Modeling of Artificial Diamond Production

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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Approved by,

(DR. NURUL HASAN)

UNIVERSITI TEKNOLOGI PETRONAS

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Hisyam Zakwan Bin Aziz

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ABSTRACT

The objective of the project is to simulate the production of artificial diamonds in a chemical vapor deposition (CVD) reactor. Diamond layers would form as layers on the substrate in the reactor. The behavior of the production of artificial diamonds in the reactor is not clear and a simulation of the process can provide valuable insight. The project will cover the nucleation and condensation phases of the diamond formation process in the CVD reactor.

The project deals with the deposition of carbon particles on a layer of substrate in a manner that causes it to arrange itself to be diamond layers. The homogeneity of the nucleation process is not considered as the main purpose it to produce a diamond layer regardless of how homogenous the layer is in terms of nuclei orientation.

The report starts with an introduction to the project, with an outline of the background, problems statement and objectives of study. Then, a section that touched on the literature review followed by the methodology of the project which covers the project activities, key milestones and tools used. Lastly, the results and discussion of the project so far is presented ending with the conclusion.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Diamonds are used in an array of fields including mechanical parts, cutting and grinding, manufacturing, abrasives, coatings, heatsinks, jewellery and more. The unique properties of diamonds are what makes it truly a valuable material. Diamonds are the hardest material known to man and it also does not wear easily, has high thermal conductivity and can tolerate high temperatures. Diamonds occur naturally in nature but it needs the right conditions which are high temperature, high pressure and it may take millions to billions of years to form.

Fast production of diamonds needs it to be produced synthetically or artificially in controlled temperatures and pressures using the right methods. One of the methods is by using Chemical Vapor Deposition (CVD) to from layers of diamond in a condition controlled chamber.

The CVD method can produce various results for the thickness of the diamonds. The thickness can depend on the temperature, pressure, gravity, chemical composition and other variables. Experiments were carried out by researches to find the optimum condition for diamond growth and there are still possibilities of better conditions.

A model of the production of artificial diamonds using software will provide insight of how is the situation in the reactor. It will show the CVD process more clearly and show the situation in the reactor under various temperatures, pressures and chemical composition hence provide a better understanding of the process.

The model developed for artificial diamond production consists of the nucleation model where the diamonds forms the first seed on the substrate surface and the condensation model where the diamond starts to grow from the nuclei. The models can be used to simulate the formation in many CVD reactors.

1.2 Problem Statement

The formation of diamonds consumes an enormous amount of energy and time. In order to use it industrially, diamonds should be made available in a shorter period of time. Diamonds need to be produced artificially to cater the needs of the industry which uses it as cutting materials, polishing materials, abrasives, and coatings.

In order to produce diamonds synthetically, chemical deposition techniques are used. This technique uses high temperatures to form plasma which creates carbon in its atomic state and deposits it onto the substrate to form the structure of diamonds in layers. More layers will result in thicker diamonds.

Models of the production of artificial diamonds are developed to provide a better understanding of the underlying processes and reactions. These models describe the production process and can be used to find new ways and better parameters to optimize the process of synthesizing diamonds.

1.3 Objective

The objectives of this project are as below:

- To develop a working simulation of the production of artificial diamonds
- To simulate the model and observe the results
- To find any parameters that might contribute to formation of thick diamond layers in through CVD process

The simulation focuses on the diamond layer condensation step that affects the growth rate of the layer on the substrate. The objectives are proposed to be feasible in the time frame that is available. A 3 dimensional reactor is drawn and meshed to study the phenomena of carbon deposition. The subject of interest is to find any parameters that can increase the deposition rate of carbon and at the same time maintain formation of diamond layer with a flat surface.

In FYP 1, the majority of the work is done to simulate the process of carbon deposition to form layers of diamond while in FYP 2, the parameters that might affect the deposition rate is experimented upon to find the optimal parameters.

1.4 Scope of Study

The project comprises the study of the phenomena of carbon deposition to form layers of diamond on a substrate. The system under study consists of a mixture of methane and hydrogen in gaseous form with a concentration of 2 mol % methane. The mixture is injected into the reactor from the inlet. The reactor is in a shape of a cylinder.

The mixture temperature and pressure is set to 500K and 10000 kPa. There are many reactions that take place in a real deposition environment for this case. To simplify it, only reactions that contribute to the deposition process are selected. They are as below:

$2H_2 \leftrightarrow H_2 + 2H$

$CH_4 + H \leftrightarrow CH_3 + H_2$

$CH_3 + H \leftrightarrow CH_2 + H_2$

$CH_2 + H \leftrightarrow CH + H_2$

$CH + H \leftrightarrow C + H_2$

The process of carbon deposition consists of 2 crucial steps which are the nucleation and condensation steps. For this project, more emphasis is given on the condensation part while the nucleation part is not totally neglected.

The end result is expected to reveal parameters that can contribute to formation of thicker diamond layers that are formed on the substrate.

CHAPTER 2
LITERATURE REVIEW

2.1 Diamonds

Diamonds are formed deep down in the earth's crust, more than 150km deep. They are created through geologic processes in the mantle of the earth. The earth consists of three concentric layers, namely, the core, mantle and crust. It takes millions to billions of years for diamonds to form. The diamonds that are recently form dated back to 45 million years ago. Diamonds usually take more than 45 million years to come into existence in their current form. Some diamonds are even one third of the age of the earth.

Diamond exhibit extraordinary physical properties with the most standing out characteristic is its luster. The lustrous properties of diamonds make it one of the most precious minerals known to man. It was formerly used as decorations for holy statues. Now, it is a very popular and everlasting jewelry item. It symbolizes status and wealth.

Besides jewelry, diamonds are also used industrially. They are used as cutting materials, polishing materials, coatings, abrasives and heatsinks. This is attributed to the remarkable physical property of diamonds which is to be the hardest material known to man. It is rated 10 on the Mohs scale with 1 being the softest and 10 being the hardest.

The hardness of diamonds is due to its strong covalent bonding between its atoms. Diamonds only consist of carbon atoms arranged in a variation of the face-centered cubic crystal structure called a diamond lattice. This structure is very stable and can withstand the stress in which it is currently used in application.

2.2 Industrial Diamonds

Diamonds consume an enormous amount of energy and time to be created. In order to use it in daily life and industries, diamonds are needed fast and must be produced in an economical manner. This became the driving force for researchers to produce diamonds synthetically in the laboratory targeting a mass production process of industrial grade diamonds.

Currently, diamonds are not being able to be produced commercially in a large scale. This is due to the high temperature and high pressure of the process needed to form diamonds. Diamonds need to be produced in the lab in a controlled chamber.

2.3 Artificial Diamonds

Research is underway in producing artificial diamonds in the laboratory. There has been a lot of research in this field that resulted many routes to produce synthetic diamonds. One of the current technology in producing artificial diamonds is through Chemical Vapor Deposition (CVD) technique.

The CVD technique is chemical process used to produce high-purity, high performance solid materials. In CVD, the substrate is exposed to gaseous molecules, called precursor, and transforms it into a solid in the form of films on the substrate surface.

There are many types of CVD techniques which differ in the way they are carried out. They can be classified according to operating pressure, physical properties of the vapor, plasma processing methods or any other ways that defines the CVD process.

Some of the most popular CVD techniques used in the production of artificial diamonds are the microwave plasma-assisted CVD (MPCVD), plasma-enhanced CVD (PECVD), hot filament CVD (HFCVD), moderate-pressure d.c. plasma CVD (MPCVD), radio-frequency thermal plasma CVD (RFCVD) and high-gravity CVD (HGCVD).

2.4 Modeling of Artificial Diamond Production

In order to obtain a better understanding of the CVD processes in making artificial diamonds, numerical models are developed to describe the mechanism of the CVD. These models are developed and simulated using computational fluid dynamic software in order to study the CVD process.

The simulation of the models will reveal conditions and situations in the process that might help in improving the CVD technique. This includes the temperature, pressure, inlet positioning, outlet positioning, chemical concentrations, substrate types, substrate holders, gravity and many more parameters[1].

Modifications are done to the existing techniques and they are retested. The results of the new experiments may be improved. The simulations can be used again to refine the results obtained experimentally. The models provide insight in what is happening in the reactors and we can study from it to get better results.

2.5 Nucleation Model

An enormous amount of effort has been put in to research on diamond films since it has remarkable properties that are useful in many applications. Most of the research focuses on understanding for preparation methods, mostly through chemical vapor deposition techniques[2]. The goal of the research is to provide coating with high quality by improving the properties. This can be achieved by increasing the nucleation density and by reducing the roughness of optical diamond behavior.

High nucleation density can reduce the void formation at the substrate-coating interface[3]. This will provide better adhesion of the diamond films to cutting tools. That is why deeper understanding into the nucleation mechanism of diamond films during chemical vapor deposition is important. The heterogeneous nucleation process with phase change at the surface was widely studied on the basis of both thermodynamic and kinetic arguments. Kinetic studies provide

- Evolution of the rate at which the new phase transforms
- The rate at which nucleation and surface coverage occur

The processes can be modeled by using rate equations. From here, we define:

N_d = the growth rate, the atom amount per unit time of the stable atomic clusters with diamond substrate

N_H = the etching rate, the etching atom amount per unit time from the surface of the clusters of atomic hydrogen

N_m = the eating rate, the eating atom amount per unit time in the trapping region of the cluster of the minute pits

N = the actual growth rate of the clusters

From here, the actual growth rate, N, can be described as follows in the kinetic equation:

$$N = N_d - N_m - N_H \qquad (1)$$

By assuming the cluster is of a spherical coronary shape, the growth rate, N, can be calculated:

$$N_d = ap(2\pi r \sin\theta)(2\pi mk)^{-1/2} \exp\left(\frac{E_a - E_d}{kT}\right) \qquad (2)$$

Where, a = the space between surface sites, r = the radius of the cluster, θ = the contact angle of the cluster, m = the mass of the adatom, k = the Boltzman constant, E_a = the adsorption energy, E_d = the energy barrier to hopping between surface sites, p = pressure in CVD, T = temperature in CVD

The area of the trapping region of the clusters is defined as $2a\pi r \sin\theta$ in the equation.

