



SCHOOL OF CHEMISTRY

Growth of Free-Standing Diamond Wafers by Pulsed DC Plasma
Assisted Chemical Vapour Deposition

Helen Harris

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Supervisor: Neil Fox
Second Assessor: Paul May
Physical and Theoretical Group

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Abstract

Diamond exhibits many remarkable properties, making it an extremely desirable material for a multitude of industrial uses. Cost and availability are limiting factors of natural diamond, and drive the development of synthesis techniques. A pulsed DC plasma assisted chemical vapour deposition reactor was built by members of the University of Bristol Diamond Group, with intent to grow diamond films at a faster rate than currently obtained by the other reactors in the laboratory. Prior to the investigation, a new electrode system had been recently installed with the purpose of improving plasma stability. The primary aim of this project was to optimise certain parameters in the new set-up, with the objective of improving both the quality of the diamond grown and the growth rate.

A Taguchi optimisation experiment was performed, to investigate the effects of methane concentration, argon concentration, pulse frequency and pressure on the growth rate and quality of the diamond films produced. Nine runs were performed with a fixed plasma power of 2500 W, lasting 1 hour each, and were analysed using optical emission spectroscopy, Raman spectroscopy and scanning electron microscopy.

The results of the optical emission spectroscopy show that increasing methane concentration, increases the production of the C_2 dimer hence reducing diamond quality. The Raman spectra obtained support this conclusion, and also provide evidence to suggest that the best conditions for optimum diamond quality (in the specific set-up investigated) are: 2% CH_4 , 1% Ar, 125 kHz and 230 Torr. These are only the best parameter levels of the three levels investigated. Additional experiments would need to be performed to see if quality could be further improved.

Scanning electron microscopy was used to obtain images of each sample. These were used to determine a lateral growth rate for each run. The results showed that increasing argon concentration improved growth rate and increasing pressure reduced growth rate. The fastest growth rate obtained in the experiment was $49.8 \mu m h^{-1}$, but the trends suggest this could be further improved if the following conditions were tested: 4% CH_4 , 2% Ar, 125 kHz and 200 Torr.

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1 Introduction

1.1 Properties and technological applications of isotopic diamond

1.1.1 Structure

There are two naturally existing, crystalline allotropes of pure carbon: graphite and diamond. Although they have exceptionally similar thermodynamic stabilities (at 300K, $\Delta G=0.04$ eV)[1], a large kinetic barrier separates graphite from its metastable counterpart. The two forms of carbon lattice have vastly different properties, which can be largely accredited to their structures, shown in Figure 1.

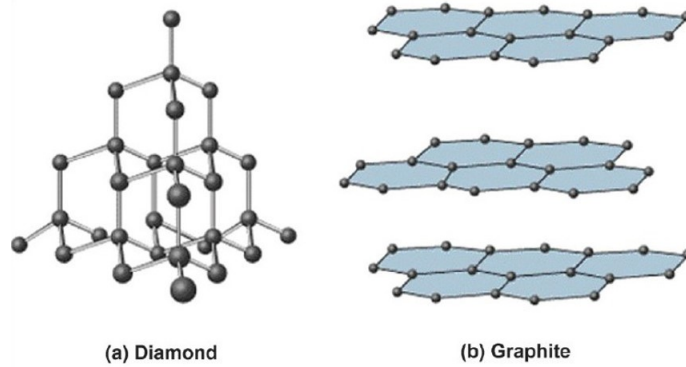


Figure 1: A diagram illustrating the structure of carbon in diamond and graphite, taken from [2].

Diamond forms a three-dimensional network of strong covalent bonds. The structure consists of one face centred cubic lattice, and another displaced by $(\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)$ where a is the lattice constant. Each carbon atom is sp^3 hybridized and a tetrahedral structure arises, with each atom bonded to four other carbon atoms. In diamond, all carbon-carbon bond lengths are equal (1.54 Å)[3]. Graphite however, forms in layers. The carbon atoms form three simple bonds with nearest neighbours, through sp^2 hybridization, with a bond length of 1.42 Å[4]. This leaves one electron per atom delocalised, and free to move anywhere in the plane. As they move, temporary dipoles are induced in the plane, which are the cause of the weak van der waals dispersion forces between the layers.

1.1.2 Hardness

The name diamond originates from the Greek word ‘adamas’, meaning invincible. Diamond is the hardest natural material on earth on both the Vickers and Mohs scale (10,000 kg mm⁻²)[5]. Carbon has four valence electrons, meaning it can form up to four bonds. In diamond, each atom forms four bonds (each covalent), rather than the three formed in graphite. This means a great deal more energy is required to separate the atoms in diamond than in graphite. Combining diamond’s hardness with its low frictional coefficient (0.05 to 0.15[6]) and chemical resistivity (100 GΩ·m to 1 EΩ·m[7]), makes it an excellent material for use as a cutting tool for non-ferrous materials, as diamond reacts with iron. Tests have shown that tools coated in CVD diamond cut faster and have longer lifetimes than conventional carbide tools[8].

1.1.3 Optics

The symmetric structure of diamond results in pure covalent bonding and hence the absence of infrared optical activity. Diamond is transparent in a very wide spectral

range, due to a large band gap (5.5 eV at 302K)[9]. The transmission spectra of type IIa diamond is displayed in Figure 2. Only UV photons have enough energy to be absorbed by diamond. Their transparency allows thin diamond membranes to be used as windows in equipment such as vacuum chambers, as they can withstand extreme pressure and allow IR radiation to pass through, and as high power laser windows[10].

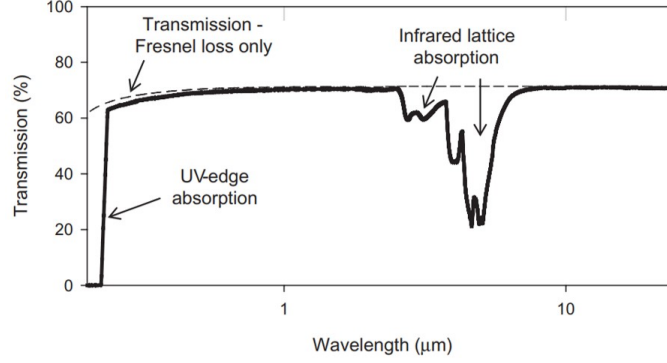


Figure 2: Type IIa diamond transmission spectra taken from [11].

1.1.4 Thermal Conductivity

The thermal conductivity of high-quality single diamond crystals is roughly 2000 W/m.K, which is five times the thermal conductivity of copper (400 W/m.K)[12]. The dominant mechanism of heat transfer in diamond is very different to that in electrically conductive solids. In copper, conduction band electrons move freely through the structure, carrying thermal energy, however in crystalline structures such as diamond, heat is transferred via the transmission of phonons. Phonon scattering reduces the rate of heat transfer, and occurs at impurities, crystal defects and boundaries. Hence, the purer and more ordered the crystalline structure, the greater the thermal conductivity of the material. Diamond exhibits particularly good thermal conductivity due to the mass of the carbon atoms and the strength of the bonds between them. The combination of light carbon atoms and strong covalent bonds between them means that diamond can support higher energy photons than other well-ordered crystals, and gives rise to a high characteristic temperature ($\theta_{\text{Debye}}=1860\text{K}$)[13]. This characteristic makes diamond a suitable material to use as a heat sink in semiconductors.

1.1.5 Isotopic Properties and Impurities

Naturally occurring diamond consists of 1.1% ^{13}C and 98.9% ^{12}C , mirroring the natural abundance of the isotopes[14]. There are in fact fifteen isotopes of carbon, although ^{12}C and ^{13}C are the only ones considered stable. These isotopes, alongside their stabilities are displayed in Table 1.

It is possible to create isotopically pure diamond, which can have favourable properties. Maximum thermal conductivity is observed when the sample is 100% C_{12} or C_{13} [15].

Table 1: A table showing the half lives of different isotopes of carbon.

Isotope	Half Life
^8C	$2.0 \times 10^{-21} \text{ s}$
^9C	126.5 ms
^{10}C	19.3 s
^{11}C	20.3 minutes
^{12}C	Stable
^{13}C	Stable
^{14}C	5730 years
^{15}C	2.4 s
^{16}C	0.7 s
^{17}C	193.5 ms
^{18}C	92.2 ms
^{19}C	46.2 ms
^{20}C	16.3 ms
^{21}C	<30 ns
^{22}C	6.2 ms

Diamond has an extremely rigid lattice and high atomic density. Because of this it is difficult to substitute an element in for carbon and therefore diamond is rarely contaminated by impurities. The most abundant form of diamond found on earth (Type Ia) contains a 0.1% concentration of nitrogen impurities[16]. Hydrogen is crucial in chemical vapour deposition diamond growth, but it can incorporate into grain boundaries during growth. Hydrogen impurities alter the properties of the material; they have been shown to deteriorate thermal conductivity and infrared transmission of the diamond[17].

1.2 Theory of CVD diamond growth

1.2.1 History

Due to its remarkable physical properties, it has always been desirable to be able to grow diamond. In 1956, the first successful synthesis of diamond from graphite, by the High Pressure High Temperature (HPHT) technique, was achieved by General Electric[®]. This technique duplicates the conditions in which diamond is formed naturally. Since then, the technique has evolved tremendously and is now the predominant method used to produce diamond for industrial consumption[18]. This method is limited due to the fact that diamond is formed as single crystals, ranging in size from nanometers to millimeters, and many properties of diamond would be best utilised if diamond was grown as a film. Around a similar time, scientists were researching using Chemical Vapour Deposition (CVD) for diamond growth. CVD is a method that encompasses a flow of precursor gases into a chamber that contains one or more heated objects. Chemical reactions occur on the hot surface which result in the formation of a thin film [19]. This method differs greatly from the HPHT technique, as diamond is formed by adding carbon atoms one-by-one to a base at low pressures, rather than compressing graphite at high pressures. In the early stages, Deryagin *et al.*[20] explored the thermal decomposition of hydrocarbon gases at low pressure, attempting to grow onto a hot natural diamond surface. There were problems however with the rate of growth, as graphite was also being deposited on the diamond surface[21]. In the 1960's a breakthrough occurred; It was discovered that if atomic hydrogen was present, the graphite would be etched, leaving pure diamond[22].

