Investigations into the plasma formed by a microwave reactor used for the chemical vapour deposition of diamond

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Abstract

Cavity ring- down spectroscopy and optical emission spectroscopy were used to probe the activated carbon, hydrogen and oxygen containing gas mixture in a microwave enhanced plasma reactor used for diamond chemical vapour deposition. In particular, it was of interest to compare previous spectroscopic results of a $CO_2/CH_4/H_2$ gas mixture to a CO/H_2 gas mixture to find out if the plasma was sensitive to the specific feed gas unlike regular C/H gas mixtures which are only dependent on the C: H ratio.

Absolute column densities of CH and OH radicals were measured using cavity ring- down spectroscopy in the plasmas formed by the $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures as a function of height above the substrate, *z*. Results showed a clear difference, with much lower column densities for both species measured in the CO/H_2 gas mixture, indicating that the plasma was sensitive to the choice of feed gas, and implying that diamond growth would be similarly sensitive to choice of the particular C/H/O source.

Optical emission spectroscopy was also used to complement the cavity ring- down results. Optical emission from excited CH, C₂, OH, CO and H were measured for both the $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures as a function of height above the substrate, *z*. The different species show different spatial profiles but, for any given species, both gas mixtures gave similar distributions – indicating that the electron temperature and density distributions were the very similar in both plasmas. However, the emission intensities from all monitored species were substantially lower in the CO/H₂ gas mixture. A slightly broader emission was measured for the CH and C₂ radicals in the $CO_2/CH_4/H_2$ gas mixture; this was attributed to a higher density of species reacting to form excited CH and C₂ radicals which chemiluminesce, thus supplementing the emission arising from the electron impact excitation.

The experimental measurements were then compared to a preliminary 2D(r, z) model of the C/H/O plasma, as made by Yuri Mankelevich of Moscow State University. This led to further refinement of the model to produce more realistic simulation of the plasma.

Two computational techniques (quantum mechanics and a hybrid technique of quantum mechanics / molecular mechanics, QM/MM) were used to simulate elementary reactions between an H-terminated diamond (100) surface and oxygen-containing species. This resulted in a possible explanation as to why oxygen is not readily incorporated into the diamond surface and to an improved understanding of other possible surface reactions being increased. QM/MM results show a high-energy barrier for the insertion of an OH radical into a diamond surface C-C bond on the diamond surface but no energy barrier for insertion into a surface C-H bond.

Abstract	2
List of Figures	4
List of Tables	5
Chapter 1 - Introduction	6
1.1 Why diamond?	6
1.2 Different Techniques for Diamond Synthesis	7
1.2.1 Chemical Vapour Deposition	7
1.2.2 Arcjet Reactors	8
1.2.3 Hot Filament Reactors	9
1.2.4 Microwave Reactors	10
1.3 Gaseous Reactions	15
1.3.1 The Role of Oxygen	16
1.4 Surface Chemistry of CVD Diamond Growth	19
1.5 Optical Diagnosis	19
1.5.1 Cavity Ring- Down Spectroscopy	21
1.5.2 Optical Emission Spectroscopy	22
1.6 Modelling and Other Computational Studies	23
1.7 Aim of the Study	23
1.8 References	24
Chapter 2 - Experimental 2.1 The Reactor 2.2 The LASER Setup 2.3 Cavity Ring- Down Spectroscopy (CRDS) Calculations 2.3.1 Spatial Profiles 2. 4 Optical Emission Spectroscopy (OES) 2.5 Computational Details 2.5.1 Computational Study: Part I 2.5.2 Computational Study: Part II 2.6 References	28 28 29 30 30 31 33 33 33 33 33
Chapter 3 - Modelling of Plasma Chemistry and Composition	36
3.1 Theory and parameters of the Bristol-Moscow model	36
3.2 Model Predictions	37
3.3 References	39
Chapter 4 - Results and Discussion	40
4.1 Optical Emission Spectroscopy	40
4.2 Cavity Ring- Down Spectroscopy	46
4.3 Computational Studies	49
4.3.1 Quantum Mechanics (QM)	49
4.3.2 Quantum Mechanics / Molecular Mechanics (QM/MM)	51
4.4 References	52
Chapter 5 - Afterword	53
5.1 Conclusion	53
5.2 Future Work	53
5.3 Acknowledgements	54
5.4 References	54
Appendices	55

List of Figures

Figure 1.1	Diagram of DC arc jet (plasma torch), left. Picture within DC arc jet reactor, right. ^[11]	8
Figure 1.2	Diagram of not filament reactor, left. Picture of a not filament reactor, right [11]	8
Figure 1.3	Top left, diagram of a NIRIM type microwave plasma reactor. Top right, diagram of an	~
	ASTEX-type microwave plasma reactor. Bottom, picture of a microwave reactor. [11]	9
Figure 1.4	Scheme showing the major H-shifting reactions and interconversion in and between L_1H_x	4.0
D: 1 F	and L_2H_y species	10
Figure 1.5	$2D(r, z)$ plots of the calculated gas temperature, I_{gas} , in Kelvin (left) and CH_3 number	
	density, (right) for reactor chamber diameter = 12cm, reactor chamber height = 6cm and $r_{\rm exp}$	
	substrate noider diameter of 3 cm. Pressure $p = 150$ forr, input power $P = 1.5$ kW and gas	
	mixture of 4.4% LH_4 , 7% Ar and 88.6% H_2 (flow rates $F(LH_4) = 25$ sccm, $F(Ar) = 40$ sccm,	
	$F(H_2) = 500$ sccm). The color scale increases in 13 equal intervals, e.g. from 303–505 to	
F igure 1 ($2729-2931$ K (left), and from $0-3.02 \times 10^{13}$ cm ⁻³ to $3.62 \times 10^{14}-3.92 \times 10^{14}$ cm ⁻³ (right). ^[5]	11
Figure 1.6	Schematic of the processes occurring during diamond UVD. [1][2]	13
Figure 1.7	Simplified Bachmann C/ H/ O phase diagram. This shows now ratio of C:H:O in the process	
	gas mixture affects the result of diamond UVD process, occurring in non-diamond carbon	10
F :	growth (pink area), diamond growth (pale blue area) or no growth (blue).	10
Figure 1.8	Idealised structures of the (111), (110) and (100)-2x1: 1H surfaces, snowing step features.	
	he large grey balls represent carbon atoms and the small white balls represent surface	17
Figure 1.0	Main radical cites important for diamond growth on the (100) diamond curface during	17
Figure 1.9	CVD. The sites are labeled A1, A2, A2, and A4 following the scheme of Skelvey at al. [65]	17
Figuro 1 10	Model clusters for the original HH mechanicm. The upper left cluster is bigyclononano and	1/
Figure 1.10	the lower right is adamantane. A det represente a radical site [67][69]	10
Figuro 1 11	The modified HH mechanicm portion of the combined CDCR and modified HH mechanicm	10
Figure 1.11	C, denotes a surface carbon atom and a dot represents a radical site [35][61]	10
Figure 1 12	Schematic of the CRDS set-up	20
Figure 1.12	2-D (r z) plots for calculated electron (left) and H atom (right) concentrations Conditions	20
rigure 1.15	modelled were for reactor chamber diameter = 12 cm reactor chamber height = 6 cm	
	substrate holder diameter of 3 cm and substrate temperature $T_{-}=973K$ Pressure $n_{-}=150$	
	Substrate holder diameter of 5 cm and substrate temperature, $r_3 = 575$ k. (1) substrate $p = 150$ Torr input power $P = 1.5$ kW and gas mixture of 4.4% CH ₄ . 7% Ar and 88.6% H ₂ (flow rates	
	$F(CH_4) = 25 \text{ sccm } F(Ar) = 40 \text{ sccm } F(H_2) = 500 \text{ sccm} [^3]$	22
Figure 2.1	Schematic of the reactor and the set-up for spatially resolved CRDS measurements [1]	28
Figure 2.2	Set-up of ontics directed to the etalon (vellow nath) and to the cavity for CRDS (the blue	20
rigare 212	nath).	29
Figure 2.3	Schematic of the OES experimental setup.	32
Figure 2.4	Diagram of the OES lens set up	32
Figure 2.5	$C_{9}H_{14}$ cluster used to model the H terminated 2 x 1 reconstructed diamond (100) surface	33
Figure 2.6	MM region (diamond lattice) and the central OM region (ball and stick C ₉ H ₁₄ cluster) used	
8	to model the diamond (100) H-terminated surface.	34
Figure 3.1	Calculated 2-D(r, z) mole fraction distributions of CO ₂ , CH ₄ , CO and H ₂ (in %), T_{gas} and n_e for	-
0	base reactor conditions ($P = 1$ kW, $p = 150$ Torr) and 35% CH ₄ / 35% CO ₂ / 30% H ₂ gas	
	mixture (<i>i.e.</i> $R = 0.5$). Given the assumed cylindrical symmetry, only half (in the radial	
	direction) of each 2-D distribution is displayed. ^[9]	38
Figure 4.1	Plot of optical emission intensities from the $CO_2/CH_4/H_2$ gas mixture of CH [*] , C_2^* , CO^* , H_{α}	
0	and H_{β} as functions of height, z, above the substrate. Each emission has been normalised to	
	unity.	40
Figure 4.2	Plot of optical emission intensities from the CO/H ₂ gas mixture of CH [*] , C ₂ [*] , CO [*] , H _{α} and H _{β}	
U	as functions of height, z, above the substrate. Each emission has been normalised to unity.	41
Figure 4.3	Plot of measured emission intensities of the CO* species as a function of height above the	
-	substrate, z, in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different	
	emission intensity scales are used for each gas mixture in order to compare the spatial	
	distribution more effectively.	42
Figure 4.4	Calculated 2-D(r , z) gas temperature, T_{gas} , (left) and electron density distributions, n_{e} ,	
	(right) for the CO ₂ /CH ₄ /H ₂ gas mixture with base reactor conditions as discussed in section	
	2.1. Given the assumed cylindrical symmetry, only half (in the radial direction) of each 2-D	
	distribution is displayed. ^[3]	43

Figure 4.5	Plot of measured emission intensities of H_{α} as a function of height above the substrate, <i>z</i> , in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more	
	effectively.	44
Figure 4.6	Plot of measured emission intensities of H_{β} as a function of height above the substrate, <i>z</i> , in both the CO ₂ /CH ₄ /H ₂ gas mixture and the CO/H ₂ gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more	
	effectively.	44
Figure 4.7	Plot of measured emission intensities of the CH* species as a function of height above the	
0	substrate, z, in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different	
	emission intensity scales are used for each gas mixture in order to compare the spatial	
	distribution more effectively.	45
Figure 4.8	Plot of measured emission intensities of the C_2^* species as a function of height above the	
	substrate, z, in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different	
	emission intensity scales are used for each gas mixture in order to compare the spatial	
	distribution more effectively.	46
Figure 4.9	Plot of the measured column density of the $OH(X, v=0)$ radical as a function of height above the substrate z for the plasmas formed from the base $OO_2/OH_2/H_2$ and OO/H_2 gas	
	mixtures All narameters are discussed in Chapter 2	47
Figure 4.10	Plot of the measured column density of the $CH(X, y=0)$ radical as a function of height above	17
0	the substrate, z, for the plasmas formed from the base $CO_2/CH_4/H_2$ and CO/H_2 gas	
	mixtures. All parameters are discussed in Chapter 2.	48
Figure 4.11	Reaction mechanisms for the rearrangement reaction of surface oxygen radical to OH, and	
	incorporation of oxygen into the diamond surface from a surface carbonyl.	49
Figure 4.12	Reaction mechanism showing the incorporation of oxygen into the diamond surface from	
	surface oxygen radical to an ether -like structure	50
Figure 4.13	Energy profile for reaction C, a large energy barrier is present for the transformation of an	
	oxygen surface radical to an ether type structure	50
Figure 4.14	C ₉ H ₁₄ cluster with C-C insertion and C-H insertion sites labelled, only the QM region is	
	shown for clarity.	51
Figure 4.15	Example of OH insertion into the C-C bond with nuclei labelled as a, b and c	51
Figure 4.16	Plot of the calculated energies against constraint value, q, calculated for the insertion of OH into the C-C bond	52

List of Tables

Table 1.1	Properties of diamond ^{[1][2]}	6
Table 4.1	Comparison of energies calculated by QM and QM/MM for reaction A and B	50

Chapter 1 - Introduction

1.1 Why diamond?

Diamond is one of the most researched materials. For centuries its beauty has meant that it is prized above all other natural gemstones, but more recently its many other extraordinary qualities have drawn scientists to it (Table 1.1).

