Modeling and Simulations of DC and RF Atmospheric Pressure Non-thermal Micro Plasma Discharges: Analysis and Applications

A Thesis

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DEDICATIONS

I dedicate this thesis to my wife Shamia who has done more than her share (while working on her own dissertation) during the past four years when I was busy working for my Ph.D. I would also like to dedicate this thesis to the people of Bangladesh; the tax payers without whom it would not have been possible for me to obtain my undergraduate degree from the public university and later pursue higher studies abroad.
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NOMENCLATURE

\begin{itemize}
\item \textit{C} capacitance
\item \textit{d} inter-electrode separation
\item \textit{D} diffusion coefficient
\item \textit{e} electron charge
\item \textit{\vec{E}} electric field vector
\item \textit{f_0} electron energy distribution function
\item \textit{\vec{F}} body force
\item \textit{h} enthalpy
\item \textit{I} current
\item \textit{j} current density
\item \textit{k} thermal conductivity
\item \textit{k_B} Boltzmann constant
\item \textit{L} inductor
\item \textit{m} mass
\item \textit{n} number density
\item \textit{N} neutral density
\item \textit{p} pressure
\item \textit{q} charge state
\item \textit{\dot{Q}} rate of enthalpy change
\item \textit{R} resistance
\item \textit{R_{im}} surface reaction rate
\item \textit{T} temperature
\item \textit{t} time
\item \textit{\vec{u}} fluid velocity vector (m/s)
\item \textit{V_d} discharge voltage
\item \textit{V_{pwr}} supply voltage
\end{itemize}
Greek Symbols

$\alpha$ volume dominated ‘alpha’ mode discharge
$\beta$ surface interaction coefficient
$\epsilon$ permittivity
$\epsilon_0$ permittivity of free space
$\epsilon_e$ electron energy
$\phi$ electric potential
$\Gamma$ flux vector
$\lambda$ mean free path
$\lambda_D$ Debye length
$\gamma$ secondary emission coefficient
$\eta$ reaction rate coefficient
$\mu$ mobility of charged species
$\mu$ dynamic viscosity
$\theta$ fraction of surface coverage
$\nu$ electron transport collision frequency
$\sigma$ plasma conductivity

Subscripts

$b$ deposited bulk species
$d$ discharge
$D$ diamond like carbon
$dexcit$ de-excitation
$diss$ dissociation
$e$ electron
$excit$ excitation
$g$ gas species
$G$ graphitic carbon
$i$ ion species
ion  ionization
k   heavy particle species
L   loading
n   neutral species
p   plasma
pwr power supply
Rx  surface species with ‘x’ dangling bonds (x = 1 – 3)
s   surface species
T   tuning
th  thermal
v   vibrationally excited species

Superscripts

+   positive ions
-   negative ions
*   electronically excited species
•   source term
ABSTRACT

Modeling and Simulations of DC and RF Atmospheric Pressure Non-thermal Plasma Discharges: Analysis and Applications
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Dr. Bakhtier Farouk and Dr. Alexander Fridman

Atmospheric pressure non-thermal plasma discharges are attractive for a wide range of applications due to their operational flexibility. Among the different atmospheric pressure non-thermal plasma sources, atmospheric pressure non-thermal micro plasma discharge is a very recent development. However, the micron scale size of these discharges makes it difficult to measure basic plasma characteristics (species density, gas and electron temperature, electric field etc) and also to analyze the different interplaying physico-chemical processes. In this work comprehensive multi-dimensional hybrid models were developed to simulate DC and RF atmospheric pressure non-thermal plasma discharges, and validated against experimental data. The basic plasma characteristics and different physico-chemical processes were explored by performing systematic parameter variations. The developed discharge models included detailed discharge physics, gas phase chemistry, surface chemistry and external circuit model.

DC micro plasma discharges in argon, hydrogen and methane-hydrogen gas were simulated. The effect of the external circuit was found to be crucial in predicting the discharge characteristics accurately. The simulations indicated the discharge to be operating as a ‘normal’ glow discharge. Predictions from the model compared favorably to the experimental measurements. A detailed surface chemistry model was developed for a DC methane-hydrogen
micro glow to study the possibility of using these micro plasma discharges in plasma enhanced chemical vapor deposition.

RF plasma discharges in argon gas together with an extensive external circuit was simulated; special attention was devoted to the effect of external circuit parameters on the discharge characteristics. The circuit elements were found to trigger change in the mode of operation. An atmospheric pressure plasma jet in helium-oxygen feed gas was also simulated to study the possibility of surface decontamination applications.

To the author’s knowledge, this is the first attempt where detailed simulation of atmospheric pressure micro plasma discharge has been conducted together with an external circuit. The discharge models were used to investigate the plasma characteristics, physico-chemical processes and study the effect of the external circuit and process parameters on the discharge. Better understanding of these processes will enable the tailoring and optimization of the operating conditions.
1 INTRODUCTION

1.1 Background

The following sections give a brief background on plasmas, plasma applications and plasma enhanced chemical vapor deposition. This information is necessary to place the motivations of this research in context.

1.1.1 Plasmas

Plasmas are gases where there are charged particles such as electrons and ions, and excited neutral species (vibrational, rotational, electronic, and radicals) in addition to the neutral gas, and are sometimes referred to as the fourth state of matter \(^1\). The density of electrons, \(n_e\), degree of ionization (ratio of electron to neutral particle density, \(\frac{n_e}{N}\)), and the average energy of the electrons (electron temperature, \(T_e\)) can be used to characterize the plasmas in a broad sense. Figure 1.1 shows the classification of plasmas based on electron density and electron energy. The interstellar plasmas are at one end of the spectrum, with very low densities and temperatures. These plasmas make up nearly all of the matter in the universe. In the other end of the spectrum, one has the high-pressure arcs where the densities, and degree of ionization can be large (\(n_e > 10^{15} \text{ cm}^{-3}\)) and fusion devices where the electron temperatures are 100s – 1000s eV (1 eV \(\approx 11,593\) K). Glow discharges and arcs having number densities from \(10^9 – 10^{15} \text{ cm}^{-3}\), and \(T_e\) ranging from 1 – 10 eV are the most common types of plasmas used in industrial and technological applications. Based on the neutral gas temperature (\(T\)) plasma discharges can be differentiated into two broad categories, thermal and non-thermal \(^1,2\). Thermal plasma discharges are typically equilibrium systems with temperatures in excess of 10,000 K. Non-thermal types, in
contrast, are in a thermodynamic and chemical non-equilibrium with the temperature of the electrons (> 10,000 K) greatly in excess of the gas temperature (~ 300 – 1000 K).

Figure 1.1: Classification of plasmas based on electron density and electron temperature.

Once the plasmas are formed they decay over time due to re-combination of the electrons and ions and by diffusion of charged species to the walls of the reactor. In the steady state, a supply of power is required to offset the losses. The energy from the power source is coupled to the electrons in the plasma through direct (DC), capacitive (CCP), and/or inductive coupling (ICP) by the electric and/or magnetic fields produced by the power source. The electrons then transfer the energy to the neutral species through collisions thereby producing the excited and ionized states which can then be used in the desired application. Due to the large difference in the masses of electrons and ions, the electrons typically oscillate about the ions which are
relatively at rest. This gives rise to fundamental oscillations leading to fundamental length and time scales. The time scale is defined by the plasma frequency $^{1-3}$:

$$\omega_p = \sqrt{\frac{4\pi n_e e^2}{m_e}}$$  \hspace{1cm} (1.1)

and the length scale is defined as the Debye length $^{1-3}$:

$$\lambda_D = \sqrt{\frac{k_B T_e}{4\pi n_e e^2}}$$  \hspace{1cm} (1.2)

where, $n_e$, $m_e$, and $T_e$ are the electron density, mass and temperature, and $e$ is the fundamental charge. In general, plasmas are electrically neutral at length scales larger than the Debye length, and time scales larger than the period of the plasma oscillation. The charge-neutrality of plasmas is valid over the bulk of the plasma but not near the walls (electrodes). The flux of electrons to the walls is higher due to their larger velocities, resulting from higher mobilities. The electrons that strike the surface are adsorbed on the walls leading to the formation of a sheath region in the plasma. Thus, there is a net positive space charge and so the charge-neutrality is no longer valid in the sheath region. This build up of a net positive space charge causes a restoring force to develop which accelerates the positively charged ions into the walls, and the negatively charged species away from it. According to the Poisson’s equation, in order to maintain quasi-neutrality, a sheath potential drop is formed that compensates for the differences in the electrons and ions near the walls. The sheath formation process is depicted in Figure 1.2. The sheath potential formed close to the surfaces accelerates the positive ions towards the wall. When the energetic ions strike the metal surfaces, they can release the bound electrons in the surface. These free ‘secondary electrons’ are then accelerated by the electric field in the sheath and produce
ionization in the bulk plasma. The source of the secondary electrons $S_j$ is dependent on the ion flux and the surface:

$$S_j = \sum_i \Gamma_i \gamma_{ij}$$  \hspace{1cm} (1.3)

where, $S_j$ is the secondary electrons from surface $j$, $\Gamma_i$ is the flux of the ionic species $i$ and $\gamma_{ij}$ is the secondary electron emission coefficient.

![Diagram showing the formation of sheath potential drop near a surface](image)

**Figure 1.2**: The formation of sheath potential drop near a surface a) the electron flux is much larger than the ion flux due to the surface due to the larger electron velocity (higher mobilities), b) a positively charged region is formed near the surface and c) the net charge produces a plasma potential drop and a sheath field.

As such, the study of the dynamics and properties of the sheath is very important in applications such as materials processing and surface modification. This is because the surfaces
are treated or modified by a combination of ion and neutral species fluxes, which are influenced by the characteristics of the sheath. For example, in a thin sheath, the ions are less collisional, as the time spent by the ion in the sheath is less than the mean time between collisions, and hence the ions are very directional.

In this dissertation, the focus is atmospheric pressure non-thermal glow discharges. For these discharges, the degree of ionization is small \( \frac{n_e}{N} \approx 10^{-6} - 10^{-5} \), and there is thermal non-equilibrium \( T_e >> T_g \) between the electrons and heavy particles. Their non-equilibrium nature allows for the creation of active species without generating excessive heat, which may cause excessive thermal dissociation and damage working surfaces/substrates. Also, the chemical processes which occur in the non-equilibrium plasma are beyond those which are accessible by the addition of only thermal energy \(^4\). Non-thermal plasmas thus find many diverse applications in the controlled treatment of materials. Operation of non-thermal plasma discharges at atmospheric pressure allows for ease of use and lower manufacturing costs, among other advantages. However, there are unique challenges in using non-thermal atmospheric pressure plasmas since they are very unstable and have the tendency to transition to thermal arc discharges \(^2\).

1.1.2 Applications of Plasmas

Among the different wide variety of plasma discharge applications some of the most common technological applications include the plasma display panels, fluorescent lamps, and semiconductor processing. In most of their applications the plasma, is used as an energy medium to breakdown the feed gas into a required product, and/or excite the gas and use a property of the
product to achieve the desired result. For example, in plasma display panels, fluorescent lamps, and metal-halide lamps the radiation from excited species is desired. The excited species are generated by electron-impact collisions. In plasma display panels, typical operating conditions are 100s Torr, in mixtures of rare gases such as Ar/Xe. The emission from excimer species such as Xe*, Xe2* is used as a source of radiation, which is then converted to visible light in the phosphor coating. In case of mercury vapor lamps for example, the emission from Hg(6^3P_1) and Hg(6^1P_1) is desired. In these applications, the efficiencies are typically governed by the fraction of the energy that is expended in producing these emitting states, which is a function of the plasma characteristics such as n_e, pressure and power density.

In semiconductor processing (typically at pressures of few – 10s mTorr), the most common use of plasmas is in etching of Si/SiO2 (using Cl, Br and F containing gas mixtures) and deposition of thin films of metals (such as copper, tungsten) or dielectric materials (silicon-nitride films). For etching SiO2, the plasma is used to breakdown the feed gas (such as C4F8) and creates ion and neutral species. The ions are then accelerated towards the substrate by application of a bias, and these ions activate (increase reactivity) the surface sites on the wafer and/or physically etch away the material. Usually, an anisotropic etch is desired, which requires the incoming ions to be highly directional (usually perpendicular to the wafer). Due to this requirement the semiconductor plasmas are at low pressures where the mean free paths are larger. In the absence of collisions in the sheath, the direction of the ion flux is parallel to the applied electric field. The control over the ion energies, angular distributions, and plasma composition is vital in achieving the desired etch or deposition properties.

Research is also being carried out to develop novel plasma discharges and apply them in other technological areas. Plasma discharges in high gas flow and relatively high pressures (>
10s Torr) is being studied for the purpose of thrusters for propulsion \(^{10}\) and actuators to control boundary layer separation \(^{11},^{12}\). In the case of plasma micro thrusters, the discharge is used as a means of adding energy and momentum to the flow, which is then used to enhance the thrust. These are similar in operation to other electro-thermal propulsion devices such as resistojets \(^{13}\) and arcjets \(^{13}\). The coupling of the power deposition to the flow is important from the standpoint of efficiency (power required per unit thrust) and makes it worthwhile to study dynamics of plasma in this regard. Plasma based actuators for aerodynamic flow control utilizes the momentum of the charged particles to infuse momentum in the boundary layer of the flow. Both DC glow \(^{12}\) and Dielectric Barrier Discharges (DBD) \(^{11}\) have been utilized for this purpose and were found to be successful in controlling and delaying the onset of boundary layer separation.

1.1.3 Plasma Enhanced Chemical Vapor Deposition (PECVD)

Plasma enhanced chemical vapor deposition (PECVD) is a type of plasma processing in which material is deposited onto surfaces in the form of thin films. It is a variant of thermal CVD in that a non-thermal plasma rather than temperature is used to activate the chemical processes. In the plasma the precursors (species from which the deposition products are forms) are partially dissociated, ionized or otherwise chemically activated. The precursor undergoes a chemical change at a solid surface leaving a solid layer, typically an amorphous or crystalline homogeneous and uniform film. A schematic diagram depicting the PECVD process is shown in Figure 1.3. All industrial applications of this processing occurs in low pressure non-thermal plasma systems \(^{14}\). This is because the necessary plasma conditions are easier to maintain at pressures of 10’s of mTorr to a few Torr. However the low operating pressure is associated with several drawbacks. These include, expensive vacuum systems, high maintenance cost of such
systems, batch manufacturing process, size constraint of work piece governed by the vacuum chamber size, and low rate of deposition/etching among the many others.

Figure 1.3: Schematic diagram of plasma enhanced chemical vapor deposition.

Plasma-enhanced chemical vapor deposition (PECVD) is widely used to coat thin films onto materials using plasmas in gas mixtures. These films serve many purposes which include wear and corrosion resistance coating (diamond-like-carbon (DLC) films), components for integrated circuit (silicon dioxide and silicon nitride layers), dielectric layers or temporary sacrificial masks in integrated circuits (polymer coatings)\textsuperscript{15}. 

8
1.2 **Motivation**

Most thin film PECVD processes\(^8\) take place in vacuum-based plasma reactors. Performing PECVD at atmospheric pressure has several advantages:

- The cost of micro fabrication is reduced significantly as there is no need for expensive vacuum pumps.
- Free from the constraints of a vacuum chamber, the processing takes place in a continuous mode and can treat any size shape or object.
- Substrates that are non-vacuum compatible can be treated by operating at an atmospheric pressure.
- The deposition/etching rate is likely to be higher, allowing for more rapid processing, due to the higher operating gas densities.
- The process uses less energy and is more environmentally-friendly because operating at ambient pressure and temperature satisfies ‘Green Chemistry’ principles\(^{16}\).

While the benefits of atmospheric pressure plasma processing are well known, significant challenges exist. The requirements for thin film deposition by PECVD are that the plasma be uniform, stable and non-thermal. Using traditional technologies, such plasma can be generated in low pressure systems. This is because at atmospheric pressure instabilities arise as a result of increased collisionality and decreased stabilizing effect of the reactor walls. These instabilities prevent the discharge from being uniform and non-thermal. Depending on the type of discharge, these instabilities include glow to arc transition, ionization overheating instability, alpha (\(\alpha\)) – gamma (\(\gamma\)) mode transition and streamer formation. Of the four, the first three lead to thermalization of the plasma discharge and the latter leads to spatial non-uniformities.
Many approaches have been proposed in recent years to overcome the problems of generating and sustaining stable, uniform and homogeneous non-thermal atmospheric pressure plasma discharges. One novel approach in generating atmospheric pressure non-thermal plasma discharge is based on Paschen’s law \( p \times d = \text{const.} \) (pressure \( \times \) inter-electrode separation = constant). Figure 1.4 shows the Paschen curves for air, nitrogen, hydrogen, helium and argon. The parameter \( pd \) is simply proportional to the ratio of the discharge gap length to the mean free path or the inverse of the Knudsen number. There is a minimum breakdown voltage on the Paschen curve, \( V_{\text{min}} \) and a corresponding \( pd_{\text{min}} \). To the left of the minimum point the discharge gap is so small that the mean free path in the discharge is insufficient to provide ignition. To the right the required voltage is higher since the gap is longer. Paschen’s law therefore suggests that in order to ignite plasma at atmospheric pressure with a minimum breakdown voltage the inter-electrode separation has to be scaled down to the micrometer range.

Figure 1.4: Paschen curves for different atomic and molecular gases.
Various designs of plasma sources to generate stable micro plasma discharges have been proposed. The reported electrode configurations include parallel plates\textsuperscript{18}, cylindrical type (e.g. hollow cathode\textsuperscript{19}), slot type\textsuperscript{20}, needle type\textsuperscript{21}, pin plate type\textsuperscript{22} etc, and the applied operation modes vary from direct current (DC) to radio frequency (RF) or microwave. These studies are motivated by numerous potential applications of micro plasmas including sensors, integrated MEMS, excimer sources or micro reactors\textsuperscript{22, 24-27}. However none of these studies were motivated towards studying the potential of micro plasma discharges in PECVD. Only recently there has been a detailed study by David Staack on PECVD using atmospheric pressure micro discharges\textsuperscript{23}.

The measurement of basic plasma characteristics, such as gas temperature, electron temperature, electron density, species concentration, electric field etc, is important for understanding discharge behavior, and for extending the range of parameter space while maintaining stable discharge operation. Although extensive investigations of micro discharge modes and voltage current (V-I) characteristics have been reported, direct plasma diagnostics of micro discharges are still limited\textsuperscript{24, 25}. The difficulties mostly arise from their small size and high operating pressure. Detailed modeling of the micro discharges can provide insight into the interplaying physico-chemical processes and the basic plasma characteristics (gas temperature, electron temperature, electron density, species concentration, electric field etc) that would be difficult to obtain via measurements. This would provide better understanding of the regime of operation and would also provide guidelines for optimizing the operating parameters.
1.3 **Objectives**

The main objective of the present research was to develop comprehensive mathematical models for atmospheric pressure micro plasma discharges for thin film deposition processes. The developed models included the modeling of the discharge physics, discharge chemistry, surface deposition mechanism as well as the external circuit parameters. In the completed research, hybrid models have been used to study plasma characteristics of atmospheric pressure micro plasma discharge which include electron density, species concentration, electric field, electron temperature and gas temperature; to study the effect of external circuit parameters on the discharge characteristics and to study thin film deposition process and the effect of operating parameters on the deposition characteristics (deposition rate and film quality). The model was used to simulate and characterize atmospheric pressure micro discharge in monatomic gas (argon), diatomic gas (hydrogen) and polyatomic gas (methane-hydrogen mixture). The DLC thin film deposition process was simulated using methane-hydrogen as the feed gas. Parametric studies were performed to identify the most favorable condition for DLC deposition. The model was used to study both DC and RF powered micro discharges. Furthermore the potential of RF powered atmospheric plasma jet in helium-oxygen feed gas for surface decontamination application was also investigated. The discharge model has been validated by comparing the model predictions with experimentally measured voltage-current (VI) characteristics, current density, gas temperature, species density and discharge visualization studies.
The objectives of the completed research were:

- Develop discharge physics models that consider self-consistent transient solutions of electron, ions, radicals, neutrals, electric field, electron energy and neutral gas temperature.
- Develop comprehensive models for both DC and RF capacitively coupled glow discharges in one-dimensional and two-dimensional axisymmetric cylindrical coordinates.
- Develop external circuit models for both DC and RF glow discharges that predict the effect of external circuit parameters on discharge characteristics.
- Develop gas phase chemistry models that predict spatial distribution of ions, radicals, excited and neutral species.
- Develop surface chemistry model that predict deposition rate and quality of DLC thin films.
- Identify the most favorable operating condition for obtaining good quality DLC films through parametric studies.
- Measure VI characteristics, current density, neutral gas temperature, species concentration and discharge visualization studies for model validation.

To a significant extent, the objectives were met in the present study. The completed work has resulted in five archival journal papers\textsuperscript{26-30}, one book section\textsuperscript{31}, four conference papers\textsuperscript{32-35} and two journal papers under preparation.
1.4 **Outline of the Thesis**

The organization of the thesis is as follows. The motivation and objectives of the present research are presented in Chapter 1. Chapter 2 describes the applications of plasma processing and manufacturing. The importance and role of mathematical modeling in plasma processing is also discussed. Chapter 3 deals with the present status of literature for simulations of plasma discharges. A literature review on modeling atmospheric pressure non-thermal micro plasma discharges is presented separately. A detailed description of the mathematical model used in this study is presented in Chapter 4. The various modules such as plasma dynamics, neutral fluid dynamics, gas phase chemical kinetics, surface kinetics and external circuit are discussed in detail.

The presentation of results begins in Chapter 5 and largely follows the chronological order of six papers published (5) or submitted (1) to journals as part of this research. In Chapter 5 simulation results of atmospheric pressure argon micro glow discharge powered by a DC power source is presented. The validation of the mathematical model through experimental measurements of VI characteristics, ‘normal’ current density and gas temperature are included. Plasma characterization of DC micro glow discharge in a diatomic gas (hydrogen) is presented in Chapter 6. The effect of different gas heating mechanisms on neutral gas temperature and the effect of secondary electron emission coefficient on cathode voltage drop are discussed. In Chapter 7 results from one dimensional simulations of DC micro glow discharge is presented. The chapter includes a detailed description of the gas phase and surface chemistry model developed. The parametric studies performed to analyze the effects of process parameters on both the discharge and DLC deposition characteristics are also discussed. Results from two-dimensional axisymmetric simulations of methane-hydrogen micro glow discharge are presented.
in Chapter 8. These simulations were conducted to obtain deposition rate profiles and determine the quality and uniformity of the deposited films.

The simulation results for a RF capacitively coupled plasma (CCP) together with an external matching circuit are presented in Chapter 9. The details of the external circuit model are also discussed in the chapter. The transition in mode of operation and the effect of the matching circuit on the transition were also reported. Chapter 10 presents the study of atmospheric pressure RF plasma jet in helium-oxygen feed gas and its potential as a possible decontamination agent. Finally Chapter 11 summarizes and concludes the research presented in this thesis with a discussion on the future work that might be undertaken.
2 BACKGROUND

2.1 Plasma Processing in Manufacturing

Plasma aided manufacturing encompasses a vast range of industrial applications \cite{8, 36}, including thin film deposition/etching, plasma polymerization, microelectronics fabrication, tool hardening, welding, arc melting, synthesis of powders, plasma spraying and plasma sintering. The main advantage of plasma-aided manufacturing over other manufacturing processes is the directional control in the process due to anisotropy of the ion movement. The mass of waste generated during plasma processing is considerably smaller than for liquid processes. And in many cases the waste generated is environmentally benign.

