NOVEL APPARATUS FOR HIGH-PRESSURE, HIGH-TEMPERATURE GROWTH OF DIAMOND

A Thesis

by

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ABSTRACT

There is an urgent need for high-quality fluorescent nanodiamonds for applications in biosensing and quantum information. Existing techniques provide poor diamond quality, making them unsuitable for most applications. The only exception is to etch bulk diamonds by lithography, but this is complex and not scalable to large quantities of nanodiamonds.

For bulk diamonds, the most successful growth techniques are chemical vapor deposition (CVD) and high-pressure, high-temperature (HPHT). However, for nanodiamonds, CVD is not scalable because it is surface-based. Therefore HPHT is the best option. While many decades of research have led to reliable techniques to grow high-quality bulk diamonds by HPHT, nanodiamonds have only recently been researched.

Developing novel nanodiamond growth techniques with large HPHT presses is hampered by the lack of good, real-time diagnostics. Many experiments must be performed, stopped at different times, to get a good profile of the growth process. To overcome this, diamond anvil cells (DACs) have recently been explored. These have the advantage of real-time diagnostics, and can also incorporate laser heating which in turn can access pressures, growth temperatures, and growth times that cannot be achieved in larger, closed presses.

The aim of this master's project was to investigate and improve all aspects of DAC design for future diamond growth, especially with laser heating. This includes novel DAC hardware design, real-time pressure control, different gasket and culet designs, improved loading and unloading techniques, as well as a variety of laser wavelengths and types for both heating and diagnostics.

TABLE OF CONTENTS

Page

ABSTRACT ii

TABLE OF CONTENTS iii

LIST OF FIGURES iv

CHAPTER I INTRODUCTION AND LITERATURE REVIEW 1

1.1 Diamond point defects 1
1.2 Creation of nanodiamond 2
1.3 The diamond anvil cell 3
1.3.1 Bevels 5

CHAPTER II USING THE DIAMOND ANVIL CELL (DAC) TO GROW NANODIAMONDS 7

2.1 DAC New Design 7
2.2 Gasket 10
2.3 Gasket preindentation 11
2.4 Pressure monitoring 13
2.4.1 Pressure gauge 15
2.5 Gasket drilling 16
2.6 Loading growth material 18
2.7 Pressurize the growth mixture 19
2.8 Laser heating 21
2.9 Monitor growth 24
2.10 Product extraction 27
2.11 Evidence of nanodiamonds with silicon-vacancies (SiV). 30

CHAPTER III FUTURE IMPROVEMENTS 32

3.1 Machining sapphire anvils with conical seats 32
3.2 Laser machining of titanium growth chambers 33

REFERENCES 35

LIST OF FIGURES

Page

Figure 1: (a) Brilliant cut. (b) Standard cut. (c) Boehler cut. 5

Figure 2: (a) Standerd Culet. (b) Culet with a bevel. 6

Figure 3: (a) Piston-cylinder diamond anvil cell. (b) New diamond anvil cell. 8

Figure 4: (a) A home-built diamond seat with tungsten supporters. (b) 3D model Showing the bottom part of the DAC. (c) Diamond anvils inside the DAC 10

Figure 5: 3D printed gasket holder with a preindented gasket. 12

Figure 6: Pictures for preindentation of a gasket on a Dimond with a bevel. (a) the diamond culet without any contact form the gasket. (b) The gasket is in contact with the diamond, the arrow shows the radius of the gasket indentations progression. (c) and (D) shows the progression of the indentation proses. 13

Figure 7: Shift in the ruby spectrum due to 12.6 GPa of pressure exerted from the diamond anvils. 14

Figure 8: (a) Hydraulic cylinder pressure gauge. (b) The relationship between pressure inside the DAC (y-axis) and pressure exerted by the hydraulic cylinder (x-axis). 15

Figure 9: (a) Electrical discharge machine (EDM) which consist of 100 µm molybdenum wire, x-y translation stage dielectric fluid cup made of aluminum. (b) A close-up image showcases the dielectric fluid cup with a gasket securely held in place by a stainless-steel washer. (c) The EDM circuit used for the process is depicted. (d) An image of the gaskets after drilling. 17

Figure 10: (a) The gasket hole after it's been drilled. (b) The gasket hole after loading the growth material. 19

Figure 11: The sample chamber under pressure. 20

Figure 12: Blackbody emission in the sample chamber. 22

Figure 13: (a) Defect in the diamond culet. (b) Shattered diamond. 23

Figure 14: The custom-built confocal microscope used for Raman and fluorescent monitoring......24

Figure 15. A schematic diagram of the custom-built confocal microscope shows the key elements. 26

Figure 16: Raman spectra of the growth mixture......27

Figure 17: The procedure of removing the sample from the diamond anvil......29

Figure 18: (a) SiV zero phonon line (ZPL) at 19 GPa. (b) Blackbody radiation in the same spot where the SiV spectrum was measured. 31

Figure 19: Recent improvements include replacing the diamond with sapphire. 33

Figure 20: A cut in a thin pieces of titanium metal to make a crude growth chamber. ...34

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Diamond point defects

Diamond point defects, such as the Silicon Vacancy (SiV), Nitrogen Vacancy (NV), Germanium Vacancy (GeV), and Nickel Vacancy (NiV) centers, have unique electronic and optical properties that make them attractive for quantum technologies. These properties stem from their long-lived spin coherence and efficient photon emission, which can be harnessed for quantum information processing, sensing, and communication [1].

SiV centers in diamond possess exceptional optical properties, including narrow linewidths, high spectral stability, and efficient photon emission. These characteristics make them promising candidates for applications in quantum communication, quantum computing, and quantum sensing [2]. SiV centers have been investigated for their potential as single-photon sources, and they exhibit strong coupling to optical cavities, which can be used for interfacing with other quantum systems [3].

NV centers in diamond are well-known for their long spin coherence times and high sensitivity to external magnetic fields, which make them ideal for applications in quantum sensing [4]. They have been widely studied for use in nanoscale magnetometry and are expected to play a significant role in the development of quantum technologies. Moreover, NV centers have been used as qubits in quantum computing and in quantum networks for long-distance communication [5].

Diamond point defects offer several advantages for biological applications due to their biocompatibility, photostability, versatility[6], and emission in the biological window[7]. Being an inert material, diamond does not interact with biological systems, ensuring minimal interference or adverse effects when used for sensing or imaging[8]. Moreover, the point defects are capable of withstanding repeated exposure to light without bleaching, making them ideal for long-term imaging applications[9]. Additionally, diamond point defects can be easily functionalized with specific molecules, enabling targeted sensing and imaging of biological molecules and processes[8]. The emission of diamond point defects in the biological window allows for efficient detection and minimal interference from the surrounding biological environment, further enhancing their potential in biological applications[10].

1.2 Creation of nanodiamond

Nanodiamonds can be obtained through various methods. Grinding of bulk diamonds is a mechanical process that involves reducing the size of a high-quality diamond to create smaller, lower-quality particles[11]. However, this method can produce irregularly shaped nanodiamonds with rough surfaces and a broad size distribution, limiting their potential applications[11]. To overcome this limitation, chemical etching can be employed to create rounded nanodiamonds with smoother surfaces[11]. The process involves using strong acids and oxidants to gradually remove the sharp edges and rough surfaces of mechanically ground nanodiamonds, resulting in more uniform and well-defined particles[11].

Another method for obtaining nanodiamonds is through detonation, which involves exploding explosives in the presence of carbon-containing materials such as graphite or diamond[12]. This process generates extreme temperatures and pressures, leading to the formation of nanodiamonds[12]. However, this method often produces low-quality nanodiamonds with impurities and defects due to the chaotic nature of the detonation process[12].

Chemical vapor deposition (CVD) is an alternative method for producing nanodiamonds[13]. CVD enables the controlled growth of high-quality diamond films on various substrates, resulting in surface-based nanodiamonds[3]. Although CVD-grown diamonds possess exceptional purity and crystalline quality, their applications may be limited due to their surface-bound nature[13].

High-pressure high-temperature (HPHT) growth is a method used to produce synthetic diamonds by replicating the extreme conditions that exist deep within the Earth's mantle, where natural diamonds are formed[14]. This process involves subjecting a carbon source to high pressure and high temperature, typically using a press and a catalyst, to facilitate the conversion of carbon into diamond.

1.3 The diamond anvil cell

The diamond anvil cell (DAC) is a device that can be considered a part of the high-pressure high-temperature (HPHT) family of techniques[15]. A diamond anvil cell is a high-pressure device used in scientific experiments to subject small samples to extreme pressures and temperatures[16]. The DAC consists of two opposing diamond anvils that compress a small sample placed between them. The sample is typically enclosed within a metallic gasket to prevent leakage and maintain the pressure[17]. Diamonds are chosen for their exceptional mechanical strength, high thermal conductivity, and transparency to a wide range of electromagnetic radiation, allowing for various in situ measurements and observations[18].

The cut and shape of the diamond anvils play a crucial role in determining the performance of the DAC. Different diamond cuts can impact the pressure distribution and attainable maximum pressure[19]:

1. Brilliant cut: The brilliant cut is a common gemstone cut (shown in Figure 1.1a), featuring a cone shape and multiple facets designed to maximize the reflection and refraction of light. While this cut is not typically used in DACs due to its primary focus on aesthetics, it serves as a reference point for the other cuts mentioned below[20].

2. Standard cut: Also known as the flat-top cut (shown in Figure 1.1b), this design features a flat small crown to maximize the table area and a single bevel on the pavilion of the diamond. The standard cut allows for a larger sample space and better optical access for measurements[21]. However, it may limit the maximum pressure achievable due to the flat culet, which results in a larger contact area between the anvils[22].

