(CN)₄.

<table>
<thead>
<tr>
<th>Mode Character</th>
<th>Experimental observations (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 member ring rotations</td>
<td>673</td>
</tr>
<tr>
<td>D</td>
<td>1323</td>
</tr>
<tr>
<td>G</td>
<td>1567</td>
</tr>
<tr>
<td>ν₁,₆ (N≡C)</td>
<td>2229</td>
</tr>
</tbody>
</table>

At 13.8 GPa all of the Raman modes related to the molecule, with the exception of ν₁ and ν₆, disappear after 13.8 GPa. The N≡C mode becomes significantly weaker in intensity at 13.8 GPa and has a significant decrease in frequency. These symmetric and asymmetric modes can no longer be distinguished. Signs of C-C bending can be seen at pressures as low as 5.5 GPa after 13.8 GPa this peak becomes more intense and broader.

3.4.5 Appearance of the Material
Figure 5. In-situ optical images of C(CN)$_4$ collected at several pressures.

Pure tetracyanomethane at ambient pressure is a colorless transparent material. No color change is observed in the material as the pressure is increased from 0 GPa to 10.9 GPa. As the pressure is increased to 12.9 GPa, the material begins to darken in color. Figure 5 shows that as the pressure is increased to 13.8 GPa, the material takes on a red color. By 14.9 GPa, the material appears to be opaque.

3.4.6 Recovered Material

A TEM image and Fourier transform of C(CN)$_4$ show an amorphous structure. Elemental analysis was performed through energy-dispersive x-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). The EDS spectrum confirms the presence of primarily carbon and nitrogen in the sample. Some minor impurities were present, such as silicon, oxygen, and sodium, which probably attached to the sample during processing. The copper signal from the TEM grid is also present. EELS shows the characteristic carbon and nitrogen K-edges at 284 and 400 eV, respectively. The appearance of the $\pi^*$ peak in both K-edges shows that there is multiple bonding hybridizations between the carbon and nitrogen atoms in the sample. Analysis of the carbon sp$^2$/sp$^3$ ratio was performed on the carbon K-edge, and showed 100% sp$^2$ content. Amorphous carbon is known to be readily damaged by a focused electron beam, such as what is used to generate significant inelastic scattering for EELS. The damage from the electron beam could cause a transformation from sp$^3$ to sp$^2$. Indeed, by comparing the TEM images of C(CN)$_4$ from before and after the EELS spectra were taken, it is obvious that the sample has undergone morphological changes. Interestingly, after exposure to the electron beam, there is some
Figure 6. (Top) HRTEM of recovered C(CN)$_4$ (Top left) the material is amorphous. (Top Right) The recovered material graphitizes under prolonged exposure of the electron beam. (Middle Left) Fourier transformation of the selected area in top right image. (Middle) Distance between layers. (Bottom Left) Elemental composition. (Bottom Right) EELs spectrum.

layer-like order within the previously completely amorphous sample. Measurement of the interlayer spacing shows a range of 3.2 to 3.7 Å, which is similar to the graphitic spacing.
of carbon (3.4 Å) and C\textsubscript{3}N\textsubscript{4} (3.2 Å).\textsuperscript{83-84} This suggests that the sample may be graphitizing
due to damage from the electron beam.

3.5 Discussion

The starting pressure measurements of Raman/IR spectroscopies and PXRD agree with
previous reports on C(CN)\textsubscript{4}. In addition, we report three combination modes in the IR and
several lattice modes that have previously been unreported. As the pressure on C(CN)\textsubscript{4} is
increased to 9.8 GPa, the unit cell dimensions steadily decrease. This decrease is also
evidenced by the gradual increase in frequency of the Raman and IR vibrational modes,
caused by a shorting shortening of the bond lengths. At 9.8 GPa we observed evidence that
C(CN)\textsubscript{4} has begun to react as the Raman and IR peak intensities start to decrease, shown
in figure 2 and 3. In figure 5, the material begins to darken, beginning on the left side. As
the pressure is increased, these changes become more pronounced. The reaction completes
as the pressure is raised to 13.8 GPa, and the modes in the Raman that are associated with
molecular C(CN)\textsubscript{4}, except \nu_1 and \nu_6, are no longer present. Figure 4 show the rise of Raman
modes which are typical for amorphous carbon materials at 13.8 GPa. At the same pressure
the IR \nu_7 has a decrease in intensity. The material is fully opaque at 14.9 GPa, providing
visible evidence that the reaction has completed.