Plasmas used in industry encompass a wide range of processes that can be classified based on operating pressure. Figure 2.1 shows a number of such traditional manufacturing techniques. At low pressures, the plasma operates in the non-thermal non-equilibrium regime, the electron-neutral collision frequency is low and the primary interactions are between charged particles and the materials to be processed. As the pressure increases collision becomes more important and the collision frequency increases. As the pressure approaches atmospheric pressure the common perception is that the plasma becomes thermal plasma \cite{1, 2}, however it has been shown that even in atmospheric pressure, non-thermal plasmas can be generated that maintains non-equilibrium characteristics \cite{17, 19, 37}. Most of the applications of non-equilibrium plasmas simultaneously involve competing processes such as deposition, sputtering, etching and surface modifications. The goal of the plasma aided manufacturing is to control the generation and flux of the ions, electrons, free radicals and large particles incident on a surface. The flux of
the species modify the surface, either by depositing material (deposition) or removing material (etching or sputtering) or imbedding particles (ion implantation).

![Figure 2.1: Plasma processes arranged by operating pressure](image)

Plasma processing using non-thermal plasma discharges is a complex phenomenon involving electron, ion and radical kinetics, chemical reactions in the discharge and adsorption, desorption, sputtering, and reactions at the surface. The plasma is used to activate a chain of chemical reactions from an energy source and to deliver energetic particles to a surface. Plasma contains electrons, ions both positive and negative, radicals and neutral species which are required for plasma processing. A schematic diagram showing the reactive environment in
plasma discharges is presented in Figure 2.2. The feed gas is fed into the inter-electrode separation spacing where the plasma exists. In the plasma region the electrons are energized by the electric field generated from the electrical power supply. The electrons with high energy, in the tail of the energy distribution function, contribute significantly to the electron induced reactions. They impact on the neutrals and radicals to dissociate and ionize through inelastic processes forming free radicals and ionic species. These species further chemically react with the feed gas and other radicals as they diffuse and drift towards the substrate sitting on an electrode. At the substrate, the radicals, the ions undergo adsorption, sputtering and/or chemical reactions thereby modifying the substrate, while the reaction products are released back to the plasma. The combination of neutral/radical species adsorption and positive ion bombardment can result in surface chemical reactions. If the products of the surface reactions are nonvolatile, a surface film grows by deposition. If the products of the surface reactions are volatile, they leave the surface and etching results. If the particles remain on or just below (couple of mono-layers) the surface, implantation occurs. Ion bombardment on the electrodes also causes secondary electron emissions. These electrons, after gaining energy from the electric field, also create ions and radicals through electron induced ionization and dissociation reactions. These ions and radicals once again come to the surface where deposition, etching or implantation occurs.

The main objective of plasma processing is to obtain desired process characteristics such as deposition/etching, spatial uniformity, selectivity and degree of anisotropy. The operating and design parameters (external process variables) for a plasma processing system are gas flow rate, gas composition, pressure, electric power and frequency, substrate temperature, electrode configuration and reactor geometry. The external process variables regulate the internal process variables that actually govern the process. These internal process variables are the densities,
energies and fluxes of electrons, ions, radicals and neutrals produced in the discharge as a function of both position and time. Determining the relationships between the external and internal process variables and their effect on process characteristics is crucial and requires attention and investigation for the advancement of plasma aided manufacturing.

Figure 2.2: Reactive environment in plasma processing, which involves electron induced, chemical and surface reactions. The electric potential distribution is shown at the left. The electric potential at the sheath accelerates the ions towards the grounded electrode (substrate).

2.2 **Examples of Common Industrial/Commercial Plasma Discharges**

Many different types of plasma discharges exist that are widely used in the industry. Here only the most relevant and general are mentioned.
2.2.1 **Low Pressure Discharges**

2.2.1.1 **DC Glow Plasmas**

These are non-thermal plasmas that are generated by the application of DC electric field to the gap between two metal electrodes. Probably the most common plasma; this is the plasma generated within fluorescent light tubes. It is used in materials processing and manufacturing in parallel with CCPs to modify ion energies, in sputter sources like magnetrons, and for physical mechanism of surface modification. Low pressure glow discharges operating with a DC power source is one of the most studied non-equilibrium plasma discharges. It is simple in geometry and easy to generate, complex in structure and also has a describable voltage-current characteristics. Since a significant portion of this research work concentrated on modeling and simulating atmospheric pressure DC micro glow discharges, it is necessary to provide a brief description of the voltage-current characteristics and structure of DC glow discharges operating in low pressure. This would help to draw comparisons between the characteristics of the well studied low pressure DC glow and the novel atmospheric DC micro glow discharge.

2.2.1.1.1 **Voltage-Current (V-I) Characteristics**

Figure 2.3 is an illustrative plot of voltage versus current for a DC electric discharge in a gas. As voltage is initially applied naturally occurring free electrons provide some current (A-B in Figure 2.3). As the voltage is increased the electric field becomes sufficient for the electrons to gain energy and ionize some of the gas producing more electrons, but not yet producing a sufficient number to create a self sustained discharge (C-D). In a corona (D-E) a sharp electrode is used to locally increase the electric field and in the region near the sharp electrode the plasma density is higher and a glowing region is seen. The shape of C-D-E shown in Figure 2.3 is for a
negative corona configuration. In a parallel plate configuration the C-D-E will actually be a flat line with voltage at the level of E. The entire C-D-E region is called the Townsend regime. Low current non-thermal discharges are considered to operate in the Townsend regime.

![Voltage – current characteristics of a typical low pressure DC glow discharge](image)

Figure 2.3: Voltage – current characteristics of a typical low pressure DC glow discharge.

Eventually breakdown occurs (E-F) when the discharge becomes self sustaining. Sufficient electron emission from the cathode is one of the requirements for the development of self sustained plasmas. In typical glow discharges the electron emission occurs because of secondary electron emission due to ion bombardment at the cathode surface. After breakdown at low currents the DC ‘normal’ glow discharge plasma is observed (F-G). In the ‘normal’ glow regime the discharge voltage is constant and an increase in current causes an increase in the diameter of the discharge.

In the ‘normal’ glow regime if the current is increased and the size of the electrodes is limited the current density will increase and we have the ‘abnormal’ glow discharge (G-H). The
‘abnormal’ glow is initially low temperature, but as the current is increased it can transition to the high temperature arc discharge (H-J). The transition can occur by either 1) the cathode becomes overheated or thermionically emission greatly increases the current or 2) the gas temperature increases and the dominant mechanism of ionization changes from electron impact ionization to thermal ionization. The higher the density of the gas medium the lower current at which the transition to an arc occurs. If the size of the electrode is not limited glow to arc transition will also occur but the line G-H will be relatively flat.

2.2.1.1.2 Structure of a Normal Glow Discharge

Glow discharges (F-G in Figure 2.3) are suitable for most materials processing applications. Townsend regime discharges are too weak and arc discharges are too hot. Figure 2.4 shows the structure of a typical DC normal glow discharge. This structure is well established for low pressure DC glow discharge operation. The description of various structures starts at the cathode and proceeds toward the anode.

\[ \text{Figure 2.4: Structure of a DC glow discharge} \]

\[ \text{Aston Dark Space} \] – This is the thin region to the right of the cathode with a strong electric field. The electrons are accelerated through this space away from the cathode. The region appears dark because of the low density and/or energy of the electrons.
**Cathode Glow** – In this structure to the right of Aston dark space, the electrons are energetic enough to excite the neutral atoms they collide with. The cathode glow has a relatively high ion density. The length of the cathode glow depends on the type of gas and the pressure. The cathode glow sometimes clings to the cathode and masks the Aston dark space.

**Cathode (Crooks, Hittorf) dark space** – This is a relatively dark region to the right of the cathode glow that has moderate electric field, a positive space charge and a relatively high ion density.

**Negative Glow** – Negative glow is the region with the brightest intensity of the discharge. The negative glow has relatively low electric field, is long, compared to the cathode glow and is the most intense on the cathode side. Electrons carry almost the entire current in the negative glow region. Electrons that have been accelerated in the cathode region to high speeds produce ionization and avalanches, and slower electrons that have had inelastic collisions already produce electronic excitations. These slower electrons are responsible for the negative glow. As these electrons slow down, energy for excitation is no longer available and the Faraday dark space begins.

**Faraday dark space** – The electron energy is low in this region. The electron number density decreases by recombination and diffusion to the walls, the net space charge is very low, and the axial electric field is small.

**Positive Column** – This region is quasi-neutral and has small electric field. The electric field is just large enough to maintain a constant degree of ionization along the length of the positive column. As the length of the discharge tube is increased at constant pressure, the length of the cathode structures remains constant, and the positive column lengthens. The positive column is a
long, uniform glow, except when standing or moving striations are triggered spontaneously, or ionization waves are triggered by a disturbance. Incredibly long positive columns can be created as in the case of neon tubes.

**Anode glow** – It is slightly brighter than the positive column, and is not always present. This is the boundary of the anode sheath. The voltage drop and brightness depend on the electron boundary conditions. In general ions are repelled and electrons are attached to the anode by a slightly higher electric field.

**Anode dark space** – The space between the anode glow and the anode itself is the anode sheath. It has negative space charge due to electrons traveling from the positive column to the anode. There is a higher electric field than the positive column.

### 2.2.1.2 Capacitively Coupled Plasma (CCP)

Capacitively coupled plasma (CCP) discharges are similar to glow discharge plasmas, but instead of a DC or low frequency electric fields they are generated with high frequency RF electric fields, typically 13.56 MHz. At these high frequencies the discharges operate continuously but in an alpha (α) mode (volume dominated). These differ from glow discharges in that the sheaths and power densities are much less intense. These are widely used in micro-fabrication and integrated circuit (IC) manufacturing industries for plasma etching and plasma enhanced chemical vapor deposition.

### 2.2.1.3 Inductively Coupled Plasma (ICP)

Inductively coupled plasma (ICP) discharge is similar to a CCP and has similar applications but the electrode consists of a coil wrapped around the discharge volume which inductively excites the plasma. ICP is widely used in conjunction with CCP in IC manufacturing
to intensify the plasma discharge. One of the main reasons for having an ICP is that it circumvents some of the disadvantages of CCP which include low ion density and low ion energy.

2.2.1.4 Wave Heated Plasma

They are similar to CCP and ICP in that it is typically RF (or microwave), but is heated by both electrostatic and electromagnetic means. Examples are helicon discharge, electron cyclotron resonance (ECR), and ion cyclotron resonance (ICR).

2.2.2 Atmospheric Pressure Discharges

2.2.2.1 Arc Discharges

Arc discharges are high power thermal discharges having very high gas temperature of \( \sim 10,000 \) K. The discharge is sustained by thermionic emission. It can be generated using a variety of power supplies. It is commonly used in metallurgical processes. For example it is used to melt rocks containing \( \text{Al}_2\text{O}_3 \) to produce aluminum \(^2\).

2.2.2.2 Corona Discharges

Corona discharge is a non-thermal discharge generated by the application of high voltage to sharp electrode tips. The sharp tip creates an electric field sufficient for breakdown only in the vicinity of the tip, the remaining region of discharge gap remain dark. Coronas are very weak discharges, having very low electron and ion density and are commonly used in ozone generators and particle precipitators \(^2\).
2.2.2.3 Dielectric Barrier Discharges (DBD)

Dielectric barrier discharge is non-thermal in nature and is generated by the application of high voltages across small gaps wherein a non-conducting coating prevents the transition of the plasma discharge into a self sustained glow or arc. Breakdown occurs in the form of streamers and charges build up on the electrodes during the discharge. A low frequency AC field $<100$ kHz is used to cycle the discharge and maintain it. They are widely used in the treatment of fabrics in roll to roll configuration. The application of the discharge to synthetic fabrics and plastics functionalizes the surface and allows for paints, glues and similar materials to adhere.

2.2.3 Novel Atmospheric Pressure Plasma Discharges

In addition to the traditional atmospheric pressure arcs, coronas and DBD’s several other configurations of atmospheric pressure plasma discharges have been developed. They have been found to possess non-thermal characteristics and have the potential for use in material processing.

2.2.3.1 Atmospheric Pressure Plasma Jet (APPJ)

The atmospheric pressure plasma jet (APPJ) is a type of RF CCP plasma discharge operated at atmospheric pressure. Like all atmospheric pressure discharges RF CCP is susceptible to instabilities such as the ionization overheating instability and alpha ($\alpha$) to gamma ($\gamma$) mode transition. In the APPJ the systems are stabilized by operation in helium or argon gases. The atomic noble gas operation makes it significantly easier to maintain the non-equilibrium system. Such systems can be stably operated in ‘normal’ and ‘abnormal’ modes in pure helium. However, only a very minor faction of precursor gases can be added. In SiO$_2$ deposition for example, typically only as much as 2% oxygen may be added and even less than $\sim 0.1\%$ of the
hexamethyldisiloxane (HMDSO) precursor may be added. The drawback of using helium is that it makes the operation very expensive. Even then APPJ was found to be successful in depositing thin films\textsuperscript{39} and has been commercialized\textsuperscript{40}.

### 2.2.3.2 Uniform DBD

Traditional DBD’s\textsuperscript{41} are typically seen as unsuitable for PECVD materials processing because of streamer formation. Streamers arise in DBDs because the avalanche formation is non-uniform and certain branches of the avalanches will become preferentially intensified. Eventually this leads to spatial non-uniformities in the discharge which also lead to spatial non-uniformities in deposited films. It has been observed that while operating with helium gas these non-uniformities do not occur. The precise reason for this is still unclear. However, like the APPJ, very high purity helium is required. There has been some success in depositing uniform thin films\textsuperscript{42}. Another opportunity to generate uniform DBD is to use pulsed rather than continuous wave excitation to apply the electric field sufficiently fast and with high over voltage to generate more uniform avalanches and thus prevent streamer formation\textsuperscript{43}.

### 2.2.3.3 Micro Plasmas

Micro plasmas are pressure scaled versions of the common low pressure discharges. The main idea of having micro plasma discharges at atmospheric pressure is based on the Paschen’s law (Figure 1.4). The high spatial resolution of micro discharges makes it a topic of high interest. Various designs of plasma sources have been proposed to generate stable micro plasma discharges. The reported electrode configurations include parallel plates\textsuperscript{18}, cylindrical type (e.g. hollow cathode\textsuperscript{19}), slot type\textsuperscript{20}, needle type\textsuperscript{21}, pin plate type\textsuperscript{22} etc. and the applied operation modes vary from direct current (DC) to radio frequency (RF) or microwave. These studies are
motivated by numerous potential applications of micro plasmas including sensors, integrated MEMS, excimer sources or micro reactors and PECVD\textsuperscript{21, 23, 44-47}.

2.3 **Role of Modeling in Plasma Processing**

Building and operating plasma reactors from the standpoint of diagnostics and design is expensive owing to their complexity and cost of operation. Also the shortening of product cycles (e.g. semiconductor manufacturing) implies that a good understanding of the physical and chemical processes that govern these plasmas is essential for efficient and fast product development. In this regard, modeling of these plasma reactors is a very useful tool to understand the processes and in identifying the key mechanisms and pathways, and can be especially useful when used in conjunction with experimental results. Plasma modeling can therefore play a significant role in the design and operation of plasma reactors used in manufacturing processes. In order to obtain information empirically necessary for optimizing the wide range of process parameters (e.g. pressure range 0.1 mTorr – 760 Torr, electron number density range $10^{15}$ m$^{-3}$ – $10^{20}$ m$^{-3}$) numerous costly experiments is required to be performed. However, once a validated predictive model is developed, it can be used to perform economically feasible parametric studies. In addition to being expensive, experimental measurements are also sometimes limited to discrete locations of the domain for a limited number of variables. Simulations can predict the temporal variations of all the different plasma variables at all spatial locations. A domain of particular interest can be investigated easily, including domains which are sometimes very difficult to access for experimental measurements. Modeling can also enable the study of ‘cause and effect’ between different physico-chemical processes, by investigating each of them separately. This can provide insight into the different plasma variables that can be controlled to obtain desired process output. The model can be used for different feed gases, including
hazardous gases that are difficult to handle in experiments. Modeling and simulations can also provide information about the transient variation of the plasma variables that are difficult to observe experimentally due to their very short time scales (in the order of nano seconds). For atmospheric pressure micro discharges mathematical modeling and simulations can play a major role in understanding the different interplaying physico-chemical processes and conduct optimization of the different process variables. The size and operating pressure of these discharges adds constraints to conduct successful experimental measurements of the basic plasma characteristics (gas temperature, electron density, electron temperature, electric field, etc). Predictive mathematical models for plasma discharges can reproduce all the plasma phenomena for a given design and operating conditions and can be used as a process tool to complement experimental measurements to aid the plasma manufacturing process.
3 Modeling Plasma Discharges: Literature Review

3.1 Introduction

Mathematical modeling and simulation of non-thermal plasma discharges consists of a self-consistent solution of conservation equations for charged and neutral species which must include transport and kinetics and Maxwell’s equation. For a DC and alternating current (AC) radio frequency (RF) powered CCP discharge the Maxwell’s equation reduces to the Poisson’s equation due to the absence of magnetic field. The discharge physics can be modeled by using either of the following:

- Fluid approach
- Particle-in-cell/Monte-Carlo collision approach
- Hybrid approach

The choice of approach depends on the operating regime of the discharge. The continuum fluid approach fails when the gradient of the macroscopic variables become so steep that the length scale is of the same order as the mean free path, \( \lambda \) (distance travelled by the particle between collisions) \(^{48}\). The variable that characterizes the transition from continuum to non-continuum limits is expressed by the Knudsen number, \( Kn = \frac{\lambda}{L} \), where \( \lambda \) is the mean free path and \( L \) is a characteristics dimensions. Based on Knudsen number the continuum approximation fails for \( Kn \geq 0.1 \) and a transition from continuum to non-continuum regime occurs. The significance of the transition limit can however be misleading if \( L \) is chosen to be some overall dimension of the reactor in order to define a single over all Knudsen number for the discharge. The limit can be specified more precisely if a local \( Kn \) is defined with \( L \) as the length scale of the
gradients of the macroscopic variable, such as electron density. In order to determine the local Knudsen number a local characteristics length scale is required, the local length scale for plasma discharges can be define as \( L = \frac{n_e}{\nabla n_e} \) where \( n_e \) is the local electron density. In a discharge, different charged and neutral species exist that lead to different types of collision processes, such as electron-neutral, neutral-neutral, electron-ion, ion-neutral etc. Out of these collision processes, the electron-neutral collision is the most important one for sustaining the discharge. Therefore, the mean free path for collisions should be selected as that for the electron-neutral collision process. The continuum model fails when the gradient of the macroscopic variables becomes so steep that the length scale of the variable is of the same order as the mean free path for collision. The calculation of a local Knudsen number provides a quantitative means to validate the continuum model. Particle-in-cell or Monte-Carlo collision models are suitable alternatives in regime where the continuum fluid models fail.

A brief description and detailed literature review of the three plasma discharge modeling approaches are discussed in this chapter. In addition literature review on modeling and simulation studies of atmospheric pressure micro discharges is also presented.

3.2 Fluid Approach

In models using the fluid approach, moments of the Boltzmann equation are coupled to the Poisson’s equation to calculate the density, drift velocity, and energy of the charged species and the self- consistent electric field. The models assume a continuum discharge; i.e., the mean free path for electron-neutral collision is small compared to the inter-electrode separation. Based on the number of moments used fluid models can be categorized as first, second and third moment approximation. In the single moment approximation, the continuity equations for the
charged species are solved together with the Poisson’s equation \(^{50-52}\). The drift-diffusion approximation is used instead of the momentum equations and the local field approximation is used instead of the electron energy balance. In the single moment approximation, one assumes that the electron, ion momentum and energy relax to the equilibrium state on a time scale much shorter than the period of the applied field. In the two moment approximation, an electron energy equation is added, removing the local field approximation \(^{53, 54}\). In the three moment approximation, momentum balance equations are added to the density and energy continuity equations \(^{55}\).

Graves and Jensen \(^{53}\) developed a continuum fluid model to simulate low pressure DC and RF discharges for a parallel plate electrode configuration. Their simulations indicated that in low pressure RF discharges, large electron conduction existed even in the quasi-neutral region. Graves \(^{54}\) also conducted simulations of low pressure RF argon discharge. Their predictions were found to reproduce many of the experimentally observed features of temporally and spatially resolved electron impact excitation. Boeuf \(^{52}\) developed a fluid model to numerically study the characteristics of a low pressure helium RF discharge. In his calculations the swarm parameters were calculated from the electric field using an equilibrium hypothesis. Meyyappan and Govindan \(^{56}\) conducted simulations of RF glow discharges in chlorine operating at the low pressure of 50 mTorr. In their model they included the local and convective acceleration terms in the momentum equations, instead of the drift-diffusion approximation. The gas phase discharge chemistry had a very limited four step reaction mechanism. The simulation results reproduced features observed experimentally in chlorine discharges under similar conditions. Park and Economou \(^{57}\) modeled RF glow discharges for both electropositive argon and electronegative chlorine gas. They also studied the effect of varying excitation frequency on the discharge
characteristics. The effect of metastable atoms in low pressure argon RF discharge was investigated by Lymberopoulos and Economou 58 using a one dimensional fluid model. Their study showed that the metastables played a major role in the discharge despite their very low concentrations. Step wise ionization from the metastables was found to be the main mechanism for electron production and thereby sustained the discharge. Bera et al. 59-64 developed a continuum based fluid model and conducted simulations for low pressure RF and ICP discharges. In their simulations of RF argon glow discharges 60 they solved for the electron, combined positive ion continuity equations, electron energy conservation and Poisson’s equation. A Maxwellian electron energy distribution function (EEDF) was assumed and no gas phase chemistry was taken into account. There simulations were found to be in reasonable agreement with experimental measurements. Simulations of low pressure ICP methane plasmas by Bera et al. 63 using a fluid model included simplified gas and surface chemistry to predict deposition/etching phenomena. They assumed a Durvesteynian EEDF and used swarm data for transport properties and reaction rate coefficients. Passchier and Goedheer 65 also performed two dimensional simulation of low pressure argon glow discharge using a fluid model. They conducted their simulations for a cylindrical discharge chamber. In the model, the self induced dc bias was calculated iteratively. An asymmetric axial ion density profile peaked toward the smaller, powered electrode. The electron energy in the pre-sheath region in front of the powered electrode was several electron volts higher than that in the bulk plasma. Boeuf and Pitchford 66 presented simulation results of an argon discharge in the RF Gaseous Electronic Conference reference cell. The electron and ion current densities on the powered electrode were observed to increase radially. A two dimensional fluid model for a low pressure silane-hydrogen plasma was
developed by Nienhuis and Goedheer\textsuperscript{67}. The model contained both gas and surface chemistry to predict the growth of silicon deposition.

Over the past ten years there has been exponential increase of the computing powers of computers. As a result more complex and detailed mathematical modeling and simulations of plasma discharges using fluid models have been reported in the literature. Arslanbekov\textsuperscript{68} developed a continuum based model to simulate the cathode region of a moderate pressure DC glow discharge. The model also included a neutral gas energy equation and the effect of gas temperature on the plasma characteristics was also investigated. For high current density, the simulation results showed that the power deposition profiles were strongly non-local and the assumption of Joule (local) heating to be inappropriate. Herrebout et al.\textsuperscript{69} conducted one dimensional simulations of low pressure methane-hydrogen RF discharge using a fluid model. Their model contained very detailed gas phase chemical kinetics (20 species) which also included vibrational excitation reactions. The predicted plasma characteristics were in favorable agreement with experimental measurements. The effect of operating pressure on the discharge characteristics was also studied. Herrebout et al.\textsuperscript{70} also extended their model to two-dimensional axisymmetric geometry and conducted comparison between one and two dimensional simulation results. The axial profiles of the species density obtained from the two dimensional simulations were in good agreement with the one-dimensional results. However the two-dimensional simulations indicated non uniform distribution of the species along the radial distance. Herrebout et al.\textsuperscript{71} also developed a one dimensional fluid model to simulate low pressure RF glow discharge in acetylene. Bleecker et al.\textsuperscript{72} developed a one dimensional fluid model to study capacitively coupled RF discharges operating at 0.45 Torr with silane/helium as the feed gas. Detailed gas phase chemistry was taken into account which included forty eight different species.
and a hundred and three step reaction steps. The effect of small concentrations of oxygen and nitrogen on the discharge characteristics was also studied. Their simulations indicated that small amount of oxygen and nitrogen drastically changed the plasma chemistry.