Property	Magnitude
Mechanical Hardness	90 GPa
Bulk modulus	1.2x 10 ¹² Nm ⁻²
Compressibility	8.3 x 10 ⁻¹³ m ² N ⁻¹
Thermal conductivity (at room	2 x 10 ³ Wm ⁻¹ K ⁻¹
temperature)	
Thermal expansion coefficient (at	0.8 x 10 ⁻⁶ K ⁻¹
room temperature)	
Optical Transparency	Broad (from the deep UV to the far IR region of the electromagnetic
	spectrum)
Resistivity	$\approx 10^{16} \Omega$ cm (electrical insulator at
	room temperature)
Resistance to chemical corrosion	High resistance
Radiation hardness	High hardness
Conductance	Diamond can be doped to become a semiconductor with a wide band gap of 5.4eV

Table 1.1 Properties of diamond^{[1][2]}

These properties have made it a valuable material for use in various electronic applications such as in high-power lasers and transistors (because it has a high thermal conductivity but low electrical conductivity so it acts as a heat sink) as well as in machine and cutting tools.

Since natural diamond is expensive and may have flaws, cheaper synthetic routes to make diamond have been much sought after. The problem with diamond is that it is not the most stable form of carbon at room temperature and pressure; graphite is, this is due to its lower enthalpy of formation. Interconversion between the two allotropes cannot be achieved by thermal activation due to a large activation barrier; hence other routes have had to be developed. ^{[3][4]}

1.2 Different Techniques for Diamond Synthesis

The most common synthesis of diamond is based on the natural formation of diamonds, under high temperatures and pressures. This is because diamond is the most dense allotrope of carbon, hence graphitic and amorphous forms of carbon are the less stable form of carbon under these conditions. This synthesis method is called the high-pressure high-temperature (HPHT) route (pressures of around 100,000 atm, temperatures of around 2500K and the use of a molten metal catalyst are required).^[4] This process forms diamond grit that contains single crystal diamonds ranging from micrometres (μ m) to millimetres (mm) in size. It is this diamond powder that is used to increase the strength and hardness in tools such as drill bits, saws and can be used as abrasive in dust form. HPHT diamond has got fewer flaws and much more reproducible properties than natural diamond, another reason why it is favoured in industry.

Optical transparency over a broad region of the electromagnetic spectrum, hardness, being chemically inert, high thermal conductivity and a low coefficient of thermal expansion all mean that diamond lends itself well to being brilliant for use as a window material. The HPHT process cannot form diamond films but an alternative, more recently developed process called chemical vapour deposition (CVD) can be used. ^[5]

1.2.1 Chemical Vapour Deposition

CVD is based on the concept of adding individual carbon atoms to a substrate in the required sp^3 -hybridized structure to form diamond as opposed to any other allotropes of carbon. The most commonly used diamond CVD gas mixture is CH₄/H₂, the methane acts as the carbon source for diamond growth and the hydrogen has many purposes that will be discussed in section 1.3. It is a well-established technique where gas phase reactions above a solid substrate result in deposition upon the substrate. ^{[1][6]} For diamond growth to occur the carbon containing gaseous reactants must be activated and the carbon must be deposited as an sp^3 hybridised structure as opposed to the sp^2 hybridised carbon that results in graphite and other amorphous carbon forms. There are many ways in which to activate the reactant gas mixtures, the various reactors can be put into three categories; electric discharge (DC arcjet or microwave), combustion flame and thermal (hot filament).

1.2.2 Arcjet Reactors

The DC arcjet is the most common type of plasma jet. Plasma jets form a jet of ionized particles, atoms and radicals by forcing the gas mix through a high power electrical discharge at quite high flow rates (litres per min). This jet then expands into another chamber, which has a lower pressure, and collides with the substrate at high velocities. Within a DC arc jet reactor the current is provided by a direct current, which keeps it high and fairly stable. ^{[2][7][8][9]} The DC arcjet technique is limited only by the small area that can be coated, the problems caused by cooling (thermal shock on jet ignition and extinguishing limit the substrates that can be used), and the high power required. But it has yielded the highest growth rate of all the CVD techniques (greater than 900 μ m h⁻¹)^[10] and can produce high quality diamond films.



Figure 1.1 Diagram of DC arc jet (plasma torch), left. Picture within DC arc jet reactor, right.^[11]

1.2.3 Hot Filament Reactors

Researchers at the National Institute for Research in Inorganic Materials (NIRIM) were the first to build a 'hot filament reactor' that grew quality diamond at good rates.^[12] The hot filament CVD (HFCVD) method requires that the process gases are slowly introduced to an evacuated chamber and a low pressure of 20-30Torr is maintained. The hot metal coil is electrically heated to over 2200°C and so must be an unreactive metal such as tungsten; it is this that activates the process gases. The substrate sits a few millimetres below the filament and is heated to between 700-900°C. This is the simplest CVD technique and is relatively cheap, producing acceptable quality polycrystalline diamond films and can coat large areas (industrially up to 350 mm x 375 mm,^[13] and it has been reported that research groups have coated areas up to 50cm x 100cm with diamond film).^[14] There are a few problems with this technique, the greatest being that it is difficult to avoid contaminating the film produced with filament material. Often this means diamond produced is of insufficient quality to use for some applications, such as electronics. Also the filament has a limited lifetime and so allows a maximum deposition time. It reacts with the gas mixture over time and forms a metal carbide, this affects resistivity, and the filament becomes brittle. Also it is difficult to improve growth rates or perform more complex growths such as inducing orientation, because there a few gas phase ions present in the thermal environment. ^[2] Despite this HFCVD is a useful technique and is often used in research and industry.^{[15][16]}



Figure 1.2 Diagram of hot filament reactor, left. Picture of a hot filament reactor, right [11]

1.2.4 Microwave Reactors

Microwave (MW) CVD is the most widely used industrial diamond production technique, despite its higher cost and similar set up compared to HFCVD. The advantages of this technique far outweigh the greater expense. A much wider variety of gas mixtures can be used than with other techniques, it produces cleaner diamonds (as there is no filament leading to contamination), a fairly large area can be coated and there are ions present in the discharge. This means that biasing the substrate can change the deposition conditions. Recently more research has been undertaken to increase the deposition area, the most successful techniques are with surface wave excited plasmas using microwave linear antennas, leading to a deposition area of up to 300mm x 300mm. ^{[17][18][19][20][21]}

Within the reactor, microwave power is coupled into the chamber to create a discharge via a dielectric window. The microwaves couple energy into the gas phase electrons, which transfer their energy to the gas through collisions. The collisions cause heating and dissociation and hence the gas is activated for deposition. The two main types of microwave reactors are the NIRIM- type and the ASTEX- type.^[2]

The former was invented by the NIRIM group shortly after they created the first hotfilament reactor.^{[22][23]} The electric field maximum is centred in the middle of the discharge tube, which is where the stable plasma is formed. The substrate is introduced from the bottom of the discharge tube. The ASTEX-type works in a different way, TE_{10} microwave mode is converted in the waveguide to the TM_{01} mode by an antenna, and the microwaves are then coupled into a water-cooled metal cavity through a quartz window.^[24]



Figure 1.3 Top left, diagram of a 'NIRIM type' microwave plasma reactor. Top right, diagram of an 'ASTEX-type' microwave plasma reactor. Bottom, picture of a microwave reactor. ^[11]

1.3 Gaseous Reactions

Within the CVD reactor, many complex chemical and physical processes occur. Most commonly the gas feed mixture is comprised of a hydrocarbon in excess hydrogen, other elements such as oxygen, nitrogen and boron have previously been added in various forms. Reasons for oxygen addition will be discussed in section 1.3.1. The gas mixture can be particularly difficult to understand and model, not least because of the steep gas temperature (T_{gas}) gradient present (especially within microwave plasma chemical vapour deposition (MWPCVD) reactors).^[25] Within the plasma ball T_{gas} is approximately 3000K, but near the water-cooled walls of the reactor, it is not much above room temperature. Total gas phase number densities of species are dependent on temperature (as are their relevant rates of reactions and stabilities), and so because of the steep gas temperature gradient, it is a sensitive function of location within the reactor. Reaction rates for interconversion are therefore also similarly dependent on location within the reactor.



Figure 1.4 Scheme showing the major H-shifting reactions and interconversion in and between C₁H_x and C₂H_y species

The number density of various species can be investigated using a variety of spectroscopic techniques, many of which are laser based. In favourable conditions, modern techniques can allow determinations of absolute column densities as functions of process conditions. Stable hydrocarbon species can be monitored by direct line of sight IR absorption methods using tuneable diode lasers^{[25][26]} and/or quantum cascade lasers. ^{[28][29]}

Such studies have shown that although a carbon source is required, within the plasma ball the specific input carbon source gas is irrelevant. Usually the input gas for the diamond CVD process will be CH₄, if it is not, then conditions on entering the reactor (relatively high H atom densities and low T_{gas}) allow efficient conversion of the input gas to CH₄.^[1]

The H atoms are formed within the hot plasma region through the dissociation of the input gas H₂, with a dissociation ratio of $[H]/[H_2] \sim 0.008.^{[31][32]}$ The H atoms formed do not recombine easily due to the need for a third body (see reaction 1.9), this means that H atoms are present throughout the reactor volume allowing efficient conversion between the input gas to CH₄ (for example acetylene, as shown in the reverse reaction 1.1).

$$2CH_4 \Longrightarrow C_2H_2 + 3H_2$$
 (1.1)

Figure 1.5 clearly shows the three main modelled regions within the reactor, the cool region C near the gas inlets (with $T_{gas} \sim 500\text{-}1500$ K), the peripheral region B (the annular shell around the hot plasma region with $T_{gas} \sim 1500\text{-}2000$ K) and the hot plasma region A ($T_{gas} \sim 2000\text{-}3000$ K).

The temperature change between regions affects the equilibrium of reaction 1.1. As the forward reaction is endothermic it is favoured by an increase in temperature, so the equilibrium shifts in its favour as the CH₄ rich mixture diffuses towards regions A and B with higher temperatures. CH₄ to C₂H₂ conversion occurs most efficiently in region B (figure 1.5), this is because when T_{gas} reaches ~1700 K there is a change in the sign of Gibb's energy (ΔG) from positive to negative, meaning that the products in 1.1 are favoured,^[33] especially as the change in entropy (ΔS) is significant (2 moles to 4 moles). When T_{gas} is below ~1700 K i.e. in region C, the reverse of reaction 1.1 is favoured and CH₄ dominates in this area.



Figure 1.5 2D (*r*, *z*) plots of the calculated gas temperature, T_{gas} , in kelvin (left) and CH₃ number density, (right) for reactor chamber diameter = 12cm, reactor chamber height = 6cm and substrate holder diameter of 3 cm. Pressure *p*= 150 Torr, input power *P* = 1.5 kW and gas mixture of 4.4% CH₄, 7% Ar and 88.6% H₂ (flow rates *F*(CH₄)= 25 sccm, *F*(Ar)= 40 sccm, *F*(H₂)= 500 sccm). The color scale increases in 13 equal intervals, e.g. from 303–505 to 2729–2931 K (left), and from 0–3.02 × 10¹³ cm⁻³ to 3.62 × 10¹⁴–3.92 × 10¹⁴ cm⁻³ (right).^[3]

C₂, CH and H(n=2) species can all also be measured within the reactor using cavity ringdown spectroscopy (CRDS)^[27], quantum cascade laser spectroscopy^{[28][29]} and optical emission spectroscopy (OES)^[30] (further discussed in section 1.5). These optical diagnostics seem to show that these species are also insensitive to the choice of carbon source gas.^[3] Despite the presence of C₂ and CH, these species may not be of direct importance in the diamond growth mechanism as they have a limited abundance when compared to the methyl radical (which is presumed to be the major growth species for diamond CVD) near the diamond surface. Their role in growth will be discussed later. ^[1]

Methyl radicals have also been monitored by resonance enhanced multiphoton ionisation (REMPI) (in environments with low densities of ions and electrons, so for example hot filament reactors) and line-of-sight absorption in the UV region. CRDS can quantitatively measure radical species with the use of pulsed tuneable dye lasers. Results obtained using CRDS are complemented well by those measured using OES. This is a useful qualitative technique that is fairly quick and simple, it measures emissions from excited states of species and provides a way to determine relative densities of H(n=1) atoms in MW plasmas using actinometry (use of small amount of inert tracer species).^{[1][30]} In order for all these analysis techniques to be of use, we must have a detailed understanding of gas phase chemistry of diamond CVD.