For the derivation of N_H,

R_H = the etching rate, the atom per unit time and unit area

Then, N_H is as below:

$$N_H = 2\pi r^2 (1 - \cos\theta) R_H \qquad (3)$$

The equation to obtain N_m is similar to that of N_d. It is as below:

$$N_m = p\left(2\pi r a D_o \sin\theta\right)\left[2\pi R(t) a\right]\exp\left(\frac{E_a - E_d}{kT}\right) \qquad (4)$$

Where, D_o = density of the minute pits per unit area, $R(t)$ = average radius of the minute pits

By substituting the equations (2),(3) and (4) into equation (1), the equation below is obtained:

$$N = N_d - N_m - N_H$$

$$N = \left[ap(2\pi r \sin\theta)(2\pi m k)^{-1/2}\exp\left(\frac{E_a - E_d}{kT}\right)\right] - \left[p\left(2\pi r a D_o \sin\theta\right)\left[2\pi R(t) a\right]\exp\left(\frac{E_a - E_d}{kT}\right)\right]$$
$$-\left[2\pi r^2\left(1 - \cos\theta\right)R_H\right]$$

Simplifying the first two terms will result:

$$N = ap(2\pi m k)^{-1/2}\exp\left(\frac{E_a - E_d}{kT}\right)[2\pi r \sin\theta(1 - 2\pi a D_o R(t)] - \left[2\pi r^2\left(1 - \cos\theta\right)R_H\right] \qquad (5)$$

During CVD, the diamond critical nucleus is so large that its contained atomic amount could reach several hundred carbon atoms on the Si substrate due to the large formation energy of diamond critical nuclei[2]. The nucleation density of diamond films on the smooth surface of Si substrates is always very low and seems to be equal to the defect density of the Si substrate surface.

High oriented diamond films are obtained from an epitaxial ratio of a few percent. The subsequent diamond film quality will be better with increasing epitaxial ratio. The ratio is difficult to increase due to the extreme complexity of the physical and chemical substrate environment during the pretreatment step. The bias-enhanced nucleation (BEN) step precedes in superimposing a discharge which is in contact with the substrate with a d.c. glow discharge created by negative biasing of the substrate relative to the reactor wall or relative to an additional anode located above the substrate.

The size and nature of the reactor, shape and size of substrate holder, electric field distribution of microwave plasma and d.c. bias and the large synthesis parameter variations such as nature and composition of the plasma producing gas mixture, substrate temperature, microwave power, pressure ans bias conditions may lead to a high dispersion of results in terms of diamond quality, epitaxial ratio, deposit homogeneity and in terms of synthesis reproducibility.

The lack of result uniformity does not permit to clearly determine the main mechanisms of diamond formation during the bias step and the multiple nucleation models presented in the literature illustrate this dicersity. In BEN step for MPCVD synthesis, the chemical and electrical behavior of the double discharge which has been strongly studied and the substrate modifications submitted to these discharges that interest many research groups and whose knowledge constitutes today a real stake foe the optimization of this process.

Increasing homogeneity requires a strict control of the double-discharge. The d.c. discharge homogeneity is directlylinked ti the microwave location over the substrate/ substrate holder system and to the electric-field distribution of the d.c.voltage. A graphite electrode located above the substrate has been added to minimize the d.c. electric field gradient near the substrate holder.

The distance between the substrate and the electrode must be chosen to avoid microwave plasma disturbance. It can be qualitatively foreseen by calculating the electric field distribution of the microwave inside the reactor when the microwave plasma is not initiated yet. With a system with symmetry of revolution, the calculation of the electromagnetic field in transverse magnetic modes is carried out with the relationship below:

$$\frac{\partial}{\partial z}\left(\frac{1}{\varepsilon . r}\frac{\partial\left(r.H_\theta\right)}{\partial z}\right)+\frac{\partial}{\partial r}\left(\frac{1}{\varepsilon . r}\frac{\partial\left(r.H_\theta\right)}{\partial r}\right)+\frac{\left(2\pi v\right)^2}{rc^2}\left(r.H_\theta\right)=0$$

Where

ε is the relative permittivity of the environment, v is the eigen frequency of the cavity and c is the speed of light.

The presence of high microwave electric field at the extremities of the substrate holder is visible in the figure below.

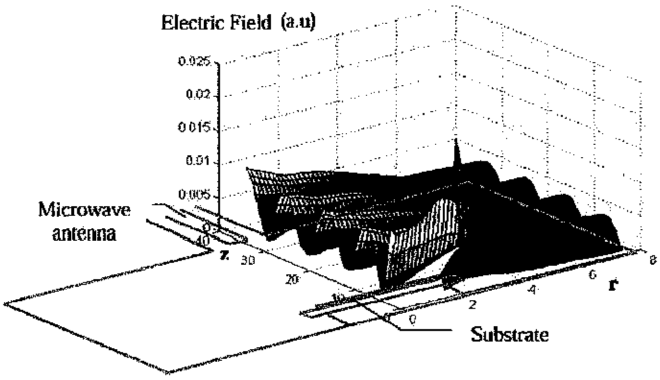


Figure 1: Microwave electric-field distribution in the reactor chamber[2]

This induces very strong point effects when the microwave plasma is switched on and corresponds to the catching areas, usually observed when the microwave plasma is ignited. Its homogeneity is all the more difficult than point effects exist.

Simulations of the microwave electric field distribution with various substrate holder geometries show that point effects can be strongly decreased for particular shapes[4]. Fig 3 shows the final configuration of the system substrate/substrate-holder that minimizes the microwave plasma heterogeneity and favours the d.c. discharge spreading over the substrate surface.

Below is the table of parameters used for the deposition of oriented diamond crystals.

Time	Heating (5 min)	Etching (3 min)	Bias (30 s)	Growth (20min/20hour)
Total pressure (hPa)	13	13	13	13
Microwave power (W)	-	300	300	300
Total flow rate (sccm)	400	400	400	190
Gas composition (vol %)	100% (H_2)	100% H_2	4% CH_4 (in H_2)	1 %CH_4 (in H2)
Bias voltage (V)	0	0	-150	0
Temperature (K)	813	1073	1113	1073
Substrate	Silicone (100) square of 10 x 10 mm^2			
Substrate-holder	Molybdenum			
Electrode	Graphite = 30mm			

Table 1: Experimental parameters used for the deposition of oriented diamond crytals and films

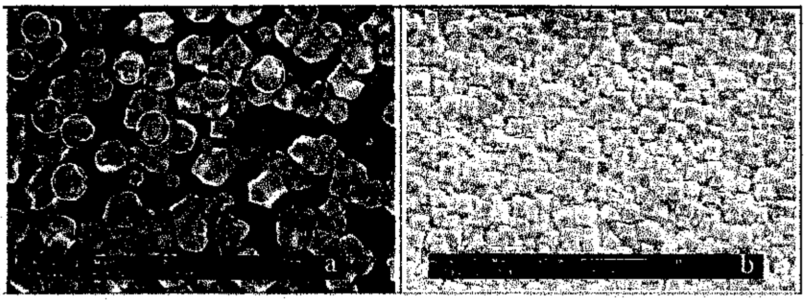


Figure 2: SEM micrographs[2]

Figure 2 shows the diamond deposites after (a) 20 min if growth step where white circles point out some epitaxial crystals and (b) 20 hours of growth step. The selection of epitaxial crystals at the expense of others, leading to a homogeneous surface mainly constituted by epitaxied crystals is observed. The very short bias duration with low bias voltage does not strongly modify the silicon substrate but sufficient to have nucleation and orientation.

The homogeneity of the highly oriented diamond films can be improved by increasing the localization and the stability of the double-discharge[5, 6] (d.c and microwave). This improvement can be done by modifying the nature and the geometry of the substrate-holder by increasing the electric field homogeneity associated to the d.c. polarization.

2.6 Condensation Model

The condensation model is also known as the step growth model. This is where the diamond increases in thickness after the nucleation step. The carbon atoms start to deposit to form layers of diamond films on the nucleus which has formed on the surface of the substrate[7]. The layers will continue on growing and this is modeled by equations.