Simulation of atmospheric pressure non-thermal plasma discharges using a fluid model was also conducted by several researchers. Yuan and Raja\textsuperscript{73} reported the development of a fluid model to study atmospheric helium RF discharges. The structure of the discharge was investigated using a one dimensional fluid model and a Maxwellian EEDF. The effect of trace amount of nitrogen levels on the discharge was also studied. Their simulations showed that at atmospheric pressure the dimer helium ions dominated, however the main ionization pathway was dimer nitrogen ions due to their lower ionization potential. Their predicted voltage-current characteristics were in good agreement with experimental measurement. Shi and Kong\textsuperscript{74} employed a one dimensional fluid model to study the different operation modes of atmospheric pressure RF glow discharge. In their study special attention was given to investigate the effect of secondary electron emission coefficient and gas phase chemistry on the transition. The evolution of sheath dynamics in atmospheric pressure helium RF glow discharges over a wide range of current density was also investigated by Shi and Kong\textsuperscript{75} using a one dimensional fluid model. Shi and Kong\textsuperscript{76} also reported a fluid modeling study in expanding the stability range of RF powered atmospheric pressure glow discharges. Their simulations demonstrated that high frequency operation substantially expands the stability range of the discharge. Simulation of atmospheric pressure helium dielectric barrier glow discharge was conducted by Zhu and Kong\textsuperscript{77}. They compared results obtained from a fluid and hybrid model and showed that the level of gas ionization and discharge current is under predicted by the fluid model.
One of the major disadvantages of fluid models is that they do not resolve the electron energy distribution function (EEDF) and assumptions must be made about the distribution function e.g. Maxwellian, Durvesteynian, which directly influences the non-equilibrium nature and misrepresents the high energy electrons at the tail of the distribution function. The relationship of electron transport parameters, electron induced reaction rate coefficients to known quantities such as reduced electric field or mean electron energy has to be assumed. Therefore care must be exercised in calculating the electron transport properties and the electron induced reaction rate coefficients in the space and time varying field 78. Despite their limitations fluid models are still popular as they are computationally efficient. They execute quite rapidly and can predict collective plasma characteristics quite well.

3.3 Particle-in-Cell/Monte-Carlo Collision Models

Particle-in-cell (PIC) and Monte Carlo collision (MCC) are kinetic models which employ Monte-Carlo techniques for resolving the governing equations. These models are applicable in the high Knudsen number regimes where the mean free path for an electron-neutral collision is comparable with the characteristics dimension of the discharge. Both PIC and MCC models are capable of fully resolving the EEDF and the ion energy distribution function (IEDF) spatially and temporally. Non-equilibrium aspects of electron energy and ion energy distributions can be well represented, and the collective effect can be well resolved. Earlier Monte Carlo studies used an assumed electric field 79. Later, PIC methods 80, 81 coupled with Monte Carlo techniques considered the Poisson’s equation for the electrostatic field instead of assuming an electric field, to arrive at a self-consistent description of the discharge.
Kushner \textsuperscript{82} developed a MCC model to study the mechanism of power deposition by electrons and the spatial dependence of electron-impact excitation rates in low pressure capacitively coupled RF discharges. The simulations were conducted for mixtures of argon and silane, since it is the common feed gas used for the plasma deposition of amorphous silicon. In the model spatially dependent Monte Carlo techniques were used to compute electron trajectories and collision probabilities while oscillating the applied potential at RF frequencies. After oscillating the applied field for many RF cycles to reach steady state conditions, the location, RF phase, and energy of the simulated particles were periodically recorded and summed to obtain the EEDF. The time averaged spatially dependent EEDF was obtained by performing integration over many RF cycles. The development of PIC simulations using Monte Carlo methods was presented by Birdsall in his 1991 paper \textsuperscript{80}. He has also written a comprehensive text book on PIC modeling titled “Plasma Physics via Computer Simulations” \textsuperscript{83}. In the self consistent PIC simulations \textsuperscript{80} the charge density at a grid point is found from the particle positions, the Poisson’s equation for the electric potential is solved in finite difference form, and then the particle forces are interpolated from the grid. The velocity and hence new positions of the particles are calculated using these forces. In the simulations, the collisional effects are considered using the Monte Carlo method. Trombley et al. \textsuperscript{84} reported a self-consistent PIC model of argon RF glow discharge for a parallel plate electrode configuration. The model showed that significant energy can be gained by the ions in the sheath region. Surendra and Graves \textsuperscript{81} reported PIC simulations to study the structure of low pressure RF glow discharges in helium between parallel plate electrodes. The difference between discharges in which secondary electrons play a key role in sustaining the discharge and those in which secondary electrons are unimportant were examined. The electron energy distribution predicted by the model was found to be highly non-Maxwellian.
Nagayama et al. 85 performed PIC Monte Carlo simulation of one dimensional capacitively coupled RF glow discharges for low pressure argon plasmas. The mathematical model employed for simulations included motions and collisions of both the neutral and charged species. The computational efforts were optimized by using different time steps for the neutral and charged species. Larger time steps compared to those for the charged species were used for the neutral species. Nagayama et al. 86 also presented PIC Monte Carlo simulations of capacitively coupled low pressure RF methane discharge. Their calculations showed that the neutral radicals were the major deposition species. Ivanov et al. 87 proposed a one dimensional particle-in-cell Monte Carlo model to simulate low pressure RF methane–hydrogen discharge. In their model, the electron behavior was kinetically simulated by solving Newton’s equations, treating the electron collisions with the Monte Carlo algorithm, and the behaviour of the ions and radicals was treated using a set of continuity equations. The study included the comparison between the fluid and the particle-in-cell model. Iza et al. 88 studied the mechanism of striation formation in plasma display panels using a PIC Monte Carlo model. There simulation identified that the combined effect of surface charge accumulation on the anode dielectric and non local electron kinetics was responsible for the observed striations in the discharges. Georgieva and Bogaerts 89 presented simulation results of plasma characterization of an argon-carbon tetra fluoride – nitrogen discharge in an asymmetric dual frequency reactor. They used a one dimensional PIC Monte Carlo for their study.

Kinetic models like PIC/MCC models can resolve the spatio-temporal variations of the particle distribution functions. They provide the most detailed information on the properties of the electrons, ions and atoms, however they have the disadvantage of having long computation time especially at high pressure (high collision frequency) and/or when many particle reactions
are taken into account. Fluid models are more robust and computationally efficient. The use of a kinetic model is justified only for large Knudsen number flows, where the continuum assumptions are not sufficient accurate.

3.4 Hybrid Models

The terminology hybrid model is used to designate models that treat one part of the problem using kinetic models but treat the other parts using fluid models. These models take advantages of both the models; the accuracy of kinetic models and robustness and computational efficiency of the fluid models. Over the past few years, different approaches were taken to obtain hybrid models for example models where one part was modeled using either Monte Carlo, multi-dimensional Boltzmann equation, or beam techniques, but other parts are modeled using continuum fluid approach. Schoenbach et al. described a one dimensional hybrid approach to simulate the cathode fall in DC abnormal glow discharges. In the model the electron kinetics was simulated using Monte Carlo techniques and fluid model together with Poisson’s equation was used to calculate the species distribution and electric field. The model was used to simulate a glow discharge in 80% helium and 20% sulfur hexa fluoride at a pressure of 8 Torr with a current density of 1 A cm\(^{-2}\). The predicted discharge voltage compared favorably with experimental measurements. Sommerer and Kushner developed a hybrid model for low pressure RF discharges. The model combined electron Monte Carlo simulations (EMCS) for the temporally and spatially varying EEDF with a self consistent fluid model (SCFM) for species densities and electric field. Electron induced reaction rates and transport coefficients were obtained from the EMCS as a function of space and time. These values are then used in the neutral chemistry/transport model (NCTM) to predict neutral species densities. Collision rates from both the EMCS and NCTM are then used to generate temporally and spatially dependent
source and sink functions for charged species. The source, sink terms and transport coefficients are used in SCFM to obtain charge density and electric field distribution. Simulation results indicated that the model was capable of accurately describing the non-equilibrium charge particle transport and plasma chemistry while executing fast enough for multi species simulations. Surendra et al. \(^9\) developed a hybrid approach to self-consistently simulate DC glow discharges in hydrogen feed gas. In the model the electrons were divided into two groups: fast electrons that originate as secondary electrons at the cathode surface and reside in the cathode sheath, and slow electrons that reside in the quasi-neutral region of the discharge. A Monte Carlo simulation was used to describe the fast energetic electrons, while the electrons and ions in the low field region of the discharge were modeled as fluid. The Poisson’s equation was solved for the self consistent electric potential. Simulation results for pure hydrogen discharges operating at 20 – 30 Torr, 1000 K and 100 – 200 A m\(^{-2}\) were in reasonable agreement with optical emission and Langmuir probe measurements.

Kolobov \(^93, 97\) developed a hybrid model where the kinetic modeling of the electrons are performed by solving the Boltzmann equation using the two-term spherical harmonics expansion. In the model, the number density of the electrons are obtained by solving a continuity equation, whereas the electron transport coefficient (mobility and diffusion coefficient) and electron induced reaction rates are found from the solution of the Boltzmann equation. Fluid models are used to describe the neutral and ionic species and the Poisson’s equation is solved to obtain the electric field. In this hybrid approach the fluid model provides the electron and ion densities, the electron mean energy and local electric field. These quantities are then used for the solution of the Boltzmann equation to obtain the EEDF. From the EEDF, electron induced reaction rates and electron transport coefficients are obtained. The transport coefficients and
reactions rates are fed into the electron continuity equation to calculate the electron density. The reaction rates are also fed into the chemical kinetic model to determine the source and sink terms of different ionic and neutral species that are required for calculating the ionic and neutral species density. These species densities, in turn are utilized in solving the Boltzmann equation. Arslanbekov and Kolobov utilised a similar model to simulate low pressure DC argon glow discharge together with an external circuit model. They conducted two dimensional simulations for a parallel plate electrode configuration operating at 3 Torr and were able to duplicate experimentally observed voltage current characteristics ranging from Townsend to ‘abnormal’ glow mode. A similar one dimensional hybrid model was also developed by Capriati et al. 98.

Surendra et al. proposed a hybrid model where fast energetic electrons in the cathode sheath region are treated using single-beam and multi-beam method. Ions and slow electrons in the bulk of the plasma are modeled using the fluid based continuity equations and the self consistent electric field is determined by solving these equations together with the Poisson’s equations. The production rates for ions and slow electrons are obtained from the fast electron models. The model was used to simulate low pressure DC glow discharges. The simulation results indicated that single beam model, while producing apparently correct results, displays some discrepancies when compared to the higher order multi beam approach. Kolobov and Tsendin also proposed a similar hybrid model where fast electrons were treated using the beam method.

3.5 Literature Review on Atmospheric Pressure Micro Plasma Modeling

At the inception of this study, very few attempts on modeling of atmospheric pressure micro plasma discharges were found in the literature. During the process of completing this
work more studies on mathematical modeling of atmospheric pressure micro plasma discharges had been reported \textsuperscript{101-105}. Even though growing interest in atmospheric pressure micro scale plasma discharges began as recently as the late 1990s \textsuperscript{19} modeling efforts only began in the early 2000s \textsuperscript{99, 100}. Kushner \textsuperscript{100} used a hybrid model to conduct two dimensional computational study of micro discharges operating in neon using a pyramidal cathode structure. The hybrid model consisted of a plasma hydrodynamics model and an electron MCC model for beam electrons. Simulations were conducted over pressure and device dimension range of 400 – 1000 Torr and 15 – 40 $\mu$m respectively. The model predictions showed that for a constant applied voltage, peak electron density increased with increasing pressure as the beam electrons were slowed in more confined regions. The study further demonstrated that micro discharges require higher applied voltages to operate at lower pressure, and so resemble discharges obeying Paschen’s curve for breakdown. Kushner \textsuperscript{99} also presented modeling of cylindrical, metal-dielectric-metal sandwich micro discharges in argon sustained by DC power. He used a hybrid model which included both plasma transport and gas dynamics. The effect of pressure, current and secondary electron emission coefficient on the discharge characteristics was also investigated. The study showed that micro discharges closely resemble negative glow discharges as they are sustained by and also sensitive to secondary electron emission from the cathode. The effect of pressure scaling identified that these discharges are density scaled version of its low pressure counter parts.

Micro plasma discharges operating in moderate pressure instead of atmospheric pressure was also modeled by researchers \textsuperscript{102, 106}. Kothnur and Raja \textsuperscript{106} employed a one dimensional, fluid model, assuming a Maxwellian EEDF to investigate the structure of DC micro discharges operating in helium. The simulations were conducted at the central axis of parallel plate electrode geometry having inter-electrode separation of 250 $\mu$m and operating pressure of 250
Torr. The simulations indicated that the micro discharges had comparable bulk plasma and cathode sheath region. Gas temperatures of the order of 1000 K were predicted, emphasizing the importance of gas heating phenomena in DC micro discharges. Deconinck et al. 102 presented fluid modeling results for discharge phenomena in a micro discharge plasma thruster device operating in argon gas and 100 Torr pressure. Strong coupling between plasma and gas dynamics was observed, resulting in a small fraction of ions escaping the device. As a consequence the thrust produced by the exiting ions was minimal.

Shi and Kong 107 proposed a one dimensional hybrid model to study the cathode fall characteristics in a meso scale DC atmospheric pressure glow discharge. The simulations were conducted for a parallel plate electrode configuration having inter-electrode separation of 4 mm, operating in helium feed gas, over a wide range of current density (Townsend – ‘abnormal’ glow regime). The predicted spatial profiles of the electric field, the electron current density, the mean electron energy and the electron and ion density were seen to exhibit distinct structures of glow discharges that have a highly non-equilibrium cathode fall region and a nearly neutral positive column. Numerical simulation of DC atmospheric pressure helium micro plasma was performed by Wang et al. 101 using a one dimensional fluid model. The model assumed a Maxwellian EEDF and included a resistive circuit model to restrict the discharge current. The micro discharge was found to resemble a macroscopic low pressure DC glow discharge in many respects. The simulation predicted the existence of electric field reversals in the negative glow under operating conditions that favor high electron diffusion flux emanating from the cathode sheath. Different mechanisms of gas heating were investigated and the simulations indicated that ion joule heating was responsible for the significantly high neutral gas temperature predictions.
Recently Hong et al. 105 conducted a detailed comparison between fluid and PIC/MCC modeling of high pressure micro plasma discharges. The simulations were conducted for helium discharges at 760 Torr and neon/xenon DBD discharges at 300 Torr with various driving currents (DC, pulsed DC and RF). It was found that the species density and electric field distribution was significantly under predicted by the fluid model only in the sheath region; in the bulk both the PIC/MCC and fluid model had similar predictions. The production of hydrogen in micro discharges sustained in argon/ammonia mixtures was computationally investigated by Arakoni et al. 103 using a two dimensional hybrid model. A detailed argon/ammonia gas phase chemistry was developed. Simulations were conducted for a cylindrical metal-dielectric-metal sandwich electrode configuration with operating pressure of 100 Torr. Modeling and scaling of micro discharges for use as micro thrusters was performed by Arakoni et al. 104. The problem geometry had a sandwich electrode configuration, operating pressure of 30 Torr and argon as the feed gas. A resistor connected to a constant voltage power supply was considered as the external circuit model. The external circuit was used to limit the discharge current. Results from the computational investigation showed that power deposition was typically concentrated near the cathode surface, leading to high power densities and high gas temperatures. The study further showed that micro discharges that were confined to the inside of the nozzle produced larger gas heating and larger thrusts ranging from 50 to 200 μN for power depositions of 0.25 – 2W.

3.6 Relevance and Significance of Present Research

Modeling of atmospheric pressure non-thermal micro plasma discharges poses unique challenges. While the atmospheric condition means high number densities, the micron-scale discharge reduces the size of the computational domain. The non-thermal nature of these micro discharges includes additional complexity of non-equilibrium characteristics which has to be
accurately accounted for. Our extensive literature survey indicated that at the inception of this project there were only two reported works on micro plasma discharge modeling; both of them by Kushner\textsuperscript{99, 100}. Even though during the completion of this project a number of papers on micro plasma discharge modeling has been published by other researchers none of them address the external circuit which is important for the discharge development and for conducting successful experiments. The role of external circuit has been found to be very crucial in maintaining the stability of atmospheric pressure micro plasma discharges in recent experimental studies\textsuperscript{23}.

In this work a multi dimensional hybrid model has been developed together with an external circuit model to simulate atmospheric pressure non-thermal micro plasma discharges. The hybrid model was found to be the most ideal, being computationally faster as well as having the capability to account for the non-equilibrium nature. In the model a Boltzmann equation solver for calculation of the EEDF was implemented. This provides an accurate calculation of the EEDF instead of making questionable EEDF assumptions. The mathematical model and simulations can play a major role in understanding the different interplaying physico-chemical processes and conduct optimization of the different process variables of atmospheric pressure micro plasma discharges. The size and operating pressure of these discharges adds constraints to conduct successful experimental measurements of the basic plasma characteristics (gas temperature, electron density, electron temperature, electric field etc). The developed model would be able to reproduce all the plasma phenomena for a given design and operating conditions and can be used as a process tool to complement experimental measurements to aid the plasma manufacturing process.
This mathematical model can therefore play a significant role in the design and operation of atmospheric pressure non-thermal micro plasma reactors. The model would be able to predict the temporal variations of all the different plasma variables irrespective of spatial locations and dimensions. In addition information about the transient variation of the plasma variables that are difficult to observe experimentally due to their very short time scales (in the order of nano seconds) can also be obtained. The study of ‘cause and effect’ between different physico-chemical processes, can be conducted using the model. This can provide insight into the different plasma variables that can be controlled to obtain desired process output. The model can be used for different feed gases, including hazardous gases that are difficult to handle in experiments. The hybrid model together with the external circuit model developed, can therefore act as a design and optimization tool for the development of novel atmospheric pressure non-thermal micro plasma discharge reactors with applications in different plasma processing and manufacturing.
4 Mathematical Model and Numerical Schemes

4.1 Introduction

In this chapter, the mathematical model to simulate atmospheric pressure non-thermal micro plasma discharge is presented. The model can be divided into five modules: plasma dynamics, fluid dynamics and neutral transport, gas phase chemical kinetics, surface chemistry and external circuit. We describe each of these modules separately and also discuss the numerical schemes employed for the solution of these coupled equations.

4.2 Mathematical Model

4.2.1 Plasma Dynamics Module

The plasma dynamics module couples the charged species (ions, electrons) transport, electric field and electron energy. The transport equations for the charged species:

Electron conservation is described by the electron density continuity equation with a drift–diffusion approximation for the electron flux:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (\mu_e n_e \phi - D_e \nabla n_e) = \dot{n}_e$$  \hspace{1cm} (4.1)

where, \(n_e\) is the electron number density, \(\mu_e\) is the electron mobility, \(D_e\) is the electron diffusion coefficient, \(\phi\) is the electrostatic potential and \(\dot{n}_e\) is the source of electrons produced or consumed due to ionization, recombination and other chemical reactions.

For the ionic species in the discharge, the conservation equation is given by:
\[
\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \tilde{u}) = -\nabla \cdot (D_i \nabla n_i + n_i q_i \mu_i \nabla \phi) + \dot{n}_i
\] (4.2)

where, \( n_i \) is the density of ionic species \( i \), \( \tilde{u} \) is the averaged species fluid velocity, \( D_i \) is the diffusion coefficient, \( q_i \) is the charge state and \( \mu_i \) is the mobility for the corresponding species. The source term \( \dot{n}_i \) represents the rate of change of \( n_i \) due to chemical kinetics. The ionic species transport has contribution from the advection flow velocity along with drift and diffusion.

In this model the electric potential \( \phi(t) \) is determined using the following modified implicit Poisson’s equation:

\[
\nabla \cdot [\epsilon e \mu_e n_e^{(t+\Delta t)} \Delta t] \nabla \phi^{(t+\Delta t)} = e \left[ \sum_{i=iions} q_i n_i^{(t+\Delta t)} - n_e^{(t)} \right] - e \Delta t [\nabla \cdot D_e \nabla n_e^{(t+\Delta t)} + \dot{n}_e] \] (4.3)

where, \( \epsilon \) is the electrical permittivity of the medium, \( q_i \) is the charge state, \( n_i \) is the ion density, \( \mu_e \) is the electron mobility, \( D_e \) is the electron diffusion coefficient, \( e \) is the elementary charge and \( \dot{n}_e \) is the source of electrons produced or consumed due to ionization, recombination and other chemical reactions. It is worth noting that for \( \Delta t \to 0 \) Equation (4.3) is reduced to the Poisson equation \( -\nabla \cdot \epsilon \nabla \phi = e \left( \sum_{i=iions} q_i n_i - n_e \right) \), and for \( \Delta t \to \infty \) it expresses the conservation of electrons described by Equation (4.1). The derivation of Equation (4.3) is shown in the Appendix. The modified implicit form of the Poisson’s equation is required so that the coupled equations can be solved implicitly. The time step taken in the charged species update requires that the fields do not reverse in a single time step. This is known as the dielectric relaxation time. It can be interpreted as the Courant limit on Poisson’s equation. If an explicit method is used to update the
charged species then the time step selection is limited by the dielectric relaxation time, \( \Delta t < \frac{\epsilon_0}{\sigma} \), which is the ratio of the permittivity of free space (\( \epsilon_0 \)) to the plasma conductivity (\( \sigma \)). The implicit formulation used in the present mathematical model allows for larger time steps.

In the model the electron energy conservation equation is expressed in the following form:

\[
\frac{3}{2} \frac{\partial}{\partial t} (n_e T_e) + \nabla \left( \frac{5}{2} T_e \Gamma_e - \frac{5}{2} n_e D_e \nabla T_e \right) = \dot{j}_e \dot{E} - n_e \sum_k n_k \eta_k - 2 n_e m_e m_{\text{neutral}} (T_e - kT_g) v_e \quad (4.4)
\]

where, \( T_e \) is the electron temperature, \( D_e \) electron diffusion coefficient, \( n_k \) is the heavy particle, \( \eta_k \) is the rate coefficient for energy loss for collisions of electrons with species \( k \), \( m_e \) and \( m_{\text{neutral}} \) are the mass of the electrons and neutral species respectively, \( T_g \) is the gas temperature and \( v_e \) is the electron momentum transfer collision frequency. The first term in the right hand side represents the energy gain due to electron joule heating and the second and third term represents the energy loss due to inelastic and elastic collisions, respectively.

### 4.2.2 Neutral Transport and Fluid Dynamics Module

The neutral transport and fluid dynamics was addressed in the model by solving neutral species conservation equations and a modified compressible form of the Navier-Stokes equation which had sources of momentum and energy due to the presence of electric fields and charged species. The Navier-Stokes equation was solved for the averaged species. The transport of the individual neutral species was addressed by taking into account the advection flow velocity
obtained from the Navier-Stokes equation along with the diffusion and sources/sinks due to chemical reaction between species.

