**COMPUTER SIMULATION OF THE METHANE PLASMA
ENHANCED DEPOSITION OF CARBON FILM**

A thesis
Presented to
the faculty of the graduate school
University of Missouri

In partial fulfillment
of the requirements for the Degree
Master of Science

by
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December, 2013

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**COMPUTER SIMULATION OF THE METAHNE PLASMA ENHANCED
DEPOSITION OF CARBON FILM**

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A candidate for the degree of Master of Science

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ACKNOWLEDGEMENTS

First and foremost, I wish to express my sincere gratitude to my advisor, Dr Retzloff for his guidance and providing me with an opportunity to work with him on this project. I will also like to express my appreciation to other members of my thesis committee:

Dr. Patrick Pinhero, and Dr. Matthew Bernards, and Dr. Stephen Lombardo for their review, input and support. I am also indebted to Rita Preckshot and Jennifer Keyzer-Andre for their various acts of kindness. I would also like to thank my friends, Peng Wan, Anthony Omosule, and Yinka Oshokoya. Finally, I wish to thank my beloved parents, siblings and relatives for their great support and for availing me of this great education.

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ABSTRACT

Graphene is a hybridized carbon sheet with a honeycomb structure and has drawn much attention for its extraordinary characteristics such as a high mechanical strength and electrical conductivity. However for the purpose of this thesis, the plasma enhanced chemical vapor deposition PECVD method for producing graphitic carbon is explored further. The purpose of this research is to model and simulate the PECVD of graphitic carbon from methane gas using a plasma spray torch. In addition, the interaction of various plasma torch parameters such as spray height, gas flow rate, and electron density among other variables are explored to find their effects on the entire spray process. A Finite Element Method was used to model this setup and was implemented using COMSOL; which is a commercially available FEM modeling software. This model was setup to consist of four coupled physics: gas flow; electrostatics, drift diffusion of electrons in the plasma, and the transport to and deposition of graphene on the substrate. Experimental reaction rates and cross-sectional collision data for the simulation was taken from published literature. The results show that deposition height varies inversely proportional to the deposited carbon film height and growth rate. Furthermore, the simulations were then used to predict qualitatively, the concentrations of reactive species as well as the influence of methane gas-flow velocity and total gas pressure on the deposition rate of graphitic carbon. The main significance of this research is to show that plasma characterization and modeling are valuable tools in plasma spray design and optimization.

CHAPTER 1 INTRODUCTION

1.1 Background

The word plasma is used to describe an assembly of partially or fully ionized gases consisting of charged particles: electrons, ions, neutral atoms, and possibly molecules that exhibit effects such as conducting electrical currents and generating magnetic fields. The electrical conductivity of a plasma is the main property that differentiates it from neutral gas which is an electric insulator.

Generally speaking, as temperature increases, molecules become more energetic and transfer matter in the sequence: solid, liquid, gas and finally plasma, which justifies the title as fourth state of matter.¹

Irving Langmuir, who pioneered the scientific study of ionized gases, gave this new state of matter the name *plasma* in 1928 when he was investigating oscillations in ionized gases. Langmuir wrote: “Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name *plasma* to describe this region containing balanced charges of ions and electrons.”²

1.1.1 The Development of Plasma Physics

The field of plasma is indeed a large one and has grown in diversity since the early studies of Nobel Prize winning American chemist Irving Langmuir and his colleague Lewi Tonks.²⁻³ Some other engineers and scientists that contributed immensely to the field of plasma physics include:

1. Edward Appleton and his colleague K.G. Budden - who basically developed the theory of electromagnetic wave propagation through non-uniform magnetized plasmas.
2. Hannes Alfvén – who developed the magnetohydrodynamics (MHD) theory; which basically treats plasma as a conducting fluid.
3. James V. Allen – who pioneered the exploration of the Earth's magnetosphere and discovered the Van Allen radiation belts surrounding the earth.

1.1.2 Occurrence of plasma

Plasmas are indeed complex and exist in differing situations by many orders of magnitude. Most importantly, plasmas do not normally exist in ordinary human experience and as a result, people do not have the sort of intuition for plasma behavior that they have for solids, liquids or gases.

Although plasma behavior seems non- or counterintuitive at first, with suitable effort a good intuition for plasma behavior can be developed. This intuition can be helpful for making initial predictions about plasma behavior in a new situation, because plasmas have the remarkable property of being extremely *scalable*; i.e., the same qualitative phenomena often occur in plasmas differing by many orders of magnitude. Plasma physics is usually not a precise science. It is rather a web of overlapping points of view, each modeling a limited range of behavior. Understanding of plasmas is developed by studying these various points of view, all the while keeping in mind the linkages between the points of view.⁴

Plasmas occur naturally and can also be manmade and comprise the majority of the universe encompassing among other phenomena, the solar corona, solar wind, nebula and the earth's ionosphere. In the earth's atmosphere, plasma is often observed as a transient event in the phenomenon of lightning strikes. Since air is normally non-conducting, large potential differences can be generated between clouds and earth during storms and these lightning discharges occur to neutralize the accumulated charge in the clouds. As one progresses further into near-space altitudes, the earth's magnetic field interacts with the charged particles streaming from the sun. These particles are diverted and often become trapped by the earth's magnetic field. The trapped particles are most dense near the magnetic poles and account for Aurora Borealis.⁵

1.1.3 Classification of plasmas

Plasmas generally have characteristics that exhibit complex phenomena and therein lies the importance of plasma classification. Based on the relative temperatures of the electrons, ions, and neutrals, plasmas are classified as either Thermal or Non-Thermal plasma.

Thermal plasmas are plasmas in which the plasma is said to approach a state of local thermodynamic equilibrium (LTE). LTE occurs when the temperatures of the electrons and the relatively heavier particles (ions and neutrals) are equal or in other words, the particles are in thermal equilibrium with each other. These thermal plasmas are generally produced by atmospheric arcs, sparks and flames.

However, with non-thermal plasmas, the thermal motion of the ions can be ignored. As a result, there is no pressure force, the magnetic force can be ignored, and only the electric force is considered to act on the particles. Furthermore, the electrons are not in thermal equilibrium with the heavier particles. The temperature of the ions and neutrals are generally at a much lower temperature sometimes around room temperature, whereas the electrons are at a much higher temperature. This is sometimes referred to as non-LTE (NLTE) Examples of non-thermal plasmas include the Earth's ionosphere, and the flow discharge in a fluorescent tube.⁶ The NLTE type plasma is modeled in this thesis.

Table 1 Comparison of plasma and gas phases

Property	Gas	Plasma
Electrical conductivity	Very low: Air is an excellent insulator until it breaks down into plasma at electric field strengths above 30 kilovolts per centimeter	Usually very high: For many purposes, the conductivity of a plasma may be treated as infinite.
Independently acting species	One: All gas particles behave in a similar way, influenced by gravity and by collisions with one another.	Two or three: Electrons, ions, protons, and neutrons can be distinguished by the sign and value of their charge so that they behave independently in many circumstances, with different bulk velocities and temperatures, allowing phenomena such as new types of waves and instabilities.
Velocity distribution	Maxwellian: Collisions usually lead to a Maxwellian velocity distribution of all gas particles, with very few relatively fast particles.	Often non-Maxwellian: Collisional interactions are often weak in hot plasmas and external forcing can drive the plasma far from equilibrium and lead to a significant population of fast particles.
Interactions	Binary: Two-particle collisions are the rule, three-body collisions extremely rare.	Collective: Waves, or organized motion of plasma, are very important because the particles can interact at long ranges through the electric and magnetic forces.

Table 1 is adapted from this reference⁷

1.1.4 Production of plasmas

There are many different methods of creating plasma in the laboratory and, depending on the method, the plasma may have a high or low density, high or low temperature, it may be steady or transient, stable or unstable, and so on.

The most commonly used method of generating and sustaining a low-temperature plasma NLTE for technological and technical application is by applying an electric field to a neutral gas; which for the purpose of this thesis, is methane.

A given volume of a neutral gas always contains a few electrons and ions that are formed. These free electrons and ions are accelerated by the electric field and new charged particles may be created when these charge carriers collide with atoms and molecules in the gas or with the surfaces of the electrodes. This leads to an avalanche of charged particles that is eventually balanced by charge carrier losses, so that a steady-state plasma develops.⁸

One characteristic of this process is that the applied electric field transfers energy much more efficiently to the light electrons than to the relatively heavy electrons. The electron temperature in gas discharges is therefore usually higher than the ion temperature, since the transfer of electrons to the heavier particles is slow. When the ionizing source is turned off, the ionization decreases gradually because of recombination until it reaches an equilibrium value consistent with the temperature of the medium. In the laboratory the

recombination usually occurs so fast that the plasma disappears in a small fraction of a second.⁹

1.1.5 Applications of plasma

Plasma technologies are numerous and involve many industries. As a result, the progress in plasma research has led to a wide range of plasma applications. The number of industrial applications of plasma technologies is extensive and involves many industries, especially electronics, lightning, coatings, treatment and processing of materials, metallurgy and energy systems. In many of these practical applications, plasma technologies compete with other approaches and successfully find their specific niche in modern industry. Such a situation takes place, for example, in thermal plasma deposition of protective coatings, in plasma stabilization of flames, in plasma conversion of fuels.⁵

The main issue for practical use of any chemical process in a particular plasma system is to find the proper regime and optimal plasma parameters among the numerous configurations available. The list below shows some of the more important practical applications of plasma physics:

1. Controlled thermonuclear fusion;
2. The magnetohydrodynamic generator;
3. Plasma propulsion;
4. Plasma enhanced chemical vapor deposition (PECVD).

1.2 Plasma enhanced chemical deposition PECVD

PECVD is a process that is used to deposit films from a gas state onto a solid surface (substrate). Typically, this involves the creation and use of plasma. Chemical reactions are sometimes involved in the process. The plasma is generally created by RF (AC) frequency or DC discharge between two electrodes, the space between which is filled with the reacting gases.

This plasma processing technique of employing low-pressure inductively coupled radio frequency (RF) plasma has become one of the most important applications in semiconductor processing. The low sheath potential reduces the damage to the surface by lowering the ion energy.¹⁰ Rather than relying solely on thermal energy to initiate and sustain chemical reactions, PECVD uses an RF-induced glow discharge to transfer energy into the reactant gases, allowing the substrate to remain at a lower temperature typically around 150 – 400 °C. Thus, one of the major advantages of PECVD is the lower substrate temperature involved and in fact, PECVD provides a method of depositing films on substrates that do not have the thermal stability to accept coating by other methods.

PECVD processes are often selected over competing techniques because they offer (one of) the following advantages:¹¹

1. High purity films can be achieved;
2. Great variety of compositions can be deposited;
3. Some films cannot be deposited with adequate film properties by any other method;
4. Good economy and process control are possible for many films.