The resulting material can be recovered to ambient conditions, is air stable and is still
transparent in the IR. The polymerization did not consume all of the cyanide groups as the
N≡C stretch is still present in the recovered Raman. Visible Raman on the recovered
material has peaks which are typical for amorphous carbon materials. The G peak position
is consistent with other reported amorphous carbon nitrides.\textsuperscript{79, 85} The presence of the D
peak is a clear indication that ring-like structures are present.\textsuperscript{79} The peak at 673 cm\textsuperscript{-1} is specific for rotation of six membered ring systems.\textsuperscript{79}

A likely product of the polymerization is the formation of 1,3,5 triazine. A proposed mechanism would be trimerization of three cyanide groups from three neighboring tetracyanomethane’s. These rings could be linked together by the starting central sp\textsuperscript{3} carbon atom, leading to an extended network solid. It is possible for central sp\textsuperscript{3} carbon atom to be bound to four 1, 3, 5, triazine rings. With this proposed reaction there is no reason for the central sp\textsuperscript{3} starting carbon to change its bonding.

For this study, we do not present a direct measurement of the sp\textsuperscript{3} carbon content. However, the material appears to have formed an extended network which is harder that stainless steel. The high hardness implies that our material has less in common with sp\textsuperscript{2} materials such as graphitic carbon nitride and more in common with sp\textsuperscript{3} materials such as cubic carbon nitrite.

3.6 Conclusions:
Using a DAC the chemical and structural changes with increasing pressure of tetracyanomethane were observed with Raman and IR spectroscopy and synchrotron X-ray diffraction data to determine the path way for polymerization. The structural and vibrational properties at low pressure are in agreement with previous reports. Upon compression, the material compresses evenly until 10 GPa, where tetracyanomethane polymerizes. Above 13.8 we observe features that are normal for amorphous carbons showing that the tetracyanomethane has polymerized into an extended network. The final product is recoverable to atmospheric pressure and unreactive in air.
Chapter Four

High Pressure Chemical Vapor Deposition

4.1 Confined High Pressure Reaction Templates

Micro glass capillaries are unique templating platforms that can have aspect ratios as high as 1:50,000. Specifically, glass fibers can be drawn kilometers in length with pore diameters down to nanometers. One reason such capillaries are produced is because they are great pressure vessels and can be useful for applications such as liquid chromatography. Their great mechanical strength stems from the fact that the silicon oxygen bond is strong. This allows micro capillaries to withstand pressures greater than 100 MPa.

Glass fibers are usually made from fused silica, which has several properties in addition to mechanical strength, which make it ideal for use as a template for HPCVD. Specifically, it is transparent between the UV and the Near IR (200 nm – 3.4 µm), which allows materials deposited inside to be characterized in situ by Raman and IR spectroscopy. It also has a high melting point around 1715 °C, meaning that heat can be used to drive reactions within silica capillaries. The capillaries can be fabricated with any number of pores with precise dimensions all the way down to several nanometers. Furthermore, silica glass is permeable to small molecules like hydrogen and helium, which allows for the removal of reaction byproducts. This last property was capitalized on with the thermal decomposition of silane (SiH₄) inside micro capillaries to deposit void free silicon wires centimeters in length, accurately reproducing the template.

4.2 HPCVD Silane
HPCVD was first demonstrated as a viable synthetic process via the high pressure pyrolysis of silane to form silicon. Silicon was chosen because it has interesting optical properties and is deposited via a simple reaction. Unlike traditional CVD, which takes place at atmospheric pressure or lower, HPCVD is performed by filling the glass capillary with silane mixed with a helium carrier gas, pressurized up to 35 MPa, which is then then heated to decompose the silane into silicon and hydrogen gas.

\[ \text{SiH}_4(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{Si}(\text{s}) \]

Normally, in a sealed container, like a hollow capillary, the extent of reaction would be limited by Le Chatelier’s principle, and the reaction would stop when a critical level of byproducts builds up, preventing further reaction, as well as limiting the transport of new reactants. However, in this case, the hydrogen is able to diffuse through the pores present in fused silica glass, allowing the reaction to progress. This process allows the creation of fully filled silicon wires inside of these hollow core capillaries.

**4.3 Thermal Decomposition of Methane**

Building on the success of the thermal decomposition of silane under pressure, methane was thermally decomposed under similar pressures as an exploratory investigation, evaluating whether diamond could be made via HPCVD. The pressure we applied during the reaction (35 MPa) is significantly lower than the expected pressure necessary for \( sp^3 \) carbon-carbon formation to be thermodynamically stable (2 GPa). As such, we expect the bulk of the material formed in our experiment to be \( sp^2 \) carbon. Using methane as the precursor gas, we find similar thermal decomposition behavior as silane. As methane is heated inside a micro glass capillary like figure 4.1, it will decompose into solid carbon.
and hydrogen gas. The hydrogen is able to exit the reaction through the glass, allowing the reaction to continue. Due to the high surface area to volume ratio of the glass capillary, this process starts by depositing a film on the surface of the capillary which grows radially inward.

Figure 4.1 A schematic of HPCVD of methane inside a microcapillary. Methane gas enters from the left and is heated while under pressure. New material grows on the surface, annularly, inward.