In the model the conservation equation for the neutral species is given as:

\[
\frac{\partial n_k}{\partial t} = -\nabla \cdot (n_k \vec{u} + D_k \nabla n_k) + \dot{n}_k \tag{4.5}
\]

In the above equation \( n_k \) is the number density of the neutral species \( k \), \( \vec{u} \) is the averaged species fluid velocity, \( D_k \) is the diffusion coefficient. The term \( \dot{n}_k \) represents the rate of change of \( n_k \) due to chemical kinetics.

For solving the flow velocity and neutral gas temperature a coupled set of continuity, momentum and energy conservation equation was utilized for the averaged species.

For the averaged density, the continuity equation is written as:

\[
\frac{\partial n}{\partial t} + \nabla \cdot (n \vec{u}) = 0 \tag{4.6}
\]

where, \( n = \sum_m n_m \) \([m = \text{positive ions, excited species, radicals and neutrals}]\) is the total density of the fluid.

The momentum equation for the averaged \( \text{(positive ions, excited species, radicals and neutrals)} \) species can be written as:

\[
\frac{\partial n \vec{u}}{\partial t} + \nabla \cdot (n \vec{u} \vec{u}) = -\nabla p + \mu \nabla^2 \vec{u} + \frac{\mu}{3} \nabla (\nabla \cdot \vec{u}) + \sum_k n_k \vec{F}_k \tag{4.7}
\]
where, $p$ is the static pressure (calculated from equation of state), $\mu$ is the dynamic viscosity and $\vec{F}$ is the body force term acting on species $k$. For ions, it is the product of ion charge $q_i$ and the electrostatic field $\vec{E}$.

The energy conservation equation for the gas mixture is expressed as:

$$\frac{\partial (nh)}{\partial t} + \nabla \cdot (nh\vec{u}) = \frac{\partial p}{\partial t} - \nabla \cdot (-\kappa \nabla T + \sum_k h_k \vec{\Gamma}_k) + \dot{Q}_k + \sum_i j_i \cdot \vec{E} + (\tau \cdot \nabla \vec{u}) \quad (4.8)$$

where, $h$ is the enthalpy of the gas mixture, $\kappa$ is the thermal conductivity of the gas mixture, $h_k$ is the partial enthalpy of species $k$, $\dot{Q}_k$ is the rate of change of enthalpy due to chemical reactions and elastic collisions and $\vec{\Gamma}_k$ is the flux of species $k$. The last two terms in Equation (4.8) account for Joule heating due to acceleration of ions in the electrostatic field having current density $j_i$ and viscous heat dissipation respectively.

### 4.2.3 Gas Phase Kinetics Module

The gas phase kinetics module calculates the electron transport coefficients (mobility and diffusivity), electron induced reaction rates and also the source and sink terms required for the different species conservation equations. The transport coefficients (mobility $\mu_e$ and diffusivity $D_e$) and rates of the electron induced chemical reactions $\eta_i$, are calculated using the electron energy distribution function (EEDF) obtained as a solution of the Boltzmann equation using the two-term spherical harmonic expansion (SHE)\textsuperscript{108}. This approach results in a four dimensional (3D in space and 1D in energy) EEDF, $f_0$\textsuperscript{97}:

$$\frac{\partial f_0}{\partial t} + \nabla.D_f \nabla f_0 + \frac{1}{\nu \partial \epsilon} \left[ \nu \left[ D_e \frac{\partial f_0}{\partial \epsilon} + V_e f_0 \right] \right] = S_f \quad (4.9)$$
where $\varepsilon = \frac{1}{2} \mu u^2 - e\phi$ is the total electron energy, $\phi$ is the electrostatic potential, $D_r = \frac{u^2}{3\nu}$ is the electron diffusion coefficient in physical space, $\nu$ is the electron transport collision frequency, $D_e$ and $V_e$ are electron diffusion and convection coefficients along the energy axis caused by the quasi-elastic collisions and $S_f$ is the source term describing inelastic collisions. The EEDF, $f_0$ is normalized to the electron density, $n_e$:

$$n_e = \int_0^{\infty} f_0(\varepsilon)\sqrt{\varepsilon} d\varepsilon$$

(4.10)

In order to simplify the numerical efforts, we used the ‘local field approximation’ $^3, 97$. According to the ‘local field approximation’ all electron parameters can be considered to be functions of local electric fields. Based on this approximation, we calculate EEDF’s as functions of the reduced electric field $\frac{E}{N}$ (ratio of electric field to neutral density) and electron number density $n_e$. In this way we produced two-dimensional look-up tables for electron transport coefficients and reaction rates. The electron parameters (rate constants of electron induced reactions $\eta_i\left(n_e, \frac{E}{N}\right)$, electron mobility $\mu_e\left(n_e, \frac{E}{N}\right)$ and electron diffusion $D_e\left(n_e, \frac{E}{N}\right)$) are expressed as functions of the electron density $n_e$ and the local reduced electric field $\frac{E}{N}$. The value of $n_e$ is obtained from the electron density conservation equation and the value of the reduced electric field $\frac{E}{N}$ is obtained from the calculated electric field from the Poisson’s equation and the neutral density from the neutral density conservation equation.
The reaction rate, electron mobility and electron diffusion coefficient are obtained by integrating the EEDF and are expressed as:

\[
\eta_e = \int_{0}^{\infty} \sigma(\varepsilon) \sqrt{\varepsilon} f_0(\varepsilon) d\varepsilon \\
\mu_e = \frac{1}{n_e} \int_{0}^{\infty} D_r \sqrt{\varepsilon} \frac{\partial}{\partial \varepsilon} f_0(\varepsilon) d\varepsilon \\
D_e = \frac{1}{n_e} \int_{0}^{\infty} D_r \sqrt{\varepsilon} f_0(\varepsilon) d\varepsilon
\]

(4.11) (4.12) (4.13)

where, \( \sigma \) is the cross section, \( \varepsilon \) is the electron energy and \( f_0 \) is the electron energy distribution function. The cross section data as a function of electron energy for different electron induced reactions were obtained from the literature. The references are given in Chapters 5, 6, 7 and 10.

The gas phase chemistry contributes to source terms in charged species and neutral transport equations. Source terms from both electron impact reactions and heavy particle collisions are included. Rate coefficients for the electron impact reactions were obtained from the look-up tables. In most cases an Arrhenius type rate coefficient was used for the heavy particle reactions.

The electron temperature can be obtained by two different approaches (a) the local field approximation or (b) solving the average electron energy equation (Equation (4.4)). In the local field approximation (commonly used in high pressure discharge modeling \(^{93}\)) the local reduced electric field \( \left( \frac{E}{N} \right) \) is used to obtain the electron temperature using tabulated data precompiled by solving the Boltzmann equation over a range of \( \frac{E}{N} \), similar to electron induced reaction rates,
electron mobility and diffusion coefficient calculations. Based on the local field approximation the electron temperature is expressed as:

\[ T_e = \frac{2}{3} \int_0^\infty \varepsilon f_0(\varepsilon) d\varepsilon \]  

(4.14)

Solving the average energy equation, which is a more general hydrodynamic approximation derived by taking moments of the Boltzmann equation, allows for accounting of the electron energy fluxes (driven by spatial gradients and electron thermal conductivity) in the calculations of \( T_e \). Under certain conditions, such as large space charge electric fields non-equilibrium electron transport occurs \(^{109}\). In this case the electron temperature cannot be considered to be only function of local electric field. The electron energy conservation equation is required to be solved in such cases to take into consideration the ‘non-local’ effects such as electron thermal conductivity. The electron temperature \( (T_e) \) and the electron number density \( (n_e) \) are used to obtain the electron transport coefficients and the reaction rates to take into account the ‘non-local’ effects.

In our work we employed the local field approximation in all our DC micro plasma simulations. The electron energy equation was solved for the RF micro plasma simulations and the electron temperature and electron number density was used to obtain the reaction rates and electron transport properties. It was shown by Sakiyama and Graves \(^{110}\) that the local field approximation fails to predict corona-glow transition in atmospheric RF glow discharges specially at high power.
4.2.4 Surface Chemistry Module

The surface chemistry module addresses the surface reactions occurring on the surfaces (electrodes). The surface chemistry module plays a dual role. First of all it provides boundary conditions for the different ionic, radicals and neutral species. The plasma and neutral transport module uses a flux in – flux out algorithm on the surfaces. The fluxes incident on the surface are consumed with a specified probability or reaction rate coefficient and returning fluxes of reactants from the surface are also produced with specified probability or reaction rate coefficient. The surface chemistry model provides these reaction rates and probabilities. Secondly the surface chemistry module computes the rates of material addition and removal on the surface. The fluxes of reactants to surfaces supplied by the plasma and neutral transport and the surface reaction chemistry are the input for the surface chemistry model. A general form of the plasma-surface reaction can be expressed as:

\[
A_g + C_s \xrightarrow{k_i} B_g + D_s \quad (4.15)
\]

\[
A_g + E_s \xrightarrow{k_j} F_d \quad (4.16)
\]

where, the subscript \(g\), \(s\) and \(d\) denotes gas species, surface species and deposited species respectively, \(k_i\) and \(k_j\) are reaction rate coefficients for the \(i\)th and \(j\)th surface reactions.

The reaction rate for the \(i\)th reaction in between species \(A_g\) and \(C_s\) (Equation (4.15)) and on material \(m\), \(R_{im}\) is given as:

\[
R_{im} = k_i \Phi_{Am} \theta_{Cm} \quad (4.17)
\]
where, \( k_i \) is the reaction probability or reaction rate coefficient for the \( i \)th reaction, \( \Phi_{i,m}^J \) is the incident flux of plasma species \( A \) on material \( m \), and \( \theta_{cm} \) is the fractional occupancy of the surface species \( C_s \). The rates of evolution of the coverage of surface species are obtained from the following expression:

\[
\frac{d\theta_{cm}}{dt} = \frac{1}{T} R_{im}
\]  

(4.18)

where, \( T \) is the total surface site density and \( R_{im} \) is the surface reaction rate for the \( i \)th reaction.

The rates of evolution of the coverage of the surface species are obtained by summing the rates of reactions generating or consuming the species (e.g. adsorption, desorption, etching, sputtering) and are integrated in time. The total fractional consumption for an incident species used in the plasma and neutral transport module is then the sum of fractional losses by all reactions removing the species from the plasma and resulting in deposition on the surface. For an evolved gas species produced by an incident species \( A_g \) on a given material, the total fractional generation used in the plasma and neutral transport module is the summation of fractional generation by all reactions of reactant \( A_g \) which produces \( D_g \) on that material. The deposition and etch rate are obtained by summing over the rates of reactions depositing material on the surface or converting surface species into volatile products respectively.

4.2.5 External Circuit Model

An external circuit was included to consider the effect of the circuit elements on the plasma characteristics. The external circuit model consisted of a fixed voltage power supply connected to resistor, capacitors and inductors. A voltage is applied to the electrodes through the means of the external circuit, and depending on the current flowing through the electrode the
voltage is changed. The current flowing through the electrode is determined from the fluxes of the charged species on to the electrode surface. The circuit solver takes this current and recalculates the voltage at the electrodes and incorporates it as an updated boundary condition. The equation solved by the circuit solver for the boundary voltages (DC micro plasma Figure 5.2) is as follows:

\[ \frac{dV_d}{dt} + \frac{1}{C} \left( I_d - \frac{V_{pwr} - V_d}{R} \right) = 0 \]  

(4.19)

where, \( C \) is the capacitance in the circuit, \( R \) is the ballast resistance, \( V_{pwr} \) is the supply voltage, \( I_d \) is the discharge current and \( V_d \) is the voltage across the boundary; the discharge voltage.

### 4.3 Numerical Schemes

The numerical scheme for solving the governing equations is based on the finite volume approach. The finite volume technique was employed for discretizing the governing equations. Figure 4.1 shows a typical mesh used for the present study. Non-uniform structured grids were used that were denser towards the electrodes and also towards the center of the axis. The denser grids near the electrodes were necessary to accurately solve the sheath regions of the discharge. The convective-diffusive terms in the charged species conservation equation is discretized using the exponential scheme of Scharfetter and Gummel. For the convective-diffusive terms in the excited and neutral species conservation a second order upwind scheme is used. A second order upwind scheme is also used for the convective-diffusive terms in the averaged species momentum conservation and the neutral energy conservation equation. Detail of the Scharfetter Gummel exponential scheme is provided in the Appendix. The Poisson’s equation is solved using a central difference scheme. Implicit time marching scheme is used with time step size
equal to $10^{-10}$ second. The time marching calculations are continued until the variation of the variables is less than $10^{-4}$ of the value of the variable from the previous time step. The solutions are then considered to be steady.

The system of equations were solved using CFD-ACE$^+$ and the general purpose circuit simulator, SPICE was used to simulate the external circuit. The CFD-ACE$^+$ solver calculates the transport of the charged and neutral particles and electric field by solving the PDE’s. The solver calculates the currents at the electrodes for a given potential at the electrodes. Based on the currents the SPICE code recalculates the voltage at the electrodes by solving the ODE’s for the external circuit. For each time step, the overall solution is iterated until the convergence of

Figure 4.1: An example of a mesh used in the present study.
voltage/current is reached. The solution procedure is shown by means of a flow diagram in Figure 4.2.

Figure 4.2: Flow diagram for atmospheric pressure micro plasma discharge simulations.
5 ATMOSPHERIC PRESSURE DIRECT CURRENT MICRO GLOW DISCHARGE IN MONOATOMIC GAS (ARGON)\textsuperscript{1}

5.1 Introduction

High pressure micro plasma discharges (or micro discharges) have received considerable attention in recent years \textsuperscript{18-20, 22, 44, 115-118}. Such discharges are characterized by their small size (characteristic dimension < 1mm) and high gas pressure operation (100 Torr – 760 Torr). They are non-equilibrium discharges, with an electron temperature (tens of thousands of Kelvins) much higher than the gas temperature (<1000 K). Various designs of plasma sources to generate stable micro plasma discharges have been proposed. The reported electrode configurations include parallel plates \textsuperscript{18}, cylindrical type (e.g. hollow cathode \textsuperscript{19}), slot type \textsuperscript{20}, needle type \textsuperscript{21}, pin plate type \textsuperscript{22} etc, and the applied operation modes vary from direct current (DC) to radio frequency (RF) or microwave. Single micro plasma sources can be integrated into arrays or matrix structures \textsuperscript{116}. These studies are motivated by numerous potential applications of micro plasmas including sensors, integrated MEMS, excimer sources or micro reactors \textsuperscript{21, 44-47}.

The measurement of basic plasma characteristics, such as gas temperature, electron temperature, electron density, species concentration, electric field etc, is important for understanding discharge behavior, and for extending the range of parameter space while maintaining stable discharge operation. Although extensive investigations of micro discharge modes and voltage current (V-I) characteristics have been reported, direct plasma diagnostics of micro discharges are still limited \textsuperscript{24, 25}. The difficulties mostly arise from their small size and high

operating pressure. Detailed modeling of the micro discharges can provide insight into the interplaying physico-chemical processes and the basic plasma characteristics (gas temperature, electron temperature, electron density, species concentration, electric field etc) that would be difficult to obtain via measurements. This would provide better understanding of the regime of operation and would also provide guidelines for optimizing the operating parameters.

In this chapter, results from computational investigations of atmospheric pressure microglow discharge in argon gas using a hybrid model are discussed. The monoatomic argon gas was chosen due to its comparatively simpler chemical kinetics. The characteristic of the discharge was studied for different ballast resistance (i.e. different discharge current). The discharge was found to have the characteristics of a ‘normal’ glow discharge which has a flat voltage-current characteristics and where the discharge current increases with a constant ‘normal’ current density. Ion-joule heating was identified to be the dominant gas heating mechanism in monoatomic argon. The neutral gas temperature predictions indicate that the discharge forms a non-thermal, non-equilibrium plasma. Experimental studies were conducted to validate the numerical model. Predictions from the numerical model compare favorably with the experimental measurements.

5.2 Geometry and Reaction Mechanism

5.2.1 Schematic of the problem geometry

Figure 5.1 depicts the computational domain for the atmospheric pressure argon micro discharge simulation between a metal wire tip and a planar metal surface (pin-plate configuration) under atmospheric pressure conditions. Due to symmetry, only half of the geometry is simulated. The line a-f is the axis of symmetry. The boundary a-b-c depicts the
anode. The boundary e-f is the grounded substrate. The distance between the electrode and the metal plate H is set to 200 µm. The domain length L and height W are chosen to be 300 µm and 500 µm respectively. Zero gradient boundary conditions are applied along the boundary c-d-e. The electrodes are coupled to an external circuit. The external circuit contains a resistance $R$ and capacitance $C$ connected in series with the discharge (see Figure 5.2). The ballast resistance $R$ is necessary in order to limit the discharge current, and thus prevent the discharge from jumping to an ‘abnormal’ (high current) mode. The capacitance $C$ is present intrinsically due to the external cables, which is known as the parasitic capacitance. This results from the insulation of the electrical wires and the optical work bench. This capacitance is in parallel to the plasma discharge. The capacitance $C$ introduces a time delay between the applied voltage $V_{pw}$, and the discharge voltage $V_d$. When enough voltage is applied between the cathode and the anode, the plasma is self-sustained by electrons emitted from the cathode by ion impact with a secondary emission coefficient $\gamma$. In these simulations, the supply voltage $V_{pw}$, is fixed at 500 V, the ballast resistance is varied from 1000 kΩ to 25 kΩ and the capacitance $C$, is fixed at 1 pF. The total current at the electrode is calculated using the electron and the ion conduction current, as well as the displacement current.
5.2.2 Chemical Kinetics and Source Term Treatment

We identified the dominant reactions under the operating conditions of the micro discharge to obtain expressions for the source terms in the species (electrons, ions, electronically excited and neutrals) conservation equations. At atmospheric pressure, these include: ionization, excitation and de-excitation processes by electron impact, three-body and dissociative recombination, conversion of atomic ions into molecular ions and other processes\textsuperscript{119-122}. The list of processes considered in the rate balance equations is given in Table 5.1. The method used to
calculate the reaction rates for the kinetic processes listed here is also indicated in Table 5.1 as A (Arrhenius form) or E (EEDF solver) for each reaction respectively.

Table 5.1: Kinetic processes taken into account in the modeling.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Rate</th>
<th>Rate Coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Scattering</td>
<td>( \text{Ar} + \text{e} \rightarrow \text{Ar} + \text{e} )</td>
<td>E</td>
<td>( \eta_{\text{elastic}} )</td>
<td>123</td>
</tr>
<tr>
<td>Ionization 1</td>
<td>( \text{Ar} + \text{e} \rightarrow \text{Ar}^+ + 2\text{e} )</td>
<td>E</td>
<td>( \eta_{\text{ion},1} )</td>
<td>120</td>
</tr>
<tr>
<td>Ionization 2</td>
<td>( \text{Ar}^* + \text{e} \rightarrow \text{Ar}^+ + 2\text{e} )</td>
<td>E</td>
<td>( \eta_{\text{ion},2} )</td>
<td>120</td>
</tr>
<tr>
<td>Three-body recombination</td>
<td>( \text{Ar}^+ + 2\text{e} \rightarrow \text{Ar} + \text{e} )</td>
<td>E</td>
<td>( \eta_{\text{re}} )</td>
<td>119</td>
</tr>
<tr>
<td>Molecular ion conversion 1</td>
<td>( \text{Ar}^* + 2\text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar} )</td>
<td>A</td>
<td>( \eta_{\text{mol},1} )</td>
<td>120</td>
</tr>
<tr>
<td>Molecular ion conversion 2</td>
<td>( 2\text{Ar}^* \rightarrow \text{Ar}_2^+ + \text{e} )</td>
<td>A</td>
<td>( \eta_{\text{mol},2} )</td>
<td>124</td>
</tr>
<tr>
<td>Excitation</td>
<td>( \text{Ar} + \text{e} \rightarrow \text{Ar}^* + \text{e} )</td>
<td>E</td>
<td>( \eta_{\text{excit}} )</td>
<td>125</td>
</tr>
<tr>
<td>De-excitation</td>
<td>( \text{Ar}^* + \text{e} \rightarrow \text{Ar} + \text{e} )</td>
<td>E</td>
<td>( \eta_{\text{deexcit}} )</td>
<td>125</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>( \text{Ar}_2^+ + \text{e} \rightarrow \text{Ar}^* + \text{Ar} )</td>
<td>A</td>
<td>( \eta_{\text{diss}} )</td>
<td>124</td>
</tr>
</tbody>
</table>

A: reaction rate in Arrhenius form;
E: reaction rate dependent on EEDF (electron energy distribution function)

Source terms in the governing equations are determined based on chemical reaction rates in kinetic processes. The source terms for electrons, ions, electronically excited atoms and neutrals are expressed as follows:

\[
\dot{n}_e = \eta_{\text{ion},1} n_e n_{\text{Ar}} + \eta_{\text{ion},2} n_e n_{\text{Ar}^*} - \eta_{\text{re}} n_{\text{Ar}^*}^2 n_{\text{Ar}} - \eta_{\text{diss}} n_e n_{\text{Ar}_2^*} \tag{5.1}
\]

\[
\dot{n}_i = \eta_{\text{ion},1} n_e n_{\text{Ar}} + \eta_{\text{ion},2} n_e n_{\text{Ar}^*} + \eta_{\text{mol},2} n_{\text{Ar}^*}^2 - \eta_{\text{re}} n_{\text{Ar}^*}^2 n_{\text{Ar}} - \eta_{\text{mol},1} n_{\text{Ar}}^2 n_{\text{Ar}^*} \tag{5.2}
\]

\[
\dot{n}_i^{**} = \eta_{\text{mol},1} n_{\text{Ar}^*} n_{\text{Ar}}^2 + \eta_{\text{mol},2} n_{\text{Ar}^*}^2 - \eta_{\text{diss}} n_e n_{\text{Ar}_2^*} \tag{5.3}
\]

64
\[ \dot{n}_n^* = \eta_{\text{excit}} n_{Ar} n_e + \eta_{\text{diss}} n_e n_{Ar}^2 - \eta_{\text{deexcit}} n_e n_{Ar}^* - \eta_{\text{mol2}} n_{Ar}^2 \]  
(5.4)

\[ \dot{n}_n = \eta_{\text{deexcit}} n_e n_{Ar} + \eta_{\text{re}} n_{Ar}^* n_e^2 + \eta_{\text{diss}} n_{Ar} n_e - \eta_{\text{excit}} n_{Ar} n_e - \eta_{\text{ion}} n_e n_{Ar} - \eta_{\text{mol1}} n_{Ar}^* n_{Ar}^2 \]  
(5.5)

where, \(\eta_{\text{ion,1}}, \eta_{\text{ion,2}}, \eta_{\text{re}}, \eta_{\text{diss}}, \eta_{\text{mol,1}}, \eta_{\text{mol,2}}, \eta_{\text{excit}}\) and \(\eta_{\text{deexcit}}\) are the ionization, three body recombination, dissociative recombination, molecular ion conversion, excitation and de-excitation rate coefficients as listed in Table 5.1.

5.3 **Boundary Conditions**

The boundary conditions used for the different variables are discussed in this section.

*Electron*: Assuming no reflection, the electron flux normal to the electrodes is given by:

\[ \hat{\Gamma}_{e,n} = \frac{1}{4} n_e u_{th} - \gamma \sum_i q_i \hat{\Gamma}_{i,n} \]  
(5.6)

where, \(\gamma\) is the secondary electron emission coefficient and \(u_{th}\) is the electron thermal velocity.

The coefficient of secondary electron emission coefficient due to ion impact was only included for the cathode. At the far side boundary c-d and d-e a zero gradient boundary condition for the electron density is applied.