The gas-phase reaction mechanism is obtained using brute force sensitivity analysis for various gas temperatures and hydrogen dissociation levels. Altogether there are 37 reversible reactions and 15 species. As the table below:

Reaction		Rate Constant
1	$CH_3 + CH_3 + H_2 \leftrightarrow C_2H_6 + H_2$	F(6.36 x 10^{41}, -7.03,2.762)
2	$CH_3 + H + H_2 \leftrightarrow C_4 + H_2$	F(1.6 x 10^{27}, -3.0,0)
3	$C_2H_4 + H + H_2 \leftrightarrow C_2H_5 + H_2$	F(1.27 x 10^{28}, -2.76,-0.054)
4	$C_2H_2 + H + H_2 \leftrightarrow C_2H_3 + H_2$	F(5.34 x 10^{21}, -3.5,2.41)
5	$CH_4 + H + H_2 \leftrightarrow CH_3 + H_2$	F(2.2 x 10^{4}, 3.08,8.75)
6	$CH_3 + CH_3 + H_2 \leftrightarrow C_2H_6 + H_2$	F(1.0 x 10^{16}, 0,31.792)
7	$CH_3 + CH_4 \leftrightarrow C_2H_5 + H_2$	F(1.0 x 10^{13}, 0,23)
8	$C_2H_5 + H \leftrightarrow CH_3 + CH_3$	F(1.0 x 10^{14}, 0,0)
9	$C_2H_3 + H \leftrightarrow C_2H_2 + H_2$	F(1.0 x 10^{13}, 0,0)
10	$C_2H_4 + H \leftrightarrow C_2H_5 + H_2$	F(1.1 x 10^{14}, 0,8.5)
11	$C_2H_6 + H \leftrightarrow C_2H_5 + H_2$	F(5.4 x 10^{2}, 3.5,5.21)
12	$H + H + H_2 \leftrightarrow H_2 + H_2$	F(9.2 x 10^{16}, -0.6,0)
13	$CH_3 + H \leftrightarrow CH_2 + H_2$	F(9.0 x 10^{13}, 0,15.1)
14	$CH_2 + H \leftrightarrow CH + H_2$	F(1.0 x 10^{18}, -1.56,0)
15	$CH + H \leftrightarrow C + H_2$	F(1.5 x 10^{14}, 0,0)
16	$CH + CH_2 \leftrightarrow C_2H_2 + H$	F(4.0 x 10^{13}, 0,0)
17	$CH + CH_3 \leftrightarrow C_2H_3 + H$	F(3.0 x 10^{13}, 0,0)
18	$CH + CH_4 \leftrightarrow C_2H_4 + H$	F(6.0x 10^{13}, 0,0)
19	$C + CH_3 \leftrightarrow C_2H_2 + H$	F(5.0 x 10^{13}, 0,0)
20	$C + CH_2 \leftrightarrow C_2H + H$	F(5.0 x 10^{13}, 0,0)
21	$CH_2 + CH_3 \leftrightarrow C_2H_4 + H$	F(3.0 x 10^{13}, 0,0)
22	$C_2H + H_2 \leftrightarrow C_2H_2 + H$	F(4.09 x 10^{5}, 2.39,0.864)
23	CH_2(singlet) + $CH_4 \leftrightarrow CH_3 + CH_3$	F(4.0 x 10^{13}, 0,0)
24	CH_2(singlet) + $H_2 \leftrightarrow CH_3 + H$	F(7.0 x 10^{13}, 0,0)
25	CH_2(singlet) + $H_2 \leftrightarrow CH_2 + H_2$	F(1.0 x 10^{13}, 0,0)
26	CH_2(singlet) + $H \leftrightarrow CH + H$	F(2.0 x 10^{14}, 0,0)
27	$CH_2 + CH_2 \leftrightarrow C_2H_2 + H_2$	F(4.0 x 10^{13}, 0,0)
28	$C_2H_2 + H_2 \leftrightarrow C_2H + H + H_2$	F(4.2 x 10^{16}, 0,107)
29	$C_2H_4 + H_2 \leftrightarrow C_2H_2 + H_2 + H_2$	F(1.5 x 10^{15}, 0,55.8)

30	$C_2H_4 + H_2 \leftrightarrow C_2H_3 + H + H_2$	F(1.4 x 10^{16}, 0,82.36)
31	$C_2 + H_2 \leftrightarrow C_2H + H$	F(4.0 x 10^{5}, 2.4,1)
32	$C + CH \leftrightarrow C_2 + H$	F(2.0 x 10^{14}, 0, 0)
33	$CH_2 + H_2 \leftrightarrow C + H_2 + H_2$	F(1.3 x 10^{14}, 0, 0)
34	$CH_2 + CH_4 \leftrightarrow CH_3 + CH_3$	F(1.0 x 10^{13}, 0, 0)
35	CH_2(singlet) + H $\leftrightarrow$ CH + H_2	F(3.0 x 10^{13}, 0, 0)
36	$CH_3 + H_2 \leftrightarrow CH_2 + H + H_2$	F(1.0 x 10^{16}, 0, 90.6)
37	$CH_3 + H_2 \leftrightarrow CH + H_2 + H_2$	F(.0 x 10^{15}, 0, 85)

Table 2: Reactions in carbon deposition to form diamond layer

A two-dimensional model of a hot filament chemical vapor deposition is developed to study the gas phase and surface processes of diamond growth[8]. The gas temperature, fluid flow, and species concentration fields were calculated by full transport equations numerically. Catalytic chemistry at the surface of the filament was taken into consideration for a more complete model formation[6]. The distribution of the atom concentration and the gas temperature in a HFCVD reactor were obtained analytically. Surface kinetics is used to derive the expressions for diamond growth rate and the hydrogen atom destruction coefficient at the substrate. Brute force sensitivity analysis was used to obtain the gas-phase reaction mechanism. The calculated results were then compared with experimental data.

Diamond growth in hot-filament chemical vapor deposition (HFCVD) reactors using intense numerical models is being studied here. Derivation of complex self consistent models that describes the numerous processes occurring in HFCVD reactors is very difficult[5]. Majority of the models used in this article are one-dimensional or reduces to one dimension. However, a two-dimensional spatial modeling is required as minimum. Simplified chemical reaction kinetics is used and the processes on the substrate filament surfaces are not taken into account for two-dimensional models. Surface processes, additional sources of hydrogen atoms at the filament surface and non-one-dimensional effects are some of the complicated issues that need to be addressed in developing a through model.

The temperature discontinuity at the filament was taken into account using experimental data. Correct formulation of the boundary conditions is very important in HFCVD reactor models. Additional source of H due to dissociation of H_2 at the filament must be included to explain the H-atom concentration and the sharp decrease in its concentration as carbon mole fraction in the feed is increased. The results from the model and from experiment that were carried out also suggest that the H-atom source on the filament needs to be considered[9]. Decomposition of hydrocarbons on the filament surface poisons the catalytic production of H-atom from H_2 at the filament surface[10]. Rate of H-atom generation is not known. Methods that are used to determine the rate are as below:

- From comparison of the kinetics of filament surface processes
- From comparison of the analytic and experimental H-atom distributions
- From 2D calculations with different rates Q to fit the calculated and measured H-atom concentrations near the filament
- From experimental data

A simple kinetics of two reversible reactions on the filament surface are considered. (1) is the recombination of an H atom on a hydrogen terminated surface site SH. (2) and (-2) are the adsorption and desorption of an H atom.

$$SH + H \rightleftharpoons S* + H_2 \quad (6)$$

$$S* + H \rightleftharpoons SH \quad (7)$$

Diamond growth from methyl radical as the dominant diamond precursor was proposed and the importance of H atoms, radical sites and chemisorbed CH_2 groups in the propagation of diamond growth was revealed. The probabilities of CH_3 adsorption on the dimer site, adjacent to the bridge site, as well as the filling of void sites are proportional to the rate of formation of the radical site pairs. The growth rate G (in μm/h) is obtained as below:

$$G = \frac{c1\sqrt{T_{ns}}CH_3}{c2\exp(14.6/RT_s) + c3\exp(7.3/RT_s) + 1 + f\left(T_s, T_{ns}\right)H_2/H} \qquad (8)$$

Equation (8) is the condensation model which describes the growth rate if the diamond films and reports it in µm/h.

A number of two-dimensional calculations are done for a set of reaction parameters. For reactor of Hsu, the parameters are P=20Torr, T_s=1100K, T_f=2600K, CH_4=1%, R_f=0.0125cm, R_{fs}=1.3cm, temperature discontinuity at the filament T_f-Tn_f is 900K. The rate of heterogeneous source Q is set at 1.6x10^{19} cm^{-1} $s^{-1}$and Q/(2 π Rf)=2x10^{20} cm^{-2} s^{-1} to make the H concentration near the substrate the same as in the experiment. The mole fraction of H is 2.5 times lower than the model prediction. This is due to the gas-phase reactions comparable with the heterogeneous source.The figure 1 below shows the representation of the two dimensional distributions of the gas temperature and the gas velocity.

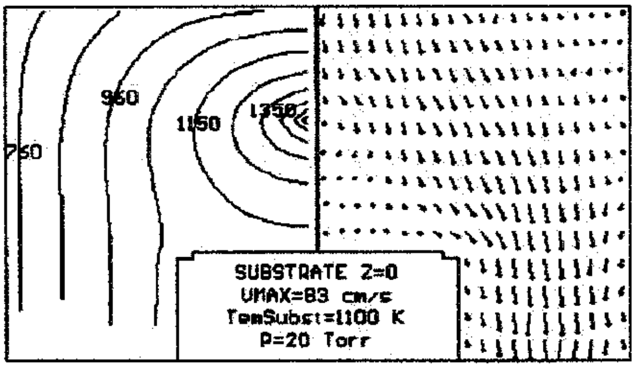


Figure 3: Gas temperature on the left and gas velocity on the right[11]

The real substrate size in the reactor is not known. The distribution of H, CH_3, C_2H_2, and CH_4 for different points of x are shown in figure 2. The diffusion effects both the z and x directions are significant in the transport of important species from near filament to substrate.