After the first few published attempts at CVD diamond growth, it was shown that when atomic hydrogen was present the diamond grew faster.^{[5][34]} This is because atomic hydrogen plays many important roles in the growth process. Apart from its part in the hydrocarbon gas processing (scheme 1.4), it etches sp²-hybridised carbon much faster than the sp³-hybridised carbon in diamond; this returns graphitic and amorphous carbon back to the gas mixture. As well as this, atomic hydrogen helps to maintain the surface by terminating surface carbon atoms, which keeps the sp³ diamond lattice stable (these H atoms can be thermally desorbed or abstracted by atomic hydrogen to create reactive surface sites). Within the gas mixture atomic H prevents the build up of large structures. These large structures could be deposited on the surface of the substrate and inhibit diamond growth. ^{[1][2][3][35][36]}

Atomic hydrogen can be formed within the chamber in the activation region, by electron impact in a plasma-enhanced system (reaction 1.2) although this is, in fact, a negligible process as the high pressures within the MW reactor (150 Torr) causes reaction 1.3 to be the predominant atomic H forming reaction. So in plasma enhanced systems most hydrogen atoms are formed through collision with heavy molecules (reaction 1.3). ^{[1][2][3][35][36]}

 $H_2 + e^- \longrightarrow H + H + e^-$ (1.2)

$$H_2 + M \implies H + H + M$$
(1.3)

Also within the activation region, other molecules get fragmented into radicals and atoms. ^{[1][2][3][5][35][36]} After this, the activated molecules can travel to the substrate via convection and/or diffusion. The dominant process out of convection and diffusion depends on the reactor system used. As well as this, it takes much longer for the transport to the surface compared to hydrocarbons reacting with atomic H, hence these latter reactions can equilibrate.

Reaction 1.4 shows abstractions that would occur in the hot regions of the reactor, whereas reaction 1.5 shows additions that would occur in cooler regions of the reactor (M is a third body). Reactions 1.6 - 1.8 show how C_2 species can be formed by radical recombination.

$$CH_y + H \longrightarrow CH_{y-1} + H_2 \qquad y = 4-1$$
 (1.4)

$$CH_{y-1} + H + M \longrightarrow CH_y + M \qquad x = 4-1$$
 (1.5)

$$CH_x + CH_y + M \implies C_2H_{x+y} + M$$
(1.6)

$$CH_{x} + CH_{y} \longrightarrow C_{2}H_{x+y-1} + H$$
(1.7)

$$CH_x + CH_y \longrightarrow C_2H_{x+y-2} + H_2$$
(1.8)

A boundary layer can form where the composition of gas is disturbed by the effect of the reactions happening at the surface of the substrate. Reactants must diffuse through this to reach the substrate surface and hence the boundary layer can limit growth rates by affecting the arrival rate of reactants to the surface. ^{[1][2][5][28][35]}



Figure 1.6 Schematic of the processes occurring during diamond CVD. [1][2]

Atomic H is in steady state levels partly due to homogeneous removal through recombination of two hydrogen atoms, reaction.

$$H + H + M \Longrightarrow H_2 + M$$
(1.9)

This is pressure dependent due to the need for a third body, M, to carry away excess heat of recombination. Other loss mechanisms are through reaction with gaseous hydrocarbon species such as the reverse of reaction 1.9. At low pressures these homogeneous removal

reactions have a very low rate and in thermal, plasma and combustion systems, H is nearly in chemical equilibrium and homogeneous recombination is only of concern within the boundary layer. So a heterogeneous mechanism must be responsible for H atom removal, this occurs primarily on the reactor walls and on the diamond surface (which is a sink for hydrogen). The recombination reactions with the surface are exothermic, as such the large amount of recombinations occurring (as shown by a large recombination coefficient of 0.16 at 1200K) ^[37] contribute to the heating of the substrate, which helps the formation of diamond over graphite.

Once the reactants reach the substrate surface, they can either adsorb and react, desorb into the gas phase (competitive loss process) or diffuse around near the surface until they reach an appropriate reaction site. A generic surface model is shown below, which represents activation of a surface site and addition to the radical site; these are all fast and in steady state (reactions 1.10 - 1.12), C_D denotes a carbon atom on the diamond surface, which is either terminated by hydrogen (C_DH) or is a radical site C_D[•]. Reactions 1.10 and 1.11 are exothermic, which contributes to the heat flow in the CVD process.

$$C_DH + H \longrightarrow C_D + H$$
 (1.10)

$$C_D^{\bullet} + H \longrightarrow C_D H$$
 (1.11)

$$C_D + C_x H_y \longrightarrow C_D C_x H_y$$
 (1.12)

As there is much more atomic H present than activated hydrocarbon species, most often another atomic hydrogen will simply terminate the vacant site (as in reaction 1.11) but occasionally a C containing radical will react and thus a new C-C bond is formed, which is able to react further to extend the lattice (as in reaction 1.12). During diamond growth, the surface is almost saturated with H, which limits the availability of sites for the hydrocarbon species to chemisorb and limit migration once they are adsorbed. [2][5][35][36][38]

It is presumed that the growth species is a C_1 species. If the hydrocarbon species has more than one carbon, it's large size relative to the C-C lattice spacings, reduce the chance of reaching the surface to effectively adsorb. If the species can adsorb, the strain and steric effects make the newly formed bond weak. This means that the species is susceptible to thermal decomposition or removal via β -scission mechanism (this mechanism is also how non-diamond sp² carbon is etched).

The C_1 species that is most important in diamond growth is the CH_3 radical. It is thought that this is the major growth species as concluded by the culmination of *in situ* detection at the growing diamond surface (using techniques such as IR absorption spectroscopy, REMPI and mass spectrometry), isotopic labelling studies and kinetic models of the growth mechanism in comparison to the observed growth rates of diamond. Also it is a neutral species, this is important as diamond can be grown in both ion and electron rich environments (such as in MWCVD) as well as those with few gaseous ions (HFCVD). As briefly mentioned earlier, C_1H_x species where x<3 may not be directly important to diamond growth as they have a low concentration near the growing diamond surface. Despite this they may still contribute to diamond growth as they have a much smaller size than the methyl radical and as such they can react with more types of surface radical sites than the methyl species. ^{[1][2][3][35][36][38][39]}

Modelling of CVD has also been widely used; the main models describe conditions that underpin the process of CVD, these include power absorption, gas heating, heat and mass transfer, or plasma activation of the reactive gas mixture, and the gas-surface processes. These can be used to predict concentration distributions of neutral species, radical species and ions, gas temperatures and electron temperature within the reactor and growth rates of diamond. ^{[1][3][40][41][42][43][44]}

1.3.1 The Role of Oxygen

Various groups have altered the conventional hydrocarbon and hydrogen gas mixture with the addition of oxygen to MWCVD and combustion system CVD.^{[44][45][46]} This can be in the form of molecular oxygen or within other compounds. Carbon monoxide and carbon dioxide are commonly used.

There are many reasons for doing this. Adding a small amount of oxygen (or oxygen containing gas) can increase the film quality,^[21] it is thought that this is because it forms atomic oxygen and OH radicals which could act as etchants similar to atomic hydrogen, ^{[46][47][48][49][50][51][52]} hence returning non-diamond carbon structures to the gas mixture faster. Also oxygen can suppress the wall recombinations of atomic hydrogen, resulting in an increased concentration of hydrogen atoms for etching and the other vital roles it carries out as discussed in this section.^[50] There is also a link with the increase of O₂ resulting in a decrease of C₂ radicals (these have been associated with non-diamond carbon structures on the substrate).^[53]

The biggest reason to introduce oxygen into the system is that a lower temperature can be used for the substrate and hence a lower power could be used for the CVD process. ^{[47][54][55][56]} The power needed for MWCVD is a great expense and so reducing this is a major industrial goal. It has been reported that diamond has been deposited from C/H/O gas mixtures at substrate temperatures as low as about 400°C. ^[56] Importantly this lower temperature would also allow a much wider range of substrate materials to be used. The main problem with having oxygen within the feed gas is that above a certain amount it can oxidise the substrate, preventing deposition of diamond and can react with gas phase hydrocarbons to form CO resulting in a reduced amount of active species within the plasma.^[53]

Several investigations of the thermodynamics of the CVD process have been made into C/H/O gas mixtures to determine the effect of the process variables on the driving force for deposition in order for the process to be optimized.^{[57][58]} Obviously, introducing oxygen as molecular oxygen is a problem as the process gas would form a possibly explosive and dangerous situation, introducing it as various compounds involves careful planning to get the desired C:H:O ratio. This is important as the ratio strictly directs whether diamond, non-diamond growth or no growth occurs as superbly shown by the Bachmann diagram (figure 1.7). ^[59]



Figure 1.7 Simplified Bachmann C/ H/ O phase diagram. This shows how ratio of C:H:O in the process gas mixture affects the result of diamond CVD process, occurring in non-diamond carbon growth (pink area), diamond growth (pale blue area) or no growth (blue).

Bachmann investigated the results of many of his peers' experiments, as well as his own, in order to produce a C H O phase diagram for all major diamond chemical vapour deposition methods used. This showed that there was a very narrow band for diamond growth in which the ratio of C:H:O was correct. It was assumed that, like for the C/H gas mixtures, the process gas mixture was irrelevant, just the ratio of elements was important. It also provided a useful explanation for the variations of diamond quality deposited using different gas mixtures. ^[59]

1.4 Surface Chemistry of CVD Diamond Growth

The area of most interest within the plasma is the region just above the surface of the substrate. It is here that we can look at how the diamond is actually growing atom by atom. Three of the most researched diamond surfaces are the square (100) surface, triangular (111) surface and the less-well defined (110) surface (figure 1.8). For each of these surfaces the mechanism predicted for diamond growth is slightly altered due to the differing needs for nucleation or growth of the next layer to occur. The (111) surface requires three carbon atoms. Two carbon atoms are required for growth on the (110) surface. This is why the latter has the most understood mechanism of the three. The only growth mechanism discussed here will be for the (100)-2x1 surface as this is the surface modelled for the computational part of the project.



Figure 1.8 Idealised structures of the (111), (110) and (100)-2x1: 1H surfaces, showing step features. The large grey balls represent carbon atoms and the small white balls represent surface bound hydrogen atoms. ^[3]

It is generally understood that the reactive species within the gas can either adsorb to the substrate, rebound back into the gas phase or they can remain close to the substrate until a reaction site becomes available. Computational methods using density functional theory and hybrid quantum mechanical/molecular mechanics have shown that the minimum energy pathway of inserting a CH_x species into a surface C-H bond on the H-terminated (100) surface is essentially barrier less (when x < 3). ^[60] It is widely believed that the growth species is the methyl radical ^{[35][61]} although C₁ insertions account for 5-6% of single crystal and microcrystalline diamond growth as a maximum. ^{[62][63]} To justify this, C₂ species such as acetylene have also been proposed to directly add to the diamond lattice. ^[64] This is thought to be unlikely due to the need for a biradical site; the fraction of these is about ten times lower than that of monoradical sites. ^[38]



Figure 1.9 Main radical sites important for diamond growth on the (100) diamond surface during CVD. The sites are labeled A1, A2, A3, and A4 following the scheme of Skokov *et al.* [65]

Diamond growth is a slow process as the radical sites are much more likely to come into contact with, and react with, the more prevalent H atoms within the plasma, than the C_1 radical species involved in growth. Also surface reaction sites need to be directly adjacent to each other for deposition to occur, it is this that is mostly thought to be the limiting factor in growth.