3. Boehler cut: This cut features a conical-shaped crown with a smaller contact area than the standard cut (shown in Figure 1.1c), allowing for higher pressures[23]. The Boehler cut also has a single bevel on the pavilion, which helps maintain optical access

for measurements[24]. The smaller culet size can lead to a more concentrated pressure distribution and a higher maximum pressure[25].

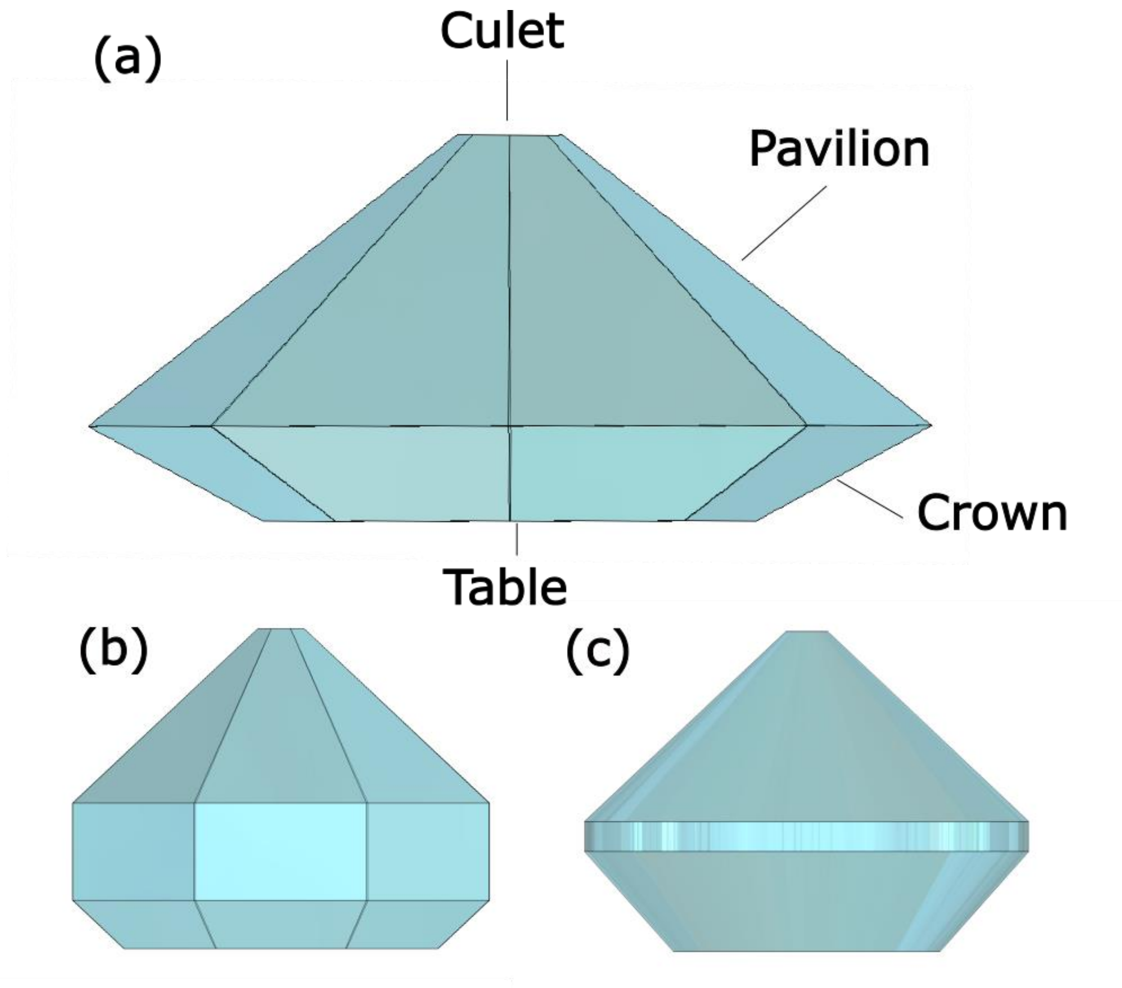

Figure 1: (a) Brilliant cut. (b) Standard cut. (c) Boehler cut.

1.3.1 Bevels

Bevels play an essential role in optimizing the performance of the DAC for various experimental conditions[26]. Bevels are the angled facets cut into the pavilion of the diamond anvil, surrounding the culet (shown in Figure 2). Bevels can influence the pressure distribution in the sample chamber[27]. A well-designed bevel can help maintain a more uniform pressure distribution across the sample, reducing the risk of localized pressure spikes that could damage the sample or the diamond anvils[28]. This aspect is particularly important when studying samples that are sensitive to pressure variations. Bevels can improve the stability and alignment of the diamond anvils within the DAC[29]. Properly designed bevels help maintain the parallelism between the anvils, ensuring an even distribution of force and reducing the risk of uneven pressure or misalignment that could compromise the experiment's results or cause damage to the diamonds[30].

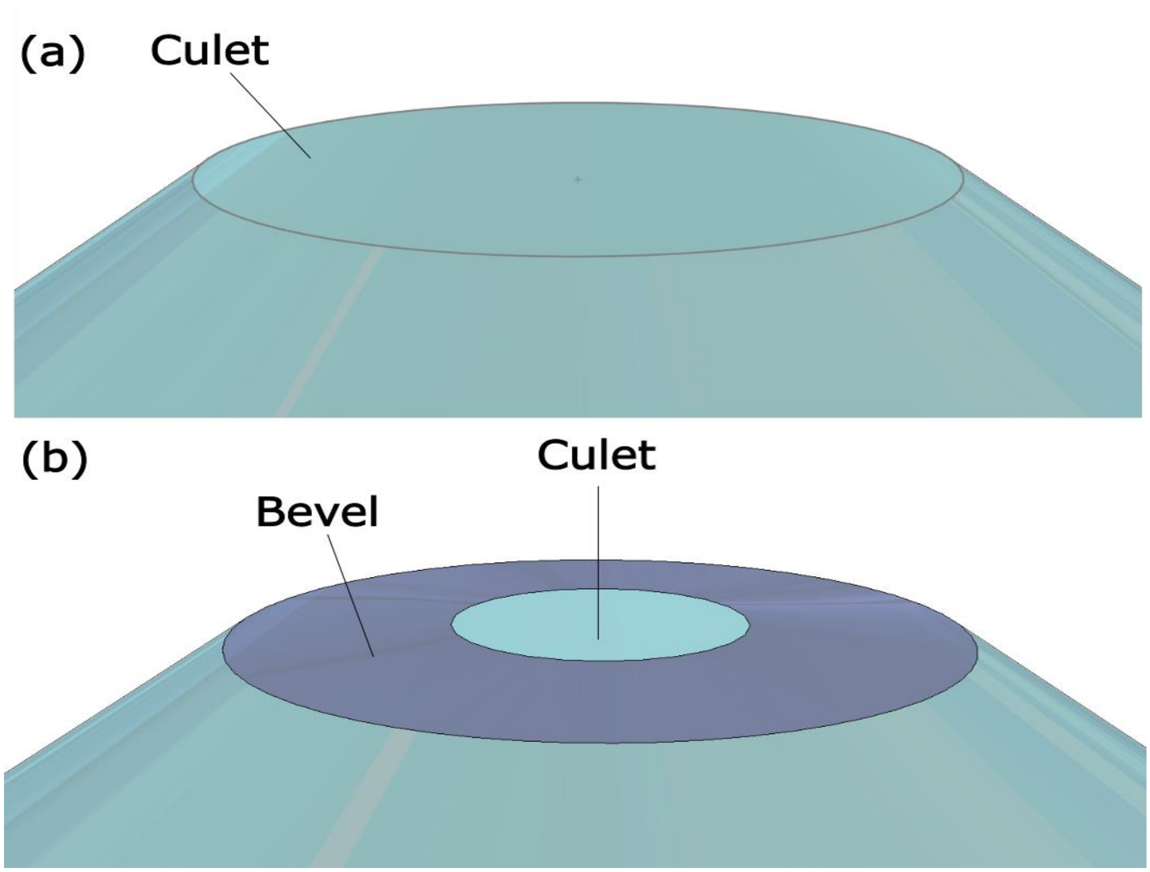

Figure 2: (a) Standerd Culet. (b) Culet with a bevel.

CHAPTER II

USING THE DIAMOND ANVIL CELL (DAC) TO GROW NANODIAMONDS

2.1 DAC new design

In the process of growing nanodiamonds, it was found that the conventional DAC design had a number of limitations. Hence it was necessary to redesign the DAC specifically for nanodiamond growth by laser heating. Conventional DACs typically have a piston-cylinder design(figure 3(a)) , where one diamond anvil is fixed, and the other is mounted on a piston that can be moved to apply pressure on the sample. However, this design can result in uneven pressure distribution and shear force on the diamonds due to its inherent asymmetry from applying force from the screws. To address this issue, we have devised a novel apparatus, shown in Figure 3(b), that incorporates a hydraulic cylinder to apply force on the diamond and create pressure on the sample. This design ensures an even pressure distribution, reducing the risk of damage to the diamonds.