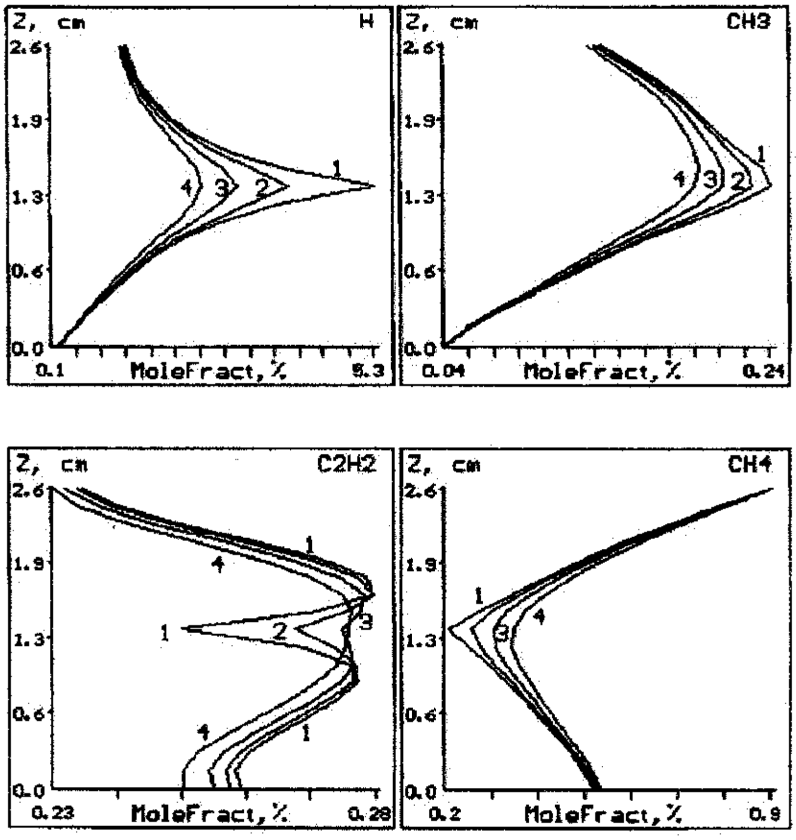


Figure 4: Gas phase distributions of H, CH_3, C_2H_2 and CH_4[11]

The variation in temperature is found out to have only a slight effect on the calculated results. It is suggested that the C_2 radical played an important role in the growth mechanis. However, the C_2 is not a dominant species. The new suggested mechanism involves competitive growth by all the C_1 radical species that are present in the gas mixture close to the growing (100) diamond surface. In HFCVD reactors at high temperatures or high CH_4 concentrations, the concentration of the other C_1 radical species near the growing diamond surface can become as high as -10^{12} cm^{-3} and may contribute to the growth process.

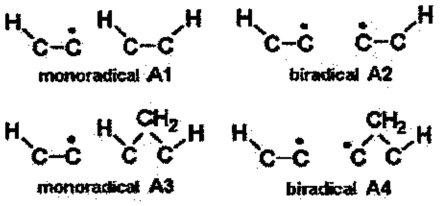


Figure 5: Mechanism of carbon deposition

In most growth models, abstraction of surface H atoms by gas phase atomic H are the reactions which drive the chemistry of growth. 2 main types of radical sites on the reconstructed (100)-(2x1) diamond surface which are mono radical sites and biradical sites.

The growth rate contribution, G (µm h^{-1}) from CH_3 is:

$$G_{bi} = 3.8\times10^{-14} T_S^{0.5}[CH_3]R^2$$

Where T is substrate temperature, $[CH_3]$ in methyl gas phase concentration in cm^{-3} at surface and R is fraction of monoradical sites.

For mono:

$$G_{mono} = 3.8\times10^{-14} T_S^{0.5}[CH_3]\times R\times 0.5\cdot k_a[H]\{1/(k_a[H]+k_d(A1))+1/(k_a[H]+k_d(A3))\}$$

And the total growth rate due to CH_3 can now be expressed as

$$G_{CH3} = 3.8\times10^{-14} T_S^{0.5}[CH_3]\cdot R\cdot\{0.5\cdot k_a[H]\cdot(1/(k_a[H]+k_d(A1))+1/(k_a[H]+k_d(A3)))+R\}$$

Where $k_d(A1)$ and $k_d(A3)$ refer to the rates of desorption of CH3 from A1 and A3 sites.

R is the fraction of surface monoradical cites given by $R = C_d^* / (C_d^* + C_dH)$ where C_d^* and C_dH are the respective densities of open and hydrogen-terminated surface sites. This fraction R mainly depends on the rate constants for the surface H abstraction and addition reactions. R is obtained as

$$R = 1/\{1 + 0.3\exp(3430/T_S) + 0.1\exp(-4420/T_S)[H_2]/[H]\}$$

After the reaction of the condensation process is known, the optimal conditions for better deposition of diamond particles should be looked into. The conditions include any aspect of the parameters such as the concentration of species, temperature and pressure and also power is applicable.

The diamond deposition rate at different power ratings is shown in the graph below.

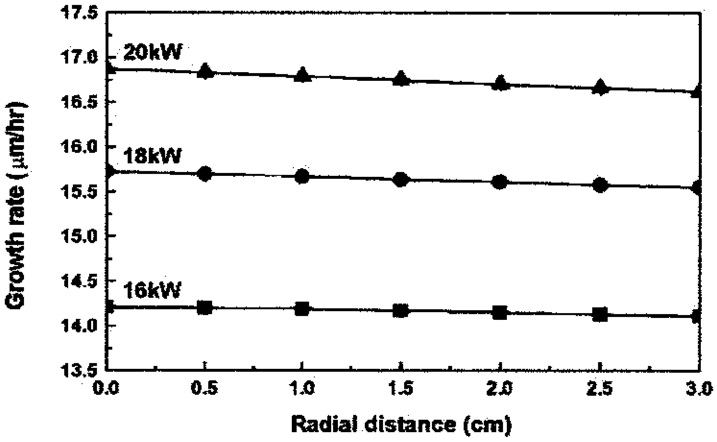


Figure 6: Diamond growth rate with varying power ratings[10]

It can clearly be seen that the power rating of 20kW gives the highest deposition rate and it can generally be said that a higher power rating will result in a higher deposition rate. The higher power used will generate more C radicals which will be deposited on the substrate. A graph below shows the C radicals concentration in a radial manner.

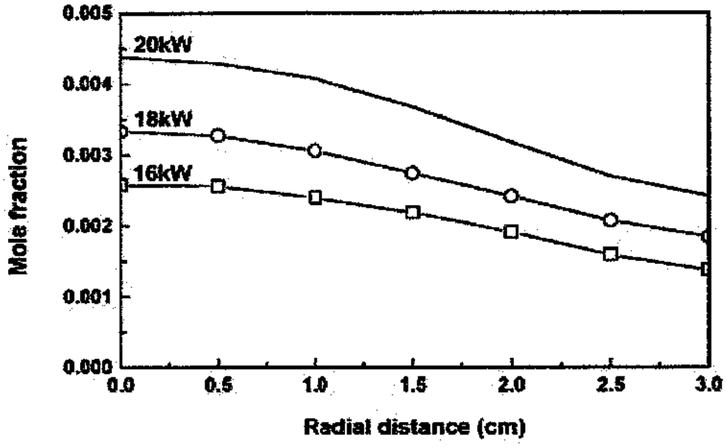
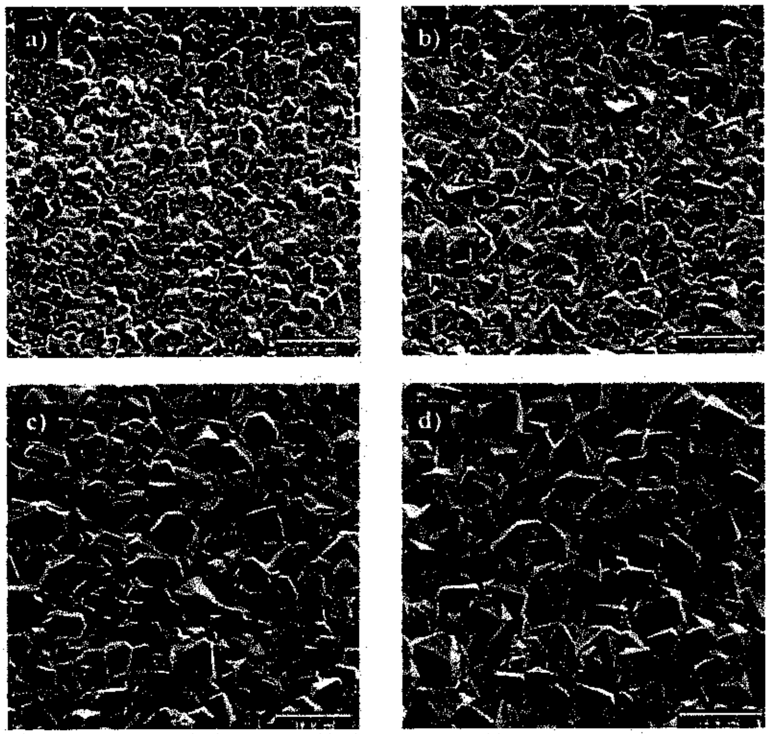


Figure 7: Mole fraction of C radicals with varying power ratings[9]

The dissociation of C_2, CH_4 and other components is much easier when the power supply used is much higher as it gives the necessary energy required for C radicals to form.

The morphology of the diamond layers is also important and needs to be taken into consideration. The figures below shows the evolving morphology based on temperature changes.



Scanning electron micrographs for diamond structures: T_{sub}=(a) 780°C; (b) 850°C; (c) 950°C; (d) 1000–1100°C.