4.4 Characterization of Amorphous Hydrogenated Carbon Films

4.4.1 Optical Microcopy

The thermal decomposition of methane takes place at 700 °C. Figure 4.2 is a cross sectional image of a carbon wire deposited inside a 50 µm I.D. capillary. The upper right portion of Figure 4.2 shows the material as-is from the cleave. The inner and outer layers appear drastically different. The outer layer is smoother and the inner layer appears rougher with some porosity. This same section was polished (figure 4.2, upper left) which confirms the observation that the outer layer has a smoother texture than the inner layer.
Figure 4.2. G – the glass capillary. O – Outer carbon layer. I – Inner carbon layer. A – Air. (Upper left) Cross section of a cleaved carbon wire. (Upper Right) Polished cross section of the carbon wire. (Lower left) Polished cross section viewed under polarized light. (Lower right) Differential interference contrast image.
In the lower images of Figure 4.2, layers can be seen that are parallel to the inner surface. When the sample is viewed with crossed polarization, the difference between the two textures are emphasized. In crossed polarization microscopy, the sample is illuminated with polarized light, then the reflected light from the sample goes through an analyzer polarizer which has a polarization perpendicular to the first. So intensities are now a function of the sample birefringence. The glass is amorphous, so it randomly rotates polarization of the light which is why it is visible. The inner layer is even in brightness, indicating a structure with no preferred orientation. The outer layer has alternating regions of light and dark. This would be consistent with a graphitic material that has sheets which are parallel to the surface. The polarization of the illumination light is vertical, so when the sheets of the outer layer are parallel or perpendicular to the incoming light, they do not rotate the light at all and appear dark. When the sheets are 45° to the incoming light, the amount of rotation is at its greatest and, thus, appears the brightest. Based on this, the outer layer is graphitic and the inner layer is not. What is observed in the lower left of figure 4.2 is known as a Maltese cross. Changing the angle between the polarizers will change the position of the light spots and eventually the 4 light spots will merge into 2 which is the extinction angle. For this sample, the extinction angle is 20°, which classifies it as rough laminar pyrolytic carbon.

Other features that are revealed under the cross polarized light are the radial conical defects. Delhaes has reported observing similar defects in pyrolytic carbon. His conclusion is that carbon particles were being deposited on the surface, then further material would be deposited on the particle, as well as the surface giving rise to the conical shape. By lightly polishing, we revealed that these defects are numerous and distributed throughout the
sample. Differential interference contrast (DIC) microscopy shows that these conical defects are not attached to the greater material and can fall out during polishing. The DIC image in the lower right of figure 4.2 shows differences in height as changes in contrast and color. The DIC image of the inner layer shows a surface composed of particles that have been fused together. Furthermore, each of these layers polish at different rates suggesting the inner layer is much softer than the outer layer.

Figure 4.3. SEM micrograph of a carbon wire that has been removed from the silica template.

**4.4.2 SEM Characterization**

Figure 4.3 shows an SEM micrograph of a carbon wire that has been selectively etched from the silica template. Hydrofluoric acid is used to etch the silica, but does not damage the carbon fiber in any perceptible way. The SEM shows that the surface of the wire is incredibly smooth, with no defects observed by the SEM. This is consistent with other applications of HPCVD, by which smooth interfaces can be created in many materials templated by silica microcapillaries.
4.4.3 Stress Strain Measurements

For stress strain measurements, carbon fibers were deposited in 8 µm pores and then etched out with hydrofluoric acid. Figure 4.4 is a carbon wire tied into a knot to show its flexibility. To test the tensile strength of the fibers, they were attached to a fixed base and a load cell with epoxy. Given that the carbon fibers were not especially strong, the epoxy was adequate to secure the fibers for this application. Results revealed that the deposition temperature affected the tensile strength of carbon fibers. Figure 4.5 shows that wires deposited at lower temperatures have superior physical properties. Table 4.1 compares the material which has been deposited at different temperatures. The lower temperature material has almost five times the tensile strength. The material deposited at lower temperature has tensile strengths comparable to other carbon fibers, meaning that the structure is, likely, similar to carbon fiber made by other techniques.
Figure 4.5 Stress-strain Measurements of thermally deposited carbon wires.

Table 4.1 Physical properties of thermally deposited carbon fibers.

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>730 °C</th>
<th>920 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (GPa)</td>
<td>2.77</td>
<td>0.63</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>80</td>
<td>21</td>
</tr>
<tr>
<td>Strain at breaking</td>
<td>3.5%</td>
<td>2.9%</td>
</tr>
</tbody>
</table>

4.4.4 Micro-Raman Spectroscopy

The Raman in figure 4.6 was collected with 514 nm excitation. The position of the G peak in both inner and outer layers are at the same position, 1596 cm\(^{-1}\). The D peak’s position of the outer peak at 1363 cm\(^{-1}\) is slightly shifted compared with the inner peak at 1355 cm\(^{-1}\). The FWHM is very different between the layers, with the outer layer having a larger
FWHM in the G and D peak. The smaller FWHM indicates that the inner layer has greater order than the outer layer.