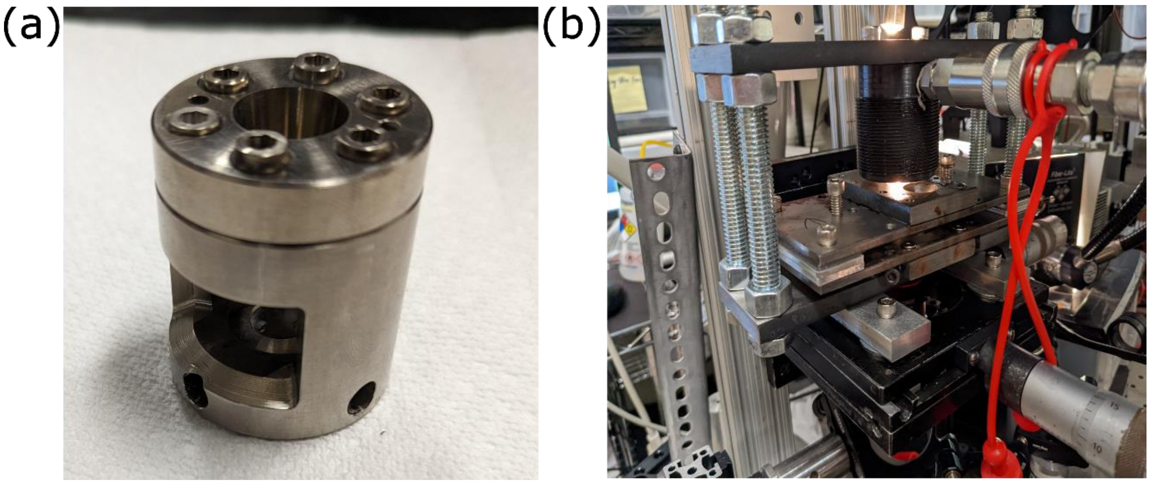

Figure 3: (a) Piston-cylinder diamond anvil cell. (b) New diamond anvil cell.

A key problem for diamond anvil cells is to avoid shear forces on the diamond anvils during compression. Shear forces will cause the anvils to break. Shear forces can be produced if the compression force is slightly off-axis. Although care is taken to prevent this, it can still happen for a number of reasons. For example, the metal seats holding the base of the diamond anvils could be slightly tilted. Even if they are not tilted initially, the strong forces applied can often cause deformation (or indentation) of the seats by the anvils. To avoid this, hard metal is used for the seats. Typically either tungsten-carbide or hardened tool steel are used, depending on the design of the anvil base, as discussed above.

In Figure 4a the diamond anvil is a standard anvil cut placed on a tungsten seat embedded in a grade 8 steel screw (Figure 4a). The seat has a 1mm conical hole on the back side (opposite the anvil) to allow wide-angle optical access for spectrometry and laser heating. In this design, the top anvil is stationary while the bottom anvil can be positioned with three set screws to align the two culets (Figure 4b). The distance between the two anvils is 1mm-1.5mm (Figure 4c).

As shown in Figure 4b,c the screw holding the diamond anvil is mounted on a thin steel sheet, which acts as a steel leaf spring. The advantage of using a leaf spring is that off axis forces and motion are strongly suppressed. Nonetheless, due to the large forces produced by the hydraulic cylinder, some tilting or twisting of the steel springs is sometimes seen. If this happens the diamond culets can both tilt and slide relative to each other. While the tilt is of minor importance, the sliding produces shear forces the break the culets. To alleviate this problem, both diamond anvil are mounted on identical leaf springs, bolted together in a symmetric design. The high-symmetry ensures that any off-axis tilting that does still occurs, will not cause sliding of the culets relative to one another. With this design, the problem of diamond anvil breakage was virtually eliminated. This greatly reduced the operating cost of our DACs and improved their stability.

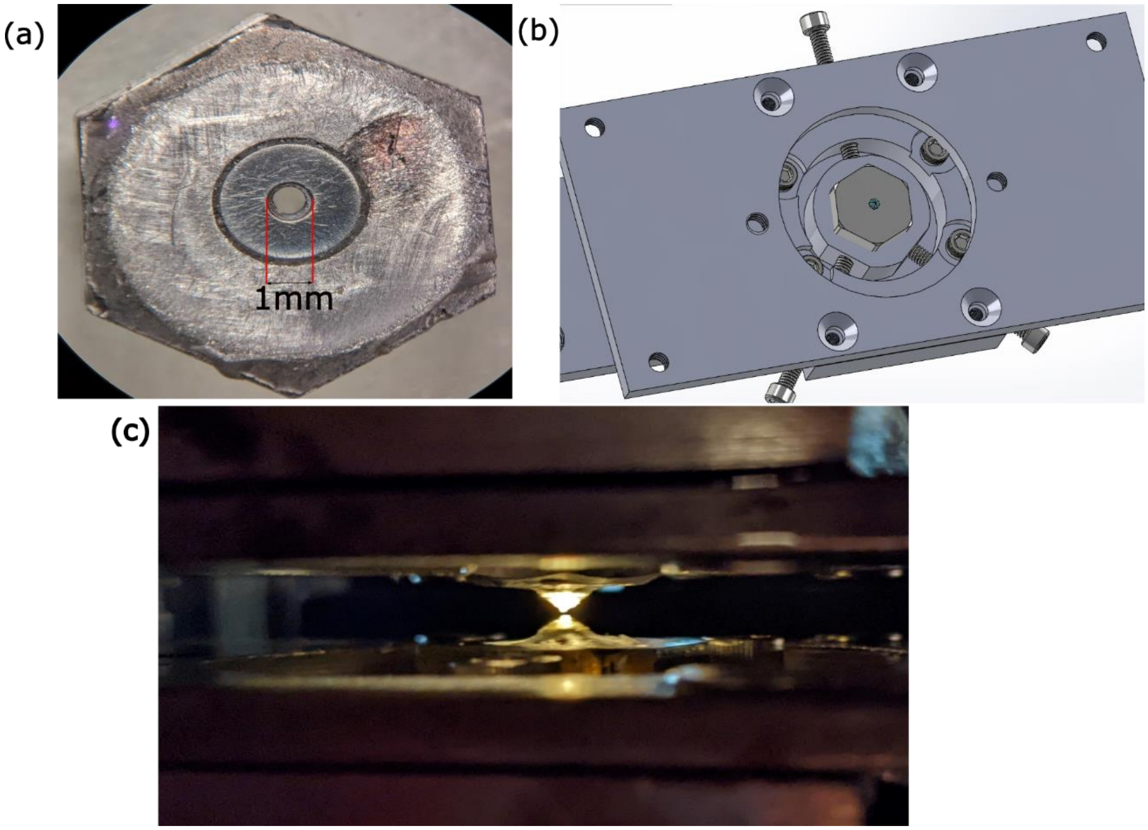

Figure 4: (a) A home-built diamond seat with tungsten supporters. (b) 3D model Showing the bottom part of the DAC. (c) Diamond anvils inside the DAC

2.2 Gasket

Gaskets in a Diamond Anvil Cell (DAC) are essential for high-pressure operation. Due to the brittleness of diamond anvils, any direct contact causes chipping and breaking. Therefore, some less-brittle material, usually metal, is needed to cushion the junction. In addition to cushioning the gasket is also needed to seal the sample chamber, since otherwise the growth material would squeeze out through any small gap between the anvils.

Originally it was believed that no pressure chamber incorporating a gasket could operate at a pressure higher than the yield pressure of the metal which is typically only a few GPa. However, experiments soon proved that this is not the case. Although the reason for this is still not totally understood, the performance of gaskets has been sufficiently well researched that it is now well-known how to design the gaskets to reach extremely high pressures. For diamond growth experiments, the gasket is typically made from a metallic foil, such as Inconel or rhenium, and is situated between the two diamond anvils.

For this experiment, we used a gasket made of rhenium due to its high melting point of 3186°C, which makes it suitable for laser heating under high-pressure conditions. Rhenium is also chemically inert, which helps prevent contamination of the sample.

2.3 Gasket preindentation

A crucial step in DAC experiments is gasket preindentation. The importance of gasket preindentation lies in its ability to ensure a good seal between the diamond anvils and the gasket. In addition, preindentation can help to minimize plastic deformation of the gasket during sample compression. Basically, when the DAC is compressed to generate high pressures, the gasket experiences significant stress. This causes the metal to flow until it reaches a critical thickness where the pressure at the center begins to rise rapidly as the force is further increased. It is important for the gasket to reach this critical thickness before machining the sample chamber. Otherwise the flow of material out from between the anvils will cause the sample chamber to expand beyond the size of the culets and the sample will be lost.

In practice, after aligning the diamond anvils, a gasket is placed between them, and pressure is applied to preindent it. For this process, the gasket's underside is coated with fine ruby particles that allow monitoring of the pressure a different positions. Then the gasket is carefully positioned with a unique, 3D printed holder, as shown in Figure 5, ensuring it lies exactly between the two anvils.

Figure 5: 3D printed gasket holder with a preindented gasket.

One way to ensure that the two diamond anvils stay aligned and that pressure is evenly distributed on the culet, is to monitor the flow of gasket metal. For example unidirectional flow means that the anvils are moving off-axis, and the compression process must be stopped until the source of the problem is identified. In the new DAC design, hydraulics enable real-time monitoring of the gasket metal flow as shown in Figure 6.