1.2.2 CVD Process

In a CVD reactor, gases (usually methane and hydrogen) are introduced into the chamber. There are various techniques employed to activate these gases, which will be explored in more detail in sections 1.2.3 and 1.2.4. Upon activation, the gases fragment into radicals, and create ions and electrons. The gas can reach many thousand Kelvins, and when the gases mix they undergo many complex reactions. Many possible outcomes can occur when the reactive fragments strike the substrate; one potential mechanism is outlined in Figure 3.

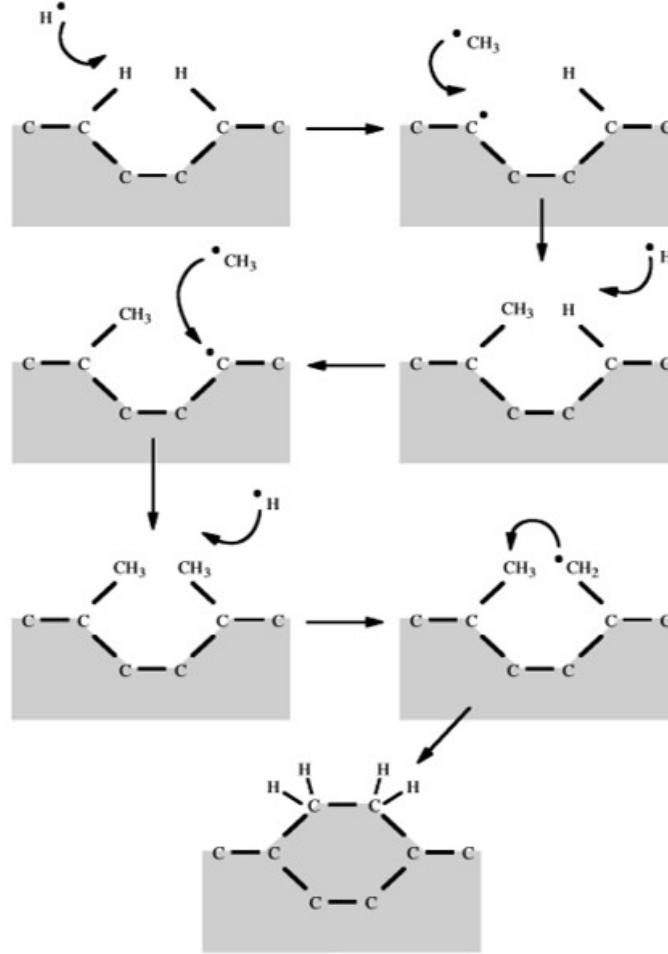


Figure 3: A schematic of one of the reactions that occurs at the diamond surface, taken from [21].

Atomic hydrogen is absolutely vital for successful synthesis of diamond via the CVD method, for many reasons. As outlined in the fifth stage in Figure 3, atomic hydrogen terminates the ‘dangling’ CH_3 bonds by removing a H atom from CH_3 , leaving CH_2 . This stabilizes the system and prevents cross-linkage of lattice rearrangement to form graphite. Atomic hydrogen is also required to create the reactive CH_3 radicals from CH_4 molecules, as shown in Equation 1.



Atomic hydrogen also etches sp^2 graphitic carbon bonds at a faster rate than it etches sp^3 diamond-like carbon bonds, hence removing clusters of graphite and leaving behind diamond. Another useful property of atomic hydrogen is that it

reacts with long chain polymers that may be present in the gas phase. They are broken down, preventing them from depositing onto the substrate surface.

As well as the presence of atomic hydrogen, it is also vital that the temperature is kept below 1860 K (Debye temperature of diamond[13]) in order to avoid spontaneous bulk rearrangement into graphite. The two dominant techniques adopted to convert hydrogen to atomic hydrogen are the use of a hot filament or a plasma.

1.2.3 Hot Filament Deposition

Using a hot filament as the means of converting hydrogen to atomic hydrogen was the first method to achieve continuous diamond growth onto a substrate[23]. The method includes a filament that is electrically heated to an excess of 2200 °C. The filament is typically made out of tungsten or tantalum as they have melting points in excess of 2200 °C. The set-up is displayed in Figure 4.

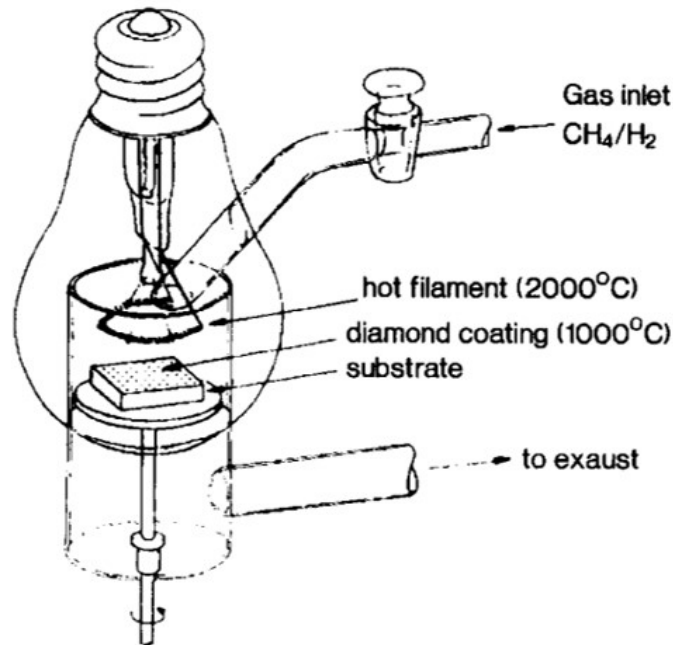


Figure 4: A diagram showing the set-up of a hot filament reactor, from [24].

The benefits of a hot filament CVD include large deposition areas, relatively cheap equipment and low electrical power consumption. A disadvantage of the system is the high temperatures meaning the filament eventually reacts with the gases, forming metal carbides. These are brittle and have a reduced lifetime. It is also challenging to escape contaminating the diamond with filament material, meaning the synthesised diamond does not always have perfect purity. Recent studies, modeling the environment inside a hot filament reactor, have contributed greatly to the understanding of the diamond deposition processes that occur in the system[25][26][27].

1.2.4 Plasma Assisted Deposition

Another common method of creating atomic hydrogen involves the use of a plasma. Plasma was first described by Langmuir in the 1920s as “a region containing balanced charges of ions and electrons”[28]. It is the fourth fundamental state of matter, however the only state to not freely exist under earth surface conditions and therefore must be artificially generated.

Plasma assisted deposition methods can be categorised into ‘glow discharge plasma methods’ and ‘plasma arc-jet methods’. A glow discharge plasma is formed by an electric field under low pressure, and subsequently the gas is ionised. The electrons are quickly accelerated and reach high temperatures however the heavier ions remain at low temperatures, as they cannot react to the swift changes in field direction. The high temperature electrons induce many reactions that would be improbable at lower temperatures, allowing the growth of materials that would be difficult to produce using thermally activated CVD methods. There is a large temperature difference between the high energy electrons and the gas, and thus the method is termed ‘non-isothermal’.

In contrast, a plasma arc-jet is generated at high powers, by DC or AC currents. Both the electrons and the ions are able to react to the slowly changing field directions and hence both acquire energy and heat up. The arc is generated at higher pressures than the glow discharge plasma and hence a smaller mean free path is established, resulting in more frequent collisions and a warmer plasma. The method is termed ‘isothermal’[29]. Plasma assisted CVD may be divided further into the following four major plasma generation methods: Microwave plasma, direct current plasma, radio-frequency plasma and plasma torch. They are all non-isothermal methods bar plasma torch, which is an isothermal process.

Microwave Plasma

After the hot filament method, the microwave plasma assisted method is the most frequently used for diamond growth. Microwave plasmas are considered stable and reproducible, which allows continuous diamond deposition for many hours. They are also highly efficient and increasingly available.

A typical system involves methane and hydrogen pumped into a chamber surrounded by a microwave applicator. At pressures between 10 and 100 Torr, microwave radiation at a frequency of around 2.45 GHz is able to maintain the electrical discharge in the mixture of gases, hence dissociating the methane and hydrogen. Diamond is able to nucleate onto the substrate surface, which is heated between 800-1100 °C. A typical set-up is depicted in Figure 5.

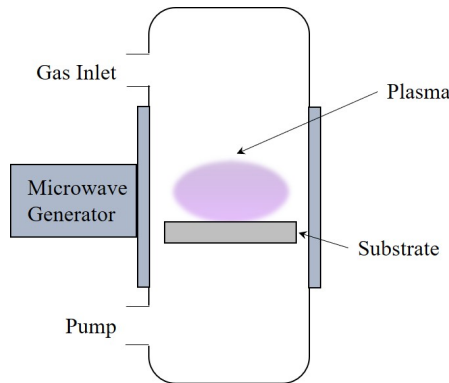


Figure 5: A simplistic diagram showing the set-up of a Microwave Plasma Assisted CVD reactor.

Some of the drawbacks of this method include slow deposition rates for high quality crystal growth and a limited diameter for uniform coatings.