Figure 4.6 Visible Raman (514 nm excitation) of thermally deposited carbon wires.

4.4.5 Powder X-ray Diffraction

Powder XRD was performed (figure 4.7) on a carbon wire which was etched out from the glass. The wire was orientated perpendicular to the beam. Diffraction reveals one peak which is close to the (002) peak in graphite. This peak provides further evidence of a layered material, with a layer spacing of ~3.45 Å, as compared to graphite’s layer spacing of 3.35 Å. The larger distance is due to disorder in the sheets which prevents the efficient stacking that is observed in graphite, for example.
Figure 4.7 An XRD pattern of thermally deposited carbon wires.

4.5 Conclusion

Exploratory work has been done on the thermal decomposition of methane inside a confined geometry. Two distinct materials are being deposited on top of each other with no external change in the deposition conditions. The transition between a smooth outer layer and a rough inner layer is sharp, occurring over a distance <1µm.

4.5.1 Outer layer

The outer layer consists of disordered layers known as a turbostratic structure.\textsuperscript{98-99} The polished optical images reveal a layered material which conforms to the inner wall of the capillary. The conformity to the surface suggests that the method for growth is a surface based reaction with the silica substrate. From the powder XRD the distance between the sheets are calculated to be \(\sim 3.46\ \text{Å}\). The extinction angle of the Maltese cross matches with the results others have reported for pyrolytic carbons.\textsuperscript{95-96}
**4.5.2 Inner layer**

The optical images show that the inner layer is made up of particles that have been fused together. These particles grow in the gas phase, and when they are too big, they precipitate onto the surface. There is still some surface growth present which causes the particles to fuse together. This creates voids in the material, and methane is no longer able to infiltrate these voids. The inner carbon layer appears to be more crystalline than the outer layer, based on the FWHM of the D and G peaks.

**4.6 Future work**

An interesting phenomenon that has been observed is the presence of two layers. No changes are made during the deposition, the pressure and temperature are held constant. This makes the sharp appearance of a second material even more surprising. The reason for this sudden transition has yet to be determined. There are two likely explanations which should be tested to determine the cause. The first set of experiments that should be done is a kinetics study to determine the growth rates of both materials and to determine at what stage during the deposition the second carbon layer forms. The results of the work presented in this chapter shows a temperature dependence on the tensile strength of the final wire, with lower temperature depositions being about five times stronger. It is unknown how each layer contributes to the overall strength of the material. The effect of temperature on the growth rate of each layer should also be investigated. The next set of experiments should be to determine the effect of hydrogen on deposition. It is well known that hydrogen can diffuse through glass, but the rate is temperature dependent.\textsuperscript{100-101} The outer material consists of graphitic sheets that conform to the inner pore of the glass capillary. Hydrogen’s rate of diffusion depends on the grain size, larger grains slow the
diffusion. Either of these phenomena would have an effect on the surface-gas interaction. Future experiments should be done varying the starting concentration of hydrogen gas to observe whether there is an effect on the boundary between the two carbon materials. Hydrogen may leave the capillary faster than it is produced, concentrating the methane within the capillary. The material of the capillary, or thickness of the capillary, might need to be changed to alter the diffusion rate of hydrogen. It would also be interesting to increase the pressure of the methane above 2 GPa, then heat it to decompose it in a confined geometry where the hydrogen can diffuse out. This would be of interest for possibly depositing sp³ carbon.
Chapter Five

Plasma Enhanced Chemical Vapor Deposition

5.1 Introduction

Plasma enhanced chemical vapor deposition (PECVD) provides a means of depositing materials at low temperature or materials which are inaccessible to thermal decomposition. This would be a powerful technique to adapt for confined geometries like micro capillaries, providing access to materials of optical interest such as diamond. PECVD deposits material by creating highly reactive intermediates through ionization. A plasma is an ionized gas composed of electrons and positively charged nuclei that move independently of each other, allowing conduction through the plasma. When molecules enter a plasma they are ionized either by collisions or the electric field, which can lead to atoms or groups of atoms being removed, forming ions or radicals. These highly reactive intermediates, facilitate the generation of high energy products, which are far from the thermodynamic equilibrium. It is the goal of this work to increase the pressure on plasma assisted depositions in order to influence kinetic and thermodynamic reactions to explore new products which are unobtainable through thermal means. It has been well established that diamond and diamond like material can be deposited by plasma enhanced, chemical vapor depositions.\textsuperscript{12,103} These depositions take place at low pressure. We would like to increase the pressure during the reaction to influence the product.

5.1.1 Townsend discharge

Townsend developed a model describing the different stages that develop with an applied electrical voltage to a gas. Figure 5.1.1 illustrates the different stages that lead to plasma
generation as the voltage is increased. Approaching the breakdown voltage near 600 V, there is an exponential growth in the current for minute changes in voltage. This region is labeled Townsend discharge where the electric field is just high enough to create a self-sustaining avalanche of electrons.