1.2.1 Methane

Methane gas (CH_4) was used in this thesis as the input gas into the plasma with the ultimate aim of depositing carbon on a substrate.

Methane, which is a principal component of most natural gas reserves, is an ideal fuel for this purpose because of it is readily available and also because of it enormous reserves that are currently underutilized.¹² Methane presents an opportunity for studying the plasma deposition of thin films of carbon. Stable glow-discharge plasmas with high deposition rates and high fractional dissociation are easily maintained over a wide range of flow rates and discharge power densities, making it possible to characterize the plasma and test the model over a broad range of parameters.¹³

Conversion of methane into more valuable compounds, such as hydrogen, synthesis gas, acetylene, and other higher hydrocarbon or black carbon is still a challenge. Many studies¹⁴⁻¹⁹ have been done intensively for several decades especially for direct methane conversion. The major problem on this route came from the strong C-H bond of methane.²⁰

1.2.2 Carbon

Carbon films have many excellent properties including infrared transparency films, high hardness, inertness to chemical attack, and high water resistance.²¹ Carbon films can be deposited using various methods such as: radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD); thermal chemical vapor deposition (thermal CVD); microwave plasma chemical vapor deposition, and ion beam deposition. However, this thesis will focus on the RF-PECVD method.

Generally, when carbon films are prepared by RF-PECVD, hydrocarbons are mostly used as the precursor gases as is the case in this research. The methane gas is then decomposed and reacted in the plasma to create carbon species which are in turn, deposited on the substrate to form the carbon films.²² The carbon deposited has a honeycomb structure.

Hence, the characteristics of the carbon film thus formed are affected by the plasma variables such as frequency, power, etc.

1.3 Justification and structure of research

There have been number of studies^{15, 17, 19, 23-24} that have modeled methane plasma and carbon deposition; but none have successfully addressed the growth rate and height of carbon deposition film using COMSOL. There have not been any particular studies that incorporate all aspects of the plasma, i.e. laminar flow of the gas, electrostatics, electron energy and diffusion, and ion transport and deposition.

This thesis will simulate the deposition of carbon using an RF-PECVD system; this will be accomplished using COMSOL which is an FEM software, capable of handling the instabilities inherent in plasma simulation. In particular, this thesis investigates the effects of plasma pressure on the film deposition growth rate and height.

Chapter 1 introduces the subjects of plasma, its history and development. This chapter also focuses on plasma applications especially with regards to RF-PECVD. A review of literature is covered under Chapter 2; this will cover the theory, and mathematical setup of the plasma model. Chapter 3 presents the COMSOL software environment as well as a detailed simulation algorithm. Chapter 4 presents and discusses the results of the simulation, parametric studies, and sensitivity analysis on the plasma system. Finally, conclusions and recommendations for future work are covered under Chapter 5

CHAPTER 2 PLASMA THEORY

This chapter will review basic plasma theory. Plasma is an ionized medium which means conversion of a neutral atom or a molecule into a positive ion and also an electron. The main participants of the ionization process are electrons and ions.

2.1 Electrons

Electrons are negatively charged particles with its mass about three to four magnitudes of order lower than the mass of ions and neutral particles. Therefore, because of the lightness of the electrons and their high mobility, electrons are the first particles that receive energy from the electric fields. Afterwards, these electrons transmit the energy to all other plasma components through ionization, excitation, and dissociation.⁴

2.2 Positive ions

Atoms and molecules lose their electrons in ionization processes and form positive ions. In extremely hot thermonuclear plasmas, the ions are multi charged, but in quasi-cold technological plasmas of interest, their charge is usually equal to Q (1.6×10^{-19} C). Ions are heavy particles, so most of the time they cannot receive high energy directly from an electric field, because of the intense collisional energy exchange with other plasma

components. The collisional nature of the energy transfer results in the ion energy distribution function usually being not far from the quasi-equilibrium Maxwell-Boltzmann distribution function. The ion temperature T_i is close to the temperature of the neutral gas temperature T_0 .

One of the most important parameters of plasma generation is an ionization energy I , which is the energy needed to form a positive ion. Ionization requires quite a large amount of energy and, as a rule, defines the upper limit of microscopic energy transfer in plasma. The ionization energies for some different atoms and molecules are given in the following Table.⁵

Table 2 Ionization energies for some atoms and molecules

Reaction Process	I (eV)
$e^- + \text{CH}_4 = \text{CH}_4^+ + e^- + e^-$	12.7
$e^- + \text{N}_2 = \text{N}_2^+ + e^- + e^-$	15.6
$e^- + \text{CO}_2 = \text{CO}_2^+ + e^- + e^-$	13.8
$e^- + \text{C}_2\text{H}_2 = \text{C}_2\text{H}_2^+ + e^- + e^-$	11.4
$e^- + \text{SiH}_4 = \text{SiH}_4^+ + e^- + e^-$	11.4
$e^- + \text{He} = \text{He}^+ + e^- + e^-$	24.6

The figure below illustrates the cascading of an ionization process.⁷

Figure 1 Cascade process of ionization

2.3 Electron energy distribution function EEDF

Electrons are energy providers for many plasma-chemical processes. The rates of such processes depend on the number of electrons having sufficient energy to do the job. This can be described by means of the electron energy distribution function, $f(\epsilon)$, which is the probability density for an electron to have the energy, ϵ . Quite often this distribution function strongly depends on the electric field and gas composition, and can vary far from equilibrium.⁵

The evolution of the electron energy distribution function is considered as an approach to describe the electron diffusion and drift in the space of electron energy. There are two common ways of deriving EEDF: (1) Boltzmann kinetic equation and (2) Fokker-Planck kinetic equation.

2.3.1 Boltzmann kinetic equation

The Boltzmann equation, derived by Ludwig Boltzmann in 1872²⁵ describes the statistical behavior of a thermodynamic system that is not in thermodynamic equilibrium. This equation can also be used to determine how physical quantities change, such as heat and momentum energy. The most general form is as follows:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{force} + \left(\frac{\partial f}{\partial t}\right)_{diffusion} + \left(\frac{\partial f}{\partial t}\right)_{collision} \quad (2.1)$$

Where f is the function associated with the number of particles; the force term corresponds to an external force on the particles; the diffusion and collision terms account for the diffusion and collision of particles.

For the number of particles in a given state is fixed, thus:⁵

$$\frac{df}{dt} = 0; \quad \left(\frac{df}{dt}\right)_{force} = \frac{\vec{F}}{m}; \quad \left(\frac{\partial f}{\partial t}\right)_{collision} = \vec{v} \quad (2.2)$$

Where m is the particles mass and $\vec{F}$ is an external force. Equation 2.2 can then be rewritten as

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \vec{v} \nabla_r f + \frac{\vec{F}}{m} \nabla_v f = I_{col}(f) \quad (2.3)$$

Where ∇_r and ∇_v denote the electron distribution function gradient related to space and velocity coordinates and $I_{col}(f)$ is the collision integral.

$$I_{col}(f) = \int [f(v')f(v'_1) - f(v)f(v_1)] |v - v_1| \frac{1}{\varepsilon} d\omega dv_1 \quad (2.4)$$

Where v_l and v are the velocities before collision, v'_1 and v' are velocities after collision; ε is a parameter proportional to the mean free path ratio to the typical system size, $d\omega$ is

the area element in the plane perpendicular to the $(v_1 - v)$ vector. In equilibrium, the collision integral should be equal to zero and therefore, the relations between velocities become:

$$f(v')f(v_1') = f(v)f(v_1) \text{ or } \ln f(v') + \ln f(v_1') = \ln f(v) + \ln f(v_1) \quad (2.5)$$

Equation (2.5) corresponds to the conservation of kinetic energy during elastic collision, since there is no change in the kinetic energy of the particles. Thus, Equation (2.6) flows logically from Equation (2.5).

$$\frac{m(v')^2}{2} + \frac{m(v_1')^2}{2} = \frac{mv^2}{2} + \frac{mv_1^2}{2} \quad (2.6)$$

From the forgoing, $\ln f$ is proportional to $mv^2/2$, which leads to the equilibrium Maxwell distribution function of particles. The final form of the Maxwell-Boltzmann distribution of particles over translational energies is:⁵

$$f_0(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left(-\frac{mv^2}{2T}\right) \quad (2.7)$$

However, the $f(\epsilon)$, depends mostly electron temperature T_e , and can then be defined by the quasi-equilibrium Maxwell-Boltzmann distribution function:

$$f(\epsilon) = 2 \sqrt{\frac{\epsilon}{\pi(k_B T_e)^3}} \exp\left(\frac{-\epsilon}{k_B T_e}\right) \quad (2.8)$$

Where k_B is the Boltzmann constant. The mean electron energy is the first moment of the distribution function and is proportional to the temperature:

$$\langle \epsilon \rangle = \int_0^\infty \epsilon f(\epsilon) d\epsilon = \frac{3}{2} T_e \quad (2.9)$$

Numerically, the mean electron energy ranges from 1 eV to 5 eV.

2.3.2 Fokker-Planck kinetic equation

The Fokker–Planck equation describes the time evolution of the probability density function of the velocity of a particle, and can be generalized to other observables as well.²⁶ The Fokker-Planck approach is a better interpretation of the evolution of EEDF and this results in the Fokker-Planck kinetic equation (Equation (2.10)).

$$\frac{\partial f(\epsilon)}{\partial t} = \frac{\partial}{\partial \epsilon} \left[D_\epsilon \frac{\partial f(\epsilon)}{\partial \epsilon} - f(\epsilon) u_\epsilon \right] \quad (2.10)$$

$$D_\epsilon = \frac{1}{3} (mvu)^2 v_{en} = \frac{2}{3} mu^2 \epsilon v_{en} \quad (2.11)$$

Where D_e is the electron diffusion, u_e is the electron drift velocity and ν_{en} is the frequency of electron-neutral collisions. Fridman and Kennedy⁵ present a detailed derivation of the Fokker-Planck kinetic equation in their book.

Upon integration of Equation (2.10), four distribution function can be derived; namely:

1. Maxwellian distribution;
2. Druyvesteyn distribution;
3. Margenau distribution;
4. Distributions controlled by vibrational excitation

The Maxwellian distribution is used in this thesis for the methane plasma. In this case, the electron-neutral collision frequency can be approximated as constant thus:

$$T_e = \frac{e^2 E^2 M}{3m^2 \nu_{en}^2} \quad (2.12)$$

2.4 Plasma properties

This section will address some of the commonly encountered plasma properties such as: electron mobility, plasma sheaths, debye radius, ambipolar diffusion, and quasi-neutrality.