Electron-cyclotron resonance (ECR) can also be used to generate a microwave plasma. This set-up operates at much lower pressures (10 mTorr to 0.1 Torr) and is achieved by using a strong magnetic field, which causes the electrons to orbit, and matching the microwave frequency to the natural frequency of the orbiting electrons.

The resonance effect heats the electrons and generates a plasma. A benefit of using ECR plasmas is an observable reduction in substrate damages, due to relatively low operating temperatures. This method however involves expensive equipment and low growth rates are often observed. Extensive modeling of diamond grown in the microwave system has been performed[30][31][32] and many of the most recent models support the idea that CH_3 is the dominant radical involved in diamond growth.

Direct Current Plasma

The typical set-up for a DC plasma assisted system is shown in Figure 6.

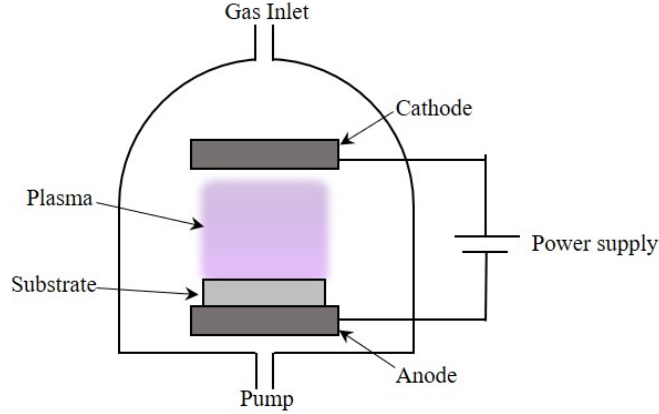


Figure 6: A simplistic diagram showing the set-up of a DC Plasma CVD reactor.

When the bias voltage is sufficiently high, a glow discharge forms between the two electrodes. The high energy electrons collide with the gas molecules and ionise them. The positive ions accelerate towards the negative cathode and, through a process called secondary electron emission, electrons are liberated from the electrode. An electron avalanche, commonly termed the ‘Townsend discharge’, is succeeded by a series of complex mechanisms which form the reactive radicals desired to grow diamond. The electron avalanche occurs at a specific breakdown voltage, V_b , given by Paschen’s law[33]:

$$V_b = \frac{Bpd}{\ln(Apd) - \ln \left[\ln \left(1 + \frac{1}{\gamma_{se}} \right) \right]} \quad (2)$$

where A and B are constants, p is pressure, d is plate separation and γ_{se} is the secondary electron coefficient at the cathode.

The method is relatively simple and has been successful in coating large substrate plates[34]. A characteristic feature of this method is the formation of an arc, if specific steps are not followed. To prevent this, it is necessary to ignite the plasma with little power, at low pressure and before occupying the chamber with methane. The voltage and current must be increased gradually up to growth conditions, and only then can the methane be introduced. This pre-growth stage generally takes 10-20 minutes, depending on the gas flow rate and chamber size[35]. Many groups have struggled to maintain a stable plasma over a long period of time.

The pulsed-DC method was introduced by Hartmann et. al. [36], and has been shown to reduce the probability of arcing, maintaining an increased plasma stability. High power pulses, with a duty cycle of less than a few percent, are used to achieve higher plasma densities in comparison to non-pulsed DC plasma. The increased

density is beneficial as it generates a higher dissociation rate of the precursor gas molecules, as well as a higher degree of ionization of the growth species[37]. This makes it possible to steer the growth species onto the substrate by applying a bias. The method has increased growth rates over larger areas which can be attributed to the use of higher powers.

Radio-Frequency Plasma

The method involves a glow discharge being formed at low pressures (~ 1 Torr), generated by an electric field at a frequency of 13.56 MHz. The method is used predominantly to form diamond-like carbon (DLC) rather than pure diamond, for use as a coating on silicon or stainless-steel substrates[38]. The set-up is very similar to the set-up for DC plasma assisted CVD, shown in Figure 6.

Plasma Torch

A stream of ionized particles is formed when hydrogen or argon gas flows through an electrical discharge. The gases in the reactor chamber rapidly expand as they are heated by the hydrogen/argon plasma arc, and form a high-speed arc-jet. This isothermal plasma can reach temperatures above 5000 K, causing a large portion of the hydrogen molecules to dissociate and react with the methane to form active carbon species. The high-speed arc jet transports this to the substrate, where diamond is grown. The most frequently used plasma jet is the DC arc jet, depicted in Figure 7.

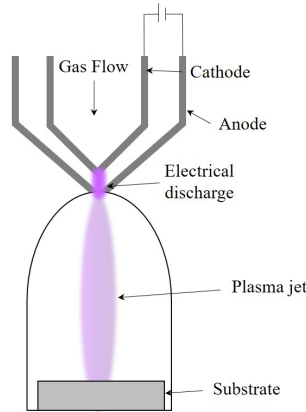


Figure 7: A diagram showing the set-up of a DC arc-jet CVD reactor.

This method uses a DC power supply to advance large currents through the ionized process gases. Very high deposition rates have been observed in DC arc-jet experiments; the highest ever recorded diamond growth rate ($>900 \mu\text{mh}^{-1}$) was obtained using this method[39]. The downfalls however include small deposition areas and difficulty cooling the substrate temperature to an acceptable level.

1.3 Taguchi method for optimising an experimental process

The Taguchi method is a statistical tool developed by Genichi Taguchi, to optimize the design of manufacturing systems. It offers an efficient and relatively simple approach to improve the quality or performance of a design[40][41]. In an experiment there are many factors that cause variability. Some of these parameters can be controlled (control factors), however some design parameters can be difficult or expensive to control (noise factors). The Taguchi method aims to optimize the

control factors in such a way that the effects of the noise factors are minimised, as this will create a more consistent and reliable process.

A factor, typically with a range of settings, controlled during the experiment by the user is termed a ‘signal factor’. If there are no signal factors present, and the aim is to determine the optimum control factor settings to achieve an output closest to the target value, it is a ‘static problem’. If the product does have a signal factor, and the optimization of the process involves finding the desired relationship between the signal factor and the output, the problem is termed ‘dynamic’.

Orthogonal arrays are used; these estimate how a factor affects the response mean and variation. In these arrays, factor levels are equally weighted, meaning each factor can be independently assessed. The advantages of the Taguchi method are that fewer experiments need to be performed to extract the quantitative data, and that multiple factors can be optimized simultaneously[42].

In the case of growing diamond films in a CVD reactor, the problem is a static one, with two desired outcomes: maximum growth rate and greatest diamond quality. The control factors include parameters such as input power, chamber pressure and methane flow rate etc. In theory, substrate temperature is also a control factor, however for the reactor in question for this experiment, there was not a system in place to measure or control the temperature of the substrate. Therefore for this experiment, substrate temperature was a noise factor. The Taguchi method has been used to optimise CVD processes before[43][44] however there are no published papers showing the optimisation of a DC plasma assisted CVD reactor using the Taguchi method.

1.4 Analytical tools for characterising physical properties of CVD diamond

1.4.1 Scanning Electron Microscopy (SEM)

A SEM is used to produce incredibly high magnification images of a sample. Following the same principles as a light microscope, a SEM fires a focused beam of high energy electrons at a sample, rather than photons used in a light microscope. The incident electrons strike the sample surface, and due to inelastic scattering, cause low energy secondary electrons to be ejected from the sample. The scattering patterns are deduced by a detector and can expose details less than 1 nm in size. Some electrons are elastically scattered from deeper locations in the sample. The intensity of these back-scattered electrons are strongly correlated to the atomic number of the sample. It is also possible for the electron beam to remove electrons from low energy shells, causing higher energy electrons to drop down and release X-rays. If the SEM is fitted with X-ray microanalysis tools, these X-rays can be detected and used to provide an insight into the composition of the sample.

Figure 8 illustrates a typical SEM set-up.

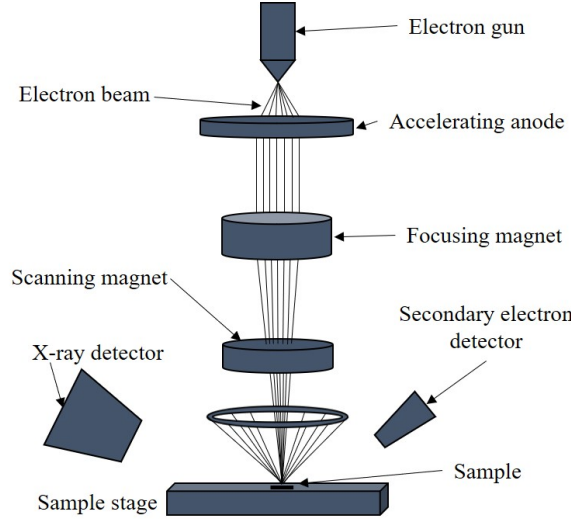


Figure 8: A diagram showing the set-up of an SEM machine.

1.4.2 Raman Spectroscopy

Raman spectroscopy, named after the physicist C. V. Raman, is a technique commonly used to characterise molecules based on their change in polarizability when interacting with light. The sample is illuminated with a beam of monochromatic light. Almost all of the scattered light is unchanged in energy (Rayleigh scattered) however a very small fraction of photons are inelastically scattered (Raman scattered). This phenomenon arises when the photon exchanges energy with the electric dipole of a molecule. The scattering can be depicted as the photon being excited to a virtual state. It can de-excite to a higher energy vibrational state than it began at (stokes scattering) or to a lower energy vibrational state (anti-stokes scattering). The amount of energy exchanged is an indicator of the vibrational frequency of the molecule; a higher frequency vibration results in a greater energy exchange. The scattered light is collected by a spectrometer and is dispersed onto a charge coupled device detector.