The first mechanism (the HH mechanism, figure 1.10) proposed growth on the (100) surface was based on the mechanism for bicyclononane (BCN) growth, and this assumed that two hydrogen atoms terminated each carbon on the surface. ^{[66][67]} This was proved to be wrong as the diamond would be highly strained due to high steric repulsion between adjacent H atoms. ^[68] Later mechanisms terminated each carbon with one hydrogen atom and bonded to the neighbouring carbon atom to fulfil valency requirements when the diamond surface was in the presence of lots of H atoms. Under CVD conditions this is the most thermodynamically stable form with the lowest enthalpy of formation, ΔH_f . STM and atomic force microscopy (AFM) images show that the diamond surface used for modelling later in the project can be described as the diamond (100)-2x1:1H surface reconstruction.



Figure 1.10 Model clusters for the original HH mechanism. The upper-left cluster is bicyclononane and the lower right is adamantane. A dot represents a radical site. [67][69]

Another mechanism to be proposed, was called the GDSB mechanism^[70] but on further analysis using MM3 molecular mechanics^[61] showed problems with the mechanism. Importantly the analysis also showed that the GDSB mechanism and the HH mechanism could be modified and combined (figure 1.11). ^[61]



Figure 1.11 The modified HH mechanism portion of the combined GDSB and modified HH mechanism. C_d denotes a surface carbon atom and a dot represents a radical site. ^{[35][61]}

The modified HH mechanism reacts preferentially through a diradical route due to steric effects. Images of the diamond surface shows distinct steps and smooth morphologies, this implies that step edges are much more reactive than isolated sites, with lower steric hindrance and migration is much more facile than previously thought.^[71] It has also been shown that methyl radicals are preferentially added to the end of dimer rows on the (100)-2x1:1H surface, this can be predicted using the GDSM mechanism.^{[1][2][3][5][35][36]}

When looking at the mechanism of growth upon the surface of the substrate, it is mostly presumed that the gas mixture used contains species made up of carbon and hydrogen only. But within my project we spent time looking at gas mixtures with oxygen containing components. So although much of the above must be considered, oxygen-containing compounds within the gaseous mixture must be looked at and what affect these may have on the growth mechanism. This is considered in more detail within chapter 3, when discussing the Bristol-Moscow model.

1.5 Optical Diagnosis

1.5.1 Cavity Ring- Down Spectroscopy

One of the major techniques used within this project is cavity ring- down spectroscopy (CRDS). It is a laser based absorption spectroscopy technique that has a high sensitivity, especially when compared with traditional absorption spectroscopy techniques. This is because it provides a large path length (up to 10s of kilometres) whilst still being a bench top size and it does not suffer from shot-to-shot variations in laser intensity.^[72] It is so sensitive that it is can be used to detect trace amounts of radical species within the

atmosphere^{[73][74]} as well as within the reactors used for chemical vapour deposition of diamond. ^{[27][75][76][77][78]}

The most important part of the CRDS technique is the two high reflectivity dielectriccoated concave mirrors (>99.9%) that form a cavity into which laser light is injected through one end mirror. This then reflects most of the incident light, but a small percentage couples into the cavity and its intensity rings down exponentially with time. Cavity losses occur due to processes such as sample absorption and mirror transmission. The time decay is determined by the mirror reflectivities, this is because they must have a high enough reflectivity to trap the laser pulse within the cavity. This causes the pulse to propagate back and forth between the mirrors. Each time it is reflected by the mirrors, a small percentage of the trapped pulse is retransmitted out of the cavity, producing a detectable signal.

The signal is measured by a photosensitive detector, and appears as an exponential decay in time. The signal is fitted by a computer to a first-order exponential function to calculate the decay time constant for each pulse.

When a gaseous sample is present within the cavity, the ring- down time is reduced. Using the ring- down time from both the empty cavity and the filled cavity, the number density of the absorbing species (dependent on the laser wavelength) can be determined. [72][78][79][80][81]

Traditional laser absorption spectroscopy methods are limited by fluctuations in the intensity of the light entering the sample, I_0 . When detecting very weak absorptions, the change in intensity of the light as it passes through the sample is very small compared to the initial intensity. CRDS differs from traditional laser absorption spectroscopy methods as the required absorbance is derived from the time dependence of the signal and not from its absolute amplitude, thus making it immune to the fluctuations I_0 .

The detection limit is also much lower than in any single pass absorption technique, as it is effectively a multipass technique. The mirrors must be precisely aligned in order to trap the laser pulse (for a few microseconds) forming a pathlength effectively kilometres long. This is 10-1000 times longer than traditional multiple reflection. This means that absorption coefficients can be obtained directly. ^{[72][81][82][83][84]}



Figure 1.12 Schematic of the CRDS set-up

CRDS can use tunable lasers with high resolution; also a doubling crystal can be used to extend the laser wavelength from visible to UV range. This makes it a very versatile tool for studies of molecular spectroscopy and molecular dynamics. If a pulsed laser source is used, the signal is not affected by the pulse-to-pulse intensity fluctuations; this is a major

source of noise when using a normal multipass cell. Nowadays there has been a significant amount of work done using continuous wave (cw) lasers, but pulse lasers remain dominant in this field.^{[74][76][78][79][80]}

1.5.2 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) is a very useful technique and has been extensively used to explore the process of chemical vapour deposition of diamond. In fact it was one of the first spectroscopic methods used to probe the plasma within a microwave (MW) reactor for CVD. ^{[30][85]} It has become widely used because it is an easy, quick, sensitive and non-invasive technique. So it doesn't affect or disturb the plasma within the microwave reactor. The most complicated part of OES is the interpretation of the data produced; this is because for the spectra to be understood you must also understand the processes of excitation and de-excitation of the species being investigated. ^[86]

Despite this, OES has found many uses, and is especially beneficial when coupled with cavity ring- down spectroscopy. It was found early on that both the density of the plasma species and the electron energy distribution function determined optical emission intensity.^[87] This meant that it could be used as a probe for these, but in order for this to be useful, a small amount of noble gas was added and monitored along with the species being looked at. This way, as the noble gas density is known, the excitation efficiency of the species could be determined by dividing the emission intensity of the excitation level by the noble gas density.^[87]

The use of a tracer species is called actinometry, and the noble gas being excited is an actinometer. This technique can be used to look at the dissociation of H_2 and to determine the concentration of a species such as H(n=1) atoms, $[^{30}]^{[88]}[^{89}]$ within the plasma, by looking at the ratio of emission intensity of actinometer and species investigated. $[^{86}]$ Actinometry can give a useful insight into the mechanism of CVD and how the feed gases are changed within the reactor.

A lot of work has been done on increasing the resolution of measurements of emissions such as those from H_{α} (this is the Balmer line emission of excited H(n=3) to H(n=2)). This is because the gas temperature, T_{gas} , can be deduced from the H_{α} Doppler line width measurements, ^{[90][91]} H₂ rotational temperature and the H₂ Fulcher (0,0) Q1 line. ^[92] The most reliable T_{gas} was given by the H₂ Doppler line width.

A radical of interest is C₂, in particular the C₂($d^3\Pi_g - a^3\Pi_u$) Swan band has been investigated within Ar - rich MW activated Ar/H₂/CH₄ gas mixtures. This is an easily detectable carbon containing radical, its absorption and emission can be detected using CRDS and OES respectively. It was found that the C₂ emission has to be directly proportional to the C₂ concentration and this correlated well when measured by white light absorption spectroscopy. ^[93] A linear relationship was discovered between the C₂ Swan band emission intensities and C₂ column densities (measured using CRDS). ^[27]

Looking at individual species within the plasma and how they correlate to column density has been one area of interest for OES. Also of interest is how these results found using OES relate to the diamond film quality and growth rate. Using the ratio of the maxima of spectral peak emission for $CH:C_2$, $CH:C_3$ and $H:C_2$ can clearly be correlated to process conditions of good quality diamond. This means that OES can be used to help find different gas mixtures and conditions for growth of good quality diamond. ^[94]

1.6 Modelling and Other Computational Studies

Modelling is an important tool when investigating the processes that occur during diamond CVD. It is very difficult to model the plasma because there are many aspects that must be considered. This includes the numerous species present within the plasma and reactions between them; these can be both thermally driven and electronically driven leading to spatial inhomogeneity due to the conditions within the reactor.

Once a model has been made, experimental results can be used to test and validate it. A successful model can be used to convert measured column densities into spatially resolved number densities to create a cross section of the plasma. So experimental results and models are mutually useful for the explanation and verification of simulated and experimental results.

Complex models such as the Bristol- Moscow model can provide a 2D description of the major processes taking place in the reactor. These processes include the activation of the gas mixture, gas-phase processes (kinetics and transport) and gas- surface reactions (active sites being created and active species being deposited). They show the variation in concentration of species throughout the reactor and how this is related to temperature, this can support theories such as H atoms react with the surface sites and hence immediately above the substrate their concentration is reduced, this is shown figure 1.13. ^[3]



Figure 1.13 2-D (*r,z*) plots for calculated electron (left) and H atom (right) concentrations. Conditions modelled were for reactor chamber diameter = 12cm, reactor chamber height = 6cm, substrate holder diameter of 3 cm and substrate temperature, T_s =973K. Pressure *p*= 150 Torr, input power *P* = 1.5 kW and gas mixture of 4.4% CH₄, 7% Ar and 88.6% H₂ (flow rates *F*(CH₄) = 25 sccm, *F*(Ar) = 40 sccm, *F*(H₂) = 500 sccm).^[3]

Other computational methods can also be useful. Modelling the surface of the diamond substrate and calculating energies of this surface undergoing processes such as hydrogen abstraction, migration across the surface and incorporation of gaseous species into the surface, can help one to understand if a process can feasibly occur and how likely it is. This has been used to look at boron doping of diamond, ^[95] how CO interacts with the surface, ^[96] growth mechanisms related to diamond crystal size, growth from different C_1 species ^[97] and other insertion mechanisms.

Simpler, 1D models have also been put to good use. Kinetic Monte Carlo simulations can be used to estimate values for the rates of processes such as desorption and a 2D model has been used to find what species (and their concentrations) adsorb on the surface. [98][99][100]

1.7 Aim of the Study

The plasma of systems with oxygen containing compounds has been fairly widely researched, but it has been presumed that, other than the ratio of C:H:O, the specific starting gases have no real effect on the plasma chemistry. This is the case for a C/H system, usually CH_4 is used but even if another carbon containing gas such as C_2H_4 is used it quickly converts the input gas to CH_4 as the gas enters the reactor where there is a relatively high H atom density and low T_{gas} .

I will be comparing the C/H/O system of CO and H_2 gas to that of a $CH_4/CO_2/H_2$ gas mixture, which has previously been investigated by this group. It is believed the stability of CO will mean that it is less likely to react as readily as CO_2 to form atomic C, this is essential for producing the C-containing radicals that lead to diamond growth. The plasma chemistry will be probed using laser techniques including optical emission spectroscopy (OES) and cavity ring-down spectroscopy (CRDS). Species being looked at within the plasma are OH, CH, C₂, CO and H radicals. The results obtained can be compared to the 2-D model in order to find out how accurate the model is and to gain understanding of the processes within the plasma. This may lead to changes being made to the model to make it more reliable and accurate.

Very little work has been reported detailing how oxygen-containing species within the gaseous mixture interact with the diamond surface. Thus it is useful to look at the energetics of processes such as abstraction of surface-bound hydrogen atoms by OH radical, to see if this is likely event, and also to look at the incorporation and migration of oxygen species on the surface. This will provide a useful insight into how oxygen affects the diamond surface within the CVD process.

1.8 References

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Chapter 2 - Experimental

2.1 The Reactor

The microwave reactor has been specially designed my Element Six Ltd. The reactor has a vertically aligned aluminium cylinder (volume of 600cm³ not including sidearms). The sidearms are stainless steel, tubular and connected with knife edge bellows to allow adjustment of height for the optics (relative to the top surface of the 30mm diameter Mo substrate). These are mounted rigidly to a platform that supports all of the beam steering optics and the entire optical assembly (figure 2.1).

The mirrors used for CRDS measurements are fitted on the end of each side arm, in finely adjustable mounts. The water-cooled base maintains temperature of the substrate. Stainless steel pipes (6.25mm diameter) feed in the pre-mixed gas near the top of the reactor, whilst the chamber is vented by six piping ports in the base (also 6.25mm diameter). Mass flow controllers (MFC) that have a 0.1% error margin control the individual gas flow rates. A two-stage rotary pump (Edwards E2M8) maintains a high vacuum (10⁻³ Torr). Stable operation occurs between 40 and 200Torr. A feedback controlled throttle valve, a Pirani gauge and a Baratron capacitance manometer enable stable monitored pressure use. ^[1]

A 2kW Muegge power supply and generator create microwaves as 2.45GHz and these are coupled into the TM_{01} mode in the chamber through a quartz window and a rectangular waveguide.