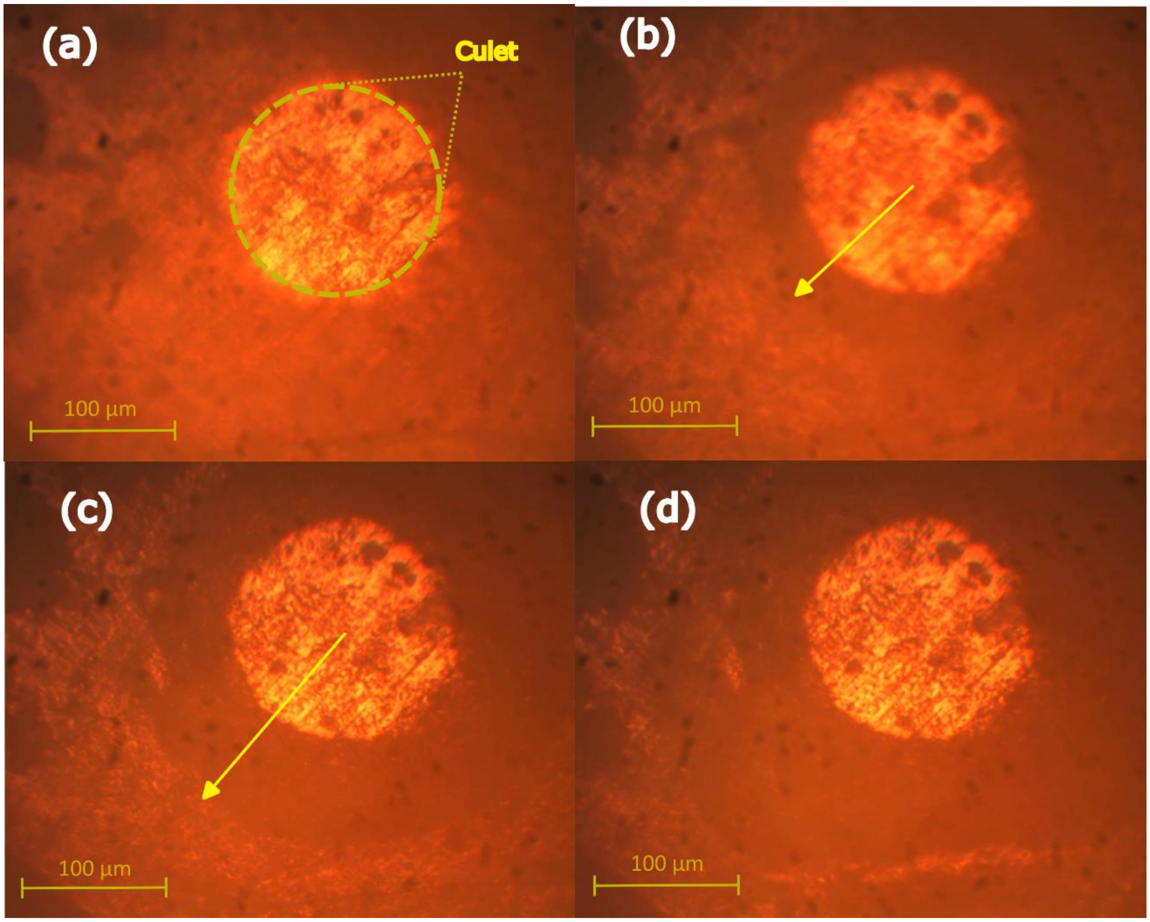

Figure 6: Pictures for preindentation of a gasket on a Dimond with a bevel. (a) the diamond culet without any contact form the gasket. (b) The gasket is in contact with the diamond, the arrow shows the radius of the gasket indentations progression. (c) and (D) shows the progression of the indentation proses.

2.4 Pressure monitoring

There are several methods for measuring pressure in a DAC, including ruby fluorescence[31,32], Raman spectroscopy [33], and electrical conductivity [34] measurements. Each method has its advantages and limitations. In this experiment, we employed ruby fluorescence, a widely used technique in DAC experiments. This technique relies on the pressure-induced shift of the ruby fluorescence emission lines. Ruby, a crystalline form of aluminum oxide (Al_2O_3) doped with a small amount of chromium (Cr), is an ideal pressure sensor due to its high-pressure stability, chemical inertness, and the well-defined fluorescence lines that are sensitive to pressure.

Under pressure, the crystal lattice is compressed, altering the crystal field around the chromium ions and causing a shift in their energy levels. This shift results in a pressure-dependent change in the wavelengths of the R_1 and R_2 fluorescence lines [31]. By measuring the pressure-induced shift in the wavelengths of these lines, as shown in figure 7, we can accurately determine the pressure inside a DAC.

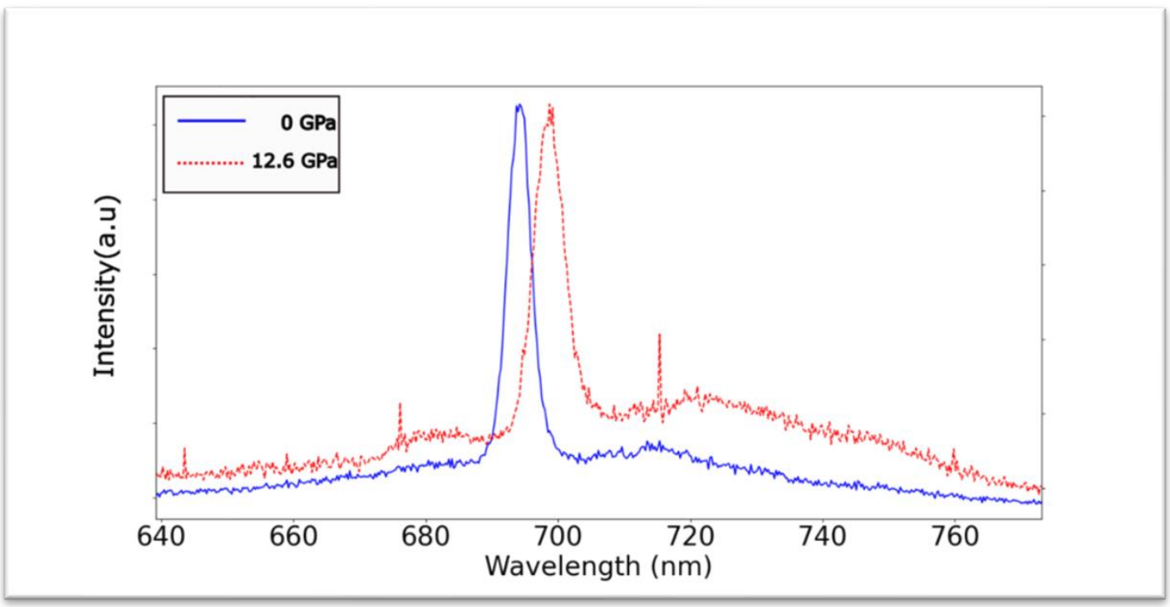

Figure 7: Shift in the ruby spectrum due to 12.6 GPa of pressure exerted from the diamond anvils.

2.4.1 Pressure gauge

During compression, it is important to monitor the pressure as a function of the applied force (as measured by a hydraulic cylinder pressure gauge, as shown in Figure 8(a)). The pressure should exhibit a non-linear increase with force, as shown in Figure 8(b). If a plateau is reached, it indicates an instability and further force application should be avoided. Gasket tilting, often caused by misaligned diamond anvils, is a common reason for such instabilities.

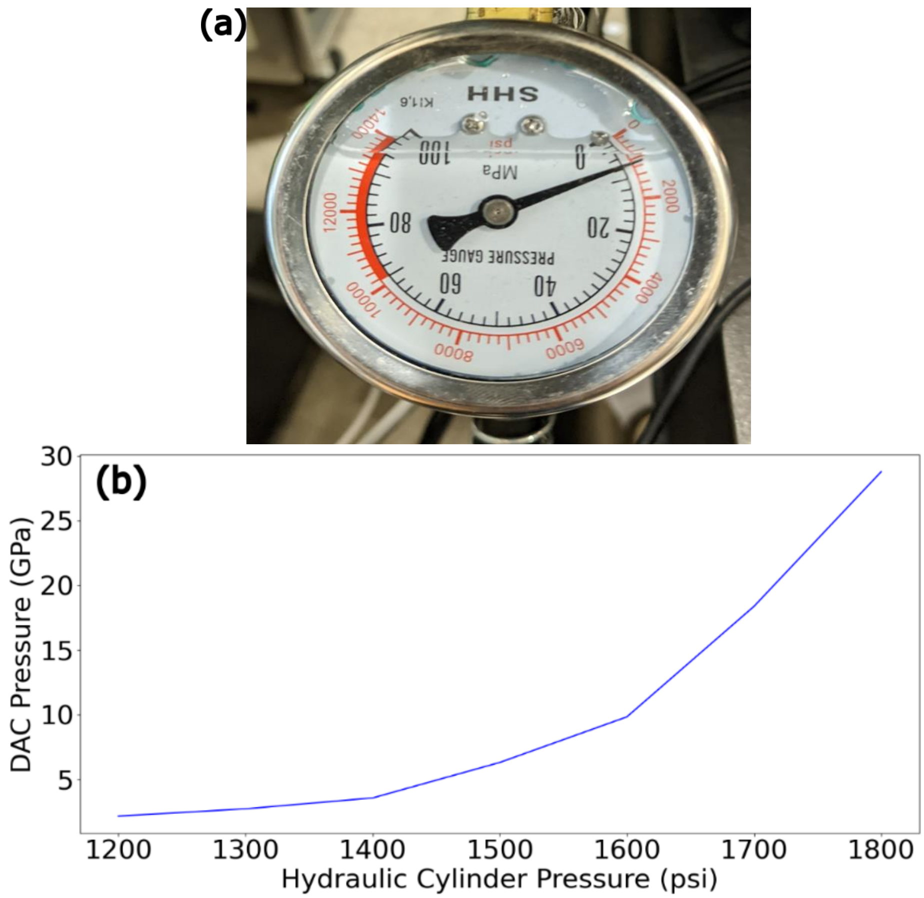

Figure 8: (a) Hydraulic cylinder pressure gauge. (b) The relationship between pressure inside the DAC (y-axis) and pressure exerted by the hydraulic cylinder (x-axis).

2.5 Gasket drilling

Once the gasket has been indented to the required growth pressure, a hole for the sample chamber must be drilled. Since the gasket is typically made from extremely hard metal and the hole is too small for mechanical drills, electric discharge machining (EDM) is a good option.