Due to varying ratios of sp^2 to sp^3 bonds, there are many different forms of carbon, with widely contrasting properties. Amorphous carbon, for example, can be a mixture of sp^2 , sp^3 and even sp^1 carbon bonds. Diamond like carbon (DLC) is an amorphous carbon with a high percentage of sp^3 bonds.

Different forms of carbon exhibit different Raman shifts. Some of these forms and their shifts are displayed in Table 2.

Table 2: A table displaying the Raman peaks expected for different forms of carbon

Carbon Form	Raman Shift / cm^{-1}
Nanocrystalline Diamond	1150[45]
Hexagonal Diamond	1315-1326[46]
Cubic Diamond	1332[46]
Amorphous Carbon (D)	1345[47]
Diamond Like Carbon	1400 and 1530[48]
Trans-polyacetylene laying in grain boundaries	1430-1470[47]
Amorphous Carbon (G)	1500-1600[47]
Disordered Graphite	1546[47]
Monocrystalline graphite	1580[47]

Crystalline graphite produces a single peak at 1580 cm^{-1} whereas all other graphitic materials, for example activated charcoal, produce a ‘G’ peak between 1500 and 1600 cm^{-1} and a second ‘D’ peak at 1345 cm^{-1} . The G peak is the only Raman active mode of the graphite lattice. The D peak arises from the breakdown of Raman selection rules and has an increased intensity depending on the magnitude of disorganised carbon and the size of the graphite crystals[49].

Raman spectroscopy can be used to non-destructively determine the quality of diamond grown, because the additional forms of carbon grown on a substrate, such as graphite, produce extra signals in the Raman spectrum. The intensity of the diamond peak compared to the additional peak allows the quality of different samples to be compared.

Another quality measure that can be drawn from a Raman spectrum is the full-width-at-half-maximum of the diamond peak. A narrower peak is indicative of better quality diamond. Figure 9 shows the widths of various diamond peaks, formed under different conditions. The broader the peak, the further the structure from the perfect crystal structure.

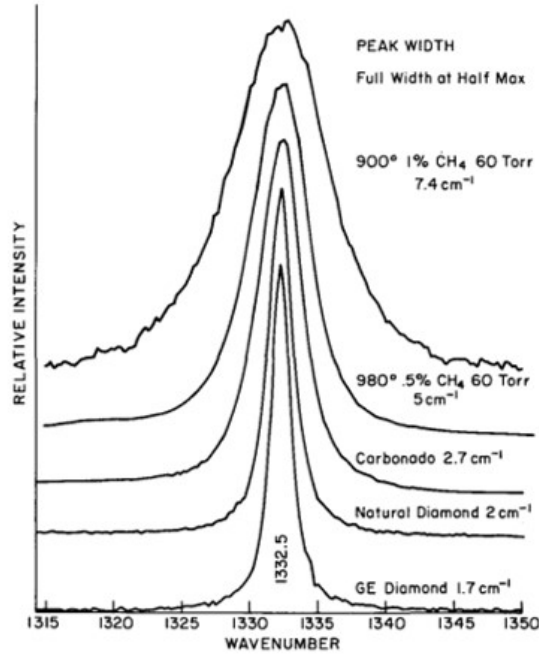


Figure 9: The shape of the diamond peak in the Raman spectrum, for various diamonds and diamond films. Taken from [46].

Photoluminescence (PL), although a separate spectroscopic tool, can be used in conjunction with Raman spectroscopy to reveal additional information about the sample. The light source causes photo-excitation in the sample and hence photoluminescence is observed, and the intensity is recorded as a function of the wavelength of light. PL is a very sensitive tool used to detect deviations in the atomic configuration of diamond, such as nitrogen atoms or vacancies in the crystal structure. It can detect these defects at concentrations of less than ten in a billion carbon atoms[50]. By combining PL with Raman analysis, it becomes possible to analyse both the electronic and vibrational properties of a sample at the same time.

1.4.3 NanoESCA

The recently built Bristol NanoESCA is a cutting-edge surface analysis instrument. It has three main characterisation tools: PhotoEmission Electron Microscopy (PEEM), X-ray Photoelectron Spectroscopy (XPS) and Spot Profile Analysis Low Energy Electron Diffraction (SPA-LEED).

PEEM uses X-rays or UV light, which is absorbed by the sample surface, causing electron excitation from core levels to unoccupied states and hence a core hole is formed. The core hole decays via the Auger effect, which produces secondary electrons. If the electrons have energy greater than the workfunction of the material, they are able to penetrate the sample surface. They are then accelerated by a strong electric field into the objective lens, where the image is magnified and recorded. Electrons generated from deeper in the material are likely to be absorbed and therefore not be detected, which is why PEEM is a highly surface-sensitive technique with a probing depth of only a few nanometers. Local variations in electron emissions are used to achieve a contrast in the image.[51]

In XPS, the sample is subject to a beam of X-rays under high vacuum conditions. The number of escaping electrons and their kinetic energy is measured and analysed. Elements emit electrons with particular characteristic energies, so the intensities and positions of peaks in a spectra can identify the composition of the sample, by acting as an elements ‘fingerprint’. The spectra is used to reveal information on the elemental composition, empirical formula and the chemical and electronic state of the atoms in the material. The electrons only tend to escape from the top 10nm of the sample, making the technique very surface-sensitive. It has been shown that XPS is a useful tool for distinguishing carbon in the diamond phase from graphite or amorphous carbon[52].

Low energy electron diffraction is the most popular method used to analyse the surface structure of single crystalline materials. It involves directing a collimated beam of low energy electrons at the sample, and using a channeltron detector to record the elastically scattered electrons. The secondary electrons released are not recorded as they are eliminated by energy filtering grids. Impurities, dislocations and atomic steps all lead to broadening of the observed diffraction spots. SPA-LEED measures the intensity of diffraction beams and forms spot profiles, which can be used to interpret surface characteristics such as roughness[53].

1.5 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) is a non-invasive tool that provides an insight into the composition of the plasma. The discharge plasma is comprised of different excited species, that each produce photons of different wavelengths corresponding to their individual energy gaps. Emission intensity does not directly correlate with the concentration of the species in the plasma, but it is proportional to the fraction of the species in the electronically excited state. This fraction is determined by the electron energy distribution function of the plasma[54]. The relationship between the spectral acquisition of the plasma and diamond quality has been investigated. It has been shown that the CH emission line at 431 nm is an indicator of good quality growth. An increased intensity of the C₂ peak between 505 and 517 nm depicts worsening of the diamond quality[55].

2 Experimental Aims and Methodology

2.1 Aims

The primary aim of the experiment was to optimize the conditions of the pulsed DC plasma assisted CVD reactor at the University of Bristol. Optimizing the conditions meant finding the best input values for various parameters in order to produce the most successful results. It was decided that, regarding diamond growth, success encompassed two things: highest quality diamond and fastest growth rate. The two dependent variables do not go hand in hand, and it was expected that different conditions would be optimum for each. There are many parameters that could be changed, that would affect growth rate and diamond quality, however there was only enough time to perform a 9-run Taguchi experiment. The maximum number of parameters and levels that can be incorporated into a 9-run Taguchi experiment is four parameters with three levels. The four parameters chosen were done so as they required no amendments to the equipment between runs. The four investigated parameters were: methane concentration, argon concentration, pulse frequency and pressure. If, for example, electrode spacing had been investigated, manual alterations would need to be performed between runs.

The carbon containing feedstock must be a gas at room temperature, for ease of use and because gases are easily ionised. This rules out butane and any longer alkane chains, because they are liquid at room temperature. Methane was chosen as the feedstock gas because, if propane for example was chosen, additional monomers would remain unbound when the carbon atom bound to the diamond surface. This reduces the uniformity of the diamond and hence increases the chances of lattice defects forming. Non-alkane feedstock gases have been used to grow diamond in the past. Ethyne has been experimented with, due to its ease in producing the C_2 radical, however it is not widely used as the rate of incorporation is slower than that achieved with a methane feedstock gas[56]. Methane concentration was investigated in this project, as previous experiments have shown there is a strong relationship between this parameter and growth rate[34]. Increasing the concentration is known to improve the growth rate however it can also encourage graphitic growth and lead to an imbalance of growth across the substrate. One of the aims of this project therefore was to find the optimum value for methane concentration to obtain the best quality diamond or to achieve best growth rate.

The addition of argon to the gas mixture has been shown to vastly improve growth rates[57][58]. It is thought that this effect is due to the addition of argon increasing the gas temperature, hence promoting the dissociation of hydrogen into H radicals[59]. The thermal conductivity of argon is ten times lower than than hydrogen, which means that when argon is added to the gas mixture, heat is transported less efficiently to the cooled reactor walls[59]. There is also evidence of argon reducing crystalline size in plasma assisted CVD methods[60][61]. By varying the argon concentration in the experiment, some light will be shed on how argon affects the growth rate and quality of diamond grown in a DC plasma assisted CVD reactor.

As previously mentioned, using a pulsed DC power supply achieves higher plasma densities which generates a higher dissociation rate of the precursor gas molecules. Minimal literature data exists comparing the quality or speed of diamond growth with varying pulse frequencies so it was an aim of this experiment to discover what effect this parameter had on the diamond results.

The final parameter investigated in the Taguchi optimisation experiment was the pressure inside the chamber. Increasing the pressure has been shown to decrease

defects in hot filament CVD experiments[62]. Increasing pressure also correlates strongly with growth rate in microwave plasma assisted CVD reactors[63]. Whether these trends would also be observed in a DC plasma assisted CVD reactor was investigated.

2.2 University of Bristol Pulsed DC Plasma Assisted CVD Reactor

A diagram of the reactor used for the experiment is detailed in Figure 10.