2.4.1 Plasma Conductivity and electron mobility

Using the conservation of momentum equation in its most general form for electrons:

$$mn \frac{d\mathbf{v}}{dt} + e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - mv_c(\mathbf{v} - \mathbf{u}) \quad (2.13)$$

Where e is the electron charge, n is the number of particles, $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields respectively. Neglecting the magnetic field, interparticle collision ($\mathbf{B}=0$, $\mathbf{u}=0$); and assuming steady state for the electrons ($d\mathbf{v}/dt=0$):

$$\mathbf{E} = -\frac{m_e v_c}{e} \mathbf{v}_e \quad (2.14)$$

And by using the relation, $\mathbf{J}=\sigma\mathbf{E}$, where $\mathbf{J}$ is the electric current and σ is the plasma conductivity, we have:

$$\sigma = \frac{n_e e^2}{m_e v_c} \quad (2.15)$$

The electron mobility, μ_e , can be defined as how fast an electron is moving when pulled by an electric field. μ_e is essentially the coefficient of proportionality between the electron drift and the electric field.

$$v_d = \mu_e \mathbf{E}; \quad \mu_e = \frac{\sigma_e}{en_e} = \frac{e}{mv_c} \quad (2.16)$$

Another important equation for determining the diffusion coefficient of particles is the Einstein relation. This Einstein relation for electrons is given as:

$$\frac{D_e}{\mu_e} = \frac{2}{3} \frac{\langle \varepsilon_e \rangle}{e} \quad (2.17)$$

2.4.2. Plasma sheath and Debye length

Any conducting medium endeavors to cut down strong electric fields and, consequently, to balance space charges. As a consequence, we know from electrostatics that free charges can be found only on the surface of metallic bodies.

In plasmas, there exists a thin layer of gas in front of the electrode in addition to the main body of the plasma gas. In principle, this region is defined as the ‘sheath’ and it exists in the regions of strong field due to the potential applied across the electrodes. The plasma is the relatively electric/magnetic field-free between the sheaths.² In general, these two regions are rather distinct and have very different properties as is illustrated in Figures 3 and 4.²⁷

Figure 2 Illustrations of plasma regions

Figure 3 Electrical potential variation in the sheaths and plasma regions

The Debye length gives the characteristic length of the plasma size necessary for screening or suppressing the electric field. It is indeed an important parameter for characterizing the quasi-neutrality of plasma.⁵ Mathematically, the Debye length, r_D , is defined as:

$$\frac{\Delta n}{n_v} \approx \frac{T_e}{e^2 n_e} \frac{1}{R^2} = \left(\frac{r_D}{R} \right)^2 \quad (2.18)$$

R is the characteristic length of the electron concentration. In addition, the Debye length can also be used as an estimate of the quasi-neutrality of the plasma. Thus, if the electron concentration is high and the Debye length is small, the deviation from quasi-neutrality is small and the diffusion can be considered as ambipolar.²⁸

2.4.3 Ambipolar diffusion

Electrons are relatively lighter than ions and as a result, the forces acting on the ions are different from those acting on the electrons in an electric field. Consequently, with the electrons moving faster than ions, a strong polarization field is formed. This electric field thus formed will alter the transport of one or both species in such a way that their rates become equal. In other words, the charge separation zone with a strong polarization field adjusts the electron and ion fluxes in order to make both species diffuse together. This phenomenon is known as the ambipolar diffusion. Ambipolar diffusion is closely related to the concept of quasi-neutrality.

If the separation of charges (polarization field) is small, the electron and positive ion number concentrations and their respective fluxes are approximately equal; $n_e \approx n_i$, $\vec{\Phi}_e = \vec{\Phi}_i$. With these approximations, the ambipolar diffusion coefficient can be calculated as follows:

$$\vec{\Phi}_e = -\mu_e E n_e - D_e \frac{\partial n_e}{\partial \vec{r}} \quad (2.19a)$$

$$\vec{\Phi}_i = -\mu_i E n_i - D_i \frac{\partial n_i}{\partial \vec{r}} \quad (2.19b)$$

$$\vec{\Phi}_e = \vec{\Phi}_i \quad (2.19c)$$

Dividing Equations 2.19a and b by μ_e and μ_i respectively and also adding the resultant equation, gives the general relation for both the electron and ion fluxes:

$$\vec{\Phi}_{e,i} = -\frac{D_i \mu_e + D_e \mu_i}{\mu_e + \mu_i} \frac{\partial n_{e,i}}{\partial \vec{r}} \quad (2.20)$$

$$D_a = \frac{D_i \mu_e + D_e \mu_i}{\mu_e + \mu_i} \quad (2.21)$$

D_a is the ambipolar diffusion. However, due to relative difference in weight of electrons and ions, the mobility and diffusion of electrons are by orders of magnitude greater than those of the ions i.e. $\mu_e \gg \mu_i$ and $D_e \gg D_i$. Equation (2.21) can be simplified further:

$$D_a \approx D_i + \frac{\mu_i}{e} T_e \quad (2.22)$$

2.5 Processes of charged particles

Ionization of atoms and molecules by electron impact, electron attachment to atoms and molecules, and ion-molecule reactions are examples of elementary plasma-chemical processes, reactive collisions accompanied by transformation of elementary plasma particles. These elementary reactive collisions, as well as others – for example, electron-ion and ion-ion recombination, excitation and dissociation of neutral species by electron impact, relaxation of excited species, electron detachment and destruction of negative ions, photo-chemical processes altogether determine the plasma behavior.

Elementary processes can be divided into two main classes: elastic and inelastic processes. The elastic collisions are those in which the internal energies of colliding particles do not change, therefore the total kinetic energy is conserved as well. Hence these processes result in only scattering. Alternately, collisions are inelastic. All elementary processes listed in previous paragraphs are inelastic ones. Inelastic collisions result in the transfer of energy. For example, the processes of excitation, dissociation, and ionization of molecules by electron impact are inelastic collisions, including transfer of

high kinetic energy of plasma electrons into the internal degrees of freedom of the molecules.

In some instances, the internal energy of excited atoms or molecules can be transferred back into the kinetic energy (particularly into the kinetic energy of plasma electrons) such elementary processes are usually referred to as superelastic collisions. According to kinetic theory, the elementary processes can be described in terms of five main collision parameters: Cross section, probability, mean free path, interaction frequency reaction rate, and reaction rate coefficient.⁵ However, for the purpose of this research, only the cross section collision process is explored further.

2.5.1 Reaction collision cross section

Methane is one of the few gases for which this key reaction cross section is known. Because of its wide use as a combustion gas, a large body of reaction rate data is available for reactions between methane and the dissociation products and synthesized species which are formed both in methane combustion and in methane plasmas.²⁹

The most fundamental characteristics of all elementary processes are their cross sections. The cross section of an elementary process between two particles can be interpreted as an imaginary circle with area π , moving together with one of the collision partners. If the center of the other collision partner crosses the circle, an elementary reaction takes place.

The cross sections of elementary processes depend strongly on the energy of the colliding species.

Typical sizes of atoms and molecules are of the order of 1-3 Å; therefore the cross section of simple elastic collisions between plasma electrons (energy 1-3 eV) and neutral particles is usually $10^{-16} - 10^{-15} \text{ cm}^2$. The cross sections of inelastic, endothermic, electron-neutral collisions are normally lower.²

The mean free path λ of one collision partner A with respect to the elementary process A + B with another collision partner B can be calculated as follows:

$$\lambda = \frac{1}{\sigma n_B} \quad (2.23)$$

Where n_B is the number density of the particles B. The collision cross section of methane is given in Appendix C.²⁹

The collision frequency ν of one collision partner A with the other collision partner B can be defined as ν/λ or as the expression below:

$$\nu_A = \sigma \nu n_B \quad (2.24)$$

Equation 2.4 taking into account, the velocity distribution function $f(v)$ and then the dependence of the cross section on the collision partner's velocity v , then, Equation 2.4 can be rewritten as:⁵

$$v_A = n_B \int f(v) \sigma(v) v dv = \langle \sigma v \rangle n_B \quad (2.25)$$

2.6 Methane plasma

At present a few studies are available to address the simulations of non-depositing and etching processes. The methane plasma is a typical electropositive discharge although both positive and negative ions are present in the discharge. Methane can be used as a feed gas to deposit/etch a diamond-like carbon thin film on a wafer. The behavior of high-density inductively coupled methane discharge in terms of plasma dynamics and deposition/etch profiles is not known.

The roles of the principal positive and negative ionic species in the high density discharge and dominant radicals like CH_3 , CH_2 and H for deposition/etch processes are not understood.³⁰

In the present research, the methane discharge physics simulation is performed to obtain species densities and their energies and fluxes, plasma potentials and electric field in a capacitively coupled reactor.

The discharge physics model is directly coupled to an electromagnetic model that calculates the electric field in the discharge. Pressure, reactor configuration and rate coefficients are input for the discharge physics model, while coil configuration, rf power, RF bias and DC bias are input for the electromagnetic model. The discharge physics model predicts the transient spatial distribution of plasma variables. The cycle-averaged plasma variables are fed into the gas phase and surface chemistry model to predict the process characteristics.

2.7 RF discharges

Radio frequency (RF) electromagnetic fields can be used to generate weakly ionized plasma at low pressures, typically in the range 1 – 103 Pa. At higher pressures, the properties of the RF discharge will change as the collision frequency increases, leading to a discharge approaching a thermal regime when close to atmospheric pressure. RF discharges usually operate at frequencies in the range 1 – 100 MHz corresponding to wavelengths in the range 300 m – 3 m.

A frequency of 13.56 MHz ($\lambda = 22$ m) is particularly common for industrial applications. The large wavelength relative to the size of the discharge chamber allows relatively homogeneous plasmas to be formed by this method.

RF discharges are particularly advantageous for applications that require the electrodes to be outside of the discharge region, thereby preventing contamination with metal vapors given off at the electrodes.

2.7.1 Types of RF discharges

The two main types of RF discharge are capacitively coupled plasmas (CCPs) and inductively coupled plasma (ICPs).

Capacitively coupled plasmas are formed by applying an RF voltage between two electrodes, which are usually spaced a few centimeters apart. When an RF voltage is applied across the discharge gap, a strong electric field is established resulting in the ignition of a plasma discharge.

The electrons respond to the electric field by rapidly oscillating back and forth within a cloud of positively charged ions. Due to the relatively large size of the ions, they respond only to time-averaged electric fields.

Inductively coupled plasmas can be formed using an inductive solenoid coil that is wrapped around the discharge chamber or a planar coil that is situated adjacent to it. When an electric current passes through the induction coil, a strong magnetic field is established in the discharge gap which induces a low electric field (in contrast to CCP, which primarily produces an electric field). ICPs can achieve high electron densities and electrical conductivities and are less suited for creating non-thermal plasma at atmospheric pressure than the previously described CCP.³⁰

2.8 Surface process model

The deposition of carbon from methane plasma is a rather complex issue, since the carbon and hydrogen containing species, interacts with the growing film.