Figure 8: Morphology of diamond layer[7]

From the morphology, the optimum condition is condition in figure c above. The size is larger than a and b. The morphology type of the diamond changes from c to d. Condition c is better as it is a flat surface while d is edged and pointed.

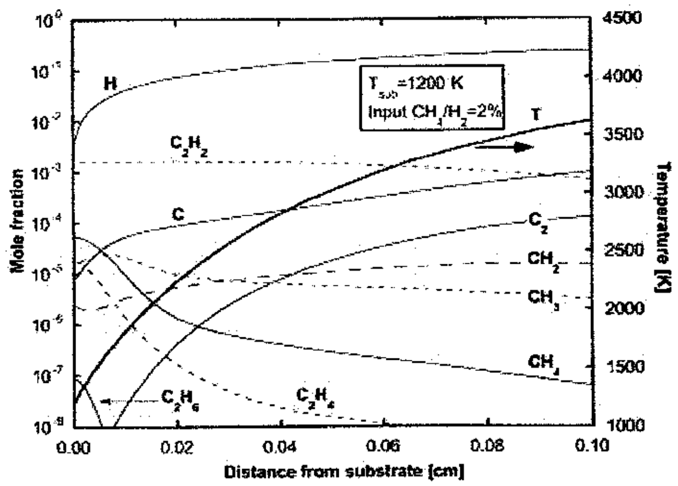


Figure 9: Concentration of components vs distance from substrate[9]

The graph shows the species profile for a system that has an inlet of CH_4/H_2 of 2%. The profile is taken at the sampling line which is located near the surface of the substrate. The temperature of the substrate is maintained at 1200K.

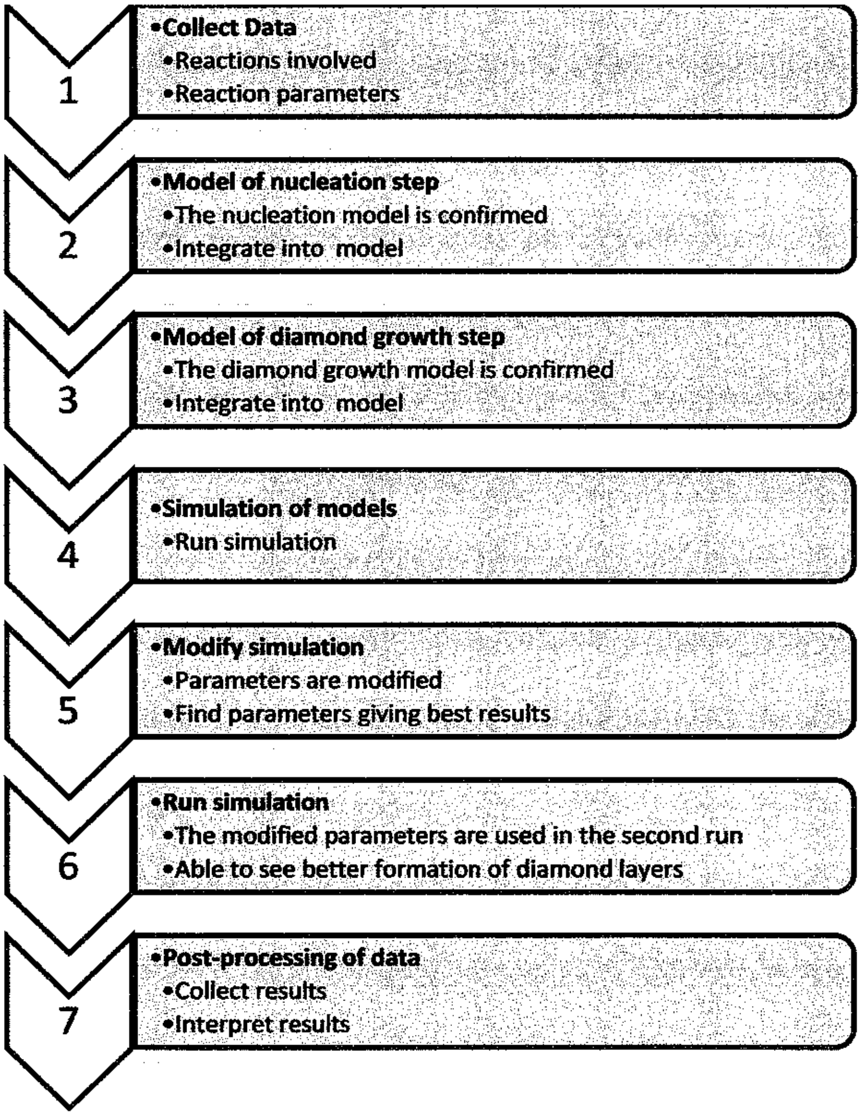
The most desirable condition is that the C radicals are high in concentration when it is nearing the deposition area. As the distance from substrate reduces, the concentration of C radicals should decrease. This shows a successful deposition on the substrate. The deposition rate is better when the concentration of the C radicals decrease drastically when it reaches the substrate surface which shows that the C radicals are deposited on the substrate. The C radicals decreasing as it gets nearer to the substrate shows that it is participating in other radical reactions.

C_2H_6 contributes to the formation of CH_3 as it decreases. Radical reactions take place at the surface of the substrate CH_3, CH_4 and C_2H_4. This is why the concentration of these species are higher at the surface of the substrate. The reactions at the surface are radical reactions that are reversible and they produce radicals of C and H and at the same time deposit C radicals on the surface.

The inlet temperature is more than 3500 K and it reduces as it reaches the surface of the substrate. This quenching effect eases condensation reactions to happen so that more C radicals will form diamonds on the surface.

CHAPTER 3
METHODOLOGY

3.1 Project Activities



1. The project starts with critical literature review of the production of diamonds artificially.

2. Then, the literature review is focused into general scopes of artificial diamond production. This includes the start of the diamond formation, the growth of the diamond, the kind of reactors used and the controlled parameter values.
3. The literature review will give insight and guidance in developing the models to describe the production of artificial diamonds.
4. Models of the nucleation step of the diamond on the substrate are developed based on the literature review done on the topic.
5. The nucleation model is compared to the existing models developed in other literatures.
6. Models of the diamond growth step are developed based on the literature review done on the topic.
7. The diamond growth model is compared to the existing models developed in the literatures.
8. Simulations of the models are done using computational fluid dynamics software to obtain results and the results are compared to experimental data.
9. Modifications are done to the model to produce results that fit the experimental results.
10. Modified parameters are used for the simulation and the simulation is done again.
11. Post-processing is done from the obtained data.

3.2 Key Milestones

1. Completion of literature review to a certain extent
2. Development of artificial diamond production models
3. Simulations of the artificial diamond production models
4. Enhancing the simulations by making it as close as possible to experimental reaction data.
5. Development of a time dependent simulation so that the behavior of the carbon deposition process can be studied.
6. Post processing the data obtained from the time dependent simulation.

3.3 Gantt Chart

Final Year Project 1

Title/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review														
i.Nucleation Model														
ii. Condensation Model														
Progress Report (3rd Sept)														
Seminar (3rd Sept)														
Calculations														
Modelling														
Simulation														
Modifications														
Interim Report (1st Nov)														
Oral Presentation (1st Nov)														

Final Year Project 2

Title/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Work Continues														
Progress Report														
Project Work Continues														
Submission of Draft Report														
Submission of Dissertation(soft bound)														
Submission of Technical Paper														
Oral Presentation														
Submission of Dissertation(hard bound)														

3.4 Tools

The tools required in order to complete this project are:

- Computer with decent computing power
- ANSYS FLUENT computational fluid dynamics software
- FLUENT GAMBIT

The main tool required in this project is the computational fluid dynamics (CFD) software. The simulation is handled through a systematic procedure line out in the methodology section. However for all CFD software, a basic procedure can be applied. Briefly during pre-processing, the geometry of the problem is first defined. The reactor where the process takes place is drawn and meshed. The physical modeling, boundary conditions and other properties are further specified. The simulation is started and solved iteratively. Lastly the results are analyzed.

FLUENT GAMBIT is used to draw and mesh the 3 dimensional computational domains for the problem. The simulation which is done to study the formation of diamond layers is done using FLUENT.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Results

The schematic diagram of a CVD reactor is as below.

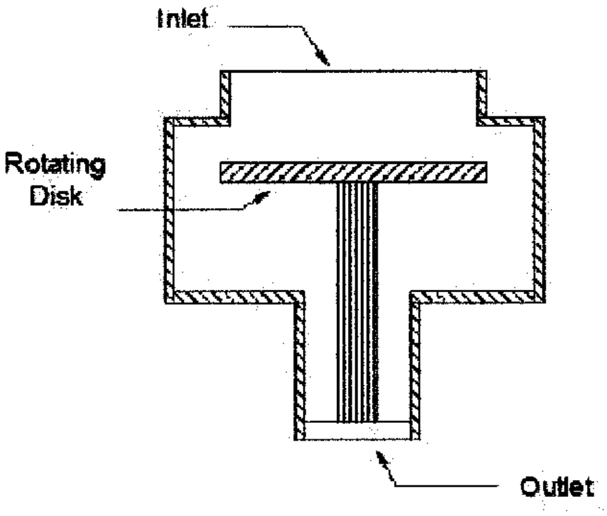


Figure 10: Schematic diagram of reactor

The conditions of the reactor is as below:

Feed inlet: Methane (80 sccm)
Hydrogen (4000 sccm)
Temperature: 1023 K
Pressure 10 000 Pa

The schematic diagram of the CVD reactor is modeled in FLUENT Gambit. The surfaces of the reactor are set as wall type except for the inlet and outlet of the reactor. The parameters and operating conditions are set in FLUENT.