![Diagram of gas discharge regions](image)

Figure 5.1.1. The relationship between current and voltage for parallel plate electrodes. 

If the voltage is maintained, then the gas will transition into an unstable corona discharge. This leads into a glow discharge plasma which requires significantly less voltage to maintain than the Townsend discharge. Glow discharge is a type of plasma commonly used for film deposition, since it can not only be maintained over an extended volume, but it also generates low nuclei temperatures required for surface depositions. Temperature
of the nuclei can be further reduced by using a high frequency alternating electric field to prevent nuclei from responding to the electric field and gathering energy. Increasing the voltage further brightens glow discharge until arc discharge occurs. An arc discharge is accompanied by temperatures in the 1000’s K and only exists between two points, limiting their use in chemical deposition techniques.\textsuperscript{106} This kind of plasma is highly destructive and will ablate anything it touches for an extended period of time.

A dielectric material can be placed on one or both of the electrodes to limit the current and prevent arc formation. This technique is called a dielectric barrier discharge (DBD), and the formed plasma is similar to glow discharge plasmas.\textsuperscript{107} Silica, a dielectric material, can only let a finite number of carriers though under an applied voltage, which prevents the high current, which forms an arc between the electrodes. The plasma reactor can be viewed electrically as a capacitor with glass and gas being the dietetic materials. To generate DBD plasma an alternating electric field is applied with sufficient voltage to reach breakdown for the gas, but not the glass dielectric. Once the plasma is ignited, it is conducting and the plasma chamber can be electrically described as a simple capacitor with a silica dielectric.

**5.1.2 Paschen’s Law**

The breakdown voltage for gases is a function of pressure described by Paschens law, Equation (5.1.1), which states that the breakdown voltage for a gas is a function of the pressure and the distance between the electrodes.\textsuperscript{108} \( V_B \) is the breakdown voltage, \( p \) is the pressure in atmospheres, \( d \) is the distance in meters, \( a \) and \( b \) are constants that depend on the gas, and \( \gamma_{se} \) is the secondary electron emission coefficient at the cathode.\textsuperscript{109}
Equation 5.1.1

\[ V_B = \frac{apd}{\ln(apd) - \ln\left(\ln 1 + \frac{1}{y_{se}}\right)} \]

This means that as pressure is increased, the breakdown voltage increases. However, if the pressure is decreased, the breakdown voltage also decreases to a minimum, after which, the breakdown voltage will increase again. For most gases this minimum is around 1.3 Pa and 0.13 Pa. Figure 5.1.2 shows the breakdown voltage for several inert gasses as a function of pressure.

This behavior of the curve can be explained by avalanche collisions. After an electron has been generated it is accelerated in the electric field. The electron can ionize another species if it gains enough energy by traveling enough distance before its next collision. This is dependent on the applied voltage and the mean free path of the gas. If \( pd \) is decreased below the minimum, \( V_b \) increases since the ion is likely to have a neutralizing collision with the surface, rather than a collision which can promote the plasma. If the pressure is increased, the mean free path decreases and the electron has a shorter distance over which to gain energy over to have an ionizing collision; thus a stronger electric field is required. Another consequence of increasing pressure is the increase in the number of collisions, which can quench the plasma, which is overcome by increasing the voltage.

5.2 Deposition methods

Micro plasma reactors were designed around micro glass capillaries because the capillaries have large surface areas to promote surface reactions and are able to withstand large internal pressures. The shape of the capillary can also be used to template the growth. The wall glass of the capillary can be used as the dielectric barrier to limit the current for a DBD plasma, and the small distance between the electrodes will keep experimental voltages low. To electrically generate plasma inside a micro capillary, there are a limited number of electrode arrangements. The electrodes need to be positioned to create an electric field parallel or perpendicular to the axis of the fiber to maximize its strength across the gas. Arrangement of the electrodes is important because electrons will always follow the path of least resistance, and it is crucial to avoid breakdowns in undesirable paths. This means that to generate plasma, the electrical path through the target gas has to have lower resistance than all other electrical paths. As an example of unintended breakdown, metal
electrodes were deposited on the outside surface of a microcapillary, creating an electric field perpendicular to the axis of the fiber. Plasma was never generated in the core of the capillary since the path of least electrical resistance was through the air traveling around the capillary and not through the glass and central hole. Alternatively, if electrodes are placed internally, in the same hole, with only a separation of a few millimeters, arcing occurs, since there is nothing to limit the current. Since the plasma generated by arching is very hot, over time, metal from the electrodes sputters, and the capillary melts if the pressure is increased above atmospheric conditions.