As shown in Figure 9(a), a drilling stage consists of a sample translation mount with x, y adjustments, along with a holder for the EDM wire that can be coarse-translated by hand. Additionally, a microscope viewer is present to allow precise positioning of the wire relative to the indented region of the gasket. The wire can also be electronically advanced and retracted using a piezo stage. In Figure 9(b), the sample stage is seen as a bowl that can be filled with dielectric liquid. In Figure 9(c), the discharge circuit is illustrated, which is basically a capacitor capable of holding approximately 1 μJ of energy. Between firings, the capacitor is charged with a high-current, high-voltage power supply through a 50 kΩ resistor. In Figure 9(d), a successful sample hole has been drilled. As seen, the gasket indent is about 300 μm at the bottom, determined by the culet tip diameter, and the hole is about 100 μm. The ratio of 1:3 hole to culet size is the maximum hole size that ensures stable pressurization.

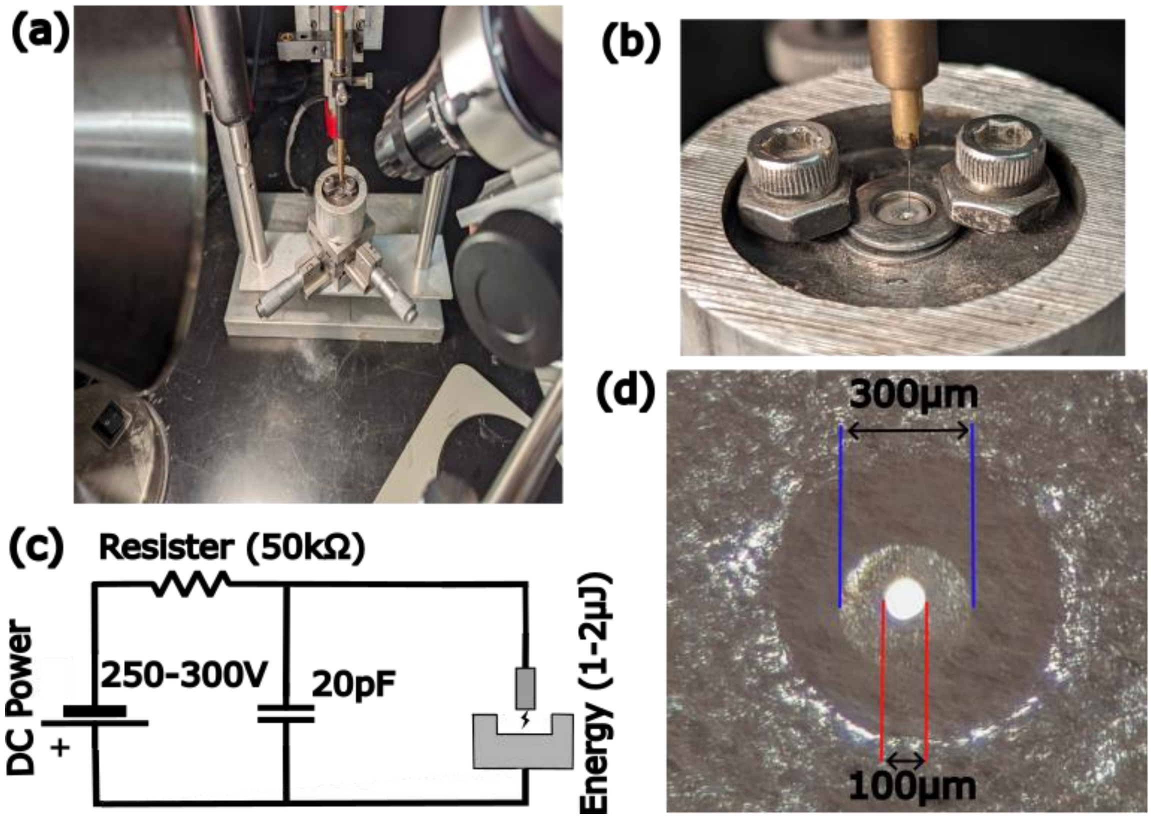

Figure 9: (a) Electrical discharge machine (EDM) which consist of 100 μm molybdenum wire, x-y translation stage dielectric fluid cup made of aluminum. (b) A close-up image showcases the dielectric fluid cup with a gasket securely held in place by a stainless-steel washer. (c) The EDM circuit used for the process is depicted. (d) An image of the gaskets after drilling.

2.6 Loading growth material

Once the hole has been drilled in the gasket, the focus shifts toward preparation and loading of the material that will be used to grow the nanodiamonds. This growth mixture consists of several components, not all of which will be present for every growth run. The components are:

a. Organic material that will decompose, or "crack", at the growth temperature to produce reactive carbon species, like methyl radicals, that will attach to the diamond surface causing it to grow.
b. A solid organic material that will make the growth mix solid at room temperature, to simplify loading.
c. "Seed" molecules that enhance nucleation for the nanodiamonds. Often these seeds will have dopant atoms, like nitrogen, that provide the raw material for diamond color centers.
d. A strong solvent, like a chlorocarbon, that enables the seed molecules, which are usually polar, to dissolve in the organic growth material, that is usually nonpolar.
e. Ruby crystals to allow pressure monitoring during growth.
f. Metal flakes or powder to absorb infrared laser energy, in the case of laser-heating. Typically titanium or gold are used most often.
g. A chemical for thermal insulation to allow high temperatures to be reached during laser heating. Typically NaCl or adamantane are used for this.

The growth mix is prepared in a separate container and homogenized. A small amount of material is then loaded into the gasket hole, either by pressing it in or loading a heated liquid that soon solidifies. In some cases, individual metal or ruby particles are added manually to ensure their presence at a specific location. If NaCl insulation is used, it is typically added as a separate layer above and/or below the rest of the growth mix. Figure 10 shows what the growth mix looks like when it is loaded into the gasket.

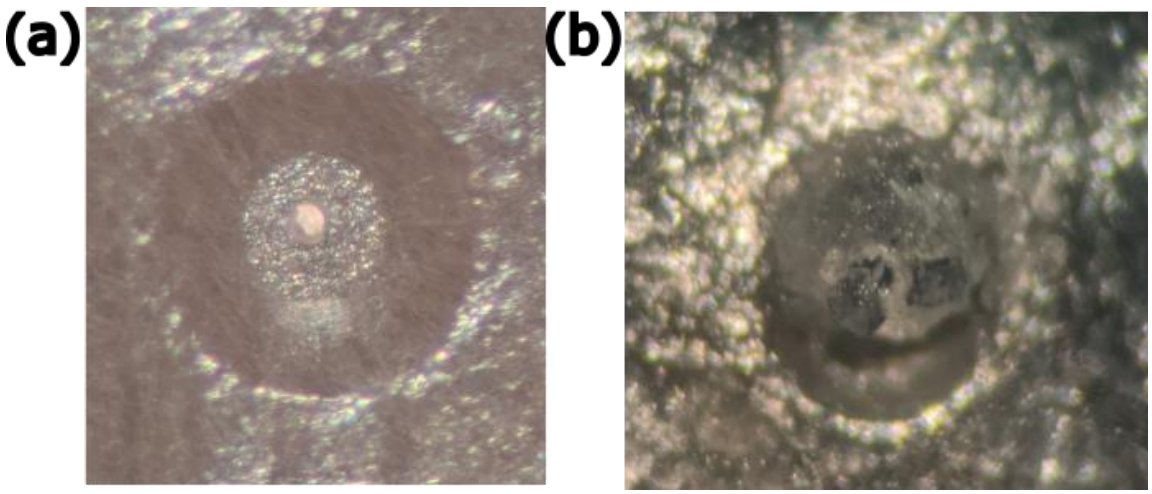

Figure 10: (a) The gasket hole after it's been drilled. (b) The gasket hole after loading the growth material.

2.7 Pressurize the growth mixture

After loading the growth material into the gasket, it is returned to the diamond anvil cell (DAC) and sealed by light pressure. At this point, the optical monitoring systems are aligned to document the subsequent growth process. It is important to identify the location of the sample chamber, as illustrated in Figure 11. Sometimes, this can be done by "backlighting" the DAC either with a lamp or a laser beam shining through the hole in the hydraulic cylinder. However, sometimes the optical transmission of the growth mix is too low due to the presence of metal particles, and so small changes in the texture of the culet image, like the one shown below, are used to outline the sample chamber location. Also, during this time, the pressure vs. force must be monitored to make sure it does not plateau, which would be another sign of instability.

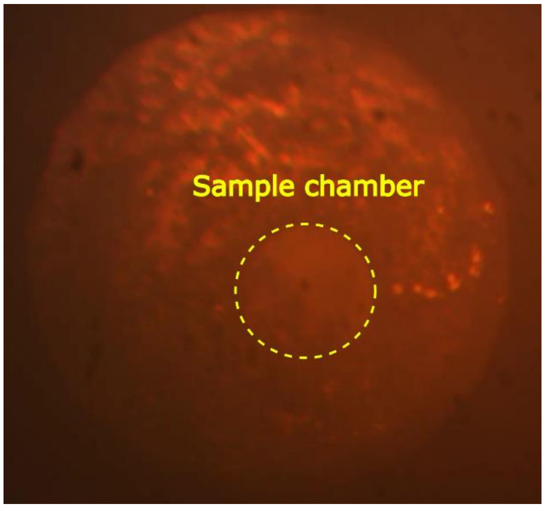

Figure 11: The sample chamber under pressure.

Once the sample chamber has been located, the system is gradually pressurized, following a similar procedure used for gasket indentation. Briefly, the hydraulic pressure is increased in small increments, and the DAC pressure, as reported by one or more rubies, is recorded and at each pressure to generate a pressure-force plot. Sometimes, the pressure at several locations is recorded to test for uniformity. Similar to gasket indentation, the pressure-force plot is analyzed to ensure that the pressure is increasing at the expected rate. In addition, the diameter of the sample chamber is also closely watched. If the sample chamber starts expanding as the force is increased, it serves as a warning sign of instability. When this happens, the pressure can no longer be increased. If it is high enough the laser heating can be started. Otherwise, a new gasket must be prepared and the whole procedure repeated.