Figure 2.1 Schematic of the reactor and the set-up for spatially resolved CRDS measurements. ^[1]

Base conditions used were chosen to be: total pressure, p = 150 Torr, input power, P = 1 kW and input flow rates $F(CH_4) = F(CO_2) = 175$ standard cm³ per minute (sccm), $F(H_2) = 150$ sccm for the CH₄/CO₂/H₂ gas mixture. For the CO/H₂ gas mixture; total pressure, p = 150 Torr, input power, P = 1 kW and input flow rates F(CO) = 206 sccm and $F(H_2) = 294$ sccm. The two gas mixtures have the same ratio of C:H:O, 35:30:35.

2.2 The LASER Setup

In order for the CH (X, v=0) radicals and OH (X, v=0) radicals to be monitored by CRDS a pulsed Nd:YAG pumped dye laser (Continuum Surelite IV plus Spectra-Physics PDL-3) was used. Each laser pulse is a few nanoseconds long, the repetition rate is 10Hz and the output was set at 355nm (for the Exalite 428 dye) and 532nm (for the Rhodamine 640 dye).

The dyes used are Exalite 428 and Rhodamine 640 (both in methanol) to probe the column densities of CH and OH radicals. This looked at the $CH(A^2\Delta \leftarrow X^2\Pi)$ transition and $OH(A^2\Sigma \leftarrow X^2\Pi)$ transition which occurred at ~431nm and ~306nm respectively. For each radical a different pair of mirrors was used, (these were both made by LayerTec, Ltd) reflectivities were approximately 0.999, and they were all plano-concave with a radius of curvature of 1m.

The separation between the two mirrors was 84cm. A photo-multiplier tube (PMT) was used to detect light escaping the cavity.



Figure 2.2 Set-up of optics directed to the etalon (yellow path) and to the cavity for CRDS (the blue path).

All data was collected and analysed using custom-built LABVIEW programs communicating with an 8 bit digital oscilloscope LeCroy 9361, dual channel, 300 MHz, 2.5 Gsamples/s via a general purpose interface bus.

2.3 Cavity Ring- Down Spectroscopy (CRDS) Calculations

Cavity ring-down spectroscopy will be used to look at the spatial distributions of OH radicals and CH radicals within the plasma.

2.3.1 Spatial Profiles

The measurement taken using CRDS can be understood using the following equations to describe transmission, ring-down time and decay rates:

The transmission intensity as a function of time, t, is given by;

$$I_t = I_0 exp\left(\frac{-t}{\tau}\right) \tag{2.1}$$

where τ is the ring-down time. The ring- down time in an empty cavity, τ_0 , is given by:

$$\tau_0 = \frac{L}{c|1-R|} \approx \frac{L}{c(1-R)} \qquad \text{for } R \approx 1$$
 (2.2)

When an absorbing species is present in the cavity;

$$\tau \approx \frac{L}{c(1-R+\alpha d)}$$
 for $R \approx 1$ (2.3)

c in these equations is the speed of light, *R* is the reflectivity of mirrors, *L* is the distance between the two mirrors and *d* is the effective path length of the absorbing species. The absorption coefficient α can be related to the number density of the absorbing species, *n*, and its absorption cross-section, σ , by the following equation:

$$\alpha = n\sigma \tag{2.4}$$

The difference between decay rates measured for the empty cavity and with the absorbing species present can be expressed as:

$$\Delta k = \frac{1}{\tau} - \frac{1}{\tau_0} = \frac{c(1 - R + \alpha d)}{L} - \frac{c(1 - R)}{L} = \frac{c\alpha d}{L} = \frac{nc\sigma d}{L}$$
(2.5)

It is this difference Δk (in s⁻¹) that is proportional to the density of absorbing species. If the transmitted intensity for the cavity with and without the species of interest (or on and off an absorption line of the species) is measured as a function of time, *t*, and the decay rates calculated, then an absolute column density, *D* and absolute concentration, *n*, can be deduced.

$$D = \frac{L \cdot \Delta k}{c\sigma}$$
 $n = \frac{L \cdot \Delta k}{c\sigma d}$ (2.6 and 2.7)

During this experiment it must be noted that the systems being probed are inhomogeneous in nature. The plasma is centred over the substrate and does not spread into the side arms. There is a steep temperature gradient present, and species are distributed non-uniformly within the reactor. The column density (equal to number density multiplied by the effective path length) can only be measured over the entire cavity length, L.

Column densities and number densities of both CH (single peak) and OH (three peaks) were calculated from spectral lines measured by CRDS. These were fitted with a Gaussian line shape in order to calculate their areas using the following formula (where $\{...\}$ denotes column density and *Y* is the relevant spectral carrier).

$$\{Y\} = \frac{8\pi L \overline{v}^2 g_l}{A_{oo} p_{line} g_u} \int_{line} \Delta k d\overline{v}$$
(2.8)

L is the length of the ring-down cavity (RDC), which in this case is 84cm; Δk is the wavenumber dependent change in the ring- down decay rate coefficient as a result of CH (or OH) absorption, which is integrated over the full width of the rotational line of interest. The electronic degeneracies of the upper and lower states are g_u and g_l . A_{00} is the Einstein A coefficient which, for the CH(*A*-*X*) (0,0) band is equal to $(1.85 \pm 0.05) \times 10^6 \, \text{s}^{-1}$.^[2] Other spectroscopic parameters used were taken from Zachwieja. ^[3] The line dependent weighting factor, p_{line}, is calculated with the PGOPHER spectral simulation program.^[4] It is temperature dependent and is the calculated ratio of the integrated intensity of the spectral line under study to the total 0,0 band intensity (where 0,0 is the absorption from the zeroth vibrational level in the ground state to the lowest vibrational level of the first excited state). For the OH (*A*-*X*) (0,0) band, the relevant Einstein A coefficient (1.3515 x $10^6 \, \text{s}^{-1}$) was obtained from the fluorescence lifetime (688 ns for the *A*, v'=0 level) ^[5] and the Franck–Condon factor, $q_{00} = 0.905$. ^[6] The degeneracy ratios in both cases were calculated using equation 2.9.

$$g_{i(j)} = \begin{cases} (2S+1) & \text{if } \Lambda = 0\\ 2(2S+1) & \text{if } \Lambda \neq 0 \end{cases}$$
(2.9)

2. 4 Optical Emission Spectroscopy (OES)

OES was used to take the spatial profiles of emitting CH and OH radicals in emission, as well as profiles of C_2 , CO and H. This can be done because within the plasma different species emit at specific wavelengths giving characteristic spectral signatures dependent on the species and the transition that results in emission.

The optical fibre II was mounted on the movable optical table (see figure 2.3); the sidearms were removed and replaced with two diamond windows. Two lenses and an iris were set up as shown in figure 2.4 to direct the light onto the quartz multicore optical fibre. The light exits the fibre as a vertical stripe and is dispersed through a small monochromator (Oriel Instaspec IV, 600 lines mm⁻¹ ruled grating) equipped with a charge couple device (CCD) strip detector, providing a spectral resolution <1 nm.



Figure 2.3 Schematic of the OES experimental setup.

The height from which optical emission is measured is adjusted using the movable bench, and hence an emission profile of each species relative to height above the top of the substrate was recorded.

The grating was set to cover wavelength range of 365-670 nm for the UV and visible light readings. The CCD detector was cooled to -10°C to reduce background noise. In the spatially resolved OES experiments, an exposure time of 0.5 seconds, with an average taken from 64 readings is used for each spectrum. The spatial resolution was calculated to be between 0.5 to 0.8 mm, and measurements were taken at vertical separations of 1mm.



Figure 2.4 Diagram of the OES lens set up

2.5 Computational Details

2.5.1 Computational Study: Part I

Reactions were investigated using two different methods, but both used a density functional theory (DFT) based method. The first had a quantum mechanical approach and only looked at a C_9H_{14} cluster as used by other studies (figure 2.5). ^{[7][8]} This was used to replicate part of an H terminated, 2 x 1 reconstructed diamond (100) surface. Potential energy minima and transition states (TSs) were found for the diamond surface interacting with oxygen containing species such as the OH radical. Full optimization was achieved using the standard BB functional with the 6-31G(d) basis set within the Gaussian03 program. ^[9] In order to confirm the nature of the stationary points found and to obtain estimates for the zero-point energy correction, vibrational frequencies were also calculated. From the B3LYP/6-31G(d) geometries single-point B3LYP energies were then computed using a larger basis set (6-311G(d,p)). The energies reported here are based on the B3LYP/6-311G(d,p) energies, using zero-point energy corrections from the B3LYP/6-311G(d) calculations.



Figure 2.5 C₉H₁₄ cluster used to model the H terminated 2 x 1 reconstructed diamond (100) surface

2.5.2 Computational Study: Part II

The second computational study investigated reactions (direct OH radical insertion into the surface, oxygen incorporation in to the surface via addition to the surface and oxygen radical migration across the diamond surface) by a quantum mechanics/ molecular mechanics (QM/MM) method using the QoMMMa program, ^{[10][11]} on the same C(100):H 2 x 1 surface. ^[12] Jaguar 5 ^[13] was used to perform calculations for the QM region (which normally consisted of a C₉ based cluster as used previously).^[7] The interactions within the MM region were modelled using TINKER. ^[14] This MM network involves a 5 x 9 x 4 slab (number of C-C dimer bonds) and the bulk diamond lattice points define the initial geometry. Figure 2.6 shows the QM and MM structure.



Figure 2.6 MM region (diamond lattice) and the central QM region (ball and stick C₉H₁₄ cluster) used to model the diamond (100) H-terminated surface.

Similar to part I of the computational study, geometry optimization within the QM region involved the use of the B3LYP density functional and the 6-31G(d) basis set. The peripheral network was described using the MM2 molecular mechanics protocol. Again the single point energies for the QM region shown were re-calculated using the larger 6-311G(d,p) basis set.

Approximate TSs for the reactions were found by calculating the highest energy of the system along a series of values of a chosen reaction coordinate, q. This was either a key bond length or a combination of several bond lengths. To hold the system close to the desired value of the reaction coordinate a harmonic constraint was used for all other degrees of freedom. The approximate TS energy was a combination of the single point energies calculated for the optimized QM region and the optimized MM energies.

2.6 References

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Chapter 3 - Modelling of Plasma Chemistry and Composition

3.1 Theory and parameters of the Bristol-Moscow model

Modelling of the plasma in diamond CVD is a very difficult and complex process although it can be of great importance. When combined with experimental results, modelling can help when trying to understand the many processes within the plasma.

Yuri Mankelevich at Moscow State University has successfully produced 2-D models for various diamond depositing plasmas (CH₄/H₂/Ar and B₂H₆/Ar/H₂ mixtures). ^{[1][2]} Most recently he has produced a preliminary 2-D model of the C/H/O plasma comparing CH₄/CO₂/H₂ and CO/H₂ mixtures. One aim of this is to show that C/H/O based plasma composition can be sensitive to the chosen source gas mixture; it also aims to provide information on the spatial distributions of the gas temperature (T_{gas}), species concentrations and power absorption.

The 2-D (r, z) model assumes cylindrical symmetry, with co-ordinates r (the radial distance from the centre axis of the reactor) and z (the vertical height above the substrate surface). The substrate has a diameter of 3 cm and the reactor radius (R_r) is 6cm, height 6cm.

Many of the plasma activation processes (such as gas heating, heat and mass transfer, species and thermal diffusion and gas surface processes) are described by a set of nonstationary conservation equations for mass, momentum, energy and species concentrations, which are solved numerically in the entire reactor volume. This is required, plus the calculation of non-equilibrium electron energy distribution function (EEDF), to describe the plasma-chemical rate coefficients for the reactions involved in plasma activation.

Experimental absorption and OES data are used to set the volume V in which microwave (MW) power is absorbed as a parameter that leads to estimations of the reduced electric fields and the electron temperature (T_e) in the plasma region for a given value of power P.