The mesh of the CVD reactor after it is imported into FLUENT is as below.

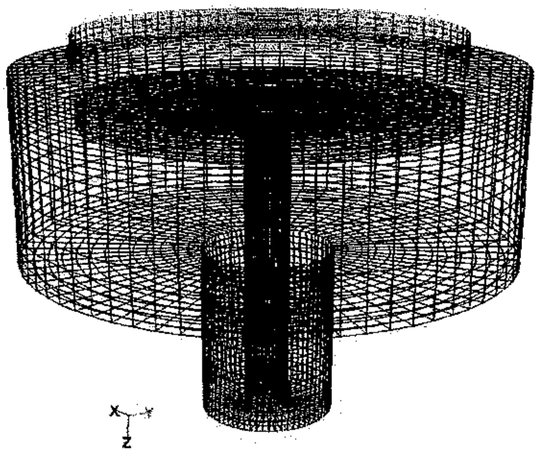


Figure 11: Mesh of reactor

For the first simulation test only one reaction is taken into consideration which is as below:

$C\_s + CH_4 + H_2 \rightarrow C + C\_s + 3H_2$

The mesh of the reactor is imported into FLUENT. The materials, boundary conditions, operating conditions and reactions are set in FLUENT. The simulation is run for 200 calculations at first without reaction and 250 calculations after that with reactions. The convergence result is as below.

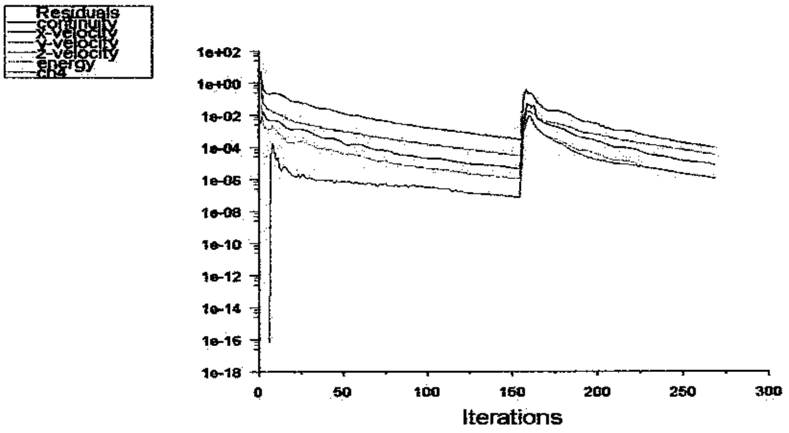
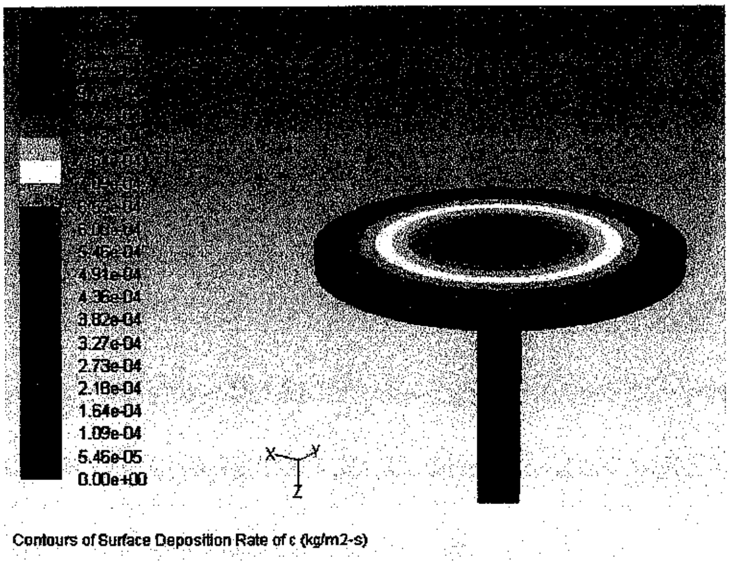


Figure 12: Convergence of simulation

The convergence shows that the values of the calculation are approaching a constant value. There are two peaks as each peak shows the beginning of a calculation. The first peak is the calculations without reaction while the other peak shows the convergence of the calculations with reactions. The calculations are done in two steps because it will be easier to converge and come to a solution.



Contours of Surface Deposition Rate of c (kg/m2-s)

Figure 13: Contours of deposition rate of carbon

Figure 4 shows the results after the calculations are complete. The red color shows that the deposition rate is high while the blue color shows that the deposition rate is low and nearly zero. From the results, it can be seen that the deposition rate is highest at the center of the deposition surface. This is expected as the precursor is fed at the center through the top of the reactor and moves radially outwards.

The diamond deposition is highest at the center. It also means that the layer of the diamonds will be thicker. The diamonds will condense at the center and lesser at the edges of the reactor surface.

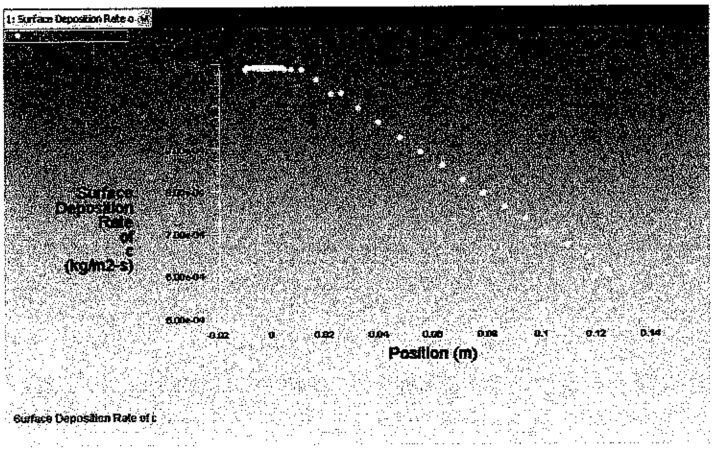


Figure 14: Deposition rate vs radial position

A plot of the deposition rate versus the radial position of the reactor surface shows the exact same results. The deposition rate at the surface center is 1.09e03 kg/m^2-s

The reactions that are to be included for the next simulation stage are as the following:

$2H_2 \leftrightarrow H_2 + 2H$

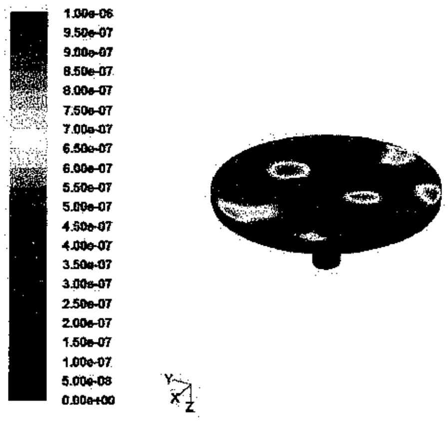
$CH_4 + H \leftrightarrow CH_3 + H_2$

$CH_3 + H \leftrightarrow CH_2 + H_2$

$CH_2 + H \leftrightarrow CH + H_2$

$CH + H \leftrightarrow C + H_2$

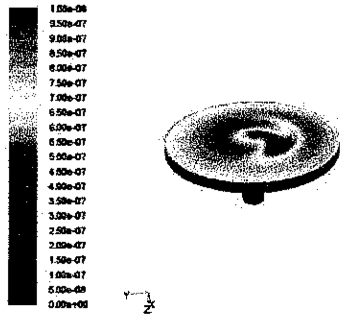
The results for the initial simulation with the reactions above is as below

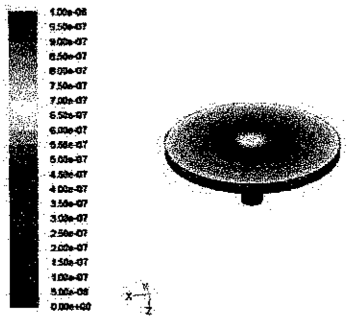


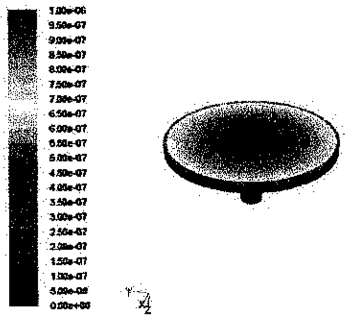
Contours of Surface Deposition Rate of c (kg/m2-s)

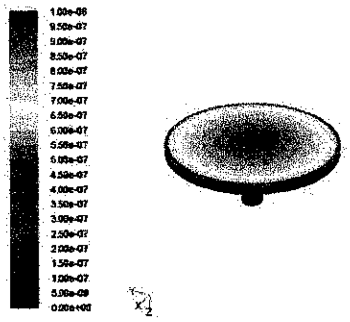
Figure 15: Contours of deposition rate for multiple reactions

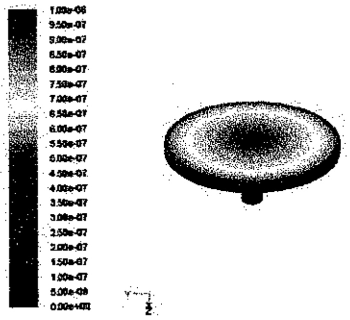
The rotational speed of the plate was experimented upon and the results are as below:

Rotational Speed (rad/s)	Carbon Deposition Rate Countour
20	 Contours of Surface Deposition Rate of c (kg/m2-s)