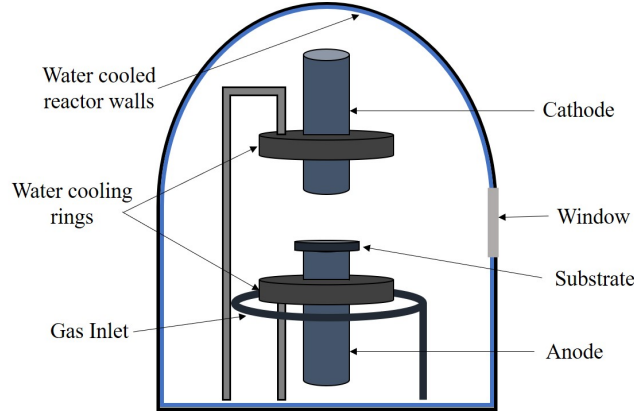


Figure 10: A diagram showing the set-up of the Bristol University CVD Reactor.

The live cathode and grounded anode are solid tungsten rods, 10 cm in length and 24.95 ± 0.05 mm in diameter. The spacing between them is 15.5 ± 0.5 mm and can be increased or decreased by adding or removing metal spacers from the frame holding the cathode. The water cooling rings are made of stainless steel and sit 11 mm above the bottom of the cathode and 27.5 mm below the top of the anode. The water flows in through copper pipes. These pipes also carry the current from the power supply to the cathode, and are surrounded by Macor[®] and glass to prevent short circuiting between the pipes and the anode. An Advanced Energy[®] Pinnacle Plus+ Pulsed-DC power supply was used. The values for power and frequency were adjusted using a dial, which allowed a power input of up to 10 kW and frequency up to 150 kHz. A visual display presented the values of voltage and current. The system included an arc suppression feature, and also stopped supplying power if voltage exceeded 660 V.

The substrates used were also tungsten, measuring 30.17 ± 0.06 mm in diameter and 4.84 ± 0.10 mm in thickness. Tungsten is a suitable substrate material for many reasons; it has a melting point higher than the temperatures reached in the reactor ($T_m=3422$ °C[64]) and it also has a thermal expansion coefficient analogous to diamond. This is important, as when the substrate and diamond cool and contract post run, they must do so in sync, else cracks and other deformations may appear. The substrate material must also be able to form carbide layers, which the diamond then grows upon. Tungsten is among the metals that satisfy this condition.[21]

The window is made of Kodial[®] glass. Borosilicate glass is used due to the fact it has a minimal thermal co-expansion coefficient and blocks UV radiation.

The gas inlet ring is made of stainless steel. The gases travel through Burkert[®] Type 8715 mass flow controllers before being introduced into the chamber via the grounded ring. A butterfly valve controls the pressure inside the chamber, which is measured using a 1000 Torr baratron at pressures above 10 Torr, and a 10 Torr

baratron at lower pressures. The vacuum pump used is an Edwards® RV12 Oil Mist Filter EMF 20 paired with an MKS® Type 252 Exhaust Valve Controller.

Figure 11 shows the inside of the reaction chamber.

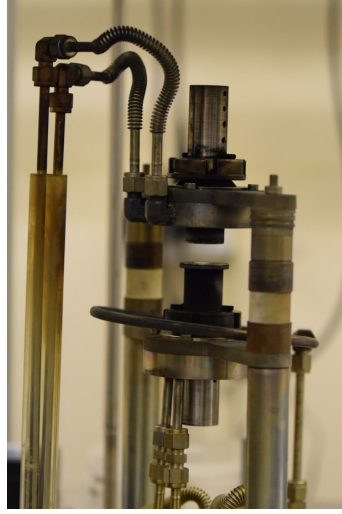


Figure 11: A picture taken of the inside of the CVD reactor.

2.3 Methodology

2.3.1 Leak Rate Tests

In order to identify possible leaks in the system, different areas were isolated and placed under vacuum until the pressure dropped below 17 mTorr. The vacuum was then turned off and the system was allowed 20 seconds to settle at a pressure. The pressure change over a period of 5 minutes was subsequently recorded.

2.3.2 Taguchi Design

Minitab® software was used to produce the Taguchi array from the list of chosen parameters and their levels. The levels were set based on the successes and failures of previous practise runs. The array is displayed in Table 3.

Table 3: A table outlining the parameters values for each run.

Run	[CH ₄] / SCCM	[Ar] / SCCM	Frequency / kHz	Set Point / Torr
1	10	0	100	200
2	10	5	125	230
3	10	10	150	260
4	20	0	125	260
5	20	5	150	200
6	20	10	100	230
7	30	0	150	230
8	30	5	100	260
9	30	10	125	200

Before each run, the substrate was cleaned using sandpaper and water, mounted centrally on the anode and left under vacuum overnight. The following day a ‘cleaning run’ was performed. The conditions followed are outlined in Table 4.

Table 4: A table outlining the conditions for a cleaning run.

Parameter	Value
Pressure	200 Torr
Power	2500 W
Frequency	150 kHz
Pause Rate	2 μ s
[H ₂]	500 sccm

The hydrogen was introduced into the chamber and when the pressure reached 1.8 Torr, the electrodes were struck with 50 W of power. The power was raised by 250 W for every 10 Torr climbed. At 80 Torr, the power was raised to 2500 W. Once the pressure inside the reactor reached 200 Torr, the system was left for an hour, before the power was switched off.

After the cleaning run, the system was put under vacuum until the pressure was below 18 mTorr. The parameters were set according to the Taguchi array and the hydrogen and argon were introduced into the chamber. The electrodes were struck with 50 W of power. The power was raised in the same manner as in the cleaning run but the methane was introduced into the chamber at 100 Torr. Once the pressure reached the set pressure, the reactor was left to run for 1 hour.

3 Results and Analysis

3.1 Leak Rate Tests

The different areas of the reactor tested for leaks are shown in Figure 12.

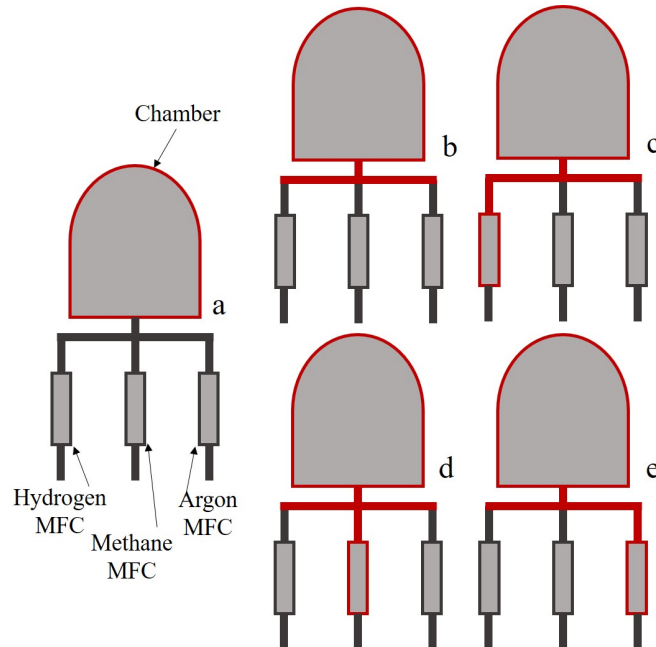


Figure 12: The areas of the reactor isolated for leak rate tests, shown in red.

The pressure changes, observed across the different areas, are shown in Table 5.

Table 5: A table showing the results of the leak rate tests performed on the pulsed DC plasma assisted CVD reactor.

Isolated Area	Start Pressure/mTorr	End Pressure/mTorr	Δ Pressure/mTorr
a	12.09	11.40	-0.69
b	11.25	12.14	0.89
c	11.55	12.32	0.77
d	13.47	24.64	11.17
e	16.45	26.56	10.10

The results show minimal pressure rise through the piping above the MFC's and the hydrogen pipes. Surprisingly, a pressure drop was observed in the chamber area. This could be caused by fluctuations in the baratron reading, as the pressure change was close to the minimum limit of detection. The pressure rise in the methane pipes and argon pipes was significant. A pressure rise that considerable suggests there was a leak, allowing nitrogen and other potential contaminants into the system. Bubble solution was used around all the nuts on the methane and argon pipes, and a positive pressure was achieved within the pipes. Where small air bubbles appeared it was evident that air was escaping and a nut was not secured tight enough. Wherever this occurred, the nuts were tightened in order to create a tighter seal. The leak rate tests were repeated and the results showed pressure rises within the noise range seen in areas a, b and c.

3.2 Taguchi Results

The first analysis performed on each run was the optical emission spectroscopy, using an Ocean Optics® USB2000 UV-Vis ES. One spectra was obtained for each run, and was taken shortly after the system had reached maximum pressure. The spectrum for run 9 is shown in Figure 13. Run 9 was representative of good quality diamond growth.

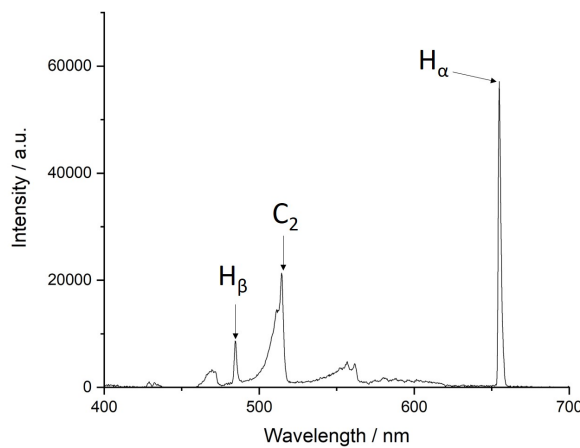


Figure 13: The optical emission spectrum obtained from run 9.