2.8 Laser heating

The ability to do laser heating is one of the big advantages of using a DAC. While oven heating can approach 700 °C and gasket heaters can go somewhat higher, direct laser heating of the growth material can reach many thousands of degrees Celsius. There are many options for laser heating. The ones tested here include a blue, green and two infrared lasers, plus a CO_2. The blue laser consisted of a laser diode operating near 480 nm, with 5 W of total power focused down to about 50 microns. The green laser consisted of a frequency doubled YAG laser, outputting several watts. This laser was close to single mode and so could focused down a few microns diameter inside the sample, giving considerable intensity. Most often this laser was used for Raman characterization, rather than heating.

A key problem is the DAC is that high pressure operation (>10 GPa) tends to require that the gasket be compressed to a thin <10 micron thickness. At this thickness the thermal conduction becomes significant, even if an insulating layer is used. To compensate for this, it is customary to use a higher laser power. The strongest laser available was a 915 nm fiber-coupled diode laser that output up to 250 W of cw power. Though multi-mode this laser could be focused down to 50 µm diameter. Since this is smaller than the typical sample chamber (~100 um) different locations in the growth mixture can be selectively heated.

Unfortunately, organic material is highly transparent near 1 µm wavelength, and so direct absorption of the laser is not sufficient to heat the sample. After investigating several materials, it was found that the best absorber of the laser light was titanium. Gold was also used sometimes because of its chemical inertness, since titanium produces carbides.

Successful laser heating can be observed using the blackbody emission, as shown in Figure 12. For this purpose, a color camera was installed in the optical monitoring setup. A successful growth experiment involves creating a “hot spot” in the growth mixture for a period of several minutes to allow diamond to grow.

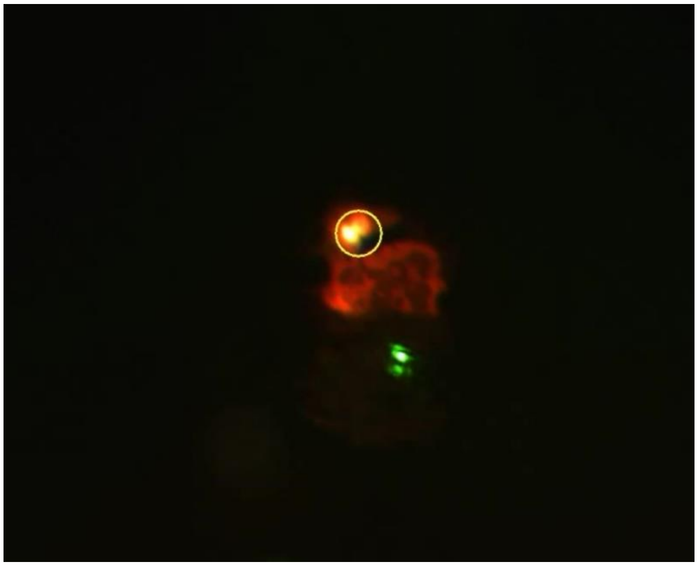

Figure 12: Blackbody emission in the sample chamber.

It sometimes happened that the growth material was modified by the laser heating and became less absorbing. In this case, a blackbody glow was observed for only a short time. Attempting to compensate by increasing the laser power would sometimes restore the blackbody glow. However, it often happened that this would work for only a short time until the laser power was increased to a very high level. At maximum power the laser heating was often explosive and damaged the gasket, reducing the pressure below that needed for diamond growth.

After many trials, it appears that a compressred gasket thickness of at least 50 μm was needed for successful laser heating. However, this typically only allowed a pressure of 10 GPa which is often not high enough for reproducible diamond growth.

In an attempt to overcome this problem we added a pulsed laser operating at 1064 nm that put out about 50 W of average power. The pulses were a few microseconds in length so that the laser energy could be delivered faster than thermal diffusion could dissipate it. The laser was close to single mode and so could be focused down to a few microns, allowing very high peak laser intensities to be applied locally to the sample. While this partially solved the laser-heating problem, it also tended to damage the diamond anvils. In fact after one or two heating steps, the diamond anvil would sometimes fail, causing the sample to be lost.An example of diamond anvil damage induced by the pulsed laser and subsequent complete failure of an anvil is shown in Figure 13.

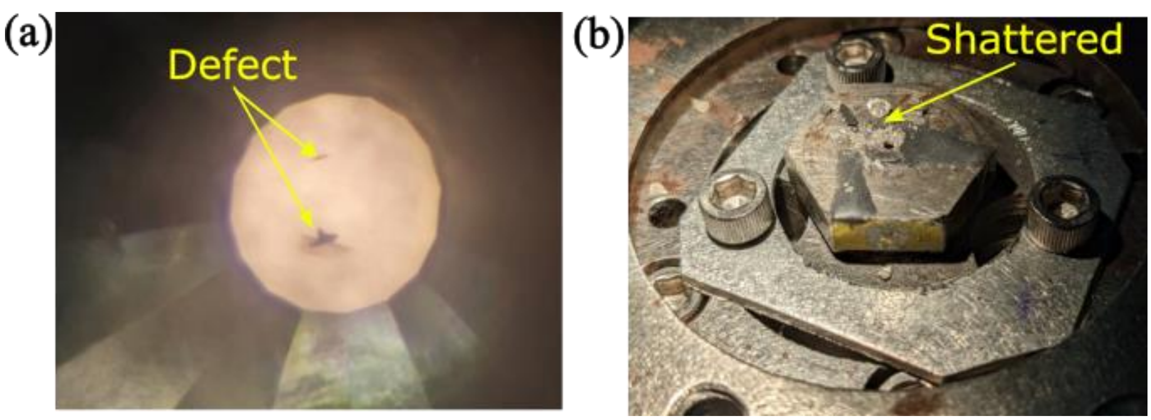

Figure 13: (a) Defect in the diamond culet. (b) Shattered diamond.

2.9 Monitor growth

A key advantage of the diamond anvil cell (DAC) is the ability to monitor the growth process in detail. For example, between pulses of laser heating, Raman spectra can be taken of the growth mixture to observe what happened to the initial growth material and also to identify any produced products. Unfortunately, the diamond anvil cell itself produces a strong Raman line that hinders the direct identification of any grown nanodiamonds.

In addition to Raman spectral, the pressure was often recorded after each laser pulse as well as other optical properties such as visible burn marks. In order to allow the comprehensive monitoring described above, a custom-built optical microscope setup was developed. This setup is shown in Figures 14 and 15.

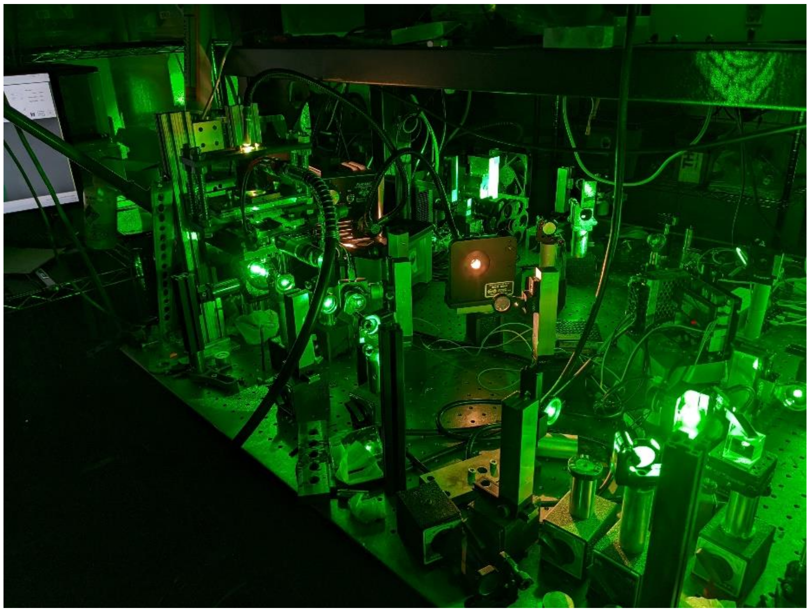

Figure 14: The custom-built confocal microscope used for Raman and fluorescent monitoring.

According to the schematic in Figure 15, the main element of the optical setup was a 10 X microscope objective with a long working distance (~ 3 cm), and color correction from visible through the near infrared regions. Laser light from the highest power lasers were was input to the objective using a dichroic mirror (DM in the figure). Following this was the color camera used to observe the growth process. A flip mirror allowed white light to illuminate the growth chamber when optical spectra were not being recorded. Following this was a galvo scanner with the 532 nm laser that could be used to generate a Raman or fluorescent image of the growth mixture. To make the microscope confocal, a pinhole was then used to spatially filter the light emitted by the sample. A notch filter was added to remove the green laser light and both an photo-multiplier and a CCD camera acting as a spectrometer were used to analyze the collected light.