Gas-phase chemistry and thermochemical input for all the C/H/O mixtures is taken from previous studies, ^{[3][4][5]} as is the ion chemistry and kinetic data for electron-molecule processes. ^{[6][7][8]} More than 500 direct and reverse reactions of neutral (and electronically excited) atoms and molecules, and 10 charged species, are included in the C/H/O plasma chemical kinetics mechanisms.

3.2 Model Predictions

For the CO₂/CH₄/H₂ gas mixture, with base conditions (P=1kW, p=150 Torr, $X_0(H_2)=0.3$, $F_{total} = 500$ sccm) the core plasma region was determined as $0 \le r \le R_{pl} \approx 3.45$ cm in the radial direction and $0 < z < H_{pl} \approx 1.6$ cm in the axial direction. T_e was assumed near constant within this region (~1eV), and declined by ~3% with increasing z. The ion temperature (T_{ion}) is close to T_{gas} in this case.

There are three main regions within the reactor; the cool region near the gas inlets (with T_{gas} < 1440-1500 K, z > 4.5cm), the hot plasma region (T_{gas} ~2600-3000 K, the localisation of which is evident from the n_e and T_{gas} distributions in fig 3.1 c, z < 2.1cm) and the peripheral region (the annular shell around the plasma region, 2.1 < z < 4.5 cm).

Within the reactor it is predicted that the feed gases will convert into a C/H/O mixture dominated by H_2 and CO. In fact, the initial feed gas mixture is only present in the cooler area within ~3cm of the feed gas inlet (figure 3.1 a).

The model can identify the dominant conversion processes within each region. Within the cool region the relatively low T_{gas} and low H atom concentration, [H], mean that the input source gases are dominant. Whereas, in the peripheral region conduction and diffusional transfer from the plasma region cause T_{gas} to be ~1500-2500K and [H] ~ 2 x 10¹⁴ – 2 x 10¹⁶ cm⁻³ which ensures that the input CH₄ is almost completely decomposed through H-shifting reactions;

$$CH_x + H \rightleftharpoons CH_{x-1} + H_2$$
 [x = 4 -1] (3.1)

and thermal decomposition:

$$CH_x + M \rightleftharpoons CH_{x-1} + H + M$$
 [x = 4 -1] (3.2)

This can lead to larger hydrocarbon species being formed, and eventually to soot particles. In C/H/O plasmas other processes occurs that break up hydrocarbon species by reaction with oxygen-containing species. For example;

$$0 + C_2 H_2 \leftrightarrow H + HCCO \tag{3.3}$$

$$0 + C_2 H_2 \leftrightarrow CO + C H_2$$
 (3.4)

and

$$OH + C_2H_2 \leftrightarrow H + CH_2CO$$
 (3.5)

$$OH + C_3H_2 \leftrightarrow C_2H_2 + HCO$$
 (3.6)

These lead to the formation of CO, which is very stable and is also formed by the reaction of the input CO_2 with H atoms:

$$H + CO_2 \leftrightarrow OH + CO$$
 (3.7)

It is reaction 3.7 that accounts for the near total destruction of the input CO_2 in the hot region, as observed in figure 3a. The OH radicals formed are mostly converted to H_2O by reaction with hydrogen, or can form O atoms by reaction with H atoms. These H atoms are mainly formed within the hot plasma region and diffuse to the peripheral region. The effect of these reactions on the spatial distribution of species can be seen in figure 3.1.



Figure 3.1 Calculated 2-D(r, z) mole fraction distributions of CO₂, CH₄, CO and H₂ (in %), T_{gas} and n_e for base reactor conditions (P = 1 kW, p = 150 Torr) and 35%CH₄/35%CO₂/30%H₂ gas mixture (*i.e.* R = 0.5). Given the assumed cylindrical symmetry, only half (in the radial direction) of each 2-D distribution is displayed.^[9]

The model can also give information on power consumption. The majority of the MW power (>90%) absorbed by the electrons is distributed into vibrational and rotational

excitation of mostly H₂ and CO. Elastic collisions of electrons with H₂ accounts for ~1.5% of the total power consumption, ~0.3% of the absorbed power is consumed in electron impact induced dissociation of H₂, and <1% is expended on electronic excitation and ionization. Rovibrationally excited H₂ and CO can collide with H atoms. This causes translational excitation of H atoms, which dissipates into gas heating. This energy transfer can be described as fast V \rightarrow T and R \rightarrow T energy transfer.

Input power is dissipated further by thermal conduction to the reactor (~14-16% to the cylinder sidewalls, ~50% to the base plate, ~12-14% to the substrate and ~3.3-5% to the top window) and chemical conversions and radiation losses (~15-20%). The major fraction of the power dissipated through chemical conversions and radiation losses is through the dissociation of H₂. As discussed previously these H atoms play a vital role in the CVD growth mechanism, converting the gas mixture to its active form and heating the substrate (the model suggests that H atom adsorption accounts for 20-25% of the total power density loading to the substrate).

Ion distributions are predicted, with main species ions being mainly formed through electron impact ionization with the reverse being dissociative recombination of the dominant ions with electrons. The distribution of particular ions is very sensitive to the local $[C_yH_x]/[H_20]$ ratio.

Experimental results obtained during this project will be used to improve this preliminary 2-D (r, z) model and give further insight into the plasma chemistries of C/H/O mixtures.

3.3 References

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Chapter 4 - Results and Discussion

4.1 Optical Emission Spectroscopy

Various optically emitting species within the plasma under the base conditions discussed for the CO₂/CH₄/H₂ gas mixture and the CO/H₂ gas mixture were measured using OES (figure 4.1 and 4.2). The measured emissions from radical species were the CH($A^2\Delta$ - $X^2\Pi$) emission ~431nm, C₂($d^3\Pi$ - $a^3\Pi$) Swan bands centred ~515nm, and OH ($A^2\Sigma^+$ - $X^2\Pi$) origin band ~308nm, referred to as CH*, C₂* and OH*. H Balmer- α and H Balmer- β lines were measured, this is the emission from H(n=3) and H(n=4), respectively, to H(n=2), both will be referred to as H*. Also emissions were measured from electronically excited CO, (referred to as CO*) this was the $B^1\Sigma^+$ - $A^1\Pi$ at ~420-600nm emission. The obvious limitations of OES are that it is only qualitative (not quantitative) and it cannot detect ground state species within the plasma as these do not emit. Despite this, OES is a useful tool to look at trends within the microwave activated C/H/O plasmas.

The plasmas of both the $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures were probed using spatially resolved OES to find out where various emitting species peaked. Clearly both show very similar findings with CO* peaking closest to the substrate at $z \sim 6-8$ mm and the H* emissions peak at $z \sim 8-9$ mm. The carbon radical species emit furthest away from the substrate at $z \sim 10-11$ mm. The OH* emission targetted was overlapped by other emissions from excited CO, this made it difficult to measure the differences in OH emissions in both the CO/H₂ and CO₂/CH₄/H₂ plasmas. Mis-calibration of the spectrometer is unlikely to be the cause of this as the H*, C₂* and CH* emission peaks agree with previous results.



Figure 4.1 Plot of optical emission intensities from the $CO_2/CH_4/H_2$ gas mixture of CH*, C_2 *, CO*, H_{α} and H_{β} as functions of height, *z*, above the substrate. Each emission has been normalised to unity.



Figure 4.2 Plot of optical emission intensities from the CO/H₂ gas mixture of CH*, C₂*, CO*, H_{α} and H_{β} as functions of height, *z*, above the substrate. Each emission has been normalised to unity.

These emission peaks occurs at different heights above the substrate because within MW activated plasmas the main route to electronically excited species is through the electron impact excitation (EIE) of the ground state of that species (for C_2 this is actually a low lying excited state). This general route to excited states means that the ground state densities and the electron density (n_e) distribution will be the main forces that govern the emissions seen.

The emissions of CO^{*} and H^{*} from the two different C/H/O plasmas overlap fairly well (figures 4.3, 4.5 and 4.6) and the emissions for CH^{*} and C₂^{*} peak in the same place for both plasmas (figures 4.7 and 4.8). The major differences between the two plasmas are that the emissions measured from the CO/H₂ plasma are of a much lower intensity and as such the baseline subtraction results in a much noisier emission profile. This is most likely due to a much lower density of the relevant ground state species to form emitting excited states. As OES is a qualitative technique this has to be confirmed by cavity ring-down spectroscopy (which is quantitative) as discussed in section 4.2.



Figure 4.3 Plot of measured emission intensities of the CO* species as a function of height above the substrate, z, in both the CO₂/CH₄/H₂ gas mixture and the CO/H₂ gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more effectively.

Most carbon is processed into CO, which means it is present throughout the reactor but it is actually most stable in slightly cooler regions. This is because the electron density is highest at towards the centre of the plasma and so reaction 4.1 (e⁻ corresponds to an electron) occurs most efficiently here, decreasing the concentration of CO, hence also decreasing the concentration of excited CO.

$$CO + e^{-} \rightarrow C + O + e^{-} \tag{4.1}$$

 T_{gas} is also greatest in this region (z = 10-12mm) thus the number density of CO is also slightly lower due to the perfect gas law (equation 4.2), so as temperature increases n decreases.

$$pV = nRT \tag{4.2}$$

Where *p* is pressure, *V* corresponds to volume, *n* the number of moles, *R* is the gas constant = 8.314 J K⁻¹mol⁻¹ and *T* corresponds to temperature. This is why CO* peaks at *z* ~6-8 mm, which is nearer to the substrate than H*, which has a higher number density nearer to the centre of the plasma at *z* ~8-9 mm.

The H atom number density peaks close to where T_{gas} is highest (z = 10-12mm) in the centre of the plasma as this is where H₂ to atomic H conversion occurs most efficiently. The position of the peak is also dependent on other factors that affect H atom density, such as H atom loss and diffusion rates. The H atoms diffuse from the centre of the plasma (where there is the most efficient production) to regions with lower concentrations and

the rates of loss processes are sufficiently low enough that H atoms can be found throughout the reactor.



Figure 4.4 Calculated 2-D(r, z) gas temperature, T_{gas} , (left) and electron density distributions, n_e , (right) for the CO₂/CH₄/H₂ gas mixture with base reactor conditions as discussed in section 2.1. Given the assumed cylindrical symmetry, only half (in the radial direction) of each 2-D distribution is displayed. ^[1]

H atoms are present at similar levels throughout the entire volume of the reactor we investigate and as such H_{α} and H_{β} atom emissions are great for determining electron density profiles. Balmer lines measured show highly excited H atom states emitting to a lower excited state, this means that a high density of electrons is need to produce the emissions observed. The model of the plasma for $CO_2/CH_4/H_2$ plasmas predicts a fairly flat n_e between 2.5< z <12.5mm but this declines as z increases and (more steeply) as z decreases further (figure 4.4). Hence this high electron density region is where H* emissions peak. It can be seen that the H* emissions are almost exactly the same for both gas mixtures (figures 4.5 and 4.6) and so we can assume that the electron density distribution changes little between the various gas mixtures (very slightly broader for $CO_2/CH_4/H_2$ mixture) and hence plasma size slightly larger for the $CO_2/CH_4/H_2$ gas mixture extending to $z\sim22mm$ which agrees with predictions made by the model discussed in chapter 3, and the CO/H_2 plasma extends to $z\sim20mm$.



Figure 4.5 Plot of measured emission intensities of H_{α} as a function of height above the substrate, z, in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more effectively.



Figure 4.6 Plot of measured emission intensities of H_{β} as a function of height above the substrate, z, in both the $CO_2/CH_4/H_2$ gas mixture and the CO/H_2 gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more effectively.

The only real differences between the plasmas formed from the two gas mixtures, as shown by OES, are when looking closely at the emissions of CH* and C₂* (figures 4.7 and 4.8). Both show a slightly wider peak from the CO₂/CH₄/H₂ gas mixture plasma, with the emissions implying that there are excited state CH and C₂ radicals at z > 24mm, where electron density is almost negligible.

The broadening is thought to be due to optical emissions from chemiluminescent (CL) reactions becoming significant and hence enhancing the emissions measured from the $CO_2/CH_4/H_2$ gas mixture plasma, which otherwise would come from EIE.