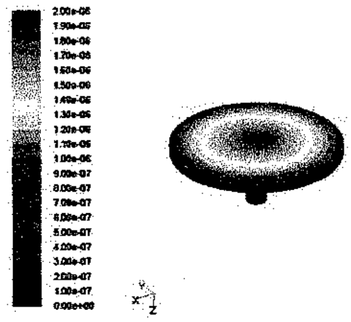
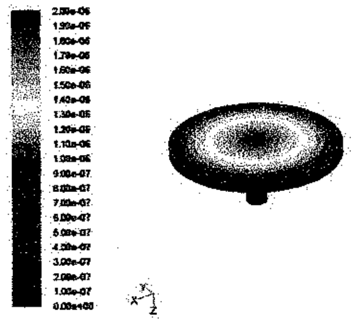
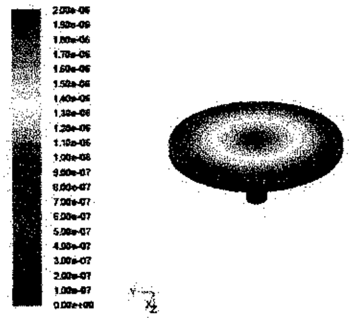
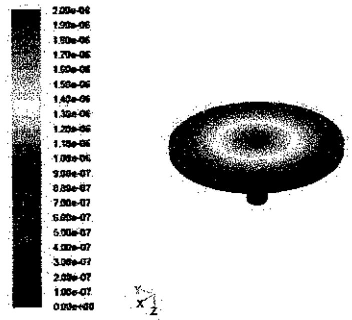
<table>
<tr><td>40</td><td>


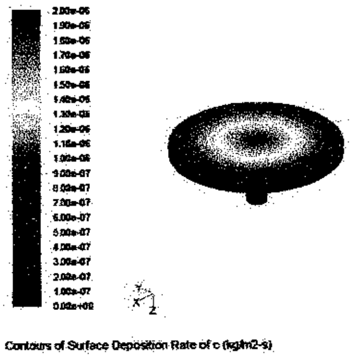
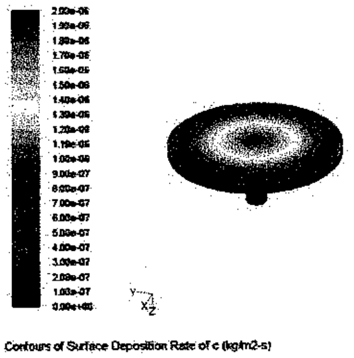
Contours of Surface Deposition Rate of c (kg/m2-s)
</td></tr>
<tr><td>60</td><td>


Contours of Surface Deposition Rate of c (kg/m2-s)
</td></tr>
<tr><td>70</td><td>


Contours of Surface Deposition Rate of c (kg/m2-s)
</td></tr>
<tr><td>80</td><td>


Contours of Surface Deposition Rate of c (kg/m2-s)
</td></tr>
</table>

100	 Contours of Surface Deposition Rate of c (kg/m2-s)
120	 Contours of Surface Deposition Rate of c (kg/m2-s)
140	 Contours of Surface Deposition Rate of c (kg/m2-s)
160	 Contours of Surface Deposition Rate of c (kg/m2-s)

180	 Contours of Surface Deposition Rate of c (kg/m2-s)
200	 Contours of Surface Deposition Rate of c (kg/m2-s)

Below is a plot of the deposition rate for each rotational speed of the plate:

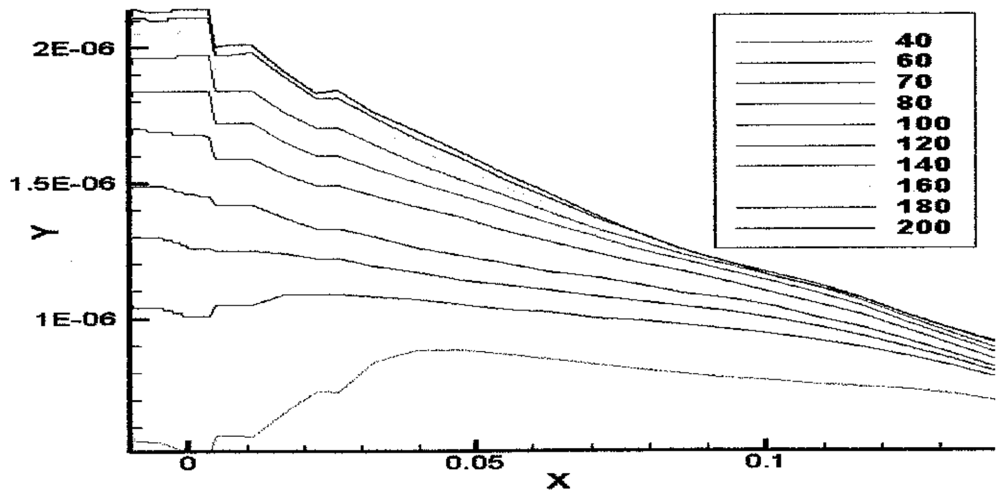


Figure 16: Deposition rate vs radial distance from center

4.2 Discussion

The reactions involved in carbon deposition to form diamonds are much more complicated than the proposed reactions to be included but not all the reactions have parameters that are readily available and studies show that the proposed reactions from one study to another study vary in the formation of side-products[9]. However, the proposed reactions are the basic reactions for most of the studies that have been carried out.

However, the newly included reactions are not easy to simulate together as the reactions are in series and reversible. The parameters of each reaction vary from one another like the activation energy and reaction rates.

The real complication is to make the reactions take place as the parameters may not be optimal for the set temperature and pressures. The temperatures pressures are set in range based on a study done by J.M. Larson et al. and most of other studies done coincide within this range.

The result for deposition rate of carbon can clearly be seen to increase as the rotational speed of the plate increases. A higher rotational speed will cause the points further from the center of the plate to have a higher velocity. This lets the gas reactants move faster relative to the center. The center on the other hand is slower in velocity. This enables the deposition rate to increase at the center causing the diamond layer to be thicker at the center of the plate.

The slight drop in deposition rate after the center as can be seen at point 0.005 m from the center is caused by the unevenness of the diamond layer. The thick center causes it to be at a higher platform and the moving gas phase have insufficient time to react with the substrate after the center (at 0.005 m) and results in a drop in deposition rate.

Although, the deposition rate increases with rotational speed, the aim is not only to achieve the highest deposition rate. It is to encourage the formation of diamond layers that are structurally strong.

The unevenness of the diamond layer can cause many problems including the formation of cracks and weak points if the layer is subjected to high stress. Uneven layers will restart the nucleation process on the diamond layer which will then make the surface much more uneven.

Uneven surfaces of the diamond layers can also be attributed to multiple nucleation points throughout the deposition process. Multiple nucleation sites will cause the new crystals to form in different orientations. Points along where independent nuclei growth meet will form layers of diamond that is not homogenous.

Homogeneity is the condition where the diamond growth orientations are in the same directions. A homogenous diamond layer exhibits higher tensile strength and minimal defects or cracks.

From the results of this simulation, the rotational speed of 70 rad/s shows that it has an even distribution of carbon deposition rate. Although this does not guarantee the homogeneity of the diamond layer, it is has a higher chance of being homogenous compared to the others.

Both deposition rate and evenness of the diamond layer are important and the parameters of the reactor should be set to create these attributes. The dimension of the reactor may also be one of the factors that contribute to these attributes.

A reactor with a larger inlet may make the supply of reactants more distributed on the entire plate. A more distributed supply may allow the rotational speed to be increased hence increasing deposition rate without affecting the evenness and homogeneity of the diamond layer.

CHAPTER 5
CONCLUSION

5.1 Conclusion

The results so far show the deposition of diamond on substrate in a reactor is possible. The addition of more reactions contribute to make it more realistic. The added reactions complicate the convergence criteria but result in a better simulation of the carbon deposition process.

Experimental work has only be done for stationary reactors and from this project, it can be seen that a reactor with a moving plate can result in a carbon deposition process that gets higher as the rotational speed is increased.

However, the homogeneity of the layer and the topology of the layer would be severely bad. Uneven surfaces would form and nucleation will start in random orientations. This will ultimately cause the diamond layer formed to be structurally weak along the lines where the orientations of the diamond meet. Cracks would form much easier as there are lots of weak points present in the diamond structure.

The best rotational speed that should be used is the one that balances the deposition rate and uniformity of the layer of diamond that is formed. For this set of parameters, it is clear that 70 rad/s will be adequate to form the diamond layer that is required.

The limit of 70 rad/s may be due to the inlet size and distribution of the initial gas phase that is exposed to the plate. Increasing the inlet area may offer a more distributed reactant exposure to the plate. This may allow the rotational speed to be cranked up higher to result in a higher deposition rate overall with uniformity and homogeneity.

5.2 Recommendation And Future Works

Recommendation and future work to improve the efficiency and to gain better insigt of the project are stated as follows:

- Increase inlet area to see relationship with uniformity of deposited diamonds on substrate layers.
- Run a time dependent simulation to find out the initial nucleation process on the substrate layers through time.