5.2.1 External coil electrodes

Techniques involving internal electrodes had many shortcomings and no immediate signs of success. The distances are so short, that it was difficult to prevent electrical conduction through unintended paths. External electrodes which applied the electric field along the axis of the capillary had the greatest success and were able to generate a DBD plasma inside the fiber. To understand why this electrical arrangement succeeded among the various methods, a close look at the possible electrical paths is needed.

![Figure 5.2.3 A schematic of the external electrode arrangement for generating atmospheric plasma.](image)

In Figure 5.2.3 the two most likely electrical paths are through the air between the two electrodes and though both the glass and capillary media. Of the two, the more desired path is through the glass, which is a good dielectric. The second path is through the gas in the micro capillary then once again through the glass. Once the gas in the capillary has been
ionized into a plasma, the plasma can be considered conductive, and requires less voltage to maintain it, as mentioned previously. The key to selecting this second pathway came from choice of flow gas. At atmospheric pressure, helium breakdown voltage is more than 6 times lower than nitrogen.\textsuperscript{110} Experimentally, it was found that for plasma to be generated inside the fiber, the majority of the gas must be helium, otherwise the electrodes will short through the air. Hydrogen’s breakdown voltage is half of nitrogen’s, but it too must be diluted with helium to achieve a plasma.

![An optical image of the arrangement of the micro plasma experiment. Green wire is ground. Red wire is the high voltage electrode. Pink is the helium plasma.](image)

The device in figure 5.2.4 was fabricated by wrapping electrodes on the outside of the micro capillary, to generate plasma inside the capillary.\textsuperscript{111} A 50 µm I.D., 125 µm O.D. micro capillary was then used for all external electrode experiments. The polymer coating on the outside of the micro capillary was removed to eliminate additional dielectric effects. The electrodes were prepared by taking copper wire and wrapping it about five times around the outside of the capillary and separating them by 2 cm. If the distance was shorter than 1 cm, arcing would occur between the electrodes and not go through the micro capillary. If it was longer than 2 cm the plasma would be visibly uneven. An experiment was done to determine the limits of the distance between the electrodes. The longest
distance over which the plasma was generated was at least 12 cm. Nothing was encountered to suggest that the distance could not be longer with sufficient voltage. In general, the plasma decreased in brightness from the high voltage electrode to the ground electrode and there also was quite a lot of plasma that traveled up stream, away from the ground electrode. Using the external electrodes, plasma generation was attempted in capillaries smaller than 50 µm. All these attempts were unsuccessful, likely due to the large surface area quenching the plasma.\(^\text{109}\) Longfei et. al. also reports failure in generated plasma in capillaries smaller than 30 µm.\(^\text{111}\)

Figure 5.2.5 Optical images of polymeric hydrogenated deposited by atmospheric pressure confined plasma. (Left) Transmitted (Right) Cross section.
Figure 5.2.6 SEM cross section of polymeric hydrogenated deposited by atmospheric pressure confined plasma.

### 5.2.2 Characterization

Many combinations of helium and methane were tried in ratios ranging from 20% methane in helium to 1% methane in helium. These mixtures did lead to the deposition of a translucent, hydrogenated amorphous carbon shown in figure 5.2.5 with almost 100% sp² bonding. The SEM images in figure 5.2.6 shows that the film has good adhesion to the glass. The material has strong photoluminescence and is easily damaged by UV. UV Raman was collected and is shown in Figure 5.2.7. However, the material proved to be highly UV sensitive, possibly damaging, on the first exposure. The large amount of photoluminescence present in figure 5.2.7 is characteristic of hydrogenated carbons.¹¹²

Figure 5.2.7. (Left) UV Raman (257 nm excitation) of polymeric hydrogenated deposited by atmospheric pressure confined plasma. (Right) Photoluminescence spectrum of polymeric hydrogenated deposited by atmospheric pressure confined plasma.
Figure 5.2.8 shows that the material grows thickest near the high voltage electrode and becomes thinner toward the ground electrode, being a total of a few millimeters in length. The thickest the film can get is limited by the inner diameter of the capillary, being no smaller than ~30 µm, since it appears plasma cannot be generated in radii smaller than 30 µm.

Figure 5.2.8 A series of optical images along the length of the capillary where the plasma was generated using external electrodes. The first image is of the high voltage, which is where methane enters first. The last image is of the ground electrode right before the gas exist the capillary.
5.2.3 Conclusions

Using the external electrodes, a carbon film was deposited using a methane helium mixture. This was successful in depositing sp$^3$ carbon; however, the material is highly hydrogenated. There is no evidence for a significant amount of sp$^3$ carbon-carbon bonding, which is needed for diamond-like properties. Though plasma was unable to be generated at high enough pressures to influence the sp$^3$ carbon-carbon bonding content, the experimental setup establishes a foundation for studies of other materials such as silicon.