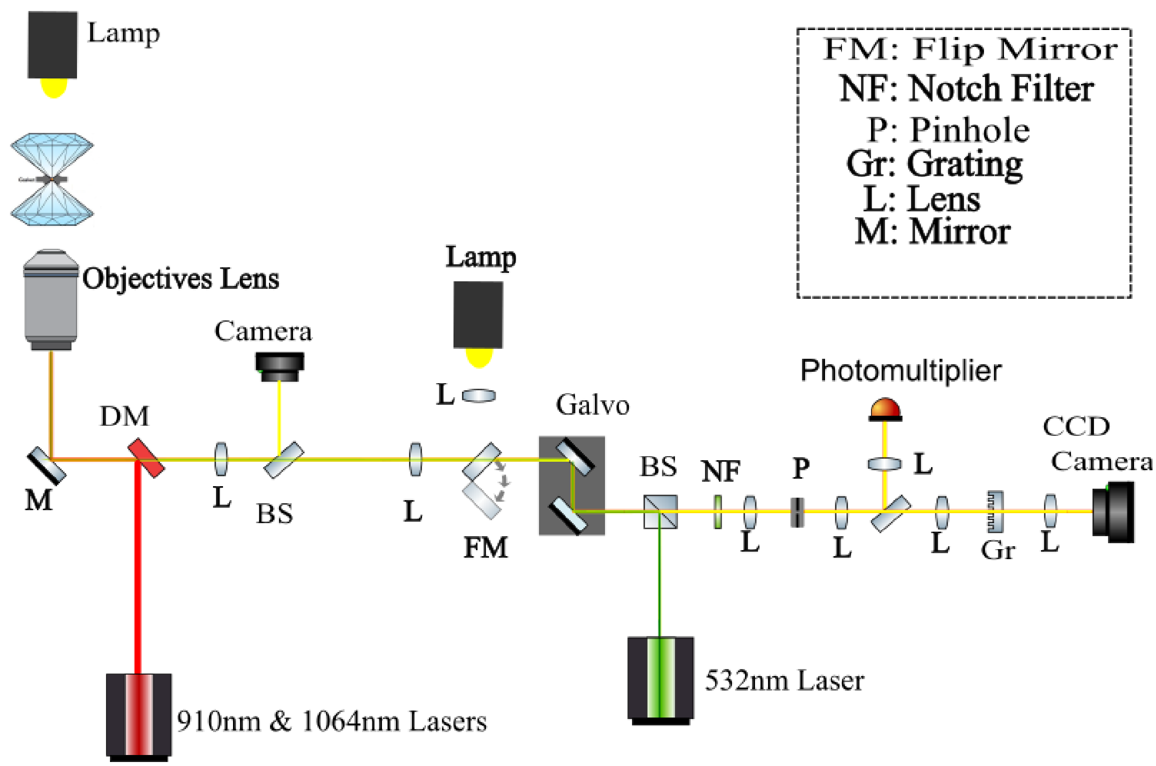

Figure 15. A schematic diagram of the custom-built confocal microscope shows the key elements.

With this optical diagnostic setup, Raman spectra of the growth mixture could be acquired in near real-time during growth. An example of this is shown in Figure 16.

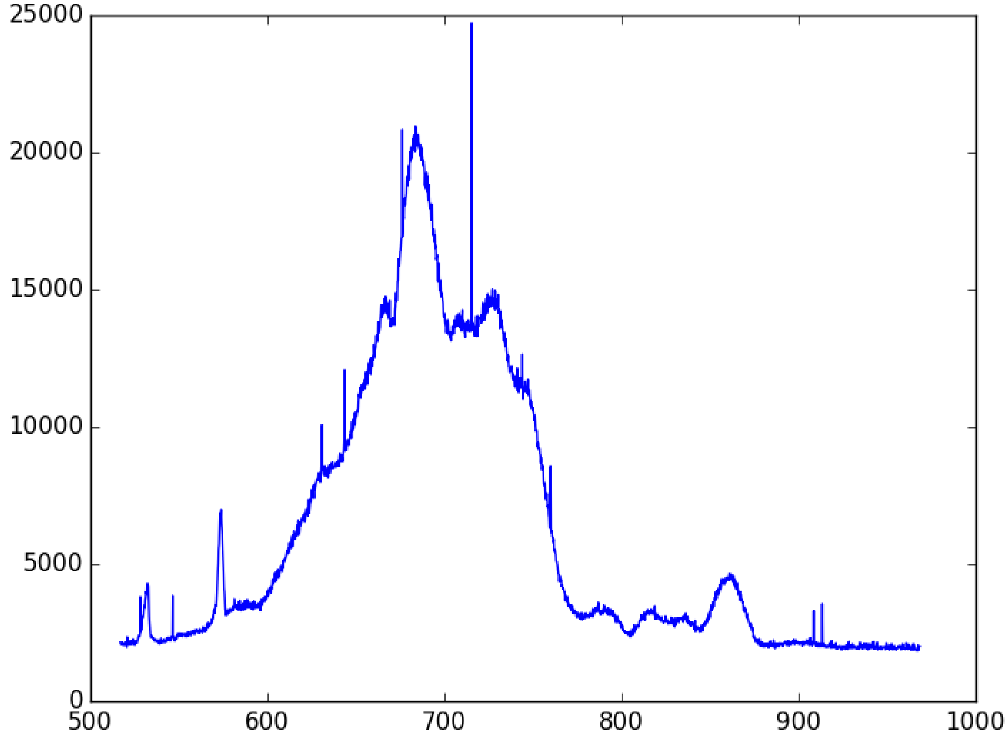

Figure 16: Raman spectra of the growth mixture.

2.10 Product extraction

Due to the Raman line from the DAC preventing direct observation of nanodiamond during growth, the sample had to be extracted from the DAC for further diagnostics. This is one of the most difficult parts of the growth process. Because the gasket hole is only about 100 um in diameter and a few 10's of microns thick, the volume of material is extremely small, ~ nanograms. This small growth volume is one of the main disadvantages of the diamond anvil cell (DAC).

To work with such small sample volumes, a number of techniques had to be developed. To begin with the gasket was slowly depressurized after the growth run. Care was taken not to let it explosively depressurize since this led to loss of the sample. Once this was done, fluorescence and Raman spectra were again taken of the growth material to verify that it was still present.

Next, the gasket was removed and examined on a separate optical setup. Often much of the growth material remained in the gasket hole. This material could carefully be removed and deposited on a glass coverslip. Often a ruled coverslip was used so that the exact location of the product could be noted. This was necessary because the sample volume was often less than that of dust and dirt that was typically present on the coverslip, even after careful cleaning. Without knowing the precise location of the sample, it was easy to lose its location among the impurities.

Often it happened that significant growth material was left on the diamond anvils. Removing this material was especially difficult. After many trials it was discovered that the best approach was to suspend it in a liquid. This was done by pipetting a few nanoliters of solvent onto the diamond anvil and then re-collecting the liquid with the same pipette. The pipette was then transferred to a ruled coverslip or TEM grid and deposited to allow the liquid to evaporate.

Using the proper solvent was important. If the growth mixture did not adequately mix with the liquid solvent, no material was extracted by the above operation, but rather it remained on the diamond culet. Eventually a mixture of H2SO4 and H2O2 was used and this performed the extraction operation successfully. Figure 17 illustrates the extraction process. As can be seen, the entire operation needed to be performed with a microscope because of the extremely small sample volume.

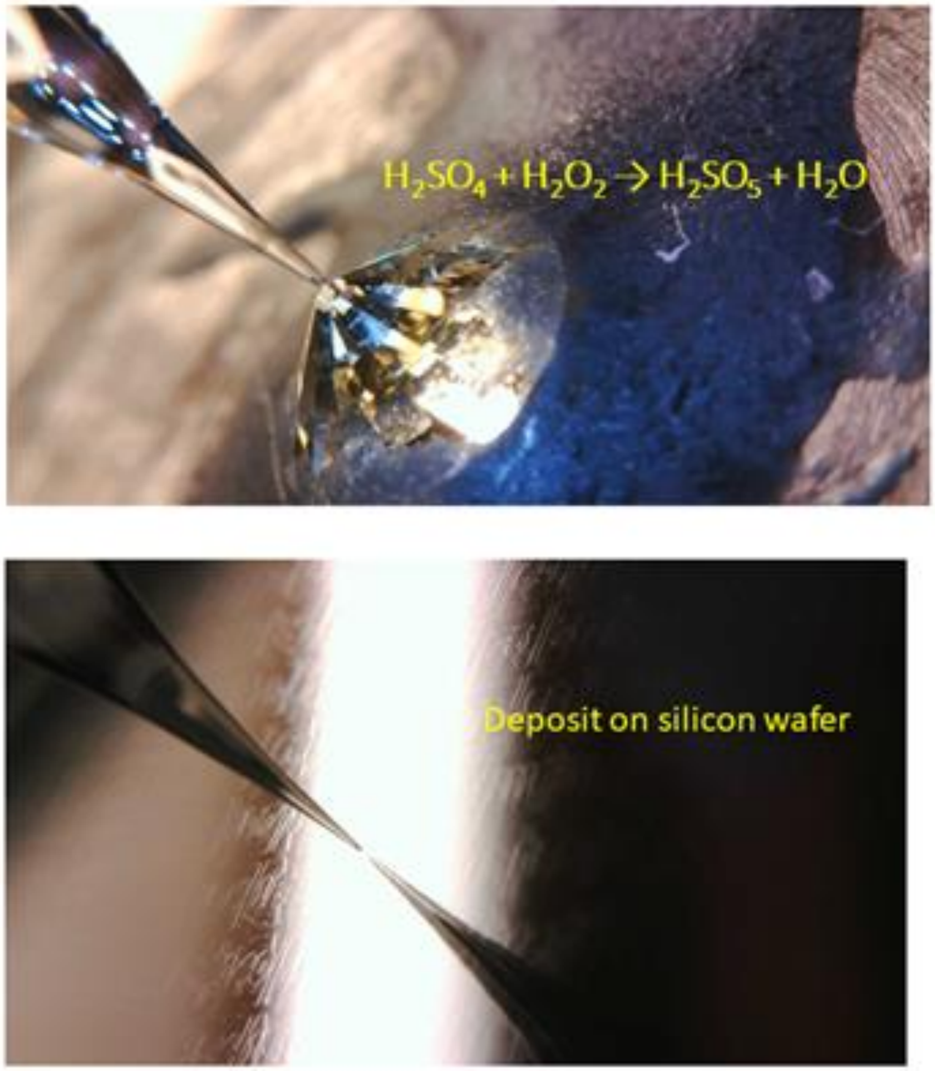

Figure 17: The procedure of removing the sample from the diamond anvil.