REFERENCES

1. Barrat, S., et al., *Three-dimensional diamond growth film simulations: correlations between nucleation and surface parameters.* Diamond and Related Materials, 1999. **8**(2-5): p. 150-154.
2. Barrat, S., et al., *Synthesis of highly oriented CVD diamond films by ultra short bias enhanced nucleation step.* Diamond and Related Materials. **10**(9-10): p. 1637-1642.
3. Yang, G.W. and B.X. Liu, *Kinetic model for diamond nucleation upon chemical vapor deposition.* Diamond and Related Materials, 2000. **9**(2): p. 156-161.
4. Juchmann, W., J. Luque, and J.B. Jeffries. *Two-photon laser-induced fluorescence of atomic hydrogen in a diamond-depositing dc arcjet.* 2005: Optical Society of America.
5. Yamada, H., et al., *Numerical analyses of a microwave plasma chemical vapor deposition reactor for thick diamond syntheses.* Diamond and Related Materials, 2006. **15**(9): p. 1389-1394.
6. May, P.W., et al., *Simulations of polycrystalline CVD diamond film growth using a simplified Monte Carlo model.* Diamond and Related Materials. **19**(5-6): p. 389-396.
7. Silva, F., et al., *Single crystal CVD diamond growth strategy by the use of a 3D geometrical model: Growth on (113) oriented substrates.* Diamond and Related Materials. **17**(7-10): p. 1067-1075.
8. Song, G.H., et al., *Heat transfer simulation of HFCVD and fundamentals of diamond vapor growth reactor designing.* Surface and Coatings Technology, 2000. **131**(1-3): p. 500-505.
9. Larson, J.M., M.T. Swihart, and S.L. Girshick, *Characterization of the near-surface gas-phase chemical environment in atmospheric-pressure plasma chemical vapor deposition of diamond.* Diamond and Related Materials, 1999. **8**(10): p. 1863-1874.
10. Liya L. Regel, W.R.W., *Diamond Film Deposition By Chemicla Vapor Transport.* Acta Astronautica, 2001. **48**: p. 129-144.
11. Mankelevich, Y.A., A.T. Rakhimov, and N.V. Suetin, *Two-dimensional simulation of a hot-filament chemical vapor deposition reactor.* Diamond and Releated Materials 5, 1996: p. 888-894.
12. Young, R.M. and J.J. Schreurs, *Evidence of supersonic flow in an arc-heated diamond film deposition reactor.* Diamond and Related Materials, 1996. **5**(2): p. 134-140.
13. Diebel, J.R., et al., *Simulation of Supersonic Flows in Inductively Coupled Plasma Tunnels*, in *Computational Fluid Dynamics 2004*, C. Groth and D.W. Zingg, Editors. 2006, Springer Berlin Heidelberg. p. 489-494.

14. Zhuang, Q.D., et al., *Effect of substrate temperature distribution on thermal plasma jet CVD of diamond.* Diamond and Related Materials, 1994. **3**(4-6): p. 319-324.
15. Laimer, J., et al., *Diamond growth in a direct-current low-pressure supersonic plasmajet.* Diamond and Related Materials, 1997. **6**(2-4): p. 406-410.
16. Juchmann, W., J. Luque, and J.B. Jeffries. *Two-photon laser-induced fluorescence of atomic hydrogen in a diamond-depositing dc arcjet.* 2005: Optical Society of America.
17. Herman, M.A., W. Richter, and H. Sitter, eds. *Epitaxy: Physical Principles and Technical Implementation.* 2004, Springer.
18. Ding, H., et al., *Basic parameters and models in simulation of CVD diamond devices.* Diamond and Related Materials. **19**(5-6): p. 500-502.

APPENDICES

Nucleation model

N_d is analyzed if it correctly gives the units

$$N_d = m \times \frac{kg}{\cancel{m}\cdot s^2}\left(\cancel{m}\right)\left(kg \times \frac{kg\cdot m^2}{s^2\cdot K}\right)^{-\frac{1}{2}} \exp\left(\frac{\cancel{J}}{\frac{\cancel{J}}{\cancel{K}}\cancel{K}}\right)$$

$$N_d = \frac{\frac{m\cdot kg}{s^2}}{\sqrt{\left(\frac{kg^2\cdot m^2}{s^2\cdot K}\right)}} = \frac{\frac{m\cdot kg}{s^2}}{\frac{kg\cdot m}{s\cdot\sqrt{K}}} = \frac{numberofatoms}{s\cdot\sqrt{K}}$$

For the derivation of N_H,

R_H = the etching rate, the atom per unit time and unit area

Then, N_H is as below:

$$N_H = 2\pi r^2\left(1-\cos\theta\right)R_H \qquad (3)$$

Units for N_H is as below

$$N_H = m^2 \times \frac{atom}{s\cdot m^2} = \frac{atom}{s}$$

The equation to obtain N_m is similar to that of N_d. It is as below:

$$N_m = p\left(2\pi raD_o \sin\theta\right)\left[2\pi R(t)a\right]\exp\left(\frac{E_a - E_d}{kT}\right) \qquad (4)$$

Where, D_o = density of the minute pits per unit area

R(t) = average radius of the minute pits

Units for Nm are as below:

$$N_m = \frac{kg}{m\cdot s^2}\times\left(m \times m \times \frac{kg}{m^3\cdot m^2}\right)\times\left(m\times m\right)\exp\left(\frac{\cancel{J}}{\frac{\cancel{J}}{\cancel{K}}\cancel{K}}\right)$$

$$N_m = \frac{kg^2}{m^2\cdot s^2}$$

The closest that I have achieved to get is as below by adding the term $(2\pi mk)^{-1/2}$

$$N_m = \frac{kg}{m \bullet s^2} \times \left(m \times m \times \frac{kg}{m^3 \bullet m^2} \right) \times \left(kg \times \frac{kg \bullet m^2}{s^2 \bullet K} \right)^{-\frac{1}{2}} \times (m \times m) \exp\left(\frac{\cancel{J}}{\frac{\cancel{J}}{\cancel{K}} \cancel{K}} \right)$$

$$N_m = \frac{\frac{kg^2}{m^2 \bullet s^2}}{\frac{kg \bullet m}{s \bullet \sqrt{K}}} = \frac{atom}{s \bullet \sqrt{K}}$$

By substituting the equations (2),(3) and (4) into equation (1), the equation below is obtained:

$$N = N_d - N_m - N_H$$

$$N = \left[ap(2\pi r \sin\theta)(2\pi mk)^{-1/2} \exp\left(\frac{E_a - E_d}{kT} \right) \right] - \left[p\left(2\pi raD_o \sin\theta\right)\left[2\pi R(t)a\right] \exp\left(\frac{E_a - E_d}{kT} \right) \right]$$
$$-\left[2\pi r^2 \left(1 - \cos\theta\right) R_H \right]$$

Simplifying the first two terms will result:

$$N = ap\left(2\pi r \sin\theta\right) \exp\left(\frac{E_a - E_d}{kT} \right) \left[(2\pi mk)^{-1/2} - 2\pi R(t)aD_o \right] - 2\pi r^2 \left(1 - \cos\theta\right) R_H$$

Condensation model

Below are representations of the equations:

$$\nabla_t \rho = -\nabla(\rho v)$$
$$\nabla_t(\rho u) = -\nabla(\rho uv) - \nabla_z P + \nabla \mathrm{W}_z + \rho g$$
$$\nabla_t(\rho v) = -\nabla(\rho xuv) - \nabla_x P + \nabla \mathrm{W}_x$$
$$\nabla_t(\rho \varepsilon) = -\nabla(\rho \varepsilon v) - P\nabla_z u - P\nabla_x v - \nabla \mathrm{Q}_\lambda - \nabla(\sum_{i=1}^{k} h_i j_i)$$
$$\nabla_t(n_i) = -\nabla(n_i v + j_i / m_i) + S_i - L_i n_i$$

where

$$\nabla_y = \partial / \partial y, y = t, z, x$$
$$\nabla(\rho v) = \partial(\rho u) / \partial z + \partial(\rho v) / \partial x$$

ρ is the density of the gas

g is the gravitational force

$v = (u, v)^T$ is the velocity vector

P is a scalar pressure

$$W_z = \left(2\mu \nabla_z u, \mu\left(\nabla_x u + \nabla_z v\right)\right)^T$$
$$W_x = \left(\mu\left(\nabla_x u + \nabla_z v\right), 2\mu \nabla_x v\right)^T$$

$\mu = \mu(T)$ is the gas viscosity
e is specific energy and h is the enthalpy

$Q_\lambda = (-\lambda\nabla_z T, -\lambda\nabla_x T)^T, \lambda = \lambda(T)$ is the thermal conductivity, T is the gas temperature, n_i and m_i are the i^th^ component concentration and mass, S_i and $L_i n_i$ are the production and loss rates in gas-phase chemical reactions. $j_i = \left(-N^2 m_k m_i D_{ik} \nabla X_i\right) / \rho - D_i^T \nabla \ln T$ is the mass diffusion flux of the i^{th} component in the molecular hydrogen . $X_i=n_i/N$,D_{ik} and D_i^T are the binary molecular diffusivities of species i and k and the thermal diffusion coefficient respectively. N is the gas concentration.
The growth rate G (in μm/h) is obtained as below:

$$G = \frac{c1\sqrt{T_{ns}}CH_3}{c2\exp(14.6/RT_s) + c3\exp(7.3/RT_s) + 1 + f\left(T_s, T_{ns}\right)H_2/H}$$

CH_3, H_2 and H are the concentrations in cm^{-3} of methyl, atomic and molecular hydrogen near the substrate
$R=1.9873x10^{-3}$ kcal(mol K)$^{-1}$
Ts and Tns are the substrate temperature and the gas temperature near the substrate.
c1=3.84x10-14
c2=0.0089
c3=0.204
$f = c4\exp(-1.5RT_s) + c5(-5.2/RT_s) + c6\exp(-8.8/RT_s) + c7\exp(-12.5/RT_s)$
c4=0.0021
c5=0.016
c6=0.1
c7=0.23