Adsorption and subsequent stitching of the neutrals into the growing film due to ion impact are believed to be important mechanisms for film growth. Recent simulation efforts have attempted to describe the growth mechanisms, despite the lack of experimental data for the rate coefficients in the plasma, and on the surface.¹⁹ This lack of experimental data for surface reaction rates is compensated for, by using Sticking Coefficients.

Lifshitz et al.³¹ in their classic paper describe a model for film growth of carbon deposition; this model is called the subplantation model. And it entails the following basic steps:

1. Penetration – this involves the impinging species into subsurface layers of the target. Some of the impinging species may be backscattered and will not contribute to net film growth.
2. Stopping - Stopping of the energetic species in the substrate via three energy-loss mechanisms.

3. Site occupation - the possible initial sites the impinging atoms occupy after being stopped are determined by the host matrix that serves as a "mold" for the structure to be formed.
4. Phase formation – this involves the formation of new phase.
5. Surface composition - during the early stages of film growth, the surface is mainly composed of substrate atoms due to the subsurface penetration of the impinging particles. These substrate surface atoms are gradually sputtered and/or diluted by ion-mixing mechanisms until a surface consisting of only projectile species evolves.
6. Film structure Several effects determine the phase and structure of the film: (i) The "mold" effect of the host matrix that determines the possible site occupancies of the penetrating species and places constraints on initial evolution of the new phase (i.e., the structure of an inclusion embedded in a surrounding matrix is highly influenced by the boundary conditions imposed by that matrix). (ii) Preferential displacement of atoms with low displacement energies (low-Ed) leaving atoms with high displacement energies (high-Ed) in their more stable positions. (iii) Diffusion rates of vacancies and interstitials created in the deposition process. When the temperature is sufficiently low, the interstitials are immobile and their concentration increases with fluence until an athermal spontaneous transformation to a new phase occurs.
7. Crystalline orientation - epitaxial growth and/or preferred orientation of films on crystalline materials is expected to result.

8. Sputtering - the film evolution of a pure film from species impinging on a substrate consisting of atoms different from that of the bombarding species is feasible only when collisional ion mixing and diffusion processes are small enough, so as to allow evolution of a film.

Some of the steps presented above are preliminary, and further rigorous theoretical treatment is needed. Atomistic calculations of phase evolution of a subplanted material in a host matrix are needed for further development of the "mold" effect. A simulation program that treats crystalline materials, rather than amorphous structures as used herein, is necessary for further development of the details of epitaxial growth.

2.8.1 Sticking coefficient

Sticking Coefficient is the term used in surface physics to describe the ratio of the number of atoms (or molecules) that adsorb, or "stick", to a surface to the total number of atoms that impinge upon that surface during the same period of time. This value is between 1 and 0 for all impinging atoms stick and none of the atoms stick respectively. The coefficient is a function of surface temperature, surface coverage (θ) and structural details as well as the kinetic energy of the impinging particles.

The modeling efforts on surface chemistry thus far have considered the one adsorbed species model, and stressed the need for a synthetic approach of the problem gas-surface chemistry.¹⁹

Reactions (1) and (2) below represent the gas phase and surface reaction. A sticking coefficient of range between 0 and 1 is used for the simulation. These reactions are modeled from the work of Nagayama et al.¹⁸

CHAPTER 3 MODEL SETUP

3.1 Plasma simulation

Plasma simulation refers to the solving of equations that describe the plasma of interest. Generally, Maxwell's equations, the Poisson's equation, Boltzmann equations and the equations of motion are coupled and solved as a system.

Since most plasma systems are in general very complicated, and are usually made up of multiple components, it is imperative that an adequate solution method is adopted. In order to have an adequate plasma simulation, the solution method/algorithm should have some of the following characteristics:

1. Conservation: the deviation from the conservation law should be minimal;
2. Stability: the total errors should not grow in time;
3. Convergence: the numerical solution should converge to the exact solution.

Finite Element Modeling FEM comes into play in solving and simulating plasma systems. COMSOL, ANSYS, and other CFD programs are examples of commercial FEM software that are capable of implementing FEM.

The algorithm shown in the figure below was developed by Bera et al,³² and it will be used for the plasma simulation in this thesis.

Figure 4 **Solution algorithm**

3.2 COMSOL Overview

COMSOL Multiphysics is a Finite Element Method FEM software for various physics and engineering applications, especially coupled phenomena, or multiphysics. In addition to conventional physics-based user interfaces, COMSOL Multiphysics also allows for entering coupled systems of ordinary and partial differential equations (ODEs and PDEs). The PDEs can be entered directly or using the so-called weak form. An early version (before 2005) of COMSOL Multiphysics was called FEMLAB.³³ COMSOL version 4.3b was used for the purpose of this research.

Due to the highly non linear plasma equations, numerical techniques have to be employed i.e. FEM to solve these equations. FEM is a weighted residual method that assumes a solution within a domain consists of piecewise polynomials. The basic idea of FEM is to find the solution of a complicated problem by replacing it with a simpler one. In other words, the actual problem is replaced by a simpler one and thus making it easier to find only an approximate solution rather than the exact solution. However, more computational effort will have to be invested in order to improve or refine this approximate solution.

Detailed plasma simulations are computationally expensive and as a result, a couple of simplifications will be made in this simulation. Some of these simplifications include: the use of an axis-symmetric model, breaking the model into individual Physics, and reducing the time steps that are solved for.

COMSOL is used in this thesis to simulate the plasma enhanced deposition of carbon and the model used consists of the following coupled sub models/physics:

1. Laminar Flow (spf);
2. Electrostatics (es);
3. Drift Diffusion (dd);
4. Heavy Species Transport (hs).

In summary, the plasma is generated by virtue of a sinusoidal voltage applied across the cathode leading to a high potential difference (V) across the cathode and anode. Methane simultaneously flows through the annular region between the cathode and anode. As a result, the methane gas is ionized and this in turn, reacts and forms the carbon which is deposited on the substrate at the end of the deposition substrate.

The remainder of this chapter logically follows the setup of the COMSOL model. A detailed step by step procedure is provided in Appendix A. In addition, a brief overview of COMSOL is provided.

3.2.1 Geometry

In practice, the geometry of a plasma spray device is rather complex as is shown in Figures 6 and 7³⁴⁻³⁵ and will therefore require more computational effort to model. Hence, this justifies the need for a simplified geometric model.

Figure 5 **Picture of a plasma spray**

Figure 6 **Schematic of a plasma spray process**

As a result of the complexity of the plasma gun, a simplified model was built using COMSOL's inbuilt CAD module; Figure 8. The simplified CAD model used for this simulation comprises of three domains: cathode, anode, and the deposition substrate. This model also consists of an annular region between the cathode and anode for the gas (methane) flow. It is important to note that the deposition chamber is in fact, a mathematical truncation of the computational domain. In other words, the deposition chamber sets an imaginary boundary on the plasma problem as well as the region that is solved for.

Figure 8 shows a 3D model of the plasma system. However, the 2D axis-symmetric equivalent of this model is used in its place because it takes less computational time to compute and run the system. Figures 9 and 10 illustrate the 2D and 2D axis-symmetric models.

Figure 7 3D plasma system

Figure 8 2D Axis-symmetric geometric model

Figure 9 Illustration of the computational domain

3.2.2 Laminar flow

This sub-model simulates the laminar flow of methane gas through the plasma system by solving the governing equations: Navier-Stokes equations. This physics is solved for the entire computational domain.

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-\rho \mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu(\nabla \cdot \mathbf{u}) \mathbf{I} \right] + \mathbf{F} \quad (3.1)$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (3.2)$$

Where $\mathbf{F}$ is the force vector, $\mathbf{I}$ is the identity matrix. The following boundary conditions were applied: no-slip ($\mathbf{u} = 0$) at the walls of the system. The initial conditions used was gas flow velocity of 5 mm/s and system pressure of 10 torr. The gas enters from the top and exits from the side of the deposition substrate. This is illustrated in the figure below.

Figure 10 Schematics showing gas inlet and outlet

This laminar model is solved using a parallel sparse direct solver (PARADISO) with an error tolerance of 0.01. The PARADISO Solver is inbuilt in COMSOL and is robust and memory efficient.

3.2.3 Electrostatics

This sub-model handles the equations, boundary conditions BC, and initial conditions IC relating to the electrostatics and charge conservation, the Gauss and Maxwell's equations in particular are solved. It is also important to note that these equations are solved for the boundaries only as opposed to the entire domain. The dependent variable is voltage, V .

$$\nabla \cdot \mathbf{D} = \rho_v \quad (3.3)$$

$$\mathbf{E} = -\nabla V \quad (3.4)$$

$\mathbf{D}$ is the electric displacement field, $\mathbf{E}$ is the electric field, and ρ_v is the free charge density. Charge conservation is the main feature, which adds the equation for the electric potential.

The Ground node is a default boundary condition and implements the BC, $V = 0$ at the anode and the top and bottoms of the deposition substrate. Conversely, a sinusoidal voltage, $V_0 = V_0 \sin(\omega t)$, is applied on the cathode. An initial condition of $V = 0$ is used. This is illustrated in the figure below.

Figure 11 Illustration showing driven and grounded electrodes

This electrostatics model is solved using a multi-frontal massively parallel sparse direct solver (MUMPS) with an error tolerance of 0.1. The MUMPS solver is inbuilt in COMSOL and is also the default solver for electrostatics physics.

3.2.4 Drift diffusion

The Drift Diffusion sub-model solves for the electron density and mean electron energy for the plasma and has coupled with the Laminar Flow and Electrostatics sub-models. A wide range of boundary conditions are available to handle secondary emission, thermionic emission, and wall losses. This sub-model also solves the equations for electron diffusivity, mobility, electron energy diffusivity and electron energy mobility. This is in addition to solving for electron density and mean electron energy. The dependent variables solved for, are the natural logarithms of electron density and electron energy density.

$$\frac{\partial n_e}{\partial t} + \nabla \cdot \mathbf{\Gamma}_e = R_e - (\mathbf{u} \cdot \nabla) n_e \quad (3.5)$$

$$\mathbf{\Gamma}_e = -(\boldsymbol{\mu}_e \cdot \mathbf{E}) n_e - \mathbf{D}_e \cdot \nabla n_e \quad (3.6)$$

$$\frac{\partial n_\varepsilon}{\partial t} + \nabla \cdot \mathbf{\Gamma}_\varepsilon + \mathbf{E} \cdot \mathbf{\Gamma}_e = S_{en} - (\mathbf{u} \cdot \nabla) n_\varepsilon + \frac{(Q + Q_{gen})}{q} \quad (3.7)$$

$$\mathbf{\Gamma}_\varepsilon = -(\boldsymbol{\mu}_{en} \cdot \mathbf{E}) n_\varepsilon - D_{en} \cdot \nabla n_\varepsilon \quad (3.8)$$

$$\mathbf{E} = -\nabla V \quad (3.9)$$

Where S_{en} represents the energy loss due to elastic and inelastic collisions; Γ_e and Γ_ε are the fluxes for electrons and mean electron energy respectively.