*Ions and electronically excited species*: Depending on the direction of the electric field at the electrode, the boundary conditions for the ions can be different. A general expression is given by introducing a parameter \(b\), which is set equal to unity if the electric field is directed towards the electrode, and zero otherwise. The boundary conditions for the ions at the cathode and the anode is given as follows:
\[ \bar{\Gamma}_i = \frac{1}{4} n_i \mu_{th,i} + b \mu_i \bar{E} n_i \]  \hspace{1cm} (5.7)

where, \( u_{th,i} \) is the thermal velocity of the ion. If the electric field is directed towards the electrode \((b = 1)\), the ion flux equals the ion thermal flux plus the ion drift flux. On the other hand if the electric field is directed away from the electrode \((b = 0)\), the ion flux equals the thermal flux.

Table 5.2: Surface reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ar}^+ \rightarrow \text{Ar} )</td>
</tr>
<tr>
<td>( \text{Ar}_2^+ \rightarrow \text{Ar}_2 )</td>
</tr>
<tr>
<td>( \text{Ar}^* \rightarrow \text{Ar} )</td>
</tr>
</tbody>
</table>

At the electrode surfaces the ions and the excited species are quenched to neutral ions due to surface reactions. The surface reactions considered in the model is listed in Table 5.2. The surface interaction at the electrodes is modeled by using the surface interaction coefficient \( \beta_j \), which specifies the probability with which species \( j \) will react at the surface. The coefficient \((1 − \beta_j)\) represents the fraction of the incident neutrals, which are reflected into the gas phase keeping initial identity. The flux of the species, which reacts at the surface of the electrodes are given as:

\[ \bar{\Gamma}_j = \beta_j n_{j,\text{surface}} \sqrt{\frac{k_B T_{\text{gas}}}{2\pi m_j}} \]  \hspace{1cm} (5.8)

For all the surface reactions the surface interaction coefficient was set to unity. A surface interaction coefficient of one indicates that all ions are quenched at the electrode surface. This assumption is reasonable for metal electrodes when the ions can easily recombine with the
electron on the surface of the metal. Zero gradient boundary condition for the far side boundary (c-d-e) is incorporated for the ions and the excited species.

**Fluid velocity:** No slip boundary conditions are set at the anode and the cathode. Zero gradient boundary condition is maintained at the far side boundary (c-d-e).

**Gas temperature:** All electrode boundaries are set to be isothermal walls at room temperature 300K and zero gradient boundary condition is maintained at the outer boundary (c-d-e) for solving the gas mixture temperature. The isothermal boundary (300 K) is an idealized condition which represents perfect heat transfer and could result in under prediction of the gas temperature.

### 5.4 Experimental Setup

Experimental studies were carried out to validate the numerical predictions. The experimental setup was similar to that used by Staack et al. A schematic diagram of the experimental setup is depicted in Figure 5.3. A DC power supply was connected in series to a ballast resistor, a shunt resistor and the discharge. Various values of the ballast resistor were used to study the ‘normal’ regime of the discharge. The shunt resistor was used to measure the discharge currents. The shunt resistor had a value of 450 Ω. The ballast resistor is used to stabilize the discharge current. The lower electrode is isolated from the ground and made from stainless steel. The upper electrode having a diameter of 500µm is also made from stainless steel. The upper electrode is connected to a micro positioning system having a resolution of ±10µm. This allowed adjustment of the gap width between the two electrodes. The entire configuration is inside a 2.54 cm x 2.54 cm x 5.08 cm discharge chamber, made of quartz. The reactor chamber was sealed with end caps and o-rings on top and bottom. The gas inlet and outlet were located at the top of the reactor chamber. A voltmeter was used to measure the voltage drop across the
shunt resistor. The discharge current is calculated from this voltage drop across the known value of the shunt resistor. The discharge voltage defined as the voltage between the two electrodes is calculated from \( V_d = V_{\text{pwr}} - I_d R \), where \( V_{\text{pwr}} \) is the power supply voltage, \( I_d \) is the measured discharge current and \( R \) is the resistance of the series resistors (ballast and shunt resistors).

![Figure 5.3: Schematic of the experimental setup.](image)

For visualization a 640 x 480 resolution DIGITAL color CCD camera WDAC-5700C was mounted on a microscope focused on the discharge. The microscope-camera setup provided a variable magnification allowing between a 2mm x 1.5mm and a 20mm x 15mm field of view. The corresponding minimum pixel size at maximum magnification was thus about 3μm. A PC was used to capture still images from the CCD camera digitally. For spectroscopic temperature measurement, an Acton Research SpectraPro 500i scanning monochromator was used. Light from the discharge was focused onto the entrance slit of the monochromator. Optical emission spectra (OES) of the discharge were taken in a range of 374-381 nm averaging emission from the
entire discharge. A Roper Scientific model 7430 CCD camera was mounted onto the exit slit to
digitally acquire the spectra at 0.01 nm resolutions.

5.5 Plasma Characteristics of Micro Glow Discharge in Monoatomic Argon

Simulations were carried out for atmospheric pressure argon discharges for six cases of
varying ballast resistance. The discharge geometry was the same for all the cases, having an
anode and cathode radius of 250 and 500 μm respectively and an inter-electrode gap width of
200 μm. The applied DC voltage $V_{pwr}$ is 500 V and the capacitance C, is 1 pF. By varying the
resistance $R$ in the load line ($V_d = V_{pwr} - I_d R$ for small C), the discharge current $I_d$, is changed
over a large range (three orders of magnitude). For varying the discharge current, the ballast
resistance had values of 1000 kΩ, 500kΩ, 250kΩ, 100kΩ, 50kΩ and 25kΩ. The operating
parameters for the cases studied are listed in Table 5.3.

Table 5.3: Operating parameters for the atmospheric pressure argon micro glow discharge
simulation studies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case 1 (Base case)</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
<th>Case 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ballast resistance ($R$)</td>
<td>500 kΩ</td>
<td>1000 kΩ</td>
<td>250 kΩ</td>
<td>100 kΩ</td>
<td>50 kΩ</td>
<td>25 kΩ</td>
</tr>
<tr>
<td>Capacitance ($C$)</td>
<td>1 pF</td>
<td>1 pF</td>
<td>1 pF</td>
<td>1 pF</td>
<td>1 pF</td>
<td>1 pF</td>
</tr>
<tr>
<td>Power supply voltage ($V_{pwr}$)</td>
<td>500 V</td>
<td>500 V</td>
<td>500 V</td>
<td>500 V</td>
<td>500 V</td>
<td>500 V</td>
</tr>
<tr>
<td>Inter-electrode separation ($d$)</td>
<td>200 μm</td>
<td>200 μm</td>
<td>200 μm</td>
<td>200 μm</td>
<td>200 μm</td>
<td>200 μm</td>
</tr>
<tr>
<td>Anode radius ($r_{anode}$)</td>
<td>250 μm</td>
<td>250 μm</td>
<td>250 μm</td>
<td>250 μm</td>
<td>250 μm</td>
<td>250 μm</td>
</tr>
</tbody>
</table>
| Secondary electron emission
  coefficient ($\gamma$)             | 0.1                | 0.1        | 0.1        | 0.1        | 0.1        | 0.1        |
The resulting voltage-current (V-I) characteristic resulting from the six cases is shown in Figure 5.4. The flat behavior of the V-I curve signifies the existence of the 'normal' glow-discharge region. In the 'normal' glow-discharge the voltage remains constant with increasing current. From the V-I characteristics it can be seen that the 'normal' glow regime starts for a discharge current greater than 0.5 mA. An onset to 'abnormal' discharge was observed for a discharge current of 10 mA. The V-I characteristics is similar to those observed for a low pressure DC discharge. Measurement data are also shown in Figure 5.4 (to be discussed in sub-section 5.5).

Figure 5.4: Voltage-current characteristics of the argon micro discharge at 760 Torr for all cases.
Figure 5.5: Ion current density profiles at the cathode for different discharge currents (0.25, 0.51, 1.02, 2.52, 5.08 and 9.9mA).

The radial profiles of the ion current density at the cathode are shown in Figure 5.5 for different discharge currents. The discharge extends laterally only across a limited region called the ‘normal’ cathode spot with a constant ‘normal’ current density. Increases of the total discharge current occur only by the growth of the cathode spot. Only when the current is so large that no additional free surface remains on the cathode does further current growth require a voltage increase. This higher voltage provides higher values of current density, resulting in the ‘abnormal’ glow-discharge. ‘Abnormal’ glow can be observed in both Figures 5.4 and 5.5. The contribution of electron current is small at the cathode and the ion current transports almost all the discharge current at the cathode. One can see that at low currents, the profile is Bessel like.
and that at larger currents the ‘normal’ current density \( j_n \) is established. In this ‘normal’ mode the discharge current increases at constant \( j_n \). The predicted ‘normal’ current density is found to be 1100 mA cm\(^{-2}\). It can be seen that once the entire cathode area has a uniform current density, the discharge voltage increases with increasing current and ‘normal’ current density does not exist anymore (see Figure 5.4 and 5.5). Voltage increase is required to provide higher values of current density for subsequent growth of the discharge current. The current density for the ‘abnormal’ glow is 1900 mA cm\(^{-2}\) which is larger by a factor of two than the ‘normal’ current density.

![Contour plots](image)

Figure 5.6: Contour plots of constant (a) \( \text{Ar}_2^+ \) density (maximum value \( 1.45 \times 10^{20} \text{ m}^{-3} \)) (b) electron density (maximum value \( 1.57 \times 10^{20} \text{ m}^{-3} \)) (c) \( \text{Ar}^* \) density (maximum value \( 1.02 \times 10^{21} \text{ m}^{-3} \)) and (d) electrostatic potential (maximum value 244.5V) for ‘normal’ discharge. Ballast resistance 500 k\( \Omega \), \( V_d = 245 \text{V} \) and \( I_d = 0.51 \text{mA} \) (Case 1).
Contour plots of constant $\text{Ar}_2^+$, $\text{Ar}^*$, electron density and electrostatic potential are shown in Figure 5.6(a) – 5.6(d) respectively for case 1. From the contours plots of $\text{Ar}_2^+$ and electron density it can be seen that both the $\text{Ar}_2^+$ and electrons have the maximum density near the cathode region. This indicates that there exists significant volumetric production of these species near the cathode of the discharge. The production of electrons by ionization is well balanced by the production of the molecular argon ions through molecular ion conversions. The plasma is found to be quasi-neutral throughout most of the discharge zone. It is known that $\text{Ar}^*$ is responsible for the brightness of the glow-discharge. According to the contour plots of $\text{Ar}^*$ we can see two regions of high intensity. This is more clear in Figure 5.7, where the number density of $\text{Ar}^*$ is plotted along the axial distance for zero radial distance for case 1. One can see two peaks for the $\text{Ar}^*$. The first and the second peaks denote the ‘negative glow’ and the ‘positive column’, which are the two most luminous regions of a glow-discharge. The region in between
the ‘negative glow’ and the ‘positive column’ is the ‘Faraday dark space’, which has less metastable argon species. These two peaks of \( \text{Ar}^* \) occurs in the regions of maximum electric field and maximum electron density. This indicates that there exists significant volumetric production of \( \text{Ar}^* \) in these regions. The meta-stable densities drop near the electrodes owing to surface quenching effect resulting from the surface reactions (Table 5.2). In Figure 5.6(d) the electrostatic potential is affected significantly by the space charge \( \lambda \), \( \lambda = e(n_i - n_e) \). The potential lines are constricted in the axial direction with the constriction happening near the cathode. Therefore most of the potential drop is observed to happen in the cathode. This denotes the ‘negative glow’ regime of the discharge. A plot of the electric potential and electric field along the axial distance is shown in Figure 5.8 (a) and (b). It can be seen in Figure 5.8 (a) that the maximum voltage drop of 240 V happens at the cathode. The maximum voltage drop starts 45 \( \mu \text{m} \) away from the cathode with the initiation of the sheath formation and decreases almost linearly to zero. Apart from the ‘negative glow’, a linear 5 V drop in the electrostatic potential occurs in the remainder of the discharge. According to the electric field distribution along the axial distance (Figure 5.8 (b)), there exists a high electric field in the cathode. This high electric field decreases almost linearly to a very low level at the cathode boundary of the ‘negative glow’. It can be seen that the electric field remains constant throughout the bulk of the plasma, with a slight increase near the anode. This slight increase of the electric field over the small region denotes the anode sheath of the discharge.
Figure 5.8: (a) Electric potential along the axial distance ($r = 0$). (b) Electric field along the axial distance ($r = 0$). Ballast resistance 500 kΩ, $V_d = 245$V $I_d = 0.51$mA (Case 1).

Figure 5.9 shows the distribution of the Ar$_2^+$ and Ar$^+$ density along the axial distance for case 1. The predicted density of Ar$_2^+$ is found to be one order of magnitude higher than that of...
Ar⁺. It is observed that at atmospheric pressure the diatomic ion is more dominant than the atomic ion in argon plasma. The combined ion (Ar₂⁺ + Ar⁺) density and electron density profiles along the gap width of the discharge are shown in Figure 5.10 for the same case. As for the bulk, the plasma was found to be neutral, other than the cathode and anode sheaths where the ion and electron number density are found to be high respectively. The cathode sheath was found to have a thickness of about 45 μm. Formation of the positively charged species is due to the fact that electrons are much faster than the ions. The fast electrons therefore leave the area near the walls. The positively charged sheaths result in the potential profile for the discharge zone as seen in Figure 5.8 earlier. Since the bulk of the plasma is quasi-neutral it is thereby also iso-potential (∅ \approx const). In Figure 5.10 a very small anode sheath is also observed due to the negative space charge. The anode sheath is found to have a thickness of about 14 μm.

Figure 5.9: Ar₂⁺ and Ar⁺ density along the axial distance (r = 0). Ballast resistance 500 kΩ, V_d = 245V I_d = 0.51mA (Case 1).
Figure 5.10: Electron and ion \((\text{Ar}_2^+ + \text{Ar}^+)\) density along the axial distance \((r = 0)\). Ballast resistance 500 kΩ, \(V_d = 245\text{V} \text{ I}_d = 0.51\text{mA} \) (Case 1).

Figures 5.11(a) –(d) and 5.12(a) –(d) show the contour plots of constant \(\text{Ar}_2^+\), \(\text{Ar}^*\), electron density and electrostatic potential for a ballast resistance of 100 kΩ (case 4) and 25 kΩ (case 6) respectively. These ballast resistances resulted in a discharge current of 2.52 mA and 9.9 mA. It is observed that with increasing discharge current the discharge starts to occupy more of the cathode area. Compared to the smaller discharge current of 0.51 mA (Figure 5.6) the discharge size is found to increase in the radial direction. The two high intensity levels of metastable argon are observed here as well. The electrostatic potential contours are constricted in the axial direction near the cathode corresponding to the positive space charge, \(\lambda\), \((\lambda = e(n_i-n_e))\). The constricted zone expands in the radial direction due to the larger size of the discharge. Finally for a discharge current of 9.9 mA (case 6) the discharge occupies the entire cathode area (Figure 5.12(a)-(d)), as also seen in the radial profiles of the ion current density at the cathode shown in
Figure 5.5. The discharge voltage begins to increase with current (see Figure 5.4), which corresponds to the ‘abnormal’ glow-discharge.

Figure 5.11: Contour plots of constant (a) $\text{Ar}_2^+$ density (maximum value $1.34 \times 10^{20} \text{ m}^{-3}$) (b) Electron density (maximum value $1.44 \times 10^{20} \text{ m}^{-3}$) (c) Ar$^+$ density (maximum value $9.8 \times 10^{20} \text{ m}^{-3}$) and (d) electrostatic potential (maximum value 246 V) for ‘normal’ discharge. Ballast resistance 100 kΩ, $V_d = 246 \text{V}$ and $I_d = 2.52 \text{mA}$ (Case 4).
Significant gas heating was observed due to joule heating. Figure 5.13 shows the temperature profile along the axial distance for various discharge currents (cases 1 – 6). It is observed that the peak temperature exists at the location of the peak electron and ion densities. Apart from 0.25 mA and 9.9 mA discharge current (case 2 and case 6) the peak temperature for the ‘normal’ glow regime is in the range of 550 K. This is 250 K above the ambient. Peak gas temperature and peak electron density as a function of discharge current are represented in Figure 5.14 for all cases studied. The peak gas temperature is found to remain fairly constant for a constant peak electron density. For the ‘normal’ glow regime the discharge has a more or less
constant peak electron density. Broadening of the discharge only happens in the radial direction with the peak intensity remaining the same for all the cases. With the onset of the ‘abnormal’ discharge the peak gas temperature is found to increase to 610 K, 60 K higher than the peak temperature of the ‘normal’ glow-discharge. For the ‘abnormal’ discharge the peak electron density is found to be higher by a factor of 1.5 than that of the ‘normal’ glow, resulting in higher joule heating.

Figure 5.13: Calculated gas temperature along the axial distance of the discharge (r = 0) for different discharge current (0.51, 0.25, 1.02, 2.52, 5.08 and 9.9mA) (Cases 1 – 6).
Figure 5.14: Maximum gas temperature and peak electron density as a function of discharge current (for all cases).

5.6 **Comparison with Experimental Measurements**

Experimental studies were conducted to validate the numerical model. A DC power supply of 500 V was used as the power source. The current was varied by changing the value of the ballast resistor. Following the computational studies (Table 5.3), the ballast resistor in the experiments were 1000 kΩ, 500 kΩ, 250 kΩ, 100 kΩ, 50 kΩ and 25 kΩ. The inter electrode gap spacing was held at 200 μm. The experimentally obtained discharge voltage versus discharge current plot can be seen Figure 5.4 together with the V-I characteristics obtained from the numerical simulations. Measurement error in the electrode spacing was ±10 μm due to the resolution of the micro positioner. Measurement errors in the discharge current were ±25 μA and errors in the discharge voltage were ±5 V. The error bars for the voltage are shown in the Figure, but are not clearly visible due to their small scale. A flat V-I characteristics was obtained which
is one of the key signatures of the ‘normal’ glow-discharge. In the experiments no onset to ‘abnormal’ glow-discharge was observed. The reason is because the cathode in the experiment was much larger than that in the numerical model. The difference in size of the cathode is responsible for the earlier onset of the ‘abnormal’ glow in the model. The discrepancy between the experimental and predicted V-I characteristics is possibly a result of the simple chemistry mechanism used in the model.

Figure 5.15: Current density in the ‘negative glow’ as a function of discharge current for an inter electrode gap spacing of 200μm (for Case 1, 3, 4, 5 and 6).

Gray scale images of the discharge were used to measure the ‘normal’ current density. The width of the ‘negative glow’ was defined at the widest point by the number of pixels over which the gray scale intensity was 50% of the maximum intensity in that region. The cross sectional area of the ‘negative glow’ was calculated assuming a cylindrical cross section. The current density was then calculated using the measured area and the discharge current. In these measurements we assume that the current corresponds to the region of emitted light and this
might result in over estimation of the current density. Figure 5.15 shows measured and predicted values of the current density in the ‘negative glow’ as a function of discharge currents for the cases considered. It can be seen in the Figure that the current density is nearly constant at a value of 2.5 A cm⁻². The error bar for current density is ±0.2 A cm⁻². An onset to ‘abnormal’ discharge is observed from the model predictions. This onset arises due to smaller size of the cathode during the simulations. In the simulations the cathode size was limited to 1000 μm, whereas in the experiments it was 2.54 cm. Due to smaller size of the cathode in the model, the entire cathode area is filled by the cathode spot at a smaller discharge current. This resulted in the earlier onset to the ‘abnormal’ glow-discharge which was not observed during the experiments at the same range of discharge current.

Figure 5.16: Measured optical emission spectra and curve fit using SPECAIR for 3.5 mA glow discharge in 770 Torr argon pressure with trace 0.01 % nitrogen, 200μm inter electrode gap spacing.
The measurement procedure similar to that reported by Staack et al.\(^{22}\) was followed to measure the gas temperature in the discharge. A trace of nitrogen was fed into the discharge since molecular spectra are needed to determine the rotational and vibrational temperatures of nitrogen. The rotational temperature of N\(_2\) and the translational temperature of Ar can be assumed equal because rotational-to-translational collisional relaxation is fast at atmospheric pressure. The vibrational temperature of N\(_2\), does not correspond to any energy mode of Ar but does indicate the non-equilibrium nature of the discharge. A detailed description of the significant spectral lines in a wavelength range of 200 – 450 nm was reported by Staack et al.\(^{22}\). Temperature measurements were performed for a discharge in argon with approximately 0.01% of nitrogen. Figure 5.16 is the measured optical emission spectra (OES) from the glow discharge in argon with trace amount of nitrogen present. The discharge conditions were argon with approximately 0.01% nitrogen at pressure of 770 Torr, a discharge current of 3.5 mA, and an inter-electrode distance of 200 \(\mu\)m. The bright lines between 374 and 381 nm are due to the \(N_2(C^3\Pi_u - B^3\Pi_g)\) (0-2) and \(N_2(C^3\Pi_u - B^3\Pi_g)\) (1-3) transitions at 375.4 nm and 380.4 nm respectively. The spectra in this range are sensitive to both \(T_{vib}\) and \(T_{rot}\). The Figure also depicts a spectra attained from SPECAIR\(^{126}\), a spectroscopic modeling code developed at Stanford University. SPECAIR code assumes a Boltzmann distribution with assumed value of rotational \(T_{rot}\) and vibrational \(T_{vib}\) temperatures. Using \(T_{rot}\) and \(T_{vib}\) as the fitting parameters a best fit between the modeled spectra and the experimental spectra was obtained by minimizing the root mean square error between the experimental and modeled spectra. At a discharge current of 3.5 mA with 200 \(\mu\)m inter-electrode spacing the discharge was measured to have a rotational and vibrational temperature of 538 K and 1614 K respectively. However these temperature measurements are spatially averaged and do not resolve any temperature variations in the
'negative glow' and the 'positive column'. These temperatures have been shown to correspond to the brightest, hottest, and largest region of the discharge, namely the 'negative glow'.

Temperature measurements for various discharge currents were conducted. The results are shown in Figure 5.17. Corresponding model predictions (cases 1, 3, 4 and 5) are also shown. The measurement error bar for temperature is ± 50K. In the 'normal' mode of the discharge the temperature was found to be fairly constant at approx. 500 K. The temperature measurements suggest the discharge to be operating as a non-thermal, non-equilibrium plasma. The measured and the predicted temperatures are found to compare favorably. However the measured temperature gives the value in the 'negative glow' whereas the simulations predict the spatial distribution of the temperature.
5.7 **Conclusions**

Plasma characteristics of a micro glow-discharge of atmospheric pressure argon have been computationally investigated using a hybrid model together with an external circuit. Experiments were also conducted to compare the numerical model predictions with measurements. The micro glow-discharge is quasi neutral in the bulk plasma region, except the sheaths that form near the electrodes. The cathode sheath region was found to be larger than that formed in the anode. The concentration of diatomic argon ion was observed to be one order of magnitude higher than that of the concentration of atomic ions. The model was able to predict the main features of a ‘normal’ discharge. These included (a) a flat voltage-current characteristics, (b) bright and dark regions corresponding to the ‘negative glow’, ‘Faraday dark space’ and ‘positive column’ and (c) ‘normal’ current density in the ‘negative glow’. The numerical results provided an insight into the physico-chemical processes in an argon micro glow-discharge operating at atmospheric pressure.

The model was able to predict the flat voltage-current characteristics of a ‘normal’ glow-discharge. An onset to the ‘abnormal’ glow-discharge was observed as well. The study further shows the development of the constant ‘normal’ current density at the cathode. Increase of the total discharge current occurred only by growth of the cathode spot through which the current flows. Radial increase of the species density was observed with increasing discharge current. Onset to the ‘abnormal’ glow-discharge occurred when the entire cathode area shows increased current density. The experimental results did not show a transition to the ‘abnormal’ glow due to the larger cathode area than that of the model. The predicted voltage-current characteristics and the ‘normal’ current density values were in fair agreement to the experimental trends. The
discrepancy could have resulted due to the simplified chemistry mechanism considered in the model.