A clear H_{α} peak can be seen at 656 nm and a smaller H_{β} peak at 486 nm. H_{α} represents an electron transitioning from the $n=3$ to the $n=2$ state, and H_{β} represents a transition from the $n=4$ to the $n=2$ state. The dominant C_2 species observed is the swan system at 516 nm. The C_2 peak intensity as a percentage of

the H_α peak intensity was determined from each spectrum. For each parameter, an average of the three runs at each level was calculated. For example, to calculate the average at 10 sccm methane flow rate, an average of runs 1, 2 and 3 was taken. Figure 14 is a plot of the peak ratios against each parameter.

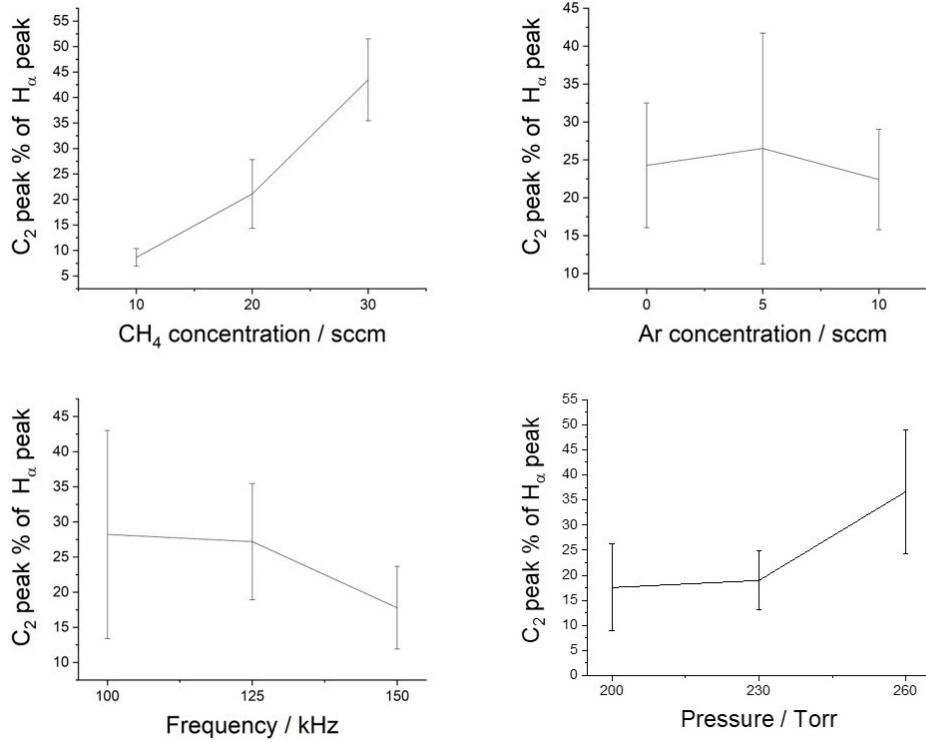


Figure 14: Graphs showing the relationships between investigated parameters and the C₂ peak intensity as a percentage of the H_α peak intensity.

Smaller error bars indicate a stronger correlation between the parameter and the result, as they show the results were more dependent on the parameter in question, rather than the other three parameters. Figure 14 shows that the C₂ peak as a percentage of the H_α peak is strongly dependent on CH₄ concentration and unsurprisingly, the larger the concentration the stronger the peak percentage. Concentration does not directly correlate to peak intensity, but an increase in C₂ radicals can be indicative of more methane in the system. As discussed in section 1.5, a lower peak percentage indicates greater diamond quality[55]. Therefore these results suggest that, at the fixed power level of 2500 W, a lower concentration of CH₄ is favourable for increased diamond quality.

There seems to be little correlation between the other parameters and peak %. Research has shown that higher pressures can increase the production of the C₂ dimer in the core region but reduce it at the substrate/plasma boundary[65]. The optical emission spectrometer was pointing at the core region of the plasma, so an increase in pressure should increase the C₂ peak %. This trend can be seen in the results, as the average value of the C₂ peak % at 260 Torr is considerably higher than at lower pressures. As the error bars overlap, statistically this conclusion cannot be drawn, and further tests would need to be performed to confirm this theory. However it does appear that 260 Torr is a less suitable pressure to grow good quality diamond than 200 or 230 Torr.

The results would tell a more conclusive story if multiple optical emission spectra had been taken at regular intervals across the duration of the runs. The effects these parameters had on the production of the C₂ dimer over time would be observed, and hence an understanding of the change in plasma quality over time would be gained. This was not done in the experiment as the equipment required manually holding in place, and so would have been difficult and time consuming to set up multiple times a run.

After the substrates were removed from the reactor (post run), they were looked at under a Leica[®] Optical Microscope. In all cases, growth was not uniform across the substrate. Quality deteriorated, and coverage increased, towards the edge of the substrate. Ideally, analysis would have been done on varying sites across the substrate, so that the contrast in diamond quality and growth rate across the sample could be evaluated. However, due to time constraints, an area of good growth was selected for each run, and an Oxford Lasers[®] laser cutter was used to cut a square of size 2 mm by 2 mm into the surface, at the selected point. This way only a comparison of the best growth, and no comparison of coverage, between runs could be made.

The substrate was taken back to the optical microscope and a site inside each corner of the square was chosen. Photos were taken of these sites using the optical microscope and a Raman spectrum using a green laser (532 nm) was obtained at each site, using a Renishaw[®] Raman microscope.

Certain features of the Raman spectra of diamond have varying intensities and positions, depending on the excitation wavelength of the laser. The optimum excitation energy for diamond films produced by various deposition methods has been investigated by Wagner et. al.[66]. Although a DC plasma formed film was not investigated, 2.33 eV (corresponding to 532 nm) resulted in optimum resolution of the diamond peak from a good quality microwave plasma assisted deposition sample, with crystal size between 50 and 100 μm . For a sample of inferior quality, and crystals between 1 to 3 μm , higher energy photons were required to achieve good resolution. For a nano-crystalline film, deposited via the hot filament method, much higher energy photons were suitable.

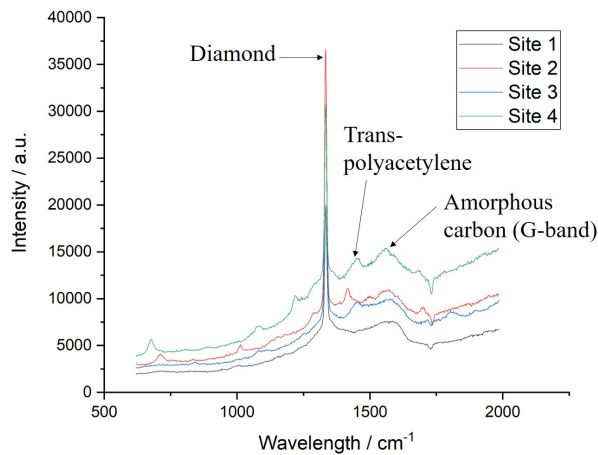


Figure 15: The Raman spectra obtained from the four sites of run 9.

The Raman spectra of the four selected sites from run 9 are shown in Figure 15. The spectra show a sharp diamond peak centred at 1332 cm^{-1} , a peak around 1450

cm^{-1} (attributed to trans-polyacetylene) and a broad peak around 1560 cm^{-1} (attributed to the amorphous carbon G-band). The ‘negative peak’ around 1700 cm^{-1} is due to a missing LED in the microscope. The presence of the trans-polyacetylene (TPA) peak has been discussed in literature, and is believed to be strongly associated with the concentration of hydrogen in the plasma[67]. It has been shown that increasing the concentration of H_2 in a H_2/CH_4 environment, or exposing the growth to a H_2 plasma after deposition, increases the amount of TPA relative to amorphous carbon[68]. To reduce TPA growth in diamond films, hydrogen-free etchants (such as oxygen) could be introduced.

Each run delivered very unique spectra; many spectra showed TPA peaks yet only some showed amorphous carbon peaks. Some runs showed no sign of a diamond peak at all. Quantitatively comparing the quality of diamond grown in each run was therefore challenging. A full table outlining which peaks were observed in each spectra can be found in the appendix (Table 2). It may be possible that had a higher energy laser been used, greater diamond peak resolution of some of the samples would have been obtained. A better comparison between the samples may have been made, had Raman spectra been obtained from each sample using a 532 nm laser and a 351 nm laser.

A sloping background is common in Raman spectra, and originates from fluorescence in the sample. For each spectrum, a fitting was made of the background, which was then subtracted from the spectra. This made the comparison between the diamond and any additional peaks more accurate. The value of the diamond peak intensity at 1332 cm^{-1} divided by the largest additional peak (whether that be from amorphous carbon, graphitic or TPA) was found. By doing this, all forms of carbon other than diamond were treated as equal ‘impurities’. An average value for each run was determined. The average of the three runs at each level was found and plotted against the parameter values on a $\log_{10}$ scale, as shown in Figure 16.