In addition to solving Equations 3.5 – 3.9, the electron diffusivity, energy mobility and energy diffusivity are automatically computed using Einstein's relation for a Maxwellian EEDF:

$$\mathbf{D}_e = \mu_e T_\varepsilon; \quad \mu_\varepsilon = \left(\frac{5}{3}\right) \mu_e; \quad \mathbf{D}_\varepsilon = \mu_\varepsilon T_e \quad (3.10)$$

This sub-model is solved using PARADISO with an error tolerance of 0.001.

3.2.5 Heavy species transport

The Heavy Species Transport sub-model user interface adds electron impact reactions, gas phase reactions, and species and surface reactions to plasma models. This was achieved by loading the methane collision cross sections from a file in the Cross Section Import section from the Heavy Species Transport node's settings window. This cross sectional data is provided in Appendix C.

In order to perform the gas phase and surface reactions, this sub-model accepts input directly from the three previously mentioned sub-models; laminar flow, electrostatics, and drift diffusion.

The ions in the now, ionized methane gas are subjected to the electric fields are affected by migration transport in addition to the existing mass transport by diffusion and convection. The flux of the ionic species in the gas phase is given by the mass flux vector, N_i with SI unit: mol/(m²·s); this is the Nernst-Planck equation.

$$\mathbf{N}_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi + c_i \mathbf{u} \quad (3.11)$$

Where c_i and D_i denote the concentration and the diffusion coefficient of the ions respectively. $\mathbf{u}$ is the velocity field vector, F refers to Faraday's constant, ϕ denotes the electric potential, z_i is the charge number of the ionic species, and $u_{m,i}$ its ionic mobility (SI unit: s·mol/kg).

3.2.6 Mesh

A free triangular mesh was used for the computational domain. A triangle mesh is a type of polygon mesh in FEM, it comprises a set of triangles in 2D (for the case in point) that are connected by their common edges or corners. A boundary effect was applied in order to make the mesh *finer* at edges and coarser away from the edges. This was done to improve on the accuracy and resolution of results. Figure 13 illustrates this:

Figure 12 **Free triangular mesh of domain**

CHAPTER 4 RESULTS

This Chapter presents the results of the simulation of the important chemical processes which lead to the deposition of carbon thin film in methane plasmas. The results are broken into the following sections: Fluid flow, Electrostatics, Drift diffusion, and Heavy species transport.

4.1 Fluid flow

The velocity profiles are plotted for methane gas flow through the plasma spray as is shown in Figures 14 to 16. The profiles thus generated, realistically represent the physical boundary conditions imposed on the system i.e. no slip. As is expected, the magnitude of the velocity is highest in the annular region between the cathode and anode this ensures that there is sufficient velocity for the gas as it enters the system and also to ensure that the carbon species generated in the plasma region have sufficient momentum to get to the substrate.

Figure 13 Streamline velocity field

Figure 14 Velocity magnitude

The ‘kink’ that can be noticed in the velocity magnitude (Figure 14), just after cathode, is as a result of the decrease in pressure once the fluid exits the high pressure annular region between the cathode and anode. This reduction in pressure is also a cause of the vortices noticed in Figure 13 above. This is essential in ensuring that there is proper mixing.

Figure 15 3D velocity magnitude

Figure 15 above shows a 3D representation of the velocity magnitude in the plasma system solved for. As was stated earlier in Chapter 3, this system was modeled as a 2D axis-symmetric geometry and thus, Figure 15 is simply a revolution about the z-axis which is also the plane of symmetry. Furthermore, this figure displays the convenience of using the axis-symmetrical simplification to solve 3D problems without the necessary extra investment in computational effort.

4.2 Electrostatics

In this section, the results for the Electrostatics sub-model are presented in Figures 16 and 17. These figures respectively show the electric potential magnitude and field lines that are necessary for generating and sustaining the plasma.

Figure 16 Electric potential (surface plot)

As is expected, the cathode has the highest magnitude of electric potential and this *potential* oscillates according to the constraint applied in this model: $\sin(\omega t)$ where ω is the angular frequency.

Although the electric potential is modeled as a stationary wave in this system, the wave could in fact, be also modeled as a travelling wave in which case, the equation takes the following form: $\sin(kz \pm \omega t)$ where k is the amplitude of the wave in the spatial domain and z represents the actual length traveled along the axis in space. The travelling wave model, however, was not used in this simulation.

In Figure 17, the electric field is greatest between cathode and anode and this is necessary to sustain the plasma and generate sufficient electrons required to ionize the methane gas.

Figure 17 **Electric field plot (streamlines)**

4.3 Drift diffusion

In this section, the results are presented from the Drift Diffusion sub-model in Figures 18 to 22. These results are further discussed in this section.

Figure 18 Surface electron density (time = 0.001 s)

Figures 18 to 20 show the variation of electron density with time. The electrons are necessary for generating the plasma and sustaining it as well; hence the importance in accurately modeling the electron densities at various points in the system.

The solution of this model starts with an initial electron density of $10^{16}/\text{m}^3$. The essence of using a value other than zero is to get the plasma system started and as time elapses, the electron density dissipates and settles down to its steady state value as is shown in Figures 19 and 20. Figure 19 shows a snapshot of the electron density after 1.13×10^{-3} s and Figure 20 shows the steady state value of the electron density at 1 s. Furthermore and as shown in Figure 20, the electron density is highest in the region between the cathode and anode and this is necessary for ionizing the methane gas flow through that region.

Figure 19 **Surface electron density (time 0.0013 s)**

Figure 20 Surface electron density (time 1 s)

Figure 21 **Electron temperature (time = 0.001 s)**

The same explanation for electron density suffices electron temperature. The electron temperature surface plots are shown in Figures 21 and 22.

Figure 22 **Electron temperature (time = 0.004 s)**

4.4 Heavy species transport

In this section, the results are presented from the Heavy Species Transport sub-model in Figures 23 to 24. Following, is a discussion of the results.

Figure 23 Surface plot of accumulated growth height (mm)

Figure 23 shows a surface plot of the carbon film deposition. In order to generate this plot, the substrate plane was extruded parametrically over the time scale. In this plot, the y-axis represents the time scale while the z-axis represents the growth height, and the x-axis represents the length of the deposition surface.

Figure 24 Accumulated growth height (nm)

Figure 24 represents a line graph plot of the accumulated growth height of the carbon film at 0.007 s. Given the atomic radii of the carbon atom to be 70 pm, this plot accounts for several layers of the carbon film deposited. It is worthy to point that the sticking coefficient used in this plot was 1 and this accounts for fast deposition rates. Plots of this kind are generally dependent on the sticking coefficient of the carbon species and as a result, the accumulated height is directly proportional to the sticking coefficient. The sticking coefficient ranges from 0 to 1, with 1 being the maximum value and 0 being the minimum value it can take. It also has to be stated that surface diffusion effects were not taken into account in the modeling of the deposition height.

Another interesting point to note about this figure, are the growth spikes at both ends of the substrate. These spikes were attributed to boundary effects because regardless of the length of the substrate the spikes still show up close to the boundaries. To buttress this point is that fact that the ‘deposition chamber’ is a computational approximation of the actual physics involved and therefore finding the optimal size of the computational domain and the appropriate boundary conditions to simulate the infinite atmosphere is crucial.

In essence, the goal is to find use boundary conditions that absorb the solution as opposed to ones that reflect. As a result, finding the optimal computational domain with non-physical boundaries is always a trade-off between numerical accuracy and model validity. On one hand, your modeling domain should be as large as possible, to minimize the influence that the exterior boundaries will have on the solution. On the other hand, making your geometry too large means that you cannot resolve it that well.

CHAPTER 5 CONCLUSIONS

The methane plasma simulation model developed in this thesis is a first approach for the observation and optimization of process variables. A 2D axis-symmetric model that included the relevant aspects of the PECVD was used as the plasma system. The height of the deposited carbon was developed as well as a discussion of the boundary effects on the plasma deposition process. In addition, the use of a very small time step allows stabilization of the model. The transport and thermodynamic properties were also simulated. The electron density gradients did not vary much with time.

Further developments of the model will focus on the improvement of the reaction paths and possibly involve more complex reactions and the use of algebraic /differential equations to model the adsorption process. In addition, the use of different geometries such as cones and spheres could be used to model the cathode and anode. The computational boundary affected the deposition heights and rates

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APPENDIX A COMSOL MODEL SETUP

A1 Model Wizard

1. Go to the **Model Wizard** window.
2. Click the **2D axisymmetric** button and then click **Next**.
3. In the **Add physics** tree, select **Fluid Flow>Single-Phase Flow> Laminar Flow (spf)** and click **Add Selected**.
4. Repeat Step 3 to add the remaining physics as follows:
5. In the Add physics tree, select **AC/DC>Electrostatics (es)** and click **Add Selected**.
6. In the **Add physics** tree, select **Plasma>Drift Diffusion (dd)** and click **Add Selected**.
7. In the **Add physics** tree, select **Plasma>Heavy Species Transport (hs)** and click **Add Selected**.
8. Find the **Studies** subsection. In the tree, select **Preset Studies for Selected Physics>Time Dependent**.
9. Click **Finish**.