Bright and dark regions in the discharge could be identified through the spatially resolved electronically excited argon (Ar*) density profiles. A peak neutral gas temperature of 550 K was predicted by the model for ‘normal’ glow discharges. The maximum temperature was observed to occur at the ‘negative glow’ region of the discharge, which is close to the cathode. The gas temperature was found to depend largely on the Joule heating. The peak neutral gas temperature was fairly constant at 550 K throughout the ‘normal’ regime of the discharge, which is 250 K above the ambient temperature. At the onset of the ‘abnormal’ glow a peak gas temperature of 610 K was predicted. Spectroscopic temperature measurements were in good agreement with the numerical predictions, thereby indicating the plasma to be a non-thermal, non-equilibrium plasma.
6 ATMOSPHERIC PRESSURE DIRECT CURRENT MICRO GLOW DISCHARGE IN DIATOMIC GAS (HYDROGEN)²

6.1 Introduction

Hydrogen plasmas have been widely used in the field of material treatments. Typically pure hydrogen plasmas are used in the microelectronics industries for surface cleaning ¹²⁷, ¹²⁸, passivation ¹²⁹ and etching of compound semiconductors ¹³⁰. The plasma sources that are commonly employed for these purposes are microwave electro cyclotron resonance (ECR) plasmas operating at pressures less than 10⁻² Torr ¹²⁸, ¹³⁰. Moderate pressure (1 – 100 Torr) hydrogen discharges are also of interest due to their application in many thin film deposition processes. Microwave generated hydrogen plasma discharges operating at moderate pressures have been successfully used for obtaining diamond or diamond like carbon (DLC) thin films ¹³¹, ¹³². All of these plasma sources require costly vacuum systems and also have low deposition/etching/reaction rates due to the low pressure operating condition. Moreover high maintenance cost of the systems results in increased manufacturing cost of the end products.

Very few experimental studies have been conducted on pure hydrogen plasma operating at high pressure ¹³³. Hydrogen being a diatomic molecule, atmospheric pressure makes the reaction kinetics complex due to the presence of different ionic and excited species (vibrational and electronic). Measurements of hydrogen atom concentration, charged species density and other plasma parameters are difficult and hard to obtain even for low pressure systems ¹³⁴. Atmospheric hydrogen plasma operating at the micron size adds more constraints further

hampering successful experimental measurements. Detailed modeling can provide insight into
the physico-chemical processes that are difficult to obtain via measurements. Several modeling
studies have been conducted for pure hydrogen plasmas \(^{91,134-138}\). Chen et al.\(^{134}\) developed a zero-
dimensional steady state model for low pressure microwave-generated hydrogen plasma. The
model included the solution of the Boltzmann equation for the electron energy distribution
function (EEDF) and solution of the species, energy and power conservation equations. The
model predicted an increase in the \(\text{H}_3^+\) ion density with an increase in pressure. A one
dimensional self-consistent particle-fluid hybrid model was proposed by Surendra et al. \(^{91}\) to
study the structure of a low pressure direct current hydrogen discharge. Monte Carlo simulation
was used to describe individual energetic electrons in the cathode sheath, while the electrons and
the ions in the low electric field region of the discharge were modeled as a fluid. Hassouni et al.
\(^{138}\) reports the development of a kinetic model to study the energy dissipation channels and the
parameters effecting dissociation and ionization kinetics in a moderate pressure \(\text{H}_2\) plasma. The
model included three groups of reactions which described the vibrational kinetics of \(\text{H}_2\), the
chemistry of \(\text{H}_2\) and \(\text{H}\) electronically excited states and ground state. All these models are
developed for low pressure systems. An extensive literature survey failed to provide any recent
modeling studies in the area of hydrogen discharges operating at atmospheric pressure.

In this chapter numerical characterization of atmospheric pressure hydrogen micro
plasma discharge using a hybrid model is presented. Low pressure plasma discharges have been
used frequently for the deposition of these DLC layers by utilizing PACVD with several kinds of
plasma sources \(^{139-141}\). These processes in general utilize methane as the carbon bearing feedstock
and dilute it with large amounts of hydrogen. Hence simulation of atmospheric pressure pure
hydrogen micro plasma discharge is the most valid primary step in order to pursue mathematical
model development and simulation of atmospheric pressure methane-hydrogen discharge for DLC deposition. A self consistent two dimensional hybrid model was utilized for the simulations and characterization of hydrogen micro plasma discharge at atmospheric pressure. The species considered were H, H₂, H⁺, H₂⁺, H₃⁺, H*(2p) H₂⁺*(C¹Π₂p), H₂v = 1 and the electrons. The electric field is obtained from the solution of the Poisson’s equation. Numerical simulations and experimental measurements indicated some of the key features of a ‘normal’ glow discharge: a flat voltage current characteristics and a constant cathode current density. Basic plasma properties such as electron number density, gas temperature, electric field and electron temperature were studied. The model predicted a constant current density of ~ 22 A cm⁻² in the ‘normal’ glow regime. The ‘normal’ current density was found to be a temperature scaled value of a low pressure ‘normal’ current density. The ion Joule heating and Frank Condon heating was found to be the dominant gas heating mechanism. Peak gas temperature of ~ 500K indicated the discharge to be a non-thermal non-equilibrium discharge. Predictions from the model compares favorably to the experimental measurements.

6.2 Geometry and Reaction Mechanism

6.2.1 Schematic of the Problem Geometry

Figure 6.1 depicts the computational domain for the simulation of an atmospheric pressure micro discharge in hydrogen for a pin plate electrode configuration (metal wire tip and a planar metal surface). The inter-electrode separation is 400 μm. A cathode radius of 500 μm was chosen so that zero-gradient boundary conditions could be applied along the boundary c-d-e. The electrodes are coupled to an external circuit. The external circuit contains a resistance R and a capacitance C connected in series and in parallel, respectively (Figure 6.2). The ballast
resistance $R$ is required in order to limit the discharge current, preventing the discharge from reaching an ‘abnormal’ (high current) mode. The capacitance $C$ represents the parasitic capacitance which is present in the experiments intrinsically due to the external cables. The parasitic capacitance $C$ introduces a time delay between the applied voltage $V_{pwr}$, and the discharge voltage $V_d$. When enough voltage is applied between the cathode and the anode, the plasma is self sustained by secondary electrons emitted from the cathode due to ion impact. In these simulations the supply voltage $V_{pwr}$, is 1200 V, because this is the breakdown voltage for hydrogen gas at atmospheric pressure. The ballast resistance is varied from 800 kΩ to 150 kΩ and the capacitance $C$, is 0.1 pF, which corresponds to the estimated value for the experimental setup. The total current at the electrode is calculated is the summation of electron conduction, ion conduction and the displacement current.

Figure 6.1: Schematic diagram of the computational domain (enclosed by the dotted line).
Figure 6.2: Resistive-capacitive (RC) circuit for the plasma discharge simulation. The numbers represent the nodes in the circuit. ‘0’ indicates grounded nodes. The supply voltage is between nodes ‘0’ and ‘1’.

### 6.2.2 Chemical Kinetics

The dominant reactions were identified under the operating conditions of the micro-discharge. The reactions were also selected so that all species had source and sink terms to bound the production rate. The reactions can be grouped into seven categories: 1) elastic collisions 2) dissociation 3) ionization 4) electron-ion collisions 5) ion-neutral collisions 6) neutral-neutral collisions and 7) excitation and de-excitation \(^{134, 138}\). The dissociation mechanism includes the dissociation of the ground state molecular hydrogen. The intermediate steps of the dissociation process involving different meta-stable species were not taken into account, since these meta-stable species are short lived and do not participate in further reactions. The excitation and de-excitation mechanisms included both electronic and vibrational excitation. Since for a diatomic molecule most of the electron energy goes into the vibrational excitation \(^2\) it is crucial to include vibrationally excited species in the chemical reaction scheme in order to obtain an accurate EEDF. In the model only the first levels of the electronic and vibrational excitations \((v = 1)\) are taken into account. This simplification is done in order to reduce the computational time. The
simplification is justified because these are the most populous excited species due to their lowest excitation energies. Table 6.1 summarizes the reactions introduced in the model. The method used to calculate the reaction rates for the kinetic processes listed here is also indicated in Table 6.1 as A (Arrhenius form) or E (calculated from cross-section data and EEDF) for each reaction, respectively. The references for the cross-section and reaction rate constant data are listed in Table 6.1 as well. The rate equations were constructed from the reactions in Table 6.1. The kinetic scheme adopted here neglects the formation of H⁻ ions following the dissociative attachment of molecular hydrogen \( [e + H_2 (v = 0 – 9) \rightarrow H + H^-] \). The reaction rate constant for the negative ion formation due to electron attachment to H₂ \( (e + H_2 \rightarrow H + H^-) \) is in the order of \( 10^{-21} \text{m}^3 \text{s}^{-1} \), which is 7 orders of magnitude less than electron impact ionization of H₂ (R4) and 6 orders of magnitude less than the dissociation of H₂ (R3). The reaction rate constants indicate the formation of negative hydrogen ions to be negligible. The formation of negative ions from the first level of vibrationally excited state was not taken into account due to the unavailability of cross-section data. Furthermore Kalache et al.\(^{143}\) reported in their work the effect of H⁻ ions to be negligible for a vibrational temperature < 3000 K. Similar results were also obtained by Salabas et al.\(^{144}\). The reaction rate for the multi-step ionization (R16) in the sheath region was found to be \( 0.25 \times 10^{-12} \text{m}^3 \text{s}^{-1} \). Reaction rates involving super-elastic collisions were neglected since our estimations indicated them to be two orders of magnitude smaller the multi-step ionization process. Super elastic collisions involving H₂* (\( ^1I\Pi_u 2p\pi \)) were neglected since they were found to be four orders of magnitude smaller than the inelastic collision processes. Hassouni et al.\(^{138}\) had also reported similar results. The simplified kinetic scheme adopted here also neglects the effect of radiative relaxation of the electronically excited species since at atmospheric pressure collisional relaxation is more dominant. Our estimations indicated
collisional relaxation rates to be larger by two orders of magnitude over the radiative relaxation rates.

Table 6.1: Kinetic processes taken into account in the modeling.

<table>
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<th>Process</th>
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<th>Reaction</th>
<th>Reaction Rate</th>
<th>Reference</th>
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<td>146</td>
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<td></td>
<td>R2</td>
<td>$e + H \rightarrow e + H$</td>
<td>E</td>
<td>146</td>
</tr>
<tr>
<td>Dissociation</td>
<td>R3</td>
<td>$e + H_2 \rightarrow 2H + e$</td>
<td>E</td>
<td>145</td>
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<td>145</td>
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<td>R5</td>
<td>$e + H \rightarrow H^+ + 2e$</td>
<td>E</td>
<td>147, 148</td>
</tr>
<tr>
<td></td>
<td>R6</td>
<td>$e + H_2 \rightarrow H^+ + H + 2e$</td>
<td>E</td>
<td>145</td>
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<tr>
<td>Electron-ion</td>
<td>R7</td>
<td>$e + H_3^+ \rightarrow 2H$</td>
<td>E</td>
<td>137</td>
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<tr>
<td></td>
<td>R8</td>
<td>$e + H_3^+ \rightarrow H_2 + H$</td>
<td>E</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>R9</td>
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<td>E</td>
<td>137</td>
</tr>
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<td>R10</td>
<td>$e + H^+ \rightarrow H$</td>
<td>A</td>
<td>144</td>
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<td>Excitation and</td>
<td>R15</td>
<td>$e + H \rightarrow e + H^*(2p)$</td>
<td>E</td>
<td>138</td>
</tr>
<tr>
<td>De-excitation</td>
<td>R16</td>
<td>$e + H^*(2p) \rightarrow H^+ + 2e$</td>
<td>E</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>R17</td>
<td>$H^*(2p) + H_2 \rightarrow H_3^+ + e$</td>
<td>A</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>R18</td>
<td>$e + H_2 \rightarrow H + H^*(2p) + e$</td>
<td>E</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>R19</td>
<td>$e + H_2 \rightarrow H_2^* (C^1\Pi_u 2p\pi) + e$</td>
<td>E</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>R20</td>
<td>$E + H_2^* (C^1\Pi_u 2p\pi) \rightarrow 2H^*(2p) + e$</td>
<td>E</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>R21</td>
<td>$E + H_2 \rightarrow H_2 v=1 + e$</td>
<td>E</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>R22</td>
<td>$H + H_2 v=1 \rightarrow H_2 + H$</td>
<td>A</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>R23</td>
<td>$H_2 + H_2 v=1 \rightarrow 2H_2$</td>
<td>A</td>
<td>154</td>
</tr>
</tbody>
</table>

A: reaction rate in Arrhenius form;
E: reaction rate dependent on EEDF (electron energy distribution function)
The electron transport coefficients (mobility $\mu_e$ and diffusion $D_e$) electron temperature ($T_e$) and rates of the electron induced reactions $\eta_i$, are calculated using the electron energy distribution function (EEDF) obtained as a solution of the Boltzmann equation using the two-term spherical harmonic expansion (SHE) $^{108}$. The local-field approximation $^{97,155}$ was employed for calculating the electron transport coefficients, electron temperature and electron induced reaction rates. In this approximation, EEDF’s are calculated as functions of the local reduced electric field $E/N$ and electron number density $n_e$, where $N$ is the neutral density. In this way we produced two-dimensional look-up tables for electron transport coefficients and reaction rates. With an inclusion of the reduced electric field as a function in the lookup table the effect of gas temperature to the electron transport coefficient and electron temperature is directly taken into account. In this calculations the electron parameters (rate constants of electron induced reactions $\eta_i(n_e, E/N)$, electron temperature $T_e(n_e, E/N)$, electron mobility $\mu_e(n_e, E/N)$ and electron diffusion $D_e(n_e, E/N)$) are expressed as functions of the electron density $n_e$ and local reduced electric field $E/N$. Instead of solving the electron energy balance equation explicitly, the electron temperature is obtained from the lookup tables as functions of electron number density $n_e$ and the reduced electric field $E/N$. The relationships obtained for the electron temperature ($T_e$) and the ionization rate constant ($\eta_{ionic}$) as functions of the local reduced electric field $E/N$ and electron number density $n_e$, are shown in Figure 6.3 (a) and 6.3 (b). It can be seen that for low values of $E/N$ the electron temperature does not have significant dependence on the electron number density. At low $E/N$ the electron temperature remains almost constant over the range of $n_e$. However with increasing $E/N$ the dependence on $n_e$ becomes significant. The electron temperature is observed to increase with an increase in $E/N$ over the entire $n_e$ range. The reduced electric field is found to have a stronger effect on the electron temperature. Similar dependence
of ionization rate constant on the reduced electric field and electron number density was also observed.

Figure 6.3: Look up table parameters for the simulations a) Electron temperature b) Ionization rate coefficient as a function of reduced electric field ($E/N$) and electron number density ($n_e$).
6.3 Boundary Conditions

The boundary conditions used for the different variables are discussed in this section.

**Electron:** Assuming no reflection, the electron flux normal to the electrodes is given by:

\[
\bar{\Gamma}_{e,n} = \frac{1}{4} n_e u_{th} - \gamma \sum q_i \bar{\Gamma}_{i,n}
\]

(6.1)

where, \( \gamma \) is the secondary electron emission coefficient and \( u_{th} \) is the electron thermal velocity.

The coefficient of secondary electron emission coefficient due to ion impact was only included for the cathode. The secondary electron emission coefficient used for the simulations are listed in Table 6.3. At the far side boundary c-d and d-e a zero gradient boundary condition for the electron density is applied.

**Ions, electronically and vibrationally excited species:** Depending on the direction of the electric field at the electrode, the boundary conditions for the ions can be different. A general expression is given by introducing a parameter \( b \), which is set equal to unity if the electric field is directed towards the electrode, and zero otherwise. The boundary conditions for the ions at the cathode and the anode are given as follows:

\[
\bar{\Gamma}_i = \frac{1}{4} n_i u_{th,i} + b \mu_i \bar{E} n_i
\]

(6.2)

where, \( u_{th,i} \) is the thermal velocity of the ion. If the electric field is directed towards the electrode \((b = 1)\), the ion flux equals the ion thermal flux plus the ion drift flux. On the other hand if the electric field is directed away from the electrode \((b = 0)\), the ion flux is only the thermal flux.
At the electrode surfaces the ions and the excited species are quenched to neutral ions due to surface reactions. The surface reactions considered in the model are listed in Table 6.2. The surface interaction at the electrodes is modeled by using the surface interaction coefficient $\beta_j$, which specifies the probability with which species $j$ will react at the surface. The coefficient $(1 - \beta_j)$ represents the fraction of the incident neutrals, which are reflected into the gas phase keeping initial identity. The flux of the species, which reacts at the surface of the electrodes is given as:

$$\vec{\Gamma}_j = \beta_j n_{j,\text{surface}} \sqrt{\frac{k_B T_{\text{gas}}}{2\pi m_j}}$$

(6.3)

For all the surface reactions the surface interaction coefficient was set to unity. A surface interaction coefficient of one indicates that all ions are quenched at the electrode surface. This assumption is reasonable for metal electrodes when the ions can easily recombine with the electron on the surface of the metal. Zero gradient boundary condition for the far side boundary (c-d-e) is incorporated for the ions and the excited species.

Table 6.2: Surface reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ \rightarrow H$</td>
</tr>
<tr>
<td>$H_2^+ \rightarrow H_2$</td>
</tr>
<tr>
<td>$H_3^+ \rightarrow H_2 + H$</td>
</tr>
<tr>
<td>$H^*(2p) \rightarrow H$</td>
</tr>
<tr>
<td>$H_2^*(C^1\Pi_u, 2p\pi) \rightarrow H_2$</td>
</tr>
<tr>
<td>$H_2 \nu=1 \rightarrow H_2$</td>
</tr>
</tbody>
</table>

Fluid velocity: No slip boundary conditions are set at the anode and the cathode. Zero gradient boundary condition is maintained at the far side boundary (c-d-e).
**Gas temperature:** All electrode boundaries are set to be isothermal walls with room temperature 300K and zero gradient boundary condition is maintained at the outer boundary (c-d-e) for solving the gas mixture temperature. The isothermal boundary (300 K) is an idealized condition which represents perfect heat transfer and could result in under prediction of the gas temperature.

### 6.4 Experimental Setup

![Experimental Setup Diagram](image)

**Figure 6.4:** Schematic diagram of the experimental setup.

Experimental studies were conducted to validate the numerical predictions. Figure 6.4 shows a schematic diagram of the experimental setup. The experimental setup is similar to that used by Staack et al. The discharge chamber is a 10 cm cube with two quartz windows to allow visualization and spectroscopic studies. The chamber is sealable and has gas inlets and outlets at the upper and lower side respectively. The sealing is required in order to conduct experiments with high purity gases. Since we were using hydrogen as the feed gas the sealing of the discharge chamber is crucial. Leakage of air into the system would result in an explosion. A thin wire electrode having a diameter of 500 μm was used as the anode. The end of the wire was
flat and the edges of the wire were rounded. The lower electrode was a 25 x 25 mm square plate having a thickness of 9.4 mm. The upper electrode was connected to a micro-positioning system having a resolution of ± 10 μm. This allowed adjustment of the gap width between the two electrodes. The circuit used to generate the glow discharge consisted of a DC power supply which was connected in series to a ballast resistor, a shunt resistor and the discharge. The ballast resistor acts to electrically stabilize the discharge current. Various values of the ballast resistor were used to study the ‘normal’ glow regime of the discharge. The ballast resistor was placed physically close to the discharge in order to reduce the stray capacitance of the circuit and to improve the stability of the discharge. The shunt resistor was connected to an oscilloscope and is used to measure DC and low frequency current. A Pearsons model 2877 current transformer probe (not shown) was connected inline to measure high frequency current oscillations up to 50 MHz. A BK-precision high impedance, 1000:1, high voltage (HV) probe connected (not shown) to an oscilloscope was used to measure the discharge voltage and voltage oscillations of up to 1 MHz. For visualization a 640 x 480 resolution DIGITAL color CCD camera WDAC-5700C was mounted on a microscope focused on the discharge. The microscope-camera setup provided a variable magnification allowing between a 2mm x 1.5mm and a 20mm x 15mm field of view. The corresponding minimum pixel size at maximum magnification was thus about 3μm. A PC was used to capture still images from the CCD camera digitally.

6.5 Plasma Characteristics of Hydrogen Micro Glow Discharges

Simulations were carried out for the atmospheric pressure hydrogen discharge for eleven cases (see Table 6.3). The cases were varied by changing the ballast resistance and also the secondary electron emission coefficient. The discharge geometry was the same for all the cases, having an anode and cathode radius of 250 μm and 500 μm, respectively and an inter-electrode
gap width of 400 µm. The DC supply voltage $V_{pwr}$ was 1200 V and the capacitance $C$ was 0.1 pF.

By varying the resistance $R$ in the load line ($V_d = V_{pwr} - I_d R$ for small $C$), the discharge current was changed. For varying the discharge current, the ballast resistance had values of 800 kΩ, 400 kΩ, 250 kΩ, 200 kΩ and 150 kΩ.

Table 6.3: Fixed and variable parameters for the atmospheric pressure hydrogen micro discharge simulations.

<table>
<thead>
<tr>
<th>Variable Parameter</th>
<th>Fixed Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ballast Resistance (R)</td>
<td>Secondary Electron Emission Coefficient ($\gamma$)</td>
</tr>
<tr>
<td>Case 1</td>
<td>400 kΩ</td>
</tr>
<tr>
<td>Case 2</td>
<td>800 kΩ</td>
</tr>
<tr>
<td>Case 3</td>
<td>250 kΩ</td>
</tr>
<tr>
<td>Case 4</td>
<td>200 kΩ</td>
</tr>
<tr>
<td>Case 5</td>
<td>150 kΩ</td>
</tr>
<tr>
<td>Case 6</td>
<td>400 kΩ</td>
</tr>
<tr>
<td>Case 7</td>
<td>800 kΩ</td>
</tr>
<tr>
<td>Case 8</td>
<td>200 kΩ</td>
</tr>
<tr>
<td>Case 9</td>
<td>150 kΩ</td>
</tr>
<tr>
<td>Case 10</td>
<td>400 kΩ</td>
</tr>
<tr>
<td>Case 11</td>
<td>400 kΩ</td>
</tr>
</tbody>
</table>

A plot of the electric potential, electric field and the electron temperature along the axis of the discharge is shown in Figure 6.5 (a) and (b), respectively, for case 1. The potential profile shows a very large drop of ~ 320 V at the cathode which corresponds to the cathode sheath. The predicted voltage drop at the cathode compares favorably to the literature value of 250 V for hydrogen gas and iron electrode $^2$. The corresponding electric field has a peak value of ~ 10700
kV m\(^{-1}\) at the cathode. A linear \(~ 55\) V drop in the electrostatic potential corresponding to an electric field of \(400\) kV m\(^{-1}\) occurs in the remainder of the plasma which is the positive column. A slight increase in the electric potential is observed near the anode, denoting the anode sheath. The electric field profile shows the maximum at the cathode. Within a distance of \(30\) \(\mu\)m from the cathode the electric field decreases almost linearly to a very low value. The high electric field region indicates the edge of the sheath. Following this region the Faraday dark space can be identified by the slight decrease in the electric field. The field in the Faraday dark space slightly increases and then remains constant over the entire length of the positive column. The electric field is further found to increase from \(~ 400\) kV m\(^{-1}\) to \(~ 800\) kV m\(^{-1}\) at the anode over a distance of \(17\) \(\mu\)m. This narrow zone denotes the anode glow. The electric potential and electric field profile is consistent with that observed for glow discharges \(^3\). The electron temperature distribution (Figure 6.5 (b)) shows a maximum electron temperature of \(~ 7.5\) eV in the cathode sheath and decreases rapidly to \(~ 1.75\) eV. The electron temperature remains fairly constant over the remainder of the plasma. An electron temperature of \(~ 2.4\) eV is observed in the anode sheath. The high electron temperatures in the sheaths results due to the large electric field existing there.
Figure 6.5: a) Electric potential and electric field b) Electron temperature along the axial distance 
(r = 0). Ballast resistance 400 kΩ, $V_d = 375 \text{ V}$ and $I_d = 2.06 \text{ mA}$ (Case 1).
Figure 6.6: Contour plot of constant a) $\text{H}_3^+$ ion density (maximum value $7.40 \times 10^{19}$ m$^{-3}$) and b) electron number density (maximum value $7.36 \times 10^{19}$ m$^{-3}$). Ballast resistance 400 k$\Omega$, $V_d = 375$ V and $I_d = 2.06$ mA (Case 1).