2.11 Evidence of nanodiamonds with silicon-vacancies (SiV).

Because of the problem with the thin sample chamber making it difficult to reach growth temperature under pressure, only one experiment produced a spectral line that had the correct characteristics expected for the silicon-vacancy (SiV) diamond color center. This data is shown in Figure 18(a). As seen, under pressure, a strong narrow line was observed at a wavelength of 728.5nm. This is approximately the wavelength expected for the SIV at the 19 GPa observation pressure [35]. This spectrum was only observed In the hot spot shown in Figure 18(b). Unfortunately, when the sample was completely depressurized, the growth material was lost.

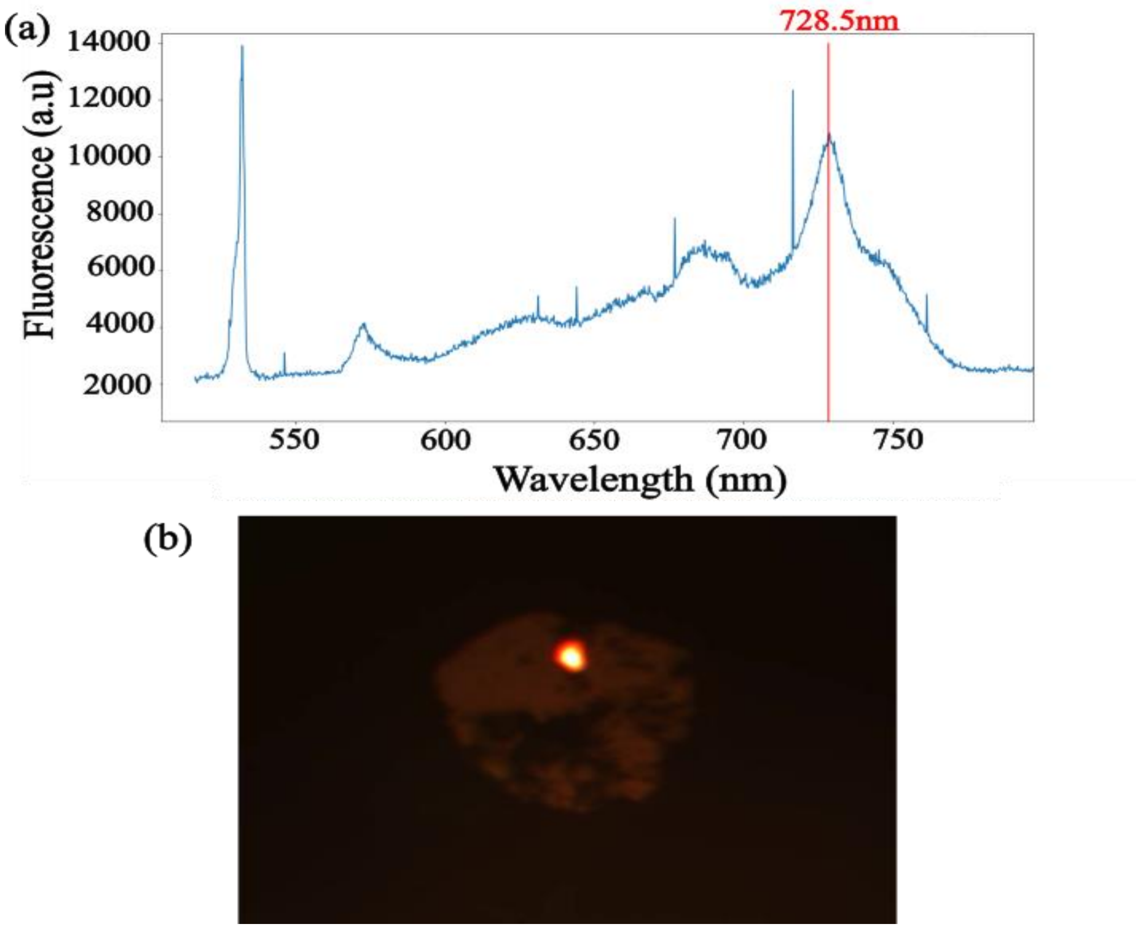

Figure 18: (a) SiV zero phonon line (ZPL) at 19 GPa. (b) Blackbody radiation in the same spot where the SiV spectrum was measured.

CHAPTER III

FUTURE IMPROVEMENTS

3.1 Machining sapphire anvils with conical seats

As mentioned above, one of the key problems with the DAC is that the diamond Raman line of the anvils obscures any Raman line in the product. This necessitates extracting the material to determine whether or not diamond was grown. Since the extraction process was wasteful and time consuming.

One way to overcome this problem is to use sapphire anvils. Unfortunately sapphire is not has hard as diamond, and so it is more difficult to reach the pressure necessary for nanodiamond growth. To overcome this second problem the well-known technique of using conical seats, to replace the conventional flat seats, was used. In this technique a conical hole is machined in the seat, consisting of hard steel, and a matching conical taper is machined onto the sapphire. One of the first attempts to make a matched pair of conical sapphire anvil and seat is shown in Figure 19. So far this design has reached pressures above 5 GPa, which is close to that needed for diamond growth.

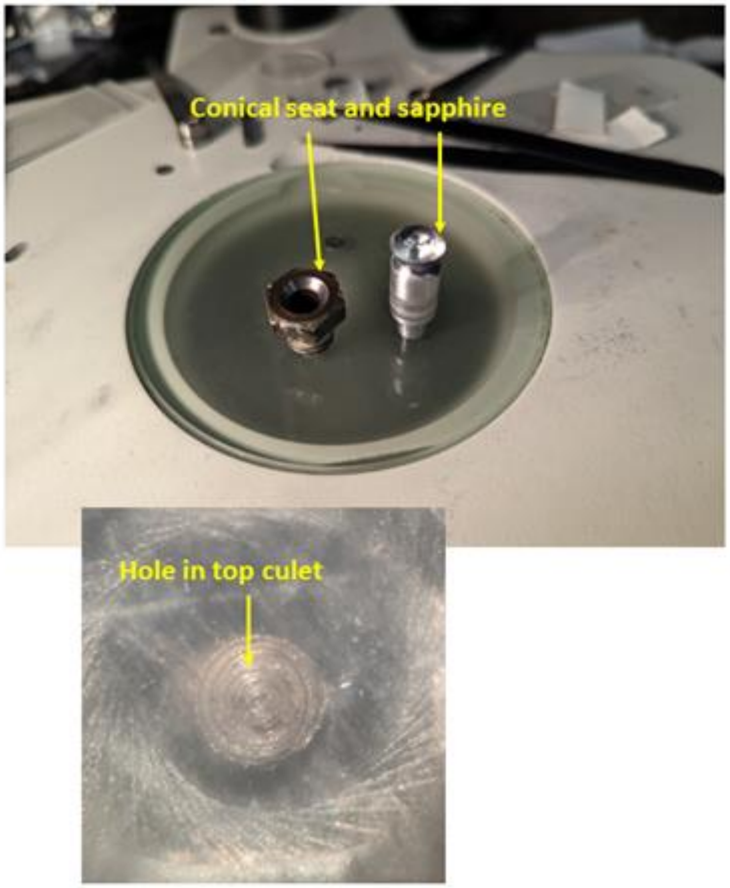

Figure 19: Recent improvements include replacing the diamond with sapphire.

Take together these advantages of using sapphire anvils promise to greatly simplify DAC growth, and make it sufficiently scalable to produce usable quantities of nanodiamonds without having to resort to expensive large-volume presses.

3.2 Laser machining of titanium growth chambers

As mentioned above, titanium is needed enhance absorption of the infrared laser used for laser-heating. It is possible to use particles of titanium. However, it is much preferable to machine a growth chamber out of titanium. This has several advantages. First, it allows the growth region to be raised to a uniformly high temperature. Material inside of the chamber will be heated from multiple sides, therby avoiding temperature gradients. Second, it marks the location of the growth and holds the product material in-place during depressurization and extraction.

For this growth chamber, the simplest design to begin with is a titanium washer. However making this washer requires precision machining. The outer diameter must be less than that of the heating laser (~50 um). At the same time, the inner diameter should be as large as possible to enable growth of a reasonable volume of diamonds. One way to machine a titanium washer with such precision is to start with a thin foil (~10 um or less) and use a pulsed laser to machine. A thin foil is used because the final growth chamber thickness is thin at the high pressures needed for growth. The first attempt to machine such a titanium gasket is shown in Figure 20.

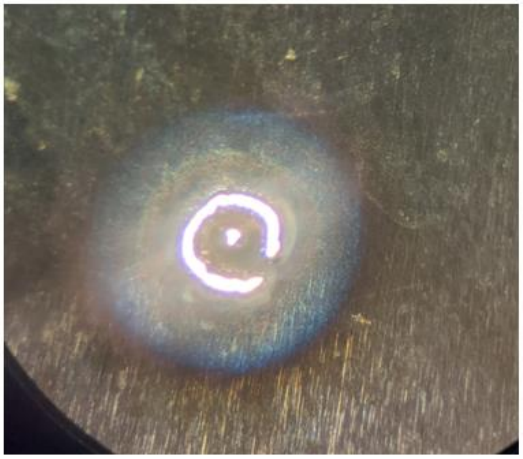

Figure 20: A cut in a thin pieces of titanium metal to make a crude growth chamber.

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