A2 Global Definitions

A2.1 Parameters

1. In the **Model Builder** window, right-click **Global Definitions** and choose **Parameters**.
2. In the **Parameters** settings window, locate the **Parameters** section.
3. In the table, enter the following settings:

Table A1 Model parameters

Name	Value [mm]	Description
h1	50	Length of substrate
h2	50	Height of 'deposition chamber'
h3	30	Height of plasma region

Figure A1 Illustration of geometric parameters

A2.2 Variables

1. In the **Model Builder** window, under **Model 1** right-click **Definitions** and choose **Variables**.
2. In the **Variables** settings window, locate the **Variables** section.
3. In the table, enter the following settings:

Table A2 Model Variables

Name	Value	Description
ramp	$\tanh(1E7[1/s]*t)$	Ramp function
TT	300[K]	Gas temperature
pp	760[torr]	Gas pressure
Nn0	$pp/k_B_const/TT$	Neutral number density
k1	$1.993039e-014*dd.Te^{0.93}*exp(-0.41/dd.Te)$	Elastic rate coefficient
k2	$8.773932e-015*dd.Te^{0.62}*exp(-18.16/dd.Te)$	Excitation rate coefficient
k3	$2.153106e-014*dd.Te^{0.49}*exp(-24.75/dd.Te)$	Ionization rate coefficient
r1	$k1*dd.Nn*dd.ne$	Elastic collision reaction rate
r2	$k2*dd.Nn*dd.ne$	Electronic excitation reaction rate
r3	$k3*dd.Nn*dd.ne$	Ionization reaction rate
de1	0[V]	Energy loss, elastic collision
de2	11.56[V]	Energy loss, electronic excitation
de3	15.8[V]	Energy loss, ionization
Re	r3	Electron production rate
Sen	$e_const*(R1*DE1+R2*DE2+R3*DE3)$	Collisional power loss
Ain	$0.5E-3^2[m^2]$	Wall area
I	2E-6[A]	Thermal emission current
influx	$I/Ain/e_const*ramp$	Electron influx
mueN	$4E24[1/(m*V*s)]$	Reduced electron mobility
freq	$(1/pi)*10^3[1/s]$	Frequency
omega	$2*pi*freq$	Angular frequency
c	299792458[m/s]	Speed of light
k	$omega/c$	Angular frequency
U0	25[mm/s]	Initial Velocity
V0	100[V]	Voltage

A3 Geometry

A3.1 Units

1. Click on **Geometry 1** and choose **length units** to mm

A3.2 Rectangle 1

1. In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Rectangle**.
2. In the **Rectangle** settings window, locate the **Size** section.
3. In the **Width** edit field, type **h1**.
4. In the **Height** edit field, type **h2**.
5. Locate the **Position** section and choose **corner** as the **base** then type **0** and **0** for the **r** and **z** edit fields.

A3.3 Rectangle 2

1. In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Rectangle**.
2. In the **Rectangle** settings window, locate the **Size** section.
3. In the **Width** edit field, type **10**.
4. In the **Height** edit field, type **h3**.
5. Locate the **Position** section and choose **corner** as the **base** then type **0** and **h2** for the **r** and **z** edit fields respectively.

A3.4 Rectangle 3

1. In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Rectangle**.
2. In the **Rectangle** settings window, locate the **Size** section.
3. In the **Width** edit field, type **5**.
4. In the **Height** edit field, type **15**.
5. Locate the **Position** section and choose **corner** as the **base** then type **0** and **(h2+h3)-15** for the **r** and **z** edit fields respectively.

A3.5 Union 1

1. Right-click **Geometry 1** and choose **Boolean Operations>Union**.
2. Select the objects **r1** and **r2** only.
3. Clear the Check Boxes for **Keep input objects** and **Keep interior boundaries**.

A3.6 Difference 1

1. Right-click **Geometry 1** and choose **Boolean Operations>Difference**.
2. In the **Objects to add** window, click on **uni1** and in the **Objects to subtract** window, click on **r2**.
3. Check the **Keep interior boundaries** and clear the Check Box for **Keep input objects**.

A4 Laminar Flow (spf)

1. Select the entire domain.

A4.1 Inlet 1

1. Right-click **Model 1> Laminar Flow> Inlet**.
2. In the Inlet settings window, choose the **boundary 6**. Also locate the **Velocity** section and choose **Normal inflow velocity**; then type **U0** in the U_0 edit field.

A4.2 Outlet 1

1. Right-click **Model 1> Laminar Flow> Outlet**.
2. In the **Outlet** settings window, and choose the **boundary 9**.
3. Locate the **Boundary Condition** section and choose **Pressure, no viscous stress** and then type **pp** in the **pressure** edit field.

A5 Electrostatics (es)

A5.1 Ground 1

1. Right-click **Model 1** > **Electrostatics** > **Ground**.
2. In the **Ground** settings window, and choose the **boundaries: 2, 7, and 8**.

A5.2 Electric Potential 1

1. Right-click **Model 1** > **Electrostatics** > **Electric Potential**.
2. In the **Electric Potential** settings window, and choose the **boundaries: 4 and 5**.
3. Locate the **Electric Potential** section and type $V_0 \sin(\omega t)$ in the V_0 edit field.

A6 Drift Diffusion

1. In the **Drift Diffusion** settings window, locate the **Electron Properties** section.
2. Check the **Use reduced electron transport properties** check box.

A6.1 Drift Diffusion Model 1

1. In the **Model Builder** window, under **Model 1** > **Drift Diffusion** click **Drift Diffusion Model 1**.
2. In the **Drift Diffusion Model** settings window, locate the **Model Inputs** section.
3. In the N_n edit field, type $Nn0$.
4. In the V edit field, choose **Electric Potential (es)**.
5. In the S_{en} edit field, type Sen .
6. Locate the **Electron Density and Energy** section. In the $\mu_e N_n$ edit field, type $\mu_e N_n$.

A6.2 Initial Values 1

1. In the **Initial Values** settings window, locate the **Initial Values** section.
2. In the $n_{e,0}$ edit field, type $1E16 [1/m^3]$.
3. In the ϵ_0 edit field, type $3 [V]$.

A6.3 Velocity 1

1. Right-click **Model 1** > **Drift diffusion** > **Velocity**.
2. In the **Velocity** settings window, and choose **domain 1**.
3. Locate the **Velocity** section and choose **Velocity field (spf1/fp1)** from the drop down box.

A6.4 Wall 1

1. In the **Model Builder** window, right-click **Drift Diffusion** and choose the boundary condition **Wall**.
2. In the **Wall** settings window, locate the **General Wall Settings** section.
3. Select the **Include migration effects** check box.
4. Select **Boundaries 2, 7, and 8**.

A6.5 Electron Density and Energy 1

1. In the **Model Builder** window, right-click **Drift Diffusion** and choose the boundary condition **Electron Density and Energy**.
2. Select **Boundaries 4 and 5**.
3. In the **Electron Density and Energy** settings window, locate the **Electron Density and Energy** section.
4. Select the **Fix mean electron energy** check box.

A6.6 Wall 2

1. In the **Model Builder** window, right-click **Drift Diffusion** and choose the boundary condition **Wall**.
2. Select **Boundaries 4 and 5**.
3. In the **Wall** settings window, locate the **Electron Density Wall Settings** section.
4. In the Γ_{in} edit field, type **influx**.
5. Locate the **Electron Energy Wall Settings** section. Clear the **Use wall for electron energy** check box.

A7 Heavy Species Transport

1. In the **Heavy Species Transport** settings window, locate the **Transport Settings** section.
2. Check the following check boxes: **Convection**, **Migration in electric field**, and **Calculate thermodynamic properties**.
3. Clear the following check boxes: **Full expression for diffusivity** and **Compute tensor ion transport properties**.

A7.1 Surface Reaction 1

1. Right-click **Model 1>Heavy Species Transport** and choose **Surface Reaction**.
2. In the **Surface Reaction** settings window, locate the **Reaction Formula** section.
3. In the **Formula** edit field, type: **CH4=>CH4(s)**.
4. Select **Boundary 2**.
5. Locate the **Kinetics Expressions** section. In the **Forward sticking coefficient, γ_r** edit field, type **1**.

A7.2 Surface Reaction 2

1. In the **Model Builder** window, right-click **Heavy Species Transport** and choose **Surface Reaction**.
2. In the **Surface Reaction** settings window, locate the **Reaction Formula** section.
3. In the **Formula** edit field, type: **CH4(s)=>C9b)+2H2**.
4. Select **Boundary 2**.
5. Locate the **Kinetics Expressions** section. In the **Forward sticking coefficient, γ_r** edit field, type **1**.

A7.3 Species: CH4

1. In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: CH4**.
2. In the **Species** settings window, locate the **Species Formula** section.
3. Select the **From mass constraint** check box.

4. Locate the **General Parameters** section. From the **Preset species data** list, choose **CH4**.

A7.4 Species: H2

1. In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: H2**.
2. In the **Species** settings window, locate the **General Parameters** section.
3. From the **Preset species data** list, choose **H2**.
4. In the **X₀** edit field, type **1E-3**.

A7.5 Species: CH4(s)

1. In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: CH4(s)**.
2. In the **Surface Species** settings window, locate the **General Parameters** section.
3. From the **Preset species data** list, choose **User defined**.
4. Locate the **Surface Species Parameters** section. In the **Z_{k,0}** edit field, type **0**.

A7.6 Species: C(b)

1. In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Species: C(b)**.
2. In the **Surface Species** settings window, locate the **General Parameters** section.
3. From the **Preset species data** list, choose **User defined**.

A7.7 Convection, Diffusion, and Migration

1. In the **Model Builder** window, under **Model 1>Heavy Species Transport** click **Convection, Diffusion, and Migration**.
2. In the **Convection and Diffusion** settings window, locate the **Model Inputs** section.
3. From the **u** list, choose **Velocity field (spf/fp1)**.
4. From the **T** list, choose **User defined** and type **TT** in the **T** edit field.
5. From the **P_A** list, choose **Pressure (spf/fp1)**.

6. From the **V** list, choose **Electric potential (es)**.

A8 Mesh

A8.1 Edge 1

1. In the **Model Builder** window, right-click **Mesh 1** and choose **More Operations>Edge**.
2. Select **Boundaries: 2, 4, 5, 7-9**.

A8.1.1 Size 1

1. Right-click **Model 1>Mesh 1>Edge 1** and choose **Size**.
2. In the Size settings window, locate the Element Size section and choose **Extra fine** from the **Element Size** section.

A8.1.2 Free Triangular 1

1. In the **Model Builder** window, right-click **Mesh 1** and choose **Free Triangular**.
2. In the Settings window, click **Build All**.

Figure A2 Model mesh development

A9 Study 1

- 1 In the **Model Builder** window, expand the **Study 1** node, then click **Step 1: Time Dependent**.
2. In the **Physics and Variables Selection** section of the **Time Dependent** settings window, disable the other physics to be solved for except for **Laminar Flow (spf)**.
3. Also, in the **Time Dependent** settings window, locate the **Study Settings** section and type the range **(0, 0.1, 20)** in the **Times** edit field.
4. In the **Model Builder** window, right-click **Study 1** and choose **Compute**.

A10 Study 2

- 1 In the **Model Builder** window, right-click on the **root** node and choose **Add Study** then choose **Time Dependent** from the **Studies** section.
2. Choose **Finish**.
3. In the **Physics and Variables Selection** section of the **Time Dependent** settings window, disable the other physics to be solved for except for **Electrostatics (es)**.
4. Also, in the **Time Dependent** settings window, locate the **Study Settings** section and type the range **(0, 0.1, 2)** in the **Times** edit field.
5. In the **Model Builder** window, right-click **Study 2** and choose **Compute**.