Contour plots of constant $\text{H}_3^+$ ion and electron density are shown in Figure 6.6 for case 1. From the contour plots of $\text{H}_3^+$ and electron density it can be seen that both the $\text{H}_3^+$ ions and electrons have the maximum density near the cathode region. This indicates that there exists a significant volumetric production of these species near the cathode of the discharge. The high electric field at the cathode is responsible for the large volumetric production of electrons and $\text{H}_3^+$ ions near the cathode. The production of electrons is well balanced by the production of $\text{H}_3^+$.
ions resulting from the ion-neutral collisions of H\(^+\) and H\(_2^+\) ions with hydrogen molecules and also the collisions of electronically excited atomic hydrogen with hydrogen molecules. Peaks in electrons and H\(_3^+\) ion concentration corresponds to the ‘negative glow’ of the discharge. The combined ion (H\(^+\) + H\(_2^+\) + H\(_3^+\)) density and the electron density profiles along the gap width of the discharge are shown in Figure 6.7 (case 1). As for the bulk, the plasma was found to be neutral, other than the cathode and the anode sheaths where the ion and the electron density were, respectively found to be high. The cathode sheath was found to have a thickness of about 30 \(\mu\)m. Creation of the cathode sheath occurs due to the multiplication of the cathode emitted electrons in the strong electric field near the cathode, leading to an increase in the ion density. A sheath having a thickness of about 17 \(\mu\)m in the anode is also observed. The anode sheath results from the diffusion current of the electrons exceeding the drift current. At the anode the drift velocity of the electron is small due to the low electric field and the diffusion current dominates.

![Figure 6.7: Electron and ion (H\(^+\) + H\(_2^+\) + H\(_3^+\)) density along the axial distance. Ballast resistance 400 k\(\Omega\), V\(_d\) = 375 V and I\(_d\) = 2.06 mA (Case 1).](image-url)
Figure 6.8: Species density along the axial distance \((r = 0)\) a) Electronically excited species \((H^+(2p) \text{ and } H_2^+(C^1Π_u, 2pν))\) b) Ionic species \((H^+, H_2^+ \text{ and } H_3^+)\). c) Radical species \((H)\). Ballast resistance \(400 \text{kΩ}\), \(V_d = 375 \text{ V}\) and \(I_d = 2.06 \text{ mA}\) (Case 1).
Figure 6.9: Contour plot of constant electronically excited species \( \text{H}_2^* (C^1 \Pi_u, 2p \pi) + \text{H}^* (2p) \) density (maximum value \( 6.95 \times 10^{19} \text{ m}^{-3} \)). Ballast resistance \( 400 \text{ k}\Omega \), \( V_d = 375 \text{ V} \) and \( I_d = 2.06 \text{ mA} \) (Case 1).

Figure 6.8 summarizes the different species (ions, electronically excited states, radicals) density distribution along the axial distance for case 1. The predicted \( \text{H}_2^* (C^1 \Pi_u, 2p \pi) \) is found to be three orders of magnitude higher than that of \( \text{H}^* (2p) \). The axial distribution of the electronically excited hydrogen species indicates higher density of \( \text{H}_2^* (C^1 \Pi_u, 2p \pi) \) and \( \text{H}^* (2p) \) near the electrodes, with larger density near the cathode. The electronically excited species density drop near the electrodes owing to the surface quenching effect resulting from the surface
reactions. It is known that the electronically excited species \( (H^*(2p) \text{ and } H_2^* (C^1Π_u 2p_π)) \) are responsible for the brightness of the glow discharge. The electronically excited species distribution indicates two luminous zones, existing near the electrodes. A contour plot of the combined electronically excited species \( (H_2^*(C^1Π_u 2p_π) + H^*(2p)) \) (Figure 6.9) clearly shows the two bright zones in the discharge. The large density of the excited state is due to the large rate of excitation that is produced by the large electron temperatures (7.5 eV and 2.4 eV) in the cathode and the anode. The luminous regime near the cathode and the anode denotes the ‘negative glow’ and the ‘anode glow’, respectively. The ‘negative glow’ is found to be much larger than the ‘anode glow’. Distribution of the ionic species (\( H^+, H_2^+ \text{ and } H_3^+ \)) along the axial distance (Figure 6.8 (b)) shows the heavier \( H_3^+ \) ion to be the dominant ionic species. The calculations predicted the heavier \( H_3^+ \) ion to be one order of magnitude higher than \( H_2^+ \) and two orders of magnitude higher than \( H^+ \) ions. As seen for the electronically excited species the ionic species also showed a similar peak density near the cathode. Since \( H_3^+ \) ions are produced due to the ion-neutral collisions of \( H^+ \) and \( H_2^+ \) ions with \( H_2 \), the bulk of the discharge has significantly lower \( H_2^+ \) and \( H^+ \) ions. Peaks in the ion concentrations correspond with the ‘negative glow’ of the discharge. The prediction of \( H_3^+ \) to be the dominant ionic species is consistent with Chen et al.\(^{134} \). Atomic H was found to have a maximum density at the cathode. The maximum H number density obtained was \( 4.4 \times 10^{23} \text{ m}^{-3} \), resulting in a dissociation degree of 0.014.

The ionization rate profiles are shown in Figure 6.10. The processes include ground state electron impact ionization (R4, R5, R6), ionization due to electron–ion (R9) and ion–neutral collision (R11, R12), stepwise ionization (R16) and ionization due to collision between electronically excited state and neutrals (R17). The ground state ionization (R4) involving the production of \( H_2^+ \) ions is the major electron production channel. It peaks near the cathode sheath.
where the electric field and the electron temperature is the maximum. The ground state electron impact ionization reaction R5 and R6 involving H$^+$ ion, were found to be two and one orders of magnitude lower than R4. Similar to R4 their maximum also existed in the cathode sheath. The H$_3^+$ ion formation due to ion-neutral collision (R12) is dominant ion production mechanism. The H$_3^+$ ion production rates (R11, R12) was also found to peak near the cathode sheath, where the H$_2^+$ and the H$^+$ density is higher. The ionization process due to the collision between H$^*$ and H$_2$ (R17) is one order magnitude lower than R12. The maximum reaction rate is located at the cathode sheath, which has the maximum H$^*$ density. Compared to all the ion production channels the contribution from the stepwise ionization (R16) and electron – ion collision (R9) was the least. All the ionization rate profiles showed an increase at the anode due to the presence of a slightly higher electron temperature there.

Figure 6.10: Reaction rates for the formation of H$^+$, H$_2^+$ and H$_3^+$ ions along the axial distance.

Ballast resistance 400 kΩ, $V_d = 375$ V and $I_d = 2.06$ mA (Case 1).
The reaction chemistry model used in the simulations included the first level of the vibrationally excited hydrogen molecule (H$_2$ v =1). The vibrationally excited species were produced by electron collisions with the neutral hydrogen molecules. The vibrationally excited species were lost through vibrational to translational (V-T) relaxation where the vibrationally excited species collided with neutral hydrogen molecule and neutral hydrogen atom. The vibrationally excited species got de-excited in these reactions and produced neutral hydrogen molecules. Contour plots of constant H$_2$ v =1 density for case 1 is shown in Figure 6.11 (a). It can be seen that H$_2$ v = 1 has the maximum density near the cathode. This indicates a significant volumetric production of the vibrationally excited species in the ‘negative glow’. This is similar to that observed for H$_3^+$ ion and electrons. Near the electrode surfaces the density of the vibrationally excited hydrogen molecules drops owing to a surface quenching effect resulting from the surface reactions. A Boltzmann distribution of the vibrationally excited molecules was employed to calculate the vibrational temperature $T_{vibrational}$. $T_{vibrational} = -\frac{\hbar \omega}{\log(\frac{n_{v=1}}{n_{2}})}$, was used where H$_2$ v = 1 and H$_2$ are the density of the vibrationally excited and neutral hydrogen molecules respectively, $\hbar \omega$ is the excitation energy which is 0.54 eV for the first level of vibrational excitation of a hydrogen molecule. Figure 6.11 (b) shows the contour plot of constant $T_{vibrational}$ in the entire discharge domain. It is observed that the maximum vibrational temperature exists near the cathode. A maximum vibrational temperature of 1560 K is observed due to the maximum H$_2$ v =1 density of 4.26 x 10$^{23}$ m$^{-3}$. Vibrational temperature distribution along the axial distance is shown in Figure 6.12. The distribution profile shows a sharp increase of the vibrational temperature in the cathode region. The maximum vibrational temperature of 1560 K is found to occur 30 μm away from the cathode corresponding with maximum $n_e$. The temperature gradually
decreases in the bulk of the plasma, with a sharp decrease near the anode. Near the cathode and the anode surfaces the vibrational temperature is observed to be 650 K and 900 K, respectively.

Figure 6.11: Contour plot of constant a) $H_2 v = 1$ density (maximum value $4.26 \times 10^{23} \text{ m}^{-3}$) and b) $T_{\text{vibrational}}$ (maximum value 1560 K). Ballast resistance 400 kΩ, $V_d = 375$ V and $I_d = 2.06$ mA (Case 1).
Figure 6.12: Vibrational temperature $T_{\text{vibrational}}$, along the axial distance. Ballast resistance 400 kΩ, $V_d = 375$ V and $I_d = 2.06$ mA (Case 1).

Contour plots of constant electron and $\text{H}_3^+$ ion number density for a ballast resistance of 800 kΩ (case 2) and 150 kΩ (case 5) are shown in Figure 6.13 and 6.14. These ballast resistances result in a discharge current of 1.0 mA and 5.5 mA. Compared to the discharge current of 2.06 mA (case 1) Figure 6.6) the discharge for a discharge current of 1.0 mA (Figure 6.13 (a), 6.14 (a)) is smaller in diameter. With an increase in the discharge current to 5.5 mA, the discharge size was found to increase in the radial direction (Figure 6.13 (b), 6.14 (b)). Comparing the density profile for the combined electronically excited states for case 1, 2 and 5 (Figure 6.15) it can be clearly seen that with an increase in the discharge current the size of the discharge increases. Both the ‘negative glow’ and the ‘anode glow’ are observed to increase in the radial
direction and starts to occupy more of the electrode area. Since the electronically excited states represent light emission, these profiles were compared to the experimental visualization studies.

Figure 6.13: Contour plots of constant electron number density for a) Ballast resistant 800 kΩ, $V_d = 405$ V, $I_d = 1.00$ mA; $\gamma = 0.10$ (Case 2) b) Ballast resistant 150 kΩ, $V_d = 368$ V, $I_d = 5.50$ mA; $\gamma = 0.10$ (Case 5).
Figure 6.14: Contour plots of constant $\text{H}_3^+$ ion number density for a) Ballast resistant 800 kΩ, $V_d = 405 \text{ V}$, $I_d = 1.00 \text{ mA}$; $\gamma = 0.10$ (Case 2) b) Ballast resistant 150 kΩ, $V_d = 368 \text{ V}$, $I_d = 5.50 \text{ mA}$; $\gamma = 0.10$ (Case 5).
Figure 6.15: Contour plot of constant electronically excited species \( \left( \text{H}_2^* \left( \text{C}^1\Pi_u \ 2\pi \right) + \text{H}^*(2p) \right) \) density for a) Ballast resistant 800 kΩ, \( V_d = 405 \text{ V} \), \( I_d = 1.00 \text{ mA} \); \( \gamma = 0.10 \) (Case 2) b) Ballast resistance 400 kΩ, \( V_d = 375 \text{ V} \) and \( I_d = 2.06 \text{ mA} \); \( \gamma = 0.10 \) (Case 1) and c) Ballast resistant 150 kΩ, \( V_d = 368 \text{ V} \), \( I_d = 5.50 \text{ mA} \); \( \gamma = 0.10 \) (Case 5).
The radial profiles of the ion current density at the cathode are shown in Figure 6.16 for different discharge currents (Cases 1 – 5). The contribution of electron current is small at the cathode and the ion transports almost all the discharge current at the cathode. The discharge extends laterally only across a limited region called the cathode spot with a constant ‘normal’ current density. Increase of the total discharge current occurs only by the growth of the cathode spot. One can see that for a discharge current of 2.06 mA the ‘normal’ current density $j_n$ is established. In this ‘normal’ mode the discharge current is observed to increase at constant $j_n$. The predicted ‘normal’ current density is found to be 22 A cm$^{-2}$. The constant current density is an indication of the lateral growth of the discharge (Figure 6.15). The low pressure ‘normal’ glow current density for hydrogen and an iron electrode at room temperature from the literature$^2$ is 90 μA cm$^{-2}$ Torr$^{-2}$. Performing a temperature scaling$^{22}$ the current density can be expressed as
\[ j = j_n p^2 \left( \frac{T_n}{T} \right)^2, \]

where \( j_n \) is the ‘normal’ current density at room temperature (90 \( \mu \text{A cm}^{-2} \text{Torr}^{-2} \)), \( T_n \) is the room temperature and \( T \) is the gas temperature. For a room temperature of 300 K and gas temperature of 500 K and pressure of 760 Torr the current density is 18.7 A cm\(^{-2} \). The ‘normal’ current density predicted by the model compares favorably to the temperature scaled literature value.

![Energy source terms along the axial distance of the discharge (r = 0). Ballast resistance 400 kΩ, \( V_d = 375 \text{ V} \) and \( I_d = 2.06 \text{ mA} \) (Case 1).](image)

The contributions of the different source terms (heavy particle reaction, Frank Condon heating due to dissociation of \( \text{H}_2 \), elastic collisions and ion Joule heating) to the energy equation are shown in Figure 6.17. The contribution of Joule heating was found to be dominant gas heating mechanism. The Joule heating peaked at the cathode where the ion current density and
the electric field is the maximum. The Frank Condon effect was smaller than the Joule heating by a factor of 2.5. However apart from the cathode sheath it was more dominant in the volume of the discharge. Heat release due to the heavy particle reaction was one order of magnitude lower than Joule heating. The energy released by the heavy particle reactions involves the collision of $\text{H}_2^+$ and $\text{H}^+$ with $\text{H}_2$. The heat release due to the heavy particle reaction peaks in the cathode sheath, where the maximum density of $\text{H}_2^+$ and $\text{H}^+$ ions exists (Figure 6.8 (b)). Heat release due to elastic collisions was found to have the smallest contribution to the neutral gas heating. Compared to the ion Joule heating it was two orders of magnitude lower.

Figure 6.18: Calculated gas temperature along the axial distance of the discharge ($r = 0$) for different discharge current (1.00, 2.06, 3.31, 4.14 and 5.50 mA) (Cases 1 – 5).
Figure 6.18 shows the temperature profile along the axial distance for various discharge currents (Case 1 – 5). Significant gas temperatures are observed due to ion Joule heating and Frank Condon effect. For all the cases the gas temperature peaks at the cathode sheath where the electric field is the maximum. Positive ions gain energy from the electric field and collisionally transfer this energy to the neutral gas, thereby heating the gas. The gas heating outside the sheath was a result of the Frank Condon heating. The peak temperature for all the cases is in the range of 500 K. This is 200 K above the ambient. Peak gas temperature and peak electron density as a function of discharge current are plotted in Figure 6.19 for cases 1 – 5. The peak gas temperature was found to increase with an increase in the discharge current. Similar trend was observed for the peak electron number density. The peak electron number density increased by a factor of 1.15 in between the discharge current of 1.0 mA and 5.5 mA. The peak gas temperature for 5.5 mA discharge current was found to be 505 K, 32 K higher than that observed for a discharge
current of 1.0 mA. The temperature increases little because the electrodes provide significant cooling. The ion Joule heating would result in a constant peak gas temperature throughout the ‘normal’ glow regime, because of the fairly constant ion current density and electric field. However outside the cathode sheath the gas heating due to the Frank Condon effect dominates (Figure 6.17). With an increase in the gas temperature the reduced electric field increases, resulting in the production of more electrons. The increase in the electron number density increases the heating due to elastic collisions and Frank Condon effect. The heat release from the heavy particle reactions (ion-neutral collisions) increases as well, since more ions are produced from the increased electrons. As a result with an increase in discharge current even though the peak temperature in the cathode sheath remains fairly constant, the gas temperature in the remainder of the plasma was observed to increase as seen in Figure 6.18.

The effect of the secondary electron emission coefficient \( \gamma \) on the electrical characteristics (discharge voltage) and the plasma property (electron number density and cathode voltage) are summarized in Figure 6.20 (a) and (b). Figure 6.20 (a) and (b) depicts discharge voltage, cathode voltage and peak electron density as function of secondary electron emission coefficient. The secondary electron emission coefficient is defined as the number of electrons emitted from the electrode surface due to ion impact. Figure 6.20 (a) shows the discharge voltage and the cathode voltage as a function of \( \gamma \). Both the discharge and the cathode voltage decreases with an increase in \( \gamma \). The voltage drop in the positive column (\( V_d - V_{\text{cathode}} \)) column was constant at \( \sim 55 \) V, suggesting a stronger dependence of the cathode voltage to \( \gamma \). The peak electron density was also observed to decrease with an increase in the secondary electron emission coefficient. The cathode voltage and peak electron density decreases from 326 V and \( 7.5 \times 10^{19} \text{ m}^{-3} \) at \( \gamma = 0.09 \) to 296 V and \( 6.75 \times 10^{19} \text{ m}^{-3} \) at \( \gamma = 0.20 \). For the same ballast resistance
as $\gamma$ decreases the response of the system is to increase the sheath voltage. The resulting higher electric field increases the ionization rate. With an increase in $\gamma$ the electrode surface emits larger number of electrons thereby providing higher ionization. Similar sensitivity to the secondary electron coefficient were observed by Kothnur et al.\textsuperscript{106} and Kushner\textsuperscript{99} for a plasma discharge operating at 250 Torr.

![Graphs](image.png)

Figure 6.20: a) Discharge voltage and cathode voltage and b) Peak electron density as a function of secondary electron emission coefficient ($\gamma$) (Case 1, 6, 10 and 11).
The resulting voltage-current (V-I) characteristics from the simulations (Case 1 – 9) are shown in Figure 6.23. The flat nature of the V-I curve signifies the existence of the ‘normal’ glow discharge regime. In the ‘normal’ glow discharge the voltage remains constant, with increasing current resulting due to the formation of the ‘normal’ current density. From the V-I characteristics it can be seen that the ‘normal’ glow regime initiates for a discharge current greater than 1.0 mA. The calculated V-I characteristics are sensitive to the secondary electron coefficient $\gamma$. Model predictions agree well with the experimental data for $\gamma = 0.10$. The dependence of the V-I characteristics on the secondary electron emission coefficient is similar to that observed by Wang et al. The obtained V-I characteristics is similar to those observed for a low pressure DC discharge.

6.6 Comparison with Experimental Measurements

Experimental studies were conducted to validate the numerical model. The inter electrode gap spacing was held at $400 \pm 10 \ \mu$m for all the experiments. Figure 6.21 shows a series of the photographs of the discharge for different discharge currents. All the images were taken at the same magnification. The images show the typical dark and bright regions observed in glow discharges. It can be seen there exists a bright region near the cathode which is defined as the ‘negative glow’. Moving upwards towards the anode a dark space termed as the ‘Faraday dark space’ is observed. The ‘Faraday dark space’ is followed by a striated ‘positive column’ and the ‘anode glow’. These dark bright regions were also observed by Staack et al. The visualization studies indicate two bright luminous zones indicating the ‘negative glow’ and ‘anode glow’ as predicted by the model. With an increase in the discharge current the ‘negative glow’ and the ‘anode glow’ is found to increase in size which validates the predictions from the model. Furthermore with an increase in the discharge current the ‘Faraday dark space’ increased in size.
and the striations in the positive column diminished. The average ‘Faraday dark space’ was found to have a thickness of \(~ 130 \, \mu m\). The model predicted a ‘Faraday dark space’ thickness of \(~ 60 \, \mu m\) (Figure 6.5 (a)) which is reasonably close to the measured thickness.

![Image of discharge](image)

Figure 6.21: Experimental visualization studies of the hydrogen micro-discharge at atmospheric pressure for an inter electrode separation of \(400 \pm 10 \, \mu m\) a) \(V_d = 415.5 \, V, I_d = 2.0 \, mA\) b) \(V_d = 396.8 \, V, I_d = 2.5 \, mA\) c) \(V_d = 382.5 \, V, I_d = 3.0 \, mA\) d) \(V_d = 378.5 \, V, I_d = 3.5 \, mA\).

‘Normal’ current density was measured from gray scale images of the discharge. The width of the ‘negative glow’ was defined at the widest point by the number of pixels over which the gray scale intensity was 50% of the maximum intensity in that region. A circular cross section was assumed to calculate the cross sectional area of the ‘negative glow’. The current density was then calculated using the measured area and the discharge current. In these measurements we assume that the current corresponds to the region of emitted light which might result in under estimation of the current density. Figure 6.22 shows the measured ‘normal’ current density over the entire discharge current range. The average ‘normal’ current density was found to be \(16 \, A \, cm^{-2}\) which is of the same order of magnitude as predicted by the model (Figure 6.16). The discrepancy between the experimental measurements and model prediction could be
due to the simple reaction chemistry model. Furthermore the experimental values for the ‘normal’ current density can vary significantly depending on the cathode material, presence of impurities, surface roughness etc.

The experimentally obtained discharge voltage versus discharge current can be seen in Figure 6.23 together with the V-I characteristics obtained from the numerical simulations. Measurement error in the electrode spacing was ±10 μm due to the resolution of the micro-positioner. This leads to the error in the discharge voltage $V_d$. Measurement errors in the discharge current were ±25 μA and errors in the discharge voltage were ±5 V. The error bars for the voltage are shown in the Figure. A relatively ‘flat’ V-I shape was observed similar to that observed by Staack et al. 22. The ‘flat’ V-I characteristics is one of the key signatures of the
‘normal’ glow discharge. The experimental measurement was found to be in good agreement with the model predictions having a secondary electron emission coefficient of 0.10.

Figure 6.23: Voltage-current characteristics of the atmospheric pressure hydrogen micro-discharge (Cases 1 – 9).

The features of the discharge which included the V-I characteristics and ‘normal’ current density compared favorably to the model predictions. However the model was not able to predict the striated positive column observed at low discharge currents. Two dimensional simulations of striations in low pressure argon glow discharge have been reported by Arslanbekov et al.\textsuperscript{158}. It was stated that non-monotonic dependence of the inelastic collision rates on electron number density was the key criterion in observing the striations. The electron temperature ($T_e$) and the ionization rate constant ($\eta_{\text{ionic1}}$) in the present calculations has a monotonic dependence on the reduced electric field ($E/N$) and the electron number density ($n_e$) (Figure 6.3), which differs from
that observed by Arslanbekov et al.\textsuperscript{158} in their striation predictions. It is believed, that in order to predict striations in hydrogen discharges more detailed chemical kinetics (different levels of vibrational excitation, vibrational – translational relaxation, stepwise ionization from vibrational excited species etc) are required. The chemical kinetics govern the electron energy distribution function, which determines inelastic collision rates, electron transport parameters and electron temperature. The striations observed during the experiments could also arise due to some non-local effects, which cannot be addressed using a local field approximation.