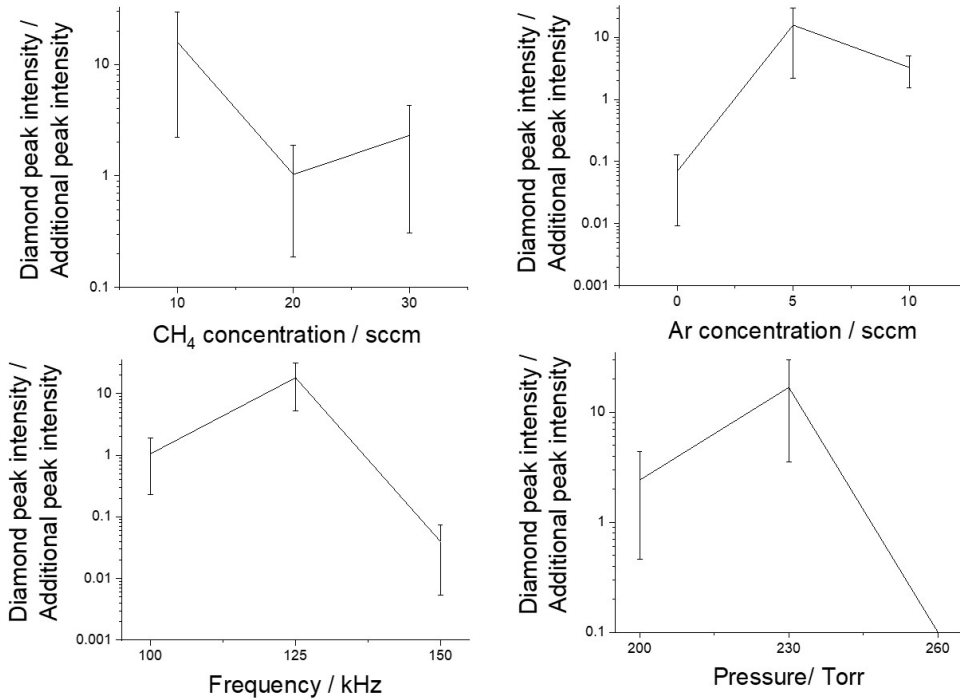


Figure 16: Graphs showing the relationship between each of the control parameters and diamond quality.

Quantitatively the results show that, at a fixed power level of 2500 W, the conditions under which the best quality diamond could be grown are 10 sccm CH₄, 5 sccm Ar, 125 kHz and 230 Torr, which are the conditions of run 2. These conditions confirm the outcome of the OES: a lower CH₄ concentration is favourable for greater diamond quality. It could be possible this trend is seen because higher CH₄ concentrations result in there being greater graphitic feedstock available, and not enough hydrogen radicals to readily remove the graphitic build up.

The OES results supported the idea that higher pressures reduced diamond quality. This conclusion can also be drawn from the Raman results, as none of the runs performed at 260 Torr produced a diamond peak in the Raman spectrum.

For the spectra containing diamond peaks, the full width at half maximum (FWHM) of the peak was also found. These values can be found in the appendix (Table 1). The FWHM provides an insight into the diamond structure; a narrower peak suggests a structure closer to that of a perfect crystal, as more defects cause increased scattering. Natural diamonds exhibit peak widths of around 2 cm⁻¹, however CVD films tend to have wider peaks. The diamond films grown in this experiment exhibited peaks with FWHM in the range 8.4 cm⁻¹ to 10.3 cm⁻¹. As a FWHM could not be found for the spectra without diamond peaks, conclusions surrounding the effects that each parameter had on the crystal structure could not be drawn. For an understanding on how, for example, the methane concentration affected the width of the diamond peak, an experiment would need to be performed changing only methane concentration whilst keeping other parameters constant. What can be gained from these results is the general crystallinity of the diamond grown in this reactor. The FWHM of the peaks are of the same order as natural diamonds, however there is scope for reducing these values and investigating what parameter changes affect this.

SEM images were collected of four sites within the square, using a Zeiss® FE-SEM. The images collected of run 9 are shown in Figure 17.

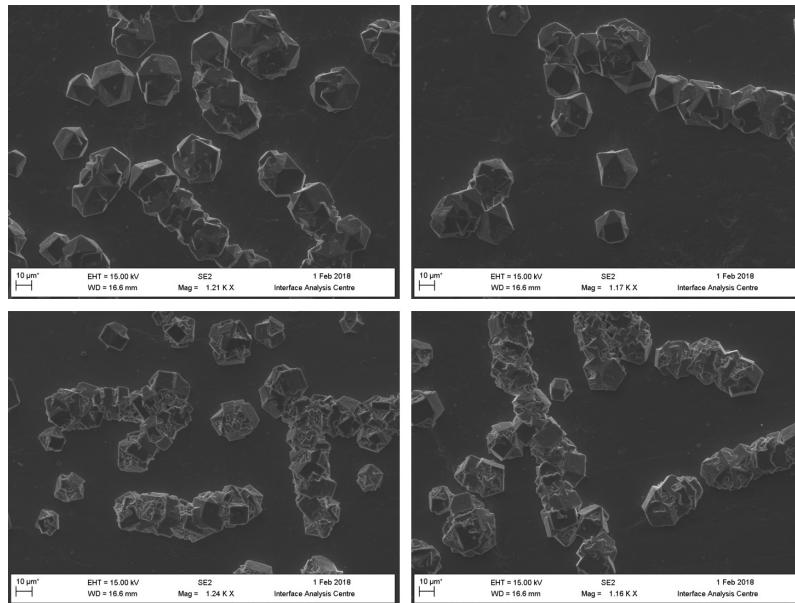


Figure 17: The SEM images taken of selected areas from run 2.

The widths of five crystals were determined, per image. An average crystal width was calculated and divided by the growth time, to determine lateral growth rate. Graphs of growth rate against parameter levels are shown in Figure 18.

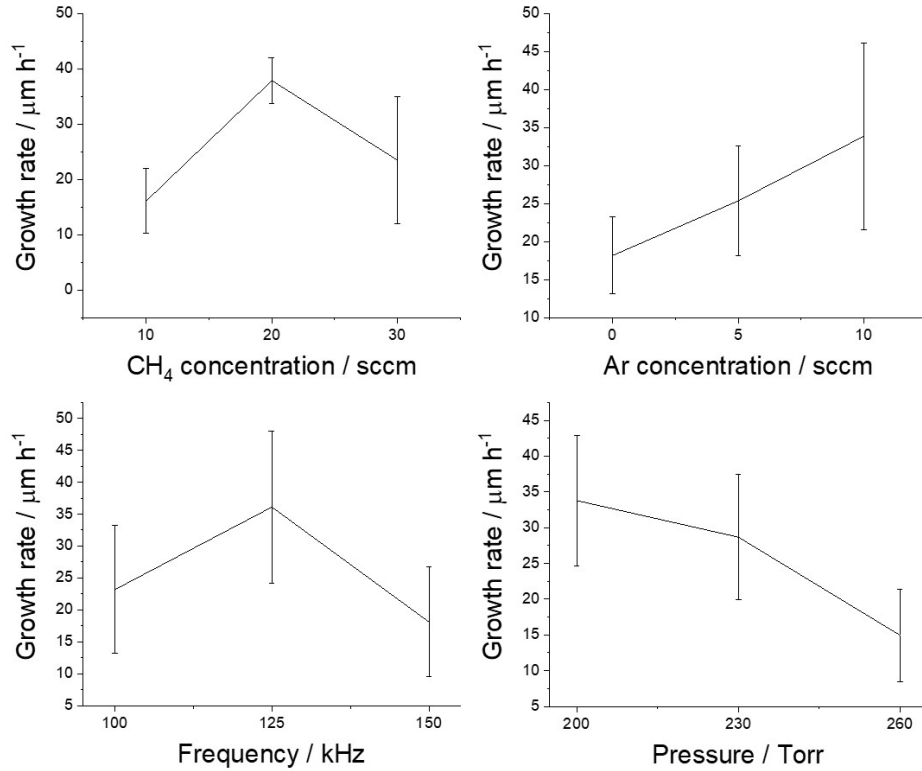


Figure 18: Graphs of the growth rate against parameter levels.

The CH₄ concentration that exhibited the greatest growth rate was 20 sccm. Literature has shown increasing CH₄ concentration leads to greater growth rates [69][70], however in these cases the growth rates do not discriminate between diamond growth and graphitic growth. As increasing CH₄ concentration also leads to worsened diamond quality, it's likely when high growth rates are observed in the cases mentioned, high levels of graphite growth were contributing to the rate. In this experiment, when selecting areas to measure, growths with crystal faces were selected where possible. The growth rate therefore was more indicative of the rate at which diamond was grown rather than a combination of diamond and amorphous carbon.

The graph of growth rate versus argon concentration shows a trend in which increasing the concentration improves the growth rate. Literature supports this trend[71][57]. Argon molecules are responsible for additional reactions between ions, excited molecules and neutral molecules in the system. They therefore influence the degree of excitation of the methane and hydrogen molecules, by energy or charge transfer. Increasing argon concentration results in enhanced deposition rates.

The effect of altering the pulse frequency on the growth rate has not been widely investigated. A trend however has been identified between pulse duration and plasma stability. Shorter pulses should be applied to low methane concentration plasmas and longer pulses should be applied to higher methane plasmas to ensure stability[36]. The results of the Taguchi experiment contradict these findings. The system used in this experiment automatically altered the pulse duration depending on pulse frequency. Frequencies of 100, 125 and 150 kHz corresponded to pulse durations of 3, 2.4 and 2 μs respectively. Run 3 (minimum CH₄ concentration and minimum pulse duration) and run 8 (maximum CH₄ concentration and maximum pulse duration) resulted in the lowest achieved growth rates of the experiment. Ac-

cording to literature these runs should have produced the most stable plasmas and therefore resulted in the best growth rates. It is therefore reasonable to assume that the other variable parameters were having a greater effect on the results than the pulse frequency.

Figure 18 shows that as pressure is increased, growth rate decreases. This trend can be understood by considering the energy per molecule in the plasma. When the pressure is increased, but the power kept constant, the energy per molecule is reduced and hence growth rate will deteriorate.

3.3 Testing Optimum Conditions

The results of the Taguchi optimisation experiment suggest that the conditions outlined in Table 6 are optimum for diamond quality or for growth rate.

Table 6: A table of the optimum conditions for diamond quality and growth rate, determined by the Taguchi experiment.