5.3 Plasma Enhanced Deposition Chemical Vapor Deposition of Silicon (PECVD)

Based on the success with using methane, silane was tried using the same plasma setup. Silane is more reactive than methane, and instead of depositing a film, gas phase reactions dominate, and particles agglomerate into clusters which collect on the capillary surface. Bright orange plasma was generated in helium with up to 10% silane (by pressure)

![Image of deposition]

Figure 5.3.1 are optical images of a 50 µm I.D. micro capillary after deposition Optical images of the deposition near the high voltage electrode. (Left) Reflected (Right) Transmitted.

at 138 KPa (20 psi). The deposition began at the upstream electrode and grew downstream. The reaction proceeded until the plasma self-extinguished. Figure 5.3.1 shows that the material’s thickness is not uniform over the length. Deposition was observed wherever plasma was seen, including 5 mm up stream of the high voltage electrode.
The particles can be seen through the side of the fiber in figure 5.3.1 and are a vibrant orange in color. When viewed in transmitted light (Figure 5.3.1 right), the inner pore can be viewed. It appears rough and uneven. In figure 5.3.2 the fiber was cleaved, revealing that the silicon particles have no adhesion to the glass or even to themselves.

Figure 5.3.2 An optical image of silicon nano particles.
Figure 5.3.3 An SEM micrograph of silicon nano particles.

Closer examination with an SEM figure 5.3.3 reveals that each particle is itself made up of smaller particle.

Figure 5.3.4 Raman (514 nm excitation) of silicon nano particles.
The Raman peak position for silicon bulk is 520 cm\(^{-1}\), but as the particle becomes smaller than 60 nm, photon confinement effects are observed.\(^{113}\) These effects cause the peak in the Raman to decrease in frequency. From this, an estimation of the particle size can be made.\(^{113}\) The greatest shift that was measured was 6 cm\(^{-1}\). According to Meier et. al. the silicon particle size is about 20 nm in diameter.\(^{113}\)

### 5.3.1 Conclusion

With the micro plasma reactor silicon nano particles are grown in the gas phase. There is no evidence of any film growth in SEM (Figure 5.3.3) or optical microscopy (Figure 5.3.2). The silane could be too reactive, preferring to react in the gas phase before plasma activated silane molecules have time to deposit on the surface. From the SEM in figure 5.3.3 and Raman in figure 5.3.4, the deposited material is silicon clusters, which are \(~250\) nm in diameter, consisting of \(~20\) nm particles of silicon. Eventually, these particles are deposited on the surface until the inner diameter of the pour become smaller than 30 µm. As stated above, the micro plasma could not be generated in capillaries smaller than 30 µm. Dongping et. al. reported similar findings.\(^ {111}\) This holds true with silane as well as methane. If deposited material makes the pore smaller than \(~30\) µm, the plasma will extinguish.

### 5.3.2 Future Work

Work is needed to explore the effect of silane concentration Experiments need to be devised to determine the effect of concentration on particle size. It might be possible to decrease the concentration and flow rate to promote surface growth, or to use magnetic fields to direct the ions toward the surface. It also would be of interest to increase the flow rate to
see if particles can be collected in the exhaust. This would allow scaled deposition of gram quantities of silicon particles. It is foreseeable that films could be deposited over long lengths by moving the capillary through the external electrodes. With some optimization it should be possible to coat the inner pore with a film of silicon. It should also be possible to collect the particles that form, in the gas phase, outside of the capillary, allowing gram scale synthesis.

5.4 Laser Induced Plasma

To realize the goal of generating micro plasmas it seems necessary to move away from metal electrodes as they are prone to shorting at the voltages necessary for high pressure plasma. One way to overcome the difficulties and challenges associated with using metal electrodes to generate plasma is to avoid using them entirely. Light has an electric field component and a magnetic field component. If enough optical density is achieved, the electric field component can become strong enough to ionize gas. Pulsed lasers are a great tool for delivering high peak powers of light, which can then be focused down to create the required field strength to generate a plasma. Equation 5.5.1 is the formula for calculating the electric field strength of light. J is the average power density, and v is the wavelength of light.

\[ E = \left( \frac{4\pi J}{\hbar v} \right)^{1/2} \]

The frequency of the electric field is in the terahertz (THz), enabling even lower nuclei temperatures than KHz voltage sources. Additionally, the generation of plasma becomes easier as pressure is increased until a minimum is reached, shown in figure 5.5.1.114 If
pressure is further increased, eventually collisions with neutrals outweighs the benefit of the increased chance for ionization.

Figure 5.4.2. (Top) An in situ demonstration that plasma can be optically generated inside 150 μm glass capillary. (Bottom) With the addition of methane gas material can be deposited on the inner surface.