Figure 4.7 Plot of measured emission intensities of the CH* species as a function of height above the substrate, z, in both the CO₂/CH₄/H₂ gas mixture and the CO/H₂ gas mixture. Different emission intensity scales are used for each gas mixture in order to compare the spatial distribution more effectively.

Excited CH radicals are mainly formed through EIE, but as reported in studies of flames $^{[2][3]}$ there are various exothermic reactions of C₂H with O and/or O₂ that result in chemiluminescence.

$$C_2H + O_2 \rightarrow CH^* + CO_2$$

$$C_2H + O \rightarrow CH^* + CO$$
(4.3)
(4.4)

The predicted O_2 densities in the hot region are much too low for reaction 4.3 to be a significant source of CH* and so reaction 4.4 is the more likely to be of interest. As CH* formed by chemiluminescent reactions is not as dependent on n_e as CH* formed by EIE, the two profiles will be very different when spatial distribution is considered and hence if CL is a considerable source of optical emission this could explain the difference in profiles from the $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures.



Figure 4.8 Plot of measured emission intensities of the C₂* species as a function of height above the substrate, z, in both the CO₂/CH₄/H₂ gas mixture and the CO/H₂ gas mixture. Different emission intensity scales are used for each gas mixture inorder to compare the spatial distribution more effectively.

Similarly there are exothermic reactions leading to excited C_2^* that produce chemiluminescence. This can usually be attributed to the following reaction:

$$C + CH \rightarrow C_2^* + H \tag{4.5}$$

The 2-D (r, z) model can predict the amount of chemiluminescence and supports this as being a contribution that extends the tail of the C₂ emission.

Other reactions that form excited species have also been investigated (such as those forming OH*). These reactions seem to produce an insufficient amount of optical emission to cause a significant difference to the optical emission produced by EIE hence why the emissions from both plasmas for CO* and H* agree well with each other.

4.2 Cavity Ring- Down Spectroscopy

Cavity ring- down spectroscopy was used to measure the column densities of the OH radical and the CH radical within the plasmas produced by both the $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures as a function of height above the substrate, *z*. These two key radicals were chosen because they are the most suitable radical species carrying oxygen and carbon within the area of plasma we are probing and hence can be considered to

represent changes to both oxygen and carbon containing species. Previous studies have shown links between these radicals and other important species within the plasma, for example CH and C_2 are linked through H-shifting reactions and interconversion within and between C_1H_x and C_2H_y species as discussed in chapter 1.

The spatially resolved profile of OH shows that the column density peaks at $z \sim 10$ mm for both the plasmas formed from the two gas mixtures (figure 4.10). It also shows a ~3-fold decrease in column density when comparing {OH(*X*, v=0)} in the CO₂/CH₄/H₂ plasma and the CO/H₂ plasma. All parameters such as power, pressure, flow rates and C:H:O ratio are kept constant and comparable for the two experimental set ups and so this difference in column densities measured can only be due to the different source gases used. This clearly shows that the chemistry and compositions of C/H/O plasmas are sensitive to the feed gases used, unlike C/H plasmas.



Figure 4.9 Plot of the measured column density of the OH(X, v=0) radical as a function of height above the substrate, z, for the plasmas formed from the base CO₂/CH₄/H₂ and CO/H₂ gas mixtures. All parameters are discussed in Chapter 2.

The measured column density of CH(*X*, v=0) also shows a peak at $z \sim 10$ mm and a large (~2-fold) decrease in the measured column density when going from the CO₂/CH₄/H₂ plasma to the CO/H₂ plasma (figure 4.11).



Figure 4.10 Plot of the measured column density of the CH(X, v=0) radical as a function of height above the substrate, z, for the plasmas formed from the base CO₂/CH₄/H₂ and CO/H₂ gas mixtures. All parameters are discussed in Chapter 2.

This difference in measured column densities of OH and CH for the different feed gases is believed to be because within the hot plasma conditions for C/H/O gas mixtures, most of the feed gas is converted to H₂ and CO throughout the reactor. The feed gases are only dominant near the inlets, in the cool region as a relatively low $T_{\rm gas}$ and low concentration of atomic H hinders decomposition as discussed in section 3.2. This means that if the feed gas mixture is CO and H₂ then there is not a big driving force to form the other key species like H₂O and C₂H₂ (and the associated OH and CH radicals), usually observed in higher column densities in CH₄/CO₂/H₂ plasmas.

The initial 2-D (r, z) model predicted that column densities of radicals would be at least one order of magnitude lower in the CO mixture than the CO₂ mixture. So CH was predicted to be <10¹² cm⁻² and OH would be < 6 x 10¹² cm⁻² (C₂ was predicted to be < 5 x 10¹⁰ cm⁻², but was not measured). The experimental results agree fairly well with these predictions, but not exactly. This could be due to the fact that the feed gas inlets in the actual experimental set up were diametrically opposed ¹/₄ inch tubes whereas the 2-D model assumes gas entry through a cylindrical ring located at r=6cm which is φ independent (φ is the azimuthal angle). Previously, asymmetry in the feed gas processing was not thought to affect the resulting plasma, and so this could be an important feature when looking at gas mixtures for diamond CVD. Also the 2- D (r, z) model revealed that within a CO/H₂ gas mixture, the major source of atomic C and O is through reaction 4.1 as discussed in section 4.1.

$$CO + e^{-} \rightarrow C + O + e^{-} \tag{4.1}$$

The resulting radicals can lead to production of other carbon and oxygen containing species through interconversions e.g. $C \leftrightarrow CH \leftrightarrow CH_2 \leftrightarrow CH_3$ etc. and $O \leftrightarrow OH \leftrightarrow H_2O$. This alters the distribution of species within the reactor compared to the $CO_2/CH_4/H_2$ gas mixture, especially in regions where electron density is high and therefore production of C and O is greater.

4.3 Computational Studies

4.3.1 Quantum Mechanics (QM)

Quantum mechanical calculations based on density functional theory were used to investigate 11 reactions. These reactions included the abstraction of surface hydrogen using the OH radical, as well as from surface methyl groups, and rearrangements and incorporation of oxygen into the diamond surface (Appendix A). The frequencies and optimized energy for each cluster modelled, for the gaseous reactant and for the transition state for every reaction were calculated. The frequencies were calculated to signal if the energies calculated were in fact those for a minimum or a transition state. The optimized single point energies calculated for each species using the larger basis set, B3LYP/6-311G(d,p), were combined with the zero- point energy corrections from the B3LYP/6-31G(d) calculations (Appendix B).



Figure 4.11 Reaction mechanisms for the rearrangement reaction of surface oxygen radical to OH, and incorporation of oxygen into the diamond surface from a surface carbonyl.

Two selected reactions (reactions A and B in figure 4.12 respectively) were modelled using both QM and QM/MM, the results agree fairly well with each other, indicating that QM is a quick and useful method to model reactions of species with the diamond surface (table 4.1). Although the MM diamond surface used in the QM/MM calculations constrains the cluster more tightly than in the QM calculation, the effect of this can be seen in the results for reaction B where the difference between the QM and QM/MM total energies calculated was much larger than that for reaction A as it involves a change in the C-C

distance on the diamond surface. This means that the QM method is much more useful for reactions with the surface such as additions, abstractions and rearrangements that do not change the C-C distance on the surface, but not for reactions that affect the C-C bond, such as insertion reactions.

Reaction	QM Total Energy / kJ mol ⁻¹	QM/MM Total Energy / kJ mol ⁻¹
Α	+25.28	+18.58
В	-16.65	-34.13

Table 4.1 Comparison of energies calculated by QM and QM/MM for reactions A and B

The most significant result found was for reaction C (figure 4.13) this shows that once an oxygen radical has been adsorbed, there is a very large energy barrier (of +172.3 kJmol⁻¹ relative to the reactants, shown in figure 4.14) to the formation of an ether structure, which would incorporate the oxygen into the diamond surface. This large energy barrier could help to explain why oxygen seems not to be incorporated into the diamond surface, unlike nitrogen.



Figure 4.12 Reaction mechanism showing the incorporation of oxygen into the diamond surface from surface oxygen radical to an ether -like structure



Figure 4.13 Energy profile for reaction C, a large energy barrier is present for the transformation of an oxygen surface radical to an ether type structure

The full reaction scheme of the H- terminated diamond surface, abstractions, additions and rearrangements can be seen in appendix C.

4.3.2 Quantum Mechanics / Molecular Mechanics (QM/MM)

As well as the two reactions modelled using QM and QM/MM for comparative reasons, other reaction minima and transition states were calculated using QM/MM. These were two insertion reactions, showing insertion of an OH radical into the surface C-C bond and a surface C-H bond, both labelled in figure 4.15.



Figure 4.14 C₉H₁₄ cluster with C-C insertion and C-H insertion sites labelled, only the QM region is shown for clarity.

The transition state was found by calculating the highest energy of the system along the reaction coordinate *q*. For an insertion reaction q = x + y - z where *x*, *y* and *z* correspond to the respective distances between nuclei *a* and *b*, *b* and *c*, and *c* and a, as shown in figure 4.16.



Figure 4.15 Example of OH insertion into the C-C bond with nuclei labelled as a, b and c

Calculated energies were plotted against the calculated constraint q to get the constraint that represents the approximate transition state. In the case shown in figure 4.17, the constraint value of 1.8Å represents the transition state for OH insertion into the C-C bond.

Results show that insertion of the OH radical into the surface C-C bond has a large energy barrier (+147 kJmol⁻¹) whereas insertion into the C-H bond had no barrier at -72 kJmol⁻¹ for insertion of the OH radical. This is in agreement with previous studies of insertion of C-containing species into the diamond surface as modelled by QM/MM.^[4]



Figure 4.16 Plot of the calculated energies against constraint value, *q*, calculated for the insertion of OH into the C-C bond

4.4 References

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Chapter 5 - Afterword

5.1 Conclusion

The work presented in this thesis provides a wider understanding of the processes occurring in C/H/O plasmas formed from both $CO_2/CH_4/H_2$ and CO/H_2 gas mixtures. Spatial profiles using optical emission spectroscopy reveal that the electron temperature and density distributions are not affected by the specific feed gas, and that exothermic reactions that result in CH and C₂ chemiluminescence have a larger role in the plasma of the $CO_2/CH_4/H_2$ gas mixture than previously recognised.

Cavity ring- down spectroscopy has quantitatively shown a dependence on specific feed gas as to the column densities of the CH and OH radicals in the plasmas, with the CO plasma having a ~3 fold and ~2-fold decrease in column densities for CH and OH radicals respectively. This indicates that diamond grown using a chemical vapour deposition technique and a C/H/O gas mixture must consider both the ratio of C:H:O and the feed gases used, unlike C/H gas mixtures that the only depend on the C:H ratio. The results agree fairly well with those predicted by the 2D (r, z) model, especially when looking at trends, but they disagree slightly on the magnitude of column densities. This is most probably due to how the model introduces the feed gas through a φ -independent cylindrical ring, whereas the reactor in reality introduces the feed gas through two diametrically opposed tubes.

Diamond surface reactions with oxygen-containing species simulated using quantum mechanics and quantum mechanics/molecular mechanics have resulted in energy minima and approximate transition states being calculated for various reactions - including H atom abstractions from the surface and O and OH additions, rearrangements and insertions into C-C bonds and C-H bonds. This preliminary study, which extends previous work investigating CH₂ radical reactions at and with a diamond surface, find OH insertion into a surface C-H bond to be a facile process, whereas insertion into a diamond surface C-C bond has a high energy barrier, making the occurrence of such an insertion reaction very improbable.

5.2 Future Work

QM/MM studies of the migration of an oxygen radical across the diamond (100) surface must be completed. This type of computational study could be expanded to calculations using other surfaces such as the (111) surface and look at a variety of reactions such as H abstractions and O (and OH) incorporation. Migrations of other species such as the C radical have been shown to occur on the step edge between (100) and (111) surfaces; this migration could be simulated for O or even OH migration across the step.