A11 Study 3

- 1 In the **Model Builder** window, right-click on the **root** node and choose **Add Study** then choose **Time Dependent** from the **Studies** section.
2. Choose **Finish**.
3. In the **Physics and Variables Selection** section of the **Time Dependent** settings window, disable the other physics to be solved for except for **Drift Diffusion (dd)**.
4. Also, in the **Time Dependent** settings window, locate the **Study Settings** section and click the **range button**.

5. Choose **Number of Values** from the **Entry method** drop-down box and then enter the following values: **Start = -5; Stop = 0; Number of values = 200; Function to apply to all values = exp10**. Click **Replace**.
6. In the **Model Builder** window, right-click **Study 3** and choose **Compute**.

A12 Study 4

1. In the **Model Builder** window, right-click on the **root** node and choose **Add Study** then choose **Time Dependent** from the **Studies** section.
2. Choose **Finish**.
3. In the Physics and variables Selection section of the **Time Dependent** settings window, disable the other physics to be solved for except for **Heavy Species transport (hs)**.
4. Also, in the **Time Dependent** settings window, locate the **Study Settings** section and click the **range button**.
5. Choose **Number of Values** from the **Entry method** drop-down box and then enter the following values: **Start = -5; Stop = -1; Number of values = 150; Function to apply to all values = exp**. Click **Replace**.
6. In the **Model Builder** window, right-click **Study 4** and choose **Compute**.

A13 Results

A13.1 Edge 2D 1

1. In the **Model Builder** window, under **Results** right-click **Data Sets** and choose **Edge 2D**.
2. Select **Boundary 2**.
3. In the **Model Builder** window, right-click **Data Sets** and choose **More Data Sets>Parametric Extrusion 1D**.

A13.2 2D Plot Group (Accumulated Growth Height)

1. Right-click **Results** and choose **2D Plot Group**.
2. In the **2D Plot Group** settings window, locate the **Data** section; then from the **Data set** list, choose **Parametric Extrusion 1D 1**.
3. Right-click **Results>2D Plot Group** and choose **Surface**.
4. In the **Surface** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Heavy Species Transport>Etching and deposition>C bulk>Accumulated growth height (h_C_bulk)**.
5. Locate the **Expression** section. From the **Unit list**, choose **nm**.
6. Right-click **Results>2D Plot Group >Surface 1** and choose **Height Expression**.
7. In the Settings window, click **Plot**.

A13.2 1D Plot Group (Accumulated Growth Height)

1. Right-click **Results** and choose **1D Plot Group**.
2. In the **1D Plot Group** settings window, locate the **Data** section; then from the **Data set** list, choose **Edge 2D 1**.
3. Right-click **Results>1D Plot Group** and choose **Line Graph**.
4. In the **Line Graph** settings window, click **Replace Expression** in the upper-right corner of the **Expression** section. From the menu, choose **Heavy Species Transport>Etching and deposition>C bulk>Accumulated growth height (h_C_bulk)**.
5. Locate the **Expression** section. From the **Unit list**, choose **nm**.
6. In the Settings window, click **Plot**.

Figure A3 1D Plot – Accumulated height (nm)

Figure A4 2D Plot – Accumulated height

Figure A5 Screen shot of COMSOL environment

APPENDIX B COMSOL REPORT

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Date

Nov 13, 2013 12:36:02 PM

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Global Definitions

Parameters

Name	Expression	Description
h1	50[mm]	Base Diameter
h2	50[mm]	Height of depostion chamber
h3	30[mm]	Height of spray neck

Variables

Selection

Geometric entity level	Domain
Selection	Domain 1

Name	Expression	Description
ramp	$\tanh(1E7[1/s]*t)$	Ramp function
TT	300[K]	Gas temperature
pp	10[torr]	Gas pressure
Nn0	$pp/k_B \text{ const}/TT$	Neutral number density
k1	$1.993039e-014*dd.Te^{0.93}*exp(-0.41/dd.Te)$	Elastic rate coefficient
k2	$8.773932e-015*dd.Te^{0.62}*exp(-18.16/dd.Te)$	Excitation rate coefficient
k3	$2.153106e-014*dd.Te^{0.49}*exp(-24.75/dd.Te)$	Ionization rate coefficient
r1	$k1*dd.Nn*dd.ne$	Elastic collision reaction rate
r2	$k2*dd.Nn*dd.ne$	Electronic excitation reaction rate
r3	$k3*dd.Nn*dd.ne$	Ionization reaction rate
de1	0[V]	Energy loss, elastic collision
de2	11.56[V]	Energy loss, electronic excitation
de3	15.8[V]	Energy loss, ionization
Re	r3	Electron production rate
Sen	$-e \text{ const}*(r1*de1 + r2*de2 + r3*de3)$	Collisional power loss
Ex	$-d(V, x)$	Electric field
Ain	$0.5E-3^2[m^2]$	Wall area
I	2E-6[A]	Thermal emission current
influx	$I/Ain/e \text{ const}*ramp$	Electron influx
mueN	$4E24[1/(m*V*s)]$	Reduced electron mobility
freq	$(1/pi)*10^3[1/s]$	Frequency
omega	$2*pi*freq$	Angular frequency
c	299792458[m/s]	Speed of light
k	$omega/c$	Angular frequency
U0	5[mm/s]	Initial Velocity

Name	Expression	Description
V0	100[V]	Voltage
mass_domain	$\text{at}(0, \text{intop1}(\text{hs.rho})) - \text{intop1}(\text{hs.rho})$	mass change in the domain
mass_bulk	$\text{intop2}(\text{h_C_bulk} * 2329[\text{kg/m}^3])$	total mass of bulk species

Coordinate Systems

Boundary System 1

Coordinate system type	Boundary system
Identifier	sys1

Geometry 1

Geometry 1

Units

Length unit	mm
Angular unit	deg

Materials

CH4 (methane) [gas]

CH4 (methane) [gas]

Selection

Geometric entity level	Domain
Selection	Domain 1

Laminar Flow (spf)

Laminar Flow

Features

Fluid Properties 1
Axial Symmetry 1
Wall 1
Initial Values 1
Inlet 1
Outlet 1

Electrostatics (es)

Electrostatics

Features

Charge Conservation 1
Axial Symmetry 1
Zero Charge 1
Initial Values 1
Ground 1
Electric Potential 1

Drift Diffusion (dd)

Drift Diffusion

Features

Drift Diffusion Model 1
Axial Symmetry 1
Insulation 1
Initial Values 1
Velocity 1
Wall 1
Electron Density and Energy 1
Wall 2

Heavy Species Transport (hs)

Heavy Species Transport

Features

Species: CH4
Species: H2
Species: CH2(s)
Species: C(b)
Species: CH4(s)
3: CH4=>CH4(s)
4: CH4(s)=>C(b)+2H2
Convection, Diffusion, and Migration
Axial Symmetry 1

Mesh 1

Mesh 1

Study 1

Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: $10^{\text{[range(-3,4/149,1)]}}$

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Laminar Flow (spf)	physics

Study 2

Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: $10^{[\text{range}(-3,4/149,1)]}$

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Electrostatics (es)	physics

Study 3

Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: $10^{[\text{range}(-3,4/149,1)]}$

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Drift Diffusion (dd)	physics

Study 4

Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: $10^{[\text{range}(-5,4/149,-1)]}$

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Heavy Species Transport (hs)	physics

Results

Data Sets

Solution 1

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 1
Model	Save Point Geometry 1

Solution 3

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 3
Model	Save Point Geometry 1

Revolution 2D

Data

Name	Value
Data set	Solution 3

Solution 4

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 4
Model	Save Point Geometry 1

Edge 2D 1

Selection

Geometric entity level	Boundary
Selection	Boundary 2

Data

Name	Value
Data set	Solution 1

Parametric Extrusion 1D 1

Data

Name	Value
Data set	Edge 2D 1

Settings

Name	Value
Level scale factor	500.05000500050113

Solution 5

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 5
Model	Save Point Geometry 1

Revolution 2D 3

Data

Name	Value
Data set	Solution 5

Revolution layers

Name	Value
Start angle	-90
Revolution angle	225

Cut Point 2D 1

Data

Name	Value
Data set	Parametric Extrusion 1D 1

Probe Solution 6

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 5
Model	Save Point Geometry 1

Boundary Probe 1

Selection

Geometric entity level	Boundary
Selection	Boundary 2

Data

Name	Value
Data set	Probe Solution 6

Settings

Name	Value
Method	Integration
Integration order	On

Probe Solution 7

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 5
Model	Save Point Geometry 1
Frame	Spatial (r, phi, z)

Domain Point Probe 1

Data

Name	Value
Data set	Probe Solution 7

Derived Values

Boundary Probe 1

Data

Name	Value
Data set	Boundary Probe 1

Expression

Name	Value
Expression	h_C_bulk
Unit	mm
Description	Accumulated growth height

Point Probe Expression 1

Data

Name	Value
Data set	Domain Point Probe 1

Expression

Name	Value
Expression	spf.U
Unit	m/s
Description	Velocity magnitude

Plot Groups

Electric Potential (es)

Time=0.019435 Streamline: Electric field

Electric Potential (es) 1

Time=0.003443 Surface: Electric potential (V)

Electron Density (dd)

Time=0.001132 Surface: Electron density ($1/m^3$)

Electron Temperature (dd)

Time=9.400574 Surface: Electron temperature (V)

Absolute Pressure (hs)

Time=9.695656e-4 Surface: Absolute pressure (Pa)

Mole Fraction

Time=1.260872e-4 Surface: Mole fraction (1)

Accumulated Height

Surface: Accumulated growth height (mm)

Velocity (spf)

Time=0.401816 Streamline: Velocity field

Pressure (spf)

Time=0.001 Contour: Pressure (Pa)

Velocity, 3D (spf)

Time=7.34128 Surface: Velocity magnitude (m/s)

Time=7.34128 Surface: Velocity magnitude (m/s)

Height vs Arc Length

Line Graph: Accumulated growth height (mm)

APPENDIX C CH₄ CROSS SECTION DATA

Each collision process is defined by a block consisting of:²⁹

1st line

Keyword in capitals indicating the type of the collision. Possible collision types are 'elastic', 'effective', 'excitation', 'ionization', or 'attachment' (capital letters required, key words are case sensitive), where 'elastic' is used to denote the elastic momentum transfer cross section and where 'effective' denotes the total momentum transfer cross section (sum of elastic momentum transfer and total inelastic cross sections). The latter is useful for solving the Boltzmann equation in the 2-term approximation.