### 5.4.1 Characterization

Exploratory work has been done using a femtosecond pulsed Ti:Sapphire laser to generate plasma. To produce light which is powerful enough to ionize a gas, pulsed lasers are normally used, which have extraordinary peak powers. As a consequence of this, the plasma will also be pulsed. The light is focused with a simple lens down the axis of the micro capillary. The top panel of Figure 5.4.2 shows plasma being generated inside a 150 μm I.D. micro capillary. As a proof of concept, material was deposited by flowing methane down the capillary during laser irradiation. Figure 5.4.2 shows how quickly material can be deposited using this technique.
The deposited material shown in figure 5.5.3 is translucent, which supports the conclusion of sp$^3$ carbon. Unfortunately, the large photoluminescence background indicates a large amount of hydrogen. From these two observations, the material is amorphous polymeric carbon, but lacks diamond like connectivity.

### 5.4.2 Future Work

A high pressure reactor was designed and built to allow the pressure inside the microcapillary to be increased while still allowing laser light to be focused axially down the fiber. Further experiments need to be done to generate plasma under these increased pressure conditions. Once successful, deposited materials may have higher amounts of diamond like sp$^3$ connectivity.
Chapter Six

Conclusion

The driving motivation for this dissertation has been toward developing new sp3 carbon bonded materials. This work contributes toward this goal in two ways. First, by furthering research in a methodology of using pressure to react small molecules together, while retaining some of their original structure. The second, by developing a confined high pressure laser induced plasma system that will allow further research on how pressure can influence plasma depositions. There is ample opportunity for future experiments based on the techniques developed and work presented in this dissertation.

Chapter 2 and 3 - Diamond Anvil Cell Work

Lithium dicyandiamide was used as a model system to demonstrate pressure induced trimerization of cyanide groups. Lithium dicyandiamide was studied under increasing pressure with Raman, IR and synchrotron x-ray diffraction to understand how the chemical nature of the material changes. This was also the first work to report measurements of low frequency Raman modes of lithium dicyandiamide. Upon compression, this crystal exhibits negative linear compressibility up to pressures of 3 GPa. This is followed by a phase transition at 8 GPa, where we observe new peaks in the IR and Raman as well as structural changes in the XRD pattern. When the pressure is increased about 15 GPa, signatures for C-N rings appear in the IR and Raman, which have strong similarities to thermally trimerized products. The final product is recoverable to atmospheric pressure, but remains air sensitive.
Guided by the results the results of lithium dicyandiamide, tetracyanomethane was selected because it is a small molecule only consisting of carbon and nitrogen and has the potential for producing ultra-hard materials. Tetracyanomethane was studied with Raman IR and synchrotron X-ray diffraction in-situ under high pressure conditions. The changes in the crystal structure and bonding environment were tracked under increasing pressure. The material was found to polymerize at ~13 GPa which can be recovered to ambient conditions and is air stable.

The future of this work should be toward the development of 3D covalent networks. The next set of experiments should be done on larger molecules with reactive side groups, with the goal of linking the molecules together, while maintaining the core of the starting molecule. How other side groups or combination of side groups react, which can lead to a covalent extended network, should be studied.

**Chapter 4 - Thermal Decomposition**

The thermal decomposition of methane led to the deposition of two different amorphous carbon layers with a sharp transition. The outer layer consists of sheets which conform to the surface of the hollow capillary. The second material is porous and appears more particulate in nature. The transition between the materials occurs over less than 1 µm and there are no external changes during the experiment. There is opportunity to investigate the exact mechanism for this transition.

**Chapter 5 - Plasma Enhanced Chemical Vapor Deposition**

A dielectric breakdown plasma was generated inside a hollow capillary, and this plasma reactor was successful in depositing both amorphous hydrogenated carbon films and silicon
nanoparticles. These two results demonstrate the potential of using this technique to deposit films as well as create nanoparticles. While the experimental setup is unsuitable for generating high pressure plasma, it is perfectly suitable for depositing other materials such as silicon carbide or germane nanoparticles. It might also be possible to modify the conditions to deposit silicon as a film instead of forming gas phase particles.

Confined, electrically generated plasma has many challenges that need to be overcome for the plasma to be generated at higher pressures. However, the future of the high pressure plasma research lies in laser induced plasma generation. Laser induced atmospheric pressure plasma has been successfully generated inside a hollow capillary. We have demonstrated that amorphous hydrogenated carbon can be deposited with this technique. For laser induced plasmas, the breakdown voltage will decrease initially as the pressure is increased, thus higher pressure plasmas are favored. This technique can take advantage of the pressure-temperature phase diagram to access new products.

In conclusion there are many directions that are available for future work. For the Diamond anvil cell, demonstrating that small molecules can be linked together with pressure, without changing the body of the molecule, would have an impact on the field. This could lead to designing covalent bond-linked materials. The thermal decomposition of methane has unanswered questions about the mechanism behind two different layered materials deposited under the same external conditions. This is a question that is mostly of a scientific interest. The preliminary research on laser generated plasmas has been completed; demonstrating that this technique is able to deposit films. The next step is to perform experiments under pressure, to study the relationship between pressure and deposition.
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