Desired Outcome	[CH ₄] / sccm	[Ar] / sccm	Frequency / kHz	Pressure / Torr
Diamond Quality	10	5	125	230
Growth Rate	20	10	125	200

A longer run was performed with the conditions found for optimum diamond quality. All other conditions were kept the same as in the Taguchi optimisation experiment. The cleaning run and start up procedure was also performed in the same manor as before. The plasma remained, for the most part, stable with occasional arcing, however at 3.5 hours a lengthy arc occurred, causing a decision to be made to stop the experiment. A Raman spectrum obtained from the sample is shown in Figure 19.

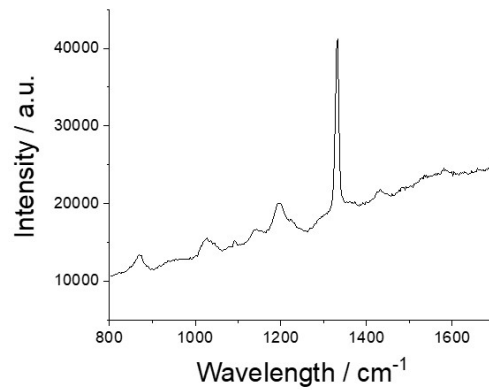


Figure 19: A Raman spectrum obtained from a 3.5 hour run with the following conditions: 10 sccm CH₄, 5 sccm Ar, 125 kHz and 230 Torr.

A clear peak at 1332 cm⁻¹, characteristic of cubic diamond, can be seen in Figure 19. Other than a very small peak attributed to trans-polyacetylene, there are minimal non-diamond phases observed in the spectra. This therefore supports the conclusion drawn from the Taguchi experiment; that these are good conditions for achieving good quality diamond.

Two SEM images taken of the sample are shown in Figure 20.

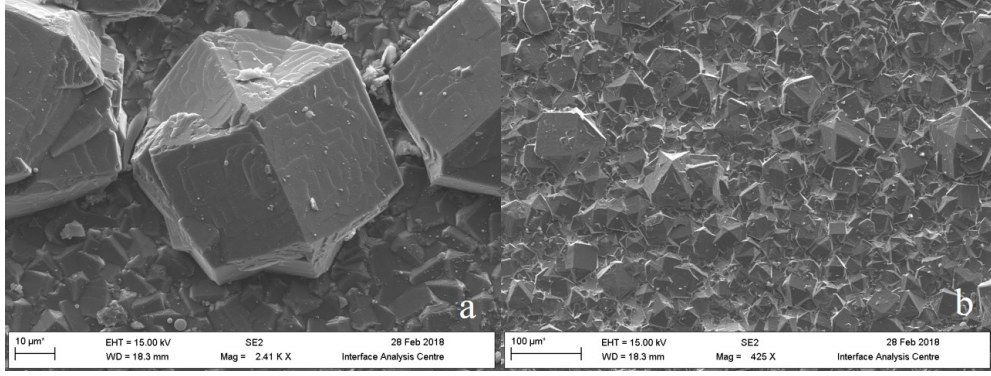


Figure 20: SEM images of a 3.5 hour run with the following conditions: 10 sccm CH_4 , 5 sccm Ar, 125 kHz and 230 Torr. a) a close up view of a crystal facet b) an overall view of the growth.

Figure 20a shows large diamond facet growth. These are the largest diamond facets grown in the pulsed DC plasma assisted CVD reactor at the University of Bristol to date. Figure 20b shows a continuous film of diamond growth on the sample.

The results of the long run exhibit good quality diamond growth, supporting the idea that 10 sccm CH_4 , 5 sccm Ar, 125 kHz and 230 Torr are the best levels of each parameter in order to grow the purest diamond. With that being said, these are only the best of the three levels chosen at the start of the experiment. It may be possible to further improve the results by performing another Taguchi optimisation experiment, but this time reducing the difference between the maximum and minimum value of each level. For example an experiment with the following three levels for each parameter, outlined in Table 7, could be performed in order to find even better parameter levels.

Table 7: A table of the proposed conditions for a second Taguchi experiment.

Level	$[\text{CH}_4]$ / sccm	$[\text{Ar}]$ / sccm	Frequency / kHz	Pressure / Torr
1	5	3	115	220
2	10	5	125	230
3	15	7	135	240

4 Future Work

It would be useful if a trial of the optimum conditions found for best growth rate was undertaken, providing evidence that the conditions predicted from the Taguchi optimisation experiment did indeed correlate to fastest diamond growth. It would then be sensible to repeat the Taguchi experiment, centring the levels around the optimum conditions found, and reduce the variance of the levels. This would allow more precise optimum conditions to be found. When repeating the Taguchi experiment, changes should be made to the way the runs were analysed. These changes include:

- Taking OES at regular intervals over the duration of a run. An insight would then be gained, of the quality of the plasma over time.
- Taking Raman spectra at several sites of the substrate, varying in distance from the centre. An understanding of the quality deterioration between the centre and the edge would be made.

- Taking Raman spectra with two different wavelength lasers (532 and 351 nm). A decision would then be made as to which wavelength laser resolved the diamond peaks best.
- Taking SEM images at several sites of the substrate, increasing in distance from the centre, to understand how the coverage varies over the sample.

There were many variable parameters that were not investigated in this project, that would almost certainly affect diamond quality and growth rate. These include, but are not limited to: electrode separation, substrate temperature, substrate size and hydrogen concentration. It is expected that the researchers working on this reactor will subsequently investigate the influence these parameters have on diamond growth.

Once all the parameters have been optimised, one of the aims of the reactor is to be able to grow with a C_{13} feedstock gas. As this feedstock gas is considerably more expensive than C_{12} methane, it is important that the optimum parameters that the reactor runs at are found before it is introduced. It would therefore also be sensible to investigate growing C_{13} diamond via a closed cycle run, to reduce process costs. A closed cycle run involves introducing the gases and bringing the chamber up to appropriate pressure, then isolating the system during the run. A long term objective of the reactor, is to be able to grow diamond in layers of C_{12} and C_{13} , for ultimate use in thermal shields for a fusion reactor.

5 Conclusion

A pulsed DC plasma assisted CVD reactor was built by members of the University of Bristol Diamond Group in 2016, with the aim of one day being able to grow continuous diamond films onto desired substrates at an acceptable rate. The system was tried and tested for many months, however due to plasma instability, inconsistent and irreproducible results continued to be produced. A new electrode set-up, with a considerably smaller anode and cathode, was introduced in July 2017, with intent to reduced plasma size and therefore increase stability. The aim of this project was to find optimum conditions at which to run the reactor, to achieve optimum diamond quality or growth rate.

The parameters chosen to investigate were methane concentration, argon concentration, pulse frequency and pressure. These were chosen as they required no alteration to the set-up of the reactor. A Taguchi experiment allows the effects of multiple parameters to be investigated simultaneously. Only nine runs needed to be performed in order to determine which level (of three possible levels) each of the four parameters should be set at, to achieve the desired results. Diamond films were grown for 1 hour onto tungsten substrates. The electrode distance was maintained at 15.5 mm, input power was kept at 2500 W and hydrogen concentration was kept at a constant 500 sccm for every run. Methane and argon concentrations were varied between 2-6% and 0-2% respectively. The pulse frequency was varied between 100 and 150 kHz and the pressure was varied between 200 and 260 Torr.

Runs were performed and analysed in three different ways. An optical emission spectrum was obtained for each run, allowing the intensity of the C_2 dimer to be compared across different runs. Raman spectra were obtained at four sites on the substrate. These allowed a comparison of the diamond peak at 1332 cm^{-1} to any additional peaks, caused by non-diamond phases, to be achieved. Hence permitting the diamond quality of each run to be distinguished. A scanning electron microscope

was used to gather images of the surfaces, which were utilised in order to determine the lateral growth rate of the diamond.

The results showed that for the configuration of the reactor, the optimum conditions in order to grow the best diamond quality are 10 sccm CH₄ (2%), 5 sccm Ar (1%), 125 kHz and 230 Torr. Both the OES and the Raman spectra supported the conclusion that higher methane concentrations lead to decreased diamond quality, and that very high pressures also lead to worsened quality. The conditions that lead to fastest diamond growth are 20 sccm CH₄ (4%), 10 sccm Ar (2%), 125 kHz and 200 Torr. These are only the optimum values of the investigated levels; another Taguchi experiment would need to be performed to further refine the exact values at which the reactor performs best.

It is also important to note that throughout the project, a fixed input power was maintained. Altering this property may have lead to very different results, especially in terms of optimum pressure levels. Increasing the gas pressure in a pulsed DC plasma system requires more power to sustain the same electrode coverage, as the electrode glow is dependent on current and hence power. Thus, it is not sensible to assume the results obtained in this experiment are transferable to higher, or lower, power levels.

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A Appendix

Table 1: A table of the Taguchi optimisation experiment results.

Run	C ₂ peak % of H _α peak	Diamond to non-diamond ratio	FWHM	Growth rate/ $\mu\text{m h}^{-1}$
1	5.5	0.208	10.1	13.8
2	8.1	47.483	9.2	28.8
3	12.3	0	-	5.6
4	36.0	0	-	29.7
5	9.8	0.119	8.4	37.7
6	17.5	2.970	10.3	46.2
7	31.3	0	-	11.0
8	61.7	0	-	9.6
9	37.4	6.935	11.1	49.8

Table 2: A table showing which peaks were observed in the Raman spectra for each run.

Run	Diamond	TPA	Amorphous carbon (D)	Amorphous carbon (G)
1	✓	✓		
2	✓			✓
3		✓		
4		✓		
5	✓	✓		
6	✓	✓		✓
7		✓	✓	✓
8			✓	✓
9	✓	✓		✓