2nd line

This line contains the name of the target particle species. This name is a character string, freely chosen by the user, e.g. 'Ar'. Optionally for excitation processes, the name of the corresponding excited state can be specified on the same line, separated from the first name either by arrow '->' or by double-head arrow " $\longleftrightarrow$ ", e.g. 'Ar -> Ar*' and 'Ar $\longleftrightarrow$ Ar*', respectively. In the later case BOLSIG+ will automatically define the inverse superelastic process, constructing the superelastic cross-section by detailed balancing, and considering the indicated excited state as the target. In this case, the ratio of statistical weights must be input in the 3rd line (see below). Alternatively, superelastic collisions

could be defined explicitly as excitation collisions with a negative electron energy loss with user input cross sections and species name, 'Ar*', for example.

3rd line

For elastic and effective collisions, the ratio of the electron mass to the target particle mass. For excitation or ionization collisions, the electron energy loss (nominally the threshold energy) in eV. For attachment, the 3rd line is missing. In case of an excitation process where an excited state has been indicated on the 2nd line using double-head arrow " $\leftrightarrow$ ", the 3rd line must specify also ratio of the statistical weights of the final state to the initial state as the second parameter in 3rd line; this is needed by BOLSIG+ to calculate the de-excitation cross-section.

ATTACHMENT

CH4 -> CH3+H⁻

COMMENT: Dissociation Attachment. Threshold 7.7eV

UPDATED: 2010-06-23 12:33:08

7.7000e+0	0.0000e+0
9.0000e+0	8.0000e-24
1.0000e+1	8.0000e-24
1.2000e+1	0.0000e+0

ATTACHMENT

CH4 -> H2+CH2^-

COMMENT: Dissociation Attachment. Threshold 9eV

UPDATED: 2010-06-23 12:33:31

9.0000e+0	0.0000e+0
1.0800e+1	4.0000e-24
1.3200e+1	0.0000e+0

ELASTIC

CH4

3.424e-5 / mass ratio

UPDATED: 2011-02-08 11:05:07

0.0000e+0	4.0000e-19
1.0000e-2	4.0000e-19
1.5000e-2	2.4354e-19
2.0000e-2	1.7000e-19
3.0000e-2	1.0188e-19
4.0000e-2	7.3000e-20
6.0000e-2	4.6000e-20
8.0000e-2	2.9000e-20
1.0000e-1	2.0000e-20
1.5000e-1	9.9000e-21
2.0000e-1	7.0000e-21
3.0000e-1	5.6000e-21
4.0000e-1	6.5000e-21
6.0000e-1	9.5340e-21
8.0000e-1	1.4000e-20
1.0000e+0	1.9000e-20
1.5000e+0	3.1000e-20
2.0000e+0	4.4000e-20
3.0000e+0	7.2000e-20
4.0000e+0	1.0500e-19
6.0000e+0	1.4739e-19
8.0000e+0	1.6080e-19
1.0000e+1	1.5500e-19
1.5000e+1	1.2000e-19
2.0000e+1	8.0300e-20
3.0000e+1	4.2800e-20
4.0000e+1	2.9007e-20
6.0000e+1	1.8459e-20

8.0000e+1	1.4173e-20
1.0000e+2	1.1851e-20
1.5000e+2	8.9450e-21
2.0000e+2	7.5000e-21
3.0000e+2	5.9530e-21
4.0000e+2	5.0980e-21
6.0000e+2	4.1340e-21
8.0000e+2	3.5770e-21
1.0000e+3	3.2000e-21

EXCITATION

CH4 -> CH4(V24)(0.162eV)

1.620e-1 / threshold energy

COMMENT: Vibrational Excitation , V24

UPDATED: 2010-06-23 12:50:08

1.6200e-1	0.0000e+0
2.0000e-1	1.3000e-21
2.5000e-1	5.5300e-21
3.0000e-1	6.8900e-21
4.0000e-1	7.5400e-21
5.0000e-1	7.0200e-21
6.0000e-1	6.0400e-21
8.0000e-1	4.3600e-21
1.0000e+0	3.1200e-21
1.2000e+0	2.4700e-21
1.5000e+0	2.2100e-21
2.0000e+0	2.2500e-21
2.5000e+0	2.5700e-21
3.0000e+0	3.0200e-21
4.0000e+0	4.1600e-21
5.0000e+0	5.8500e-21
6.0000e+0	7.9300e-21
6.5000e+0	9.2300e-21
7.0000e+0	1.0800e-20
7.5000e+0	1.1400e-20
8.0000e+0	1.1100e-20
9.0000e+0	9.2300e-21
1.0000e+1	7.9300e-21
1.5000e+1	5.2000e-21
2.0000e+1	4.6800e-21
4.0000e+1	3.4500e-21

7.0000e+1	2.0800e-21
1.0000e+2	1.3000e-21
1.5000e+2	6.0000e-22
2.0000e+2	0.0000e+0

EXCITATION

CH4 -> CH4(V13)(0.361eV)

3.610e-1 / threshold energy

COMMENT: Vibrational Excitation, V13

UPDATED: 2010-06-23 12:50:32

3.6100e-1	0.0000e+0
4.5000e-1	1.3000e-21
5.0000e-1	2.0800e-21
6.0000e-1	2.9900e-21
6.6000e-1	3.1200e-21
7.5000e-1	2.9900e-21
8.4000e-1	2.6000e-21
9.0000e-1	2.3800e-21
1.0000e+0	2.0800e-21
1.2000e+0	1.7500e-21
1.5000e+0	1.5300e-21
1.8000e+0	1.4300e-21
2.0000e+0	1.4700e-21
2.5000e+0	1.8200e-21
3.0000e+0	2.4100e-21
4.0000e+0	4.2300e-21
5.0000e+0	6.5000e-21
6.0000e+0	9.1000e-21
7.0000e+0	1.1700e-20
7.5000e+0	1.2000e-20
8.0000e+0	1.1570e-20
9.0000e+0	8.8400e-21
1.0000e+1	7.2800e-21
1.5000e+1	3.6400e-21
2.0000e+1	2.8600e-21
4.0000e+1	1.6900e-21
7.0000e+1	6.5000e-22
1.0000e+2	3.9000e-22
1.5000e+2	0.0000e+0

EXCITATION

CH4 -> CH4*(9eV-dissoc)

9.000e+0 / threshold energy

COMMENT: Dissociation Excitation

UPDATED: 2010-06-23 12:50:46

```

-----
9.0000e+0    0.0000e+0
1.0000e+1    3.0000e-21
1.3000e+1    3.0000e-21
1.5000e+1    4.0000e-21
2.0000e+1    5.4000e-21
2.5000e+1    5.4000e-21
1.0000e+2    5.4000e-21
1.5000e+2    4.8500e-21
2.0000e+2    4.5000e-21
3.0000e+2    4.0000e-21
4.0000e+2    3.7500e-21
5.0000e+2    3.5000e-21
1.0000e+3    1.5000e-21
2.0000e+3    7.5000e-22
5.0000e+3    3.0000e-22
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```

EXCITATION

CH4 -> CH4*(10eV-dissoc)

1.000e+1 / threshold energy

COMMENT: Dissociation Excitation

UPDATED: 2010-06-15 13:44:39

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-----
1.0000e+1    0.0000e+0
1.1000e+1    3.0000e-21
1.3000e+1    3.0000e-21
1.5000e+1    4.0000e-21
2.0000e+1    5.4000e-21
2.5000e+1    5.4000e-21
1.0000e+2    5.4000e-21
1.5000e+2    4.8500e-21
2.0000e+2    4.5000e-21
3.0000e+2    4.0000e-21
4.0000e+2    3.7500e-21

```

5.0000e+2	3.5000e-21
1.0000e+3	1.5000e-21
2.0000e+3	7.5000e-22
5.0000e+3	3.0000e-22

EXCITATION

CH4 -> CH4*(11eV-dissoc)

1.100e+1 / threshold energy

COMMENT: Dissociation Excitation

UPDATED: 2010-06-15 13:45:07

1.1000e+1	0.0000e+0
1.2000e+1	3.0000e-21
1.3000e+1	3.0000e-21
1.5000e+1	4.0000e-21
2.0000e+1	5.4000e-21
2.5000e+1	5.4000e-21
1.0000e+2	5.4000e-21
1.5000e+2	4.8500e-21
2.0000e+2	4.5000e-21
3.0000e+2	4.0000e-21
4.0000e+2	3.7500e-21
5.0000e+2	3.5000e-21
1.0000e+3	1.5000e-21
2.0000e+3	7.5000e-22
5.0000e+3	3.0000e-22

EXCITATION

CH4 -> CH4*(12eV-dissoc)

1.200e+1 / threshold energy

COMMENT: Dissociation Excitation

UPDATED: 2010-06-15 13:45:30

1.2000e+1	0.0000e+0
1.3000e+1	3.0000e-21
1.5000e+1	4.0000e-21
2.0000e+1	5.4000e-21
2.5000e+1	5.4000e-21
1.0000e+2	5.4000e-21
1.5000e+2	4.8500e-21
2.0000e+2	4.5000e-21
3.0000e+2	4.0000e-21

4.0000e+2	3.7500e-21
5.0000e+2	3.5000e-21
1.0000e+3	1.5000e-21
2.0000e+3	7.5000e-22
5.0000e+3	3.0000e-22

IONIZATION

CH4 -> CH4⁺

1.260e+1 / threshold energy

UPDATED: 2010-06-15 13:48:33

1.2600e+1	0.0000e+0
1.3500e+1	3.4000e-22
1.4000e+1	7.4000e-22
1.4500e+1	1.3000e-21
1.5000e+1	1.7000e-21
2.0000e+1	6.8000e-21
3.0000e+1	1.2600e-20
5.0000e+1	1.6900e-20
7.0000e+1	1.7800e-20
1.0000e+2	1.7800e-20
2.0000e+2	1.5100e-20
3.0000e+2	1.1900e-20
4.0000e+2	1.0000e-20
5.0000e+2	9.0000e-21
1.0000e+3	4.5000e-21
2.0000e+3	2.2500e-21
5.0000e+3	9.0000e-22

IONIZATION

CH4 -> H+CH3⁺

1.430e+1 / threshold energy

COMMENT: Dissociation Ionization

UPDATED: 2010-06-15 13:49:03

1.4300e+1	0.0000e+0
1.5000e+1	3.5000e-22
2.0000e+1	3.9000e-21
3.0000e+1	1.0400e-20
5.0000e+1	1.6100e-20
7.0000e+1	1.7800e-20
1.0000e+2	1.7800e-20

2.0000e+2	1.5100e-20
3.0000e+2	1.1900e-20
4.0000e+2	1.0000e-20
5.0000e+2	9.0000e-21
1.0000e+3	4.5000e-21
2.0000e+3	2.2500e-21
5.0000e+3	9.0000e-22