More CRDS for the CO/H₂ plasma would be useful as the CRDS work for $CO_2/CH_4/H_2$ plasma is extensive and so species such as C₂ and H(n=2). Further attempts on detecting the metastable triplet CO and the CH₃ radical could be made using CRDS, this has been successfully used to detect CH₃ radicals in a hot-filament reactor.^[1] If it were found that the CH₃ radical is the dominant radical species near to the substrate surface, this would

give added weight to the argument that it is the main growth species in diamond CVD. Another technique that could possibly be used to detect CH_3 radical is tunable diode laser absorption spectroscopy; this has been successfully used previously to detect methyl radicals in various CVD environments (microwave plasmas and filament-assisted).^{[2][3][4][5][6]}

Upon completion of the work regarding C/H/O plasmas, a similar investigation will be undertaken to look at C/H/N plasmas. A base mixture of CH_4/H_2 will be used with the addition of a small amount of N₂. Previous work on nitrogen containing gas mixtures for diamond CVD has concentrated on the doping of diamond by nitrogen and the morphology of diamond produced, but very little has been done to look at the plasma during diamond CVD and the dynamics involved. A quantitative approach using CRDS combined with OES will be used, also looking at other relevant species in the plasma such as CN, NH_2 and NH_3 .

The computational techniques used in this project may also be used to look at diamond surface interaction with gaseous species in the nitrogen containing plasma, investigating additions, insertions, migrations and rearrangement reactions.

5.3 Acknowledgements

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5.4 References

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Appendices

Appendix A

Reaction mechanisms of reactions 1-11 modelled using QM



55



Appendix B

Tables showing single point energies of reactions 1-11 using the B3LYP/6-31G (d) basis set and the larger basis set B3LYP/6-311(d,p) as well as zero point correction energies to calculate total energies of each species and the total energy and energy barrier for each reaction.

Reaction Number	Species	Single poi B3LYP/6	nt energy i-31G (d)	Zero point correction		
		Hartree	kJ mol ⁻¹	Hartree	kJ mol ⁻¹	
1	C9H14 + OH	-427.11	-1121389	0.22	585.60	
	TS1	-427.12	-1121393	0.22	576.42	
	C9H13 + H2O	-350.72	-920808	0.20	528.74	
2	C9H13O	-425.94	-1118314	0.20	537.97	
	TS2	-425.87	-1118132	0.20	524.90	
	C9H12OH	-425.93	-1118271	0.20	537.97	
3	C9H13CH3 + OH	-466.43	-1224614	0.25	658.20	
	TS3	-466.43	-1224620	0.25	650.91	
	C9H12CH3 + H2O	-466.44	-1224645	0.25	656.87	
4	C9H13CH3 + OH	-466.43	-1224614	0.25	658.20	
	TS4	-466.43	-1224615	0.25	650.93	
	C9H13CH2 + H2O	-466.45	-1224653	0.25	652.50	
5	C9H13OH + OH	-502.33	-1318858	0.23	594.89	
	TS5	-502.34	-1318889	0.23	592.88	
	C9H13O + H2O	-502.35	-1318926	0.23	593.55	
6	C9H13OH + OH	-502.33	-1318858	0.23	594.89	
	TS6	-502.32	-1318853	0.22	585.31	
	C9H12OH + H2O	-502.34	-1318883	0.23	593.55	
7	C9H13OH + H	-427.10	-1121357	0.22	573.09	
	TS7	-427.09	-1121326	0.22	566.15	
	C9H12OH + H2	-427.10	-1121358	0.22	564.61	
8	C9H13OH + H	-427.10	-1121357	0.22	573.09	
	TS8	-427.10	-1121343	0.21	564.20	
	C9H13O + H2	-427.12	-1121401	0.22	564.61	
9	C9H13O	-425.94	-1118314	0.20	537.97	
	TS19	-425.83	-1118018	0.20	532.13	
	C9H13O ether	-425.95	-1118343	0.21	542.69	
10	C9H13O	-425.94	-1118314	0.20	537.97	
	TS10	-425.94	-1118310	0.20	534.19	
	C9H13O carbonyl	-425.94	-1118317	0.20	537.92	
11	C9H13O carbonyl	-425.94	-1118317	0.20	537.92	
	TS11	-425.87	-1118134	0.20	532.11	
	C9H13O ether	-425.95	-1118343	0.21	542.69	

Reaction Number	Species	Single point e 311(d,p)	nergy B3LYP/6-	Single point energy - zero point energy/ kJ mol ⁻¹	TS – Reactants / kJ mol ⁻¹	Product – reactant /kJ mol ⁻¹
		Hartree	kJ mol⁻¹	kJ mol ⁻¹		
1	C9H14 + OH	-427.23	-1121114	-1121700	-21.32	-48.12
	TS1	-427.24	-1121135	-1121712		
	C9H13 + H2O	-350.80	-920506	-921034		
2	C9H13O	-426.05	-1118059	-1118597	159.60	25.28
	TS2	-425.99	-1117899	-1118424		
	C9H12OH	-426.04	-1118033	-1118571		
3	C9H13CH3 + OH	-466.56	-1224295	-1224953	-21.66	-48.34
	TS3	-466.57	-1224316	-1224967		
	C9H12CH3 + H2O	-466.58	-1224344	-1225000	-16.22	-62.97
4	C9H13CH3 + OH	-466.56	-1224295	-1224953		
	TS4	-466.56	-1224311	-1224962		
	C9H13CH2 + H2O	-466.58	-1224358	-1225011	-30.42	-66.89
5	C9H13OH + OH	-502.47	-1318649	-1319244		
	TS5	-502.48	-1318679	-1319272		
	C9H13O + H2O	-502.50	-1318716	-1319310	-13.24	-41.61
6	C9H13OH + OH	-502.47	-1318649	-1319244		
	TS6	-502.47	-1318662	-1319247		
	C9H12OH + H2O	-502.49	-1318691	-1319284	15.98	-15.52
7	C9H13OH + H	-427.22	-1121089	-1121662		
	TS7	-427.21	-1121072	-1121638		
	C9H12OH + H2	-427.22	-1121104	-1121669	4.67	-40.80
8	C9H13OH + H	-427.22	-1121089	-1121662		
	TS8	-427.21	-1121083	-1121648		
	C9H13O + H2	-427.23	-1121129	-1121694	172.34	-20.60
9	C9H13O	-426.05	-1118059	-1118597		
	TS9	-425.98	-1117886	-1118418		
	C9H13O ether	-426.06	-1118079	-1118622	-2.83	-3.94
10	C9H13O	-426.05	-1118059	-1118597		
	TS10	-426.05	-1118061	-1118596		
	C9H13O carbonyl	-426.05	-1118063	-1118600	40.35	-16.67
11	C9H13O carbonyl	-426.05	-1118063	-1118600		
	TS11	-426.03	-1118022	-1118554		
	C9H13O ether	-426.06	-1118079	-1118622		

Appendix C Full reaction scheme for reactions modelled using QM



Appendix D

Table presenting energies calculated for gaseous reactants using QM/MM

Gaseous Reactants	B3LYP/6-31g (d)		B3LYP/6-311(d,p)//	B3LPY/6-31g(d)
	Hartree	kJmol ⁻¹	Hartree	kJmol ^{⁻1}
ОН	-75.720	-198803	-75.753	-198890
H2O	-76.407	-200607	-76.447	-200713
Н	-0.500	-1313	-0.502	-1318
H2	-1.175	-3086	-1.180	-3097
0	-74.267	-194989	-74.678	-196067

Appendix E Table showing energies calculated for surface species using QM/MM using a smaller basis set of B3LYP/6-31g (d) and the larger basis set B3LYP/6-311(d,p)//B3LPY/6-31g(d)

Surface Species	B3LYP/6-	B3LYP/6-31g (d)								
	QM		MM		Total		Constrai	int 1	Constrain	t 2
	Hartree	kJmol⁻¹	Hartree	kJmol⁻¹	Hartree	kJmol⁻¹	Hartre	kJmol⁻¹	Hartree	kJmol⁻¹
							е			
С9Н14	-351.35	-922469	9.709	25491	-341.64	-896977	0.0059	15.38	0.0061	16.13
C9H13	-350.67	-920688	9.710	25495	-340.96	-895193	0.0066	17.25	0.0007	1.86
C9H13OH	-426.56	-1119925	9.709	25490	-416.85	-1094435	0.0062	16.27	0.0062	16.31
C9H13CH3	-390.66	-1025670	9.718	25516	-380.94	-1000154	0.0066	17.25	0.0061	16.12
C9H13O	-425.90	-1118194	9.709	25492	-416.19	-1092702	0.0063	16.49	0.0063	16.45
C9H12	-350.03	-919014	9.715	25506	-340.32	-893508	0.0059	15.42	0.0059	15.55
C9H12OH	-425.88	-1118157	9.710	25492	-416.17	-1092665	0.0061	16.05	0.0061	16.12
C9H12CH3	-389.98	-1023903	9.716	25511	-380.27	-998392	0.0059	15.60	0.0060	15.66
C9H13CH2	-389.99	-1023919	9.709	25492	-380.28	-998426	0.0065	17.00	0.0062	16.27
C9H13O	-425.91	-1118232	9.707	25485	-416.21	-1092747	0.0068	17.80	0.0067	17.69
ether										
C9H13O	-425.90	-1118196	9.709	25491	-416.19	-1092705	0.0060	15.84	0.0061	15.92
carbonyl										
C9H14O	-426.58	-1119986	9.710	25493	-416.87	-1094493	0.0067	17.65	0.0067	17.69
ether			_							
C9H12O	-425.28	-1116568	9.711	25495	-415.57	-1091073	0.0060	15.76	0.0061	15.90
ether										
C9H13OH2	-427.06	-1121245	9.710	25494	-417.35	-1095752	0.0060	15.78	0.0060	15.78
C9H14OH2 ether	-427.08	-1121300	9.710	25494	-417.37	-1095806	0.0069	18.19	0.0069	18.22

Surface Species	B3LYP/6-311(d,p)//B3LPY/6-31	g(d)	
	Single point energy		Total Energy (QM + MM)	
	Hartree	kJmol ⁻¹	Hartree	kJmol ⁻¹
C9H14	-351.44	-922715	-341.73	-897224
C9H13	-350.77	-920959	-341.06	-895464
С9Н13ОН	-426.68	-1120249	-416.97	-1094759
C9H13CH3	-390.76	-1025949	-381.04	-1000433
C9H13O	-426.01	-1118497	-416.30	-1093005
C9H12	-350.13	-919257	-340.41	-893751
C9H12OH	-426.01	-1118479	-416.30	-1092986
C9H12CH3	-390.09	-1024174	-380.37	-998664
C9H13CH2	-390.09	-1024194	-380.39	-998702
C9H13O ether	-426.03	-1118531	-416.32	-1093047
C9H13O carbonyl	-426.01	-1118498	-416.30	-1093008
C9H14O ether	-426.70	-1120288	-416.99	-1094795
C9H12O ether	-425.39	-1116862	-415.68	-1091367
C9H13OH2	-427.19	-1121574	-417.48	-1096081
C9H14OH2ether	-417.36	-1095769	-407.65	-1070276

Appendix F Table of energies obtained for reactions studied using QM/MM

		B3LYP/6-31 Energy	g (d) Total	B3LYP/6-311(d,p) Total Energy		TS - Reactants	Product - reactants
Reaction	Species	Hartree	kJmol⁻¹	Hartree	kJmol⁻¹	kJmol⁻¹	kJmol⁻¹
O insertion via a carbonyl	C9H13Ocarbonyl	-415.98	-1092167	-416.10	-1092470	-2.33	-34.13
	Approximate TS	-415.99	-1092169	-416.10	-1092472		
	C9H13Oether	-416.00	-1092205	-416.11	-1092504		
O radical rearrangement to OH	С9Н13О	-415.98	-1092165	-416.10	-1092467	-21	18.58
	Approximate TS	-415.99	-1092186	-416.11	-1092488		
	C9H12OH	-415.97	-1092127	-416.09	-1092449		
OH insertion into a C-C bond	C9H14	-341.43	-896414	-341.52	-896660	147	202.77
	ОН	-75.71	-198782	-75.74	-198868		
	Approximate TS	-417.08	-1095041	-417.21	-1095381		
	C9H14OH(ether)	-417.07	-1095018	-417.19	-1095326		
OH insertion into a C-H bond	C9H14	-341.43	-896414	-341.52	-896660	-72	25.30
	ОН	-75.71	-198782	-75.74	-198868		
	Approximate TS	-417.16	-1095249	-417.29	-1095601		
	C9H13OH2	-417.13	-1095174	-417.26	-1095503		