6.7 Conclusions

Atmospheric pressure micro discharge in diatomic hydrogen gas has been numerically characterized using a self consistent hybrid model. For the atmospheric pressure plasma discharges, the local-field approximation was invoked where the electron energy $T_e$ is considered to be a function of the local electron density ($n_e$) and the reduced electric field ($E/N$). The discharge operating at a 400 micron inter-electrode gap width for a pin plate configuration was studied numerically. The simulations provided detailed insight into the physico-chemical processes. The predicted electric potential and electric field profiles indicated the discharge to be a glow discharge. The cathode voltage drop obtained was found to be in good agreement with literature value. The ‘negative glow’, ‘Faraday dark space’, ‘positive column’ and ‘anode glow’ was identified from the electric field, electron and ion density profiles. The micro discharge was found to be quasi-neutral in the bulk of the plasma region, apart from the sheaths formed at the electrodes. Distinct cathode sheath ($\sim 30 \mu m$) and anode sheath ($\sim 17 \mu m$) were observed, with the cathode having a larger sheath than the anode. The model predicted the heavier species to be dominant. $H_3^+$ ion was found to be the major ionic species. The $H_3^+$ ion concentration was one
order of magnitude larger than \( \text{H}_2^+ \) and two orders of magnitude larger than \( \text{H}^+ \) ion concentration. Vibrationally excited molecular hydrogen was found to have the highest concentration among the excited species. A peak vibrational temperature of 1560 K was predicted assuming a Boltzmann distribution of the vibrationally excited species. The ion Joule heating and the Frank Condon heating were found to be the dominant gas heating mechanism. The ion Joule heating was dominant in the cathode sheath, the Frank Condon heating was dominant in the remainder of the plasma. A peak neutral gas temperature of \(~ 500\) K was predicted by the model. The maximum gas temperature was observed to occur near the cathode sheath of the discharge. Dependence of the secondary electron emission coefficient on the plasma properties was studied. With an increase in \( \gamma \) a decrease in the discharge voltage was observed. With a fairly constant voltage drop in the positive column (~ 55 V) most of the change was found to occur at the cathode voltage drop. The peak electron density showed a similar trend as that of the cathode voltage as a result of the change in the electric field in the sheath. The model was able to predict a flat voltage-current characteristic. The simulations predicted the existence of the constant ‘normal’ current density at the cathode. Increase of the total discharge current occurred only by growth of the cathode spot through which the current flows. The electronically excited states predicted by the model showed two distinct luminous zones at the cathode and the anode. These luminous zones were also found to increase radially with an increasing discharge current.

Experimental studies were conducted to validate the numerical predictions. Visualization studies showed ‘dark’ and ‘bright’ regions as observed in glow discharges. The voltage-current characteristics obtained from the experiments showed similar trends as predicted by the model. The measured ‘normal’ current density was also found to be in good agreement with the
numerical predictions. 1) Flat voltage-current characteristics 2) ‘dark’ and ‘bright’ regions and 3) ‘normal’ current density at the cathode enabled us to further conclude the discharge to be a glow discharge. Furthermore the gas temperature prediction by the model suggested the discharge to be non-thermal, non-equilibrium plasma. The discrepancy between the experimental data and numerical predictions is believed to be due to the simple reaction chemistry used in the model. The hybrid model was found to be successful in capturing the features of a pure hydrogen discharge operating at atmospheric pressure. The model can be further extended to predict the physico-chemical processes of a methane-hydrogen plasma used for thin-film deposition, where trace amount of methane is mixed with hydrogen gas.
7 ATMOSPHERIC PRESSURE DIRECT CURRENT MICRO GLOW DISCHARGE IN POLYATOMIC GAS (METHANE)³

7.1 Introduction

The physical and chemical properties of diamond-like carbon (DLC) layers make it an ideal candidate for applications such as machine tools, optical coatings and high temperature electronics. Plasma discharges have been used frequently for the deposition of these DLC layers by utilizing the plasma-assisted chemical vapor deposition (PACVD) process. DLC can be deposited on a variety of substrates by PACVD using different kinds of plasmas, i.e., a microwave plasma, an electron cyclotron resonance (ECR) plasma, an inductively coupled plasma (ICP) or a radio frequency capacitively coupled plasma (RF CCP). These processes in general utilize CH₄ as the carbon bearing feedstock and dilute it with large amounts of H₂ to obtain these DLC layers. All these plasma sources are generally maintained at low (< 1 Torr) or moderate pressure (1 – 100 Torr) for the deposition process. The low-moderate pressure operating conditions of these plasma sources results in low deposition rates and also in the requirement of costly vacuum systems. Furthermore high maintenance cost of the systems results in increased production cost.

Atmospheric pressure glow discharges are attractive for a wide range of material processing applications largely due to their operational flexibility afforded by the removal of the vacuum system. At atmospheric pressure, reaction rates are higher and chemical processes can occur more rapidly, thereby resulting in higher deposition/etching rates. The use of atmospheric

pressure plasma would therefore expand the current scope of material processing. The key to having an atmospheric pressure micro plasma discharge that can be used for PACVD is to provide conditions which maintain the non-equilibrium state. Atmospheric pressure direct current (DC) micro glow discharge of the cold type has been successfully generated. Experimental studies are performed to use the micro glow discharge for DLC deposition. In order to improve the results of DLC depositions (i.e. deposition rate, film quality, film uniformity) numerical modeling of the plasma discharge can be of great use to achieve a better understanding of the various factors involved in the DLC film deposition process. The properties of the DLC film are influenced by the plasma characteristics, which depend on the specific deposition conditions, such as power, gas mixture and gas flow. However, the reasons for change in the plasma properties (i.e. density of different species) due to change in the deposition conditions remain unclear and requires further investigation. Numerical modeling could provide this information and thus, provide a better insight into how the deposition conditions affect the film properties.

In recent years a number of methane-hydrogen plasma models have been proposed. All these models were however developed for low or moderate pressure systems. Tachibana et al. developed a zero dimensional model for a low pressure RF plasma. The study included the effect of RF power and gas flow rate on the plasma properties and the deposition rate. For the simulations a Duryvesteyn like electron energy distribution function (EEDF) was assumed. Their calculations indicated CH$_3$ to be the dominant radical and CH$_5^+$ to be the dominant ion. Keudell et al. reported the development of a model for a low pressure ECR plasma. The proposed model contained both volume and surface chemistry for predicting film growth and composition. The surface chemistry only took into account the incorporation of CH$_3$
radicals. The predicted H/C ratio in the deposited films had qualitative agreement with experimental measurements. A similar model was developed by Mantzaris et al. 163 which had a combined plasma physics, discharge chemistry and surface chemistry models to study DLC film deposition process for a low pressure RF capacitively coupled methane discharge. The film deposition in the model, took place by direct ion incorporation and ion induced stitching of adsorbed neutrals, while film removal was performed by etching and sputtering. A one dimensional fluid model for low pressure RF methane-hydrogen plasma was proposed by Herrebout et al. 69. The model contained a detailed gas chemistry consisting of twenty gas species and forty six reactions. However no detailed surface chemistry was included in the model. Results from their simulations indicated C2H6, C3H8, C2H4 and C2H2 to be present in high densities together with CH4 and H2. CH3 and CH5+ were predicted to be the dominant radical and ion respectively. Ivanov et al. 87 proposed a one dimensional particle-in-cell Monte Carlo model to simulate low pressure RF methane-hydrogen discharge. In their model, the electron behavior was kinetically simulated by solving Newton’s equations, treating the electron collisions with the Monte Carlo algorithm and the behavior of the ions and radicals were treated using a set of continuity equations. The study included the comparison between the fluid and particle-in-cell model. Over the years numerical models to simulate atmospheric methane-hydrogen plasmas have also been developed by various researchers 150, 166, 167. All these models are however developed for thermal plasmas where the reaction mechanisms are governed by the neutral gas temperature and no electron kinetics are taken into account. Frenklach and Wang 150 reported the development of a detailed chemical kinetics model for an atmospheric pressure thermal plasma with methane-hydrogen, methane-argon and methane-oxygen-hydrogen being the feed gas mixture. The model included detailed description of the gas-phase and surface processes to
predict diamond deposition. One dimensional simulation was conducted with the experimental temperature profile being the input parameter. Their predicted deposition rates reproduced the general experimental trends observed. Yu and Girshick 166 conducted one-dimensional simulations to predict diamond film growth in an atmospheric pressure methane-hydrogen thermal plasma. Their simulations indicated that for gas temperatures higher than 4000K monatomic carbon vapor has a significant contribution in diamond growth. The growth of diamond in a sub-atmospheric DC arc plasma jet was studied numerically by Coltrin and Dandy 167. The proposed model included detailed surface reaction mechanisms which included pathways for the growth of both graphite and diamond like carbon. Their simulation results indicated the growth of diamond film due to the incorporation of CH₃, C₂H₂ and C in the film.

Our literature review indicates that simulation of DC atmospheric pressure non thermal methane-hydrogen plasma has not been performed. In this chapter we report the results of a one dimensional hybrid model 97, 168 to simulate atmospheric pressure DC glow discharges in methane-hydrogen mixtures. In the model the electron energy distribution is treated kinetically to determine the EEDF and the electron induced reaction rates, electron mobility and diffusivity by solving the Boltzmann equation and the ions and neutrals are treated hydrodynamically. The model contains a detailed volume (Table 7.2) and surface chemistry (Table 7.3) to predict the quality of the deposited film. Twenty three species and an eighty one step reaction mechanism were considered for the gas-phase methane-hydrogen discharge. The surface chemistry consisted of eighteen species and eighty four reaction steps. The aim of the work was to study the effect of different operating conditions (power, gas mixture) on the plasma characteristics and hence on the deposition. The study focused in determining the best conditions required to obtain pristine DLC deposition.
7.2 Geometry and Reaction Mechanism

7.2.1 Schematic of the Problem Geometry

![Schematic of a parallel plate micro discharge](image)

Figure 7.1: Schematic of a parallel plate micro discharge with inter-electrode spacing $d$ together with the external circuit. The numbers represent the nodes in the circuit, ‘0’ indicates grounded nodes.

The schematic of the parallel plate micro discharge is shown in Figure 7.1. The electrodes are connected to an external circuit. The external circuit contains a resistance $R$ and a capacitance $C$ connected with the discharge. The ballast resistance $R$ is necessary in order to limit the discharge current. The time dependent circuit model, which includes a parasitic capacitance has been considered to model the transient (start-up) processes (stability) for the experimental system. The experimental studies indicated a strong dependence of discharge stability on the parasitic capacitance. The capacitance $C$ is present intrinsically due to the external cables, which is known as the parasitic capacitance. This results from the insulation of the electrical wires and the optical work bench. This capacitance is in parallel to the plasma discharge. The parasitic capacitance plays a significant role in the time evolution of the plasma discharge and was included in the circuit model to be closer to the experimental setup. In these simulations, the inter-electrode separation $d$ is set to 200 $\mu$m. An electrode radius of 75 $\mu$m is set to calculate the
discharge current, which is similar to the approach reported by Wang et al. \(^{169}\) for conducting one dimensional simulations of micro discharges with external circuit. The total current is calculated using the electron conduction, ion conduction and the displacement current. The power supply voltage \(V_{\text{pwr}}\) is fixed at 1200 V, so that it is larger than the required breakdown voltage for an atmospheric pressure pure hydrogen discharge. The capacitance \(C\) is fixed at 0.1 pF, corresponding to the estimated value of the experimental setup. In order to obtain different discharge currents the ballast resistance is varied from 200 k\(\Omega\) to 1200 k\(\Omega\).

### 7.2.2 Chemical Kinetics

#### 7.2.2.1 Gas Phase Chemical Kinetics

Table 7.1: Different species taken into account in the methane-hydrogen plasma model.

<table>
<thead>
<tr>
<th>Neutrals</th>
<th>Ions</th>
<th>Radicals</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>C(_2)H(_4)</td>
<td>CH(_5^+)</td>
<td>C(_2)H(_4^+)</td>
</tr>
<tr>
<td>H(_2)</td>
<td>C(_2)H(_2)</td>
<td>CH(_3^+)</td>
<td>C(_2)H(_5^+)</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>C</td>
<td>H(_2^+)</td>
<td>H(_3^+)</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>Soot</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Twenty three species were considered in the model to simulate atmospheric pressure methane-hydrogen micro discharges. An overview of the different species (electrons, ions, radicals and neutrals) is given in Table 7.1. It is important to note that in addition to CH\(_4\) and H\(_2\) (feed gas), higher order neutral molecules C\(_2\)H\(_6\), C\(_3\)H\(_8\), C\(_2\)H\(_4\), C\(_2\)H\(_2\) are also considered in the model because it is stated in the literature that they can have high densities in the plasma \(^{162, 170}\). Furthermore no negative ions (mainly CH\(_2^-\) and H\(^-\)) are incorporated since CH\(_4\) plasma has a very strong electropositive character. It was found by Gogolides et al. \(^{171}\) that negative ion density in a methane plasma is about one order of magnitude lower than the electron and the
positive ion densities. For the hydrogen ionic species, H^+ was not taken into account due to its low density at atmospheric pressure (four orders magnitude smaller than H_3^+)\(^{27}\). The chemical kinetics model employed in this study involves two major components; gas phase reaction mechanism (chemistry of hydrogen species, chemistry of neutral hydrocarbons, hydrocarbon-ion chemistry) and surface reaction mechanism. The total set of the gas phase volume reactions taken into account is summarized in Table 7.2. The gas phase reactions can be grouped into four categories 1) electron-neutral 2) electron-ion 3) ion-neutral and 4) neutral-neutral reactions. The electron-neutral reactions include momentum transfer, ionization, dissociation and vibrational excitation. Two or more vibrational excitations levels for every neutral were taken into account, since for poly atomic gases a considerable fraction of the electron energy is lost in the vibrational excitation reactions. Reactions between vibrationally excited hydrogen and hydrocarbon were not taken into account. The vibrationally excited hydrogen molecules do not participate in methane chemistry\(^2\), since it requires vibrationally excited hydrogen molecules of very high levels in order to dissociate methane. The population of these vibrationally excited species are generally very low\(^2\). Hassouni et al.\(^{172}\) had also conducted simulations of a moderate pressure and moderate temperature hydrogen/methane plasma discharge, where the influence of vibrationally excited hydrogen on methane chemistry was not taken into account using the same arguments. The vibrational excitation reactions were only considered during the solution of the Boltzmann equation for the EEDF and were not taken into account separately in order to limit the number of species in the model. Following Herrebout et al.\(^{69}\) electronic excitation reactions were not included in the model, since all the electronically excited reactions ultimately lead to dissociation of the molecule. The chemical kinetics model included the dissociation pathways. Rotational excitation reactions were not considered since their cross section data are very
difficult to find. Moreover compared to vibrational excitations much less energy of the electrons is required for the rotational excitation \(^2\). This justifies not including the different rotational excitation reactions in the model. At atmospheric pressure volume recombination is dominant. Therefore electron-ion reactions involving volume recombination were taken into account.

Table 7.2: Gas phase reaction mechanism considered in the modeling.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction No</th>
<th>Reaction</th>
<th>Reaction Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>G2</td>
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<td>G3</td>
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<td>173</td>
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<td>174</td>
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<td>G7</td>
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<td>Equation</td>
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<td>$\text{C}_2\text{H}_4 + e \rightarrow \text{C}_2\text{H}_2 + 2\text{H} + e$</td>
<td>E 174</td>
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<td>G25</td>
<td>$\text{CH}_4 + e \rightarrow \text{CH}_4^+ + 2e$</td>
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<td>G31</td>
<td>$\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$</td>
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<td>G32</td>
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<td>$\text{CH}_5^+ + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5^+ + \text{CH}_4 + \text{H}_2$</td>
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<td>G34</td>
<td>$\text{H}_3^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{H}_2$</td>
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<td>$\text{H}_3^+ + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5^+ + 2\text{H}_2$</td>
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<td>G36</td>
<td>$\text{H}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + 2\text{H}_2$</td>
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<td>G37</td>
<td>$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$</td>
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<tr>
<td>G38</td>
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<td>$\text{C}_2\text{H}_5 + \text{H} \rightarrow 2\text{CH}_3$</td>
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<td>G45</td>
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<td>G48</td>
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<td>G49</td>
<td>$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}$</td>
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<td>G50</td>
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<td>G51</td>
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<td>G52</td>
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<td>G53</td>
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<tr>
<td>G54</td>
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<tr>
<td>G55</td>
<td>CH + CH₂ → C₂H₂ + H</td>
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<td>166</td>
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<td>G56</td>
<td>CH + CH₃ → C₂H₃ + H</td>
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<td>G57</td>
<td>C + CH₃ → C₂H₂ + H</td>
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<td>C₂H₆ + CH₃ → C₂H₅ + CH₄</td>
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<td>G59</td>
<td>C₂H₆ + H → C₂H₅ + H</td>
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<td>G60</td>
<td>C₂H₄ + H → C₂H₃ + H₂</td>
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<td>G61</td>
<td>C₂H₄ + H₂ + H → C₂H₅ + H₂</td>
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<tr>
<td>G62</td>
<td>C₂H₅ + H₂ + H → C₂H₅ + H₂</td>
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<td>G63</td>
<td>C₂H₅ + H → C₂H₄ + H₂</td>
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<td>G64</td>
<td>C₂H₅ + CH₂ → C₂H₄ + CH₃</td>
<td>A</td>
<td>167</td>
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<tr>
<td>G65</td>
<td>C₂H₅ + CH → C₂H₄ + CH₂</td>
<td>A</td>
<td>167</td>
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<tr>
<td>G66</td>
<td>CH₂ + CH₂ → C₂H₂ + H₂</td>
<td>A</td>
<td>167</td>
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<tr>
<td>G67</td>
<td>C₂H₄ + H₂ → C₂H₃ + 2H₂</td>
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<tr>
<td>G68</td>
<td>C₂H₄ + H₂ → C₂H₃ + H + H₂</td>
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<td>167</td>
<td></td>
</tr>
<tr>
<td>G69</td>
<td>C₂H₄ → Soot + H₂ *</td>
<td>A</td>
<td>183</td>
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</tbody>
</table>

**Hydrogen Reactions**

**Electron-neutral**

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction Equation</th>
<th>Reaction Rate Form</th>
<th>Arrhenius Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>G70</td>
<td>H₂ + e → H₂ (v = 1) + e</td>
<td>E</td>
<td>184</td>
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<td>G71</td>
<td>H₂ + e → H₂ (v = 2) + e</td>
<td>E</td>
<td>184</td>
</tr>
<tr>
<td>G72</td>
<td>H₂ + e → H₂ (v = 3) + e</td>
<td>E</td>
<td>184</td>
</tr>
<tr>
<td>G73</td>
<td>H₂ + e → H₂ + e</td>
<td>E</td>
<td>175</td>
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<tr>
<td>G74</td>
<td>H + e → H + e</td>
<td>E</td>
<td>175</td>
</tr>
<tr>
<td>G75</td>
<td>H₂ + e → 2H + e</td>
<td>E</td>
<td>145</td>
</tr>
<tr>
<td>G76</td>
<td>H₂ + e → H₂⁺ + 2e</td>
<td>E</td>
<td>145</td>
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**Ion-neutral**

<table>
<thead>
<tr>
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<th>Reaction Equation</th>
<th>Reaction Rate Form</th>
<th>Arrhenius Constant</th>
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</thead>
<tbody>
<tr>
<td>G77</td>
<td>H₂⁺ + H₂ → H₃⁺ + H</td>
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<td>138</td>
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**Electron-ion**

<table>
<thead>
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<tbody>
<tr>
<td>G78</td>
<td>H₃⁺ + e → H₂ + H</td>
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<tr>
<td>G79</td>
<td>H₂⁺ + e → 2H</td>
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**Neutral-neutral**

<table>
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<th>Reaction Rate Form</th>
<th>Arrhenius Constant</th>
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<tbody>
<tr>
<td>G80</td>
<td>2H + H₂ → 2H₂</td>
<td>A</td>
<td>150</td>
</tr>
<tr>
<td>G81</td>
<td>H + H + H → H₂ + H</td>
<td>A</td>
<td>151</td>
</tr>
</tbody>
</table>

A: reaction rate in Arrhenius form
E: reaction rate dependent on EEDF
* Soot represents 2Cₛ, where Cₛ is the carbon atoms in soot
In the model, seven ion-neutral and thirty five neutral-neutral reactions were included to get insight into the temperature dependent heavy particle reactions on the plasma characteristics. The neutral-neutral reactions also included a simple soot formation reaction (G69, Table 7.2). The soot formation model from acetylene proposed by Kronenburg et al. 185 and Leung et al. 186 was employed. The one-step soot formation mechanism is expressed as $\text{C}_2\text{H}_2 \rightarrow \text{Soot} + \text{H}_2$, where soot represents $2\text{C}_s$ where $\text{C}_s$ represents carbon atoms in soot. This reaction step is essentially a nucleation mechanism of the soot precursor $\text{C}_s$ and treats it as a chemical species in the gaseous form 185. The rate of soot deposition in the film is addressed via a simple surface reaction. Including a detailed soot formation mechanism is perceived as a future extension of the present work.

7.2.2.2 Surface Chemistry and Deposition Model

An eighty four step reaction mechanism consisting of fifteen surface and three deposited bulk species were considered for the surface chemistry model. The complete set of the surface reactions is summarized in Table 7.3. The bulk deposited species included diamond like carbon, graphitic carbon and soot. These three bulk species provided an understanding about the quality of the film. The surface processes consisted of physisorption, chemisorption, desorption, ion induced stitching, radical-adsorbed layer reaction, neutral-adsorbed layer reaction, sputtering and etching. In addition a one step soot deposition surface reaction was also introduced (S59, Table 7.3). Soot deposition on the surface starts to occur due to their volumetric production in the plasma. A sticking coefficient of unity was used for the soot deposition reactions, assuming all the soot produced in the volume is deposited on the surface. The film deposition in the model, took place by direct ion induced stitching of adsorbed neutrals, radical-adsorbed layer reactions...
and neutral-adsorbed layer reaction, while film removal was performed by etching and sputtering. Details of the surface reaction chemistry have been presented in published works \cite{163, 167, 187}. The rates for the different surface reactions were also obtained from the literature \cite{163, 167, 187}.

Table 7.3: Surface chemistry for the deposition model.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction No</th>
<th>Reaction</th>
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<tbody>
<tr>
<td>Adsorption</td>
<td>S1</td>
<td>CH → CH(_{(s)})</td>
<td>\cite{187}</td>
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<tr>
<td></td>
<td>S2</td>
<td>CH(_2) → CH(_2)(s)</td>
<td>\cite{163}</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>CH(_3) → CH(_3)(s)</td>
<td>\cite{163}</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>C(_2)H(_5) → C(_2)H(_5)(s)</td>
<td>\cite{187}</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>H → H(_{(s)})</td>
<td>\cite{163}</td>
</tr>
<tr>
<td>Desorption</td>
<td>S6</td>
<td>CH(_{(s)}) → CH</td>
<td>\cite{187}</td>
</tr>
<tr>
<td></td>
<td>S7</td>
<td>CH(_2)(s) → CH(_2)</td>
<td>\cite{163}</td>
</tr>
<tr>
<td></td>
<td>S8</td>
<td>CH(_3)(s) → CH(_3)</td>
<td>\cite{163}</td>
</tr>
<tr>
<td></td>
<td>S9</td>
<td>C(_2)H(_5)(s) → C(_2)H(_5)</td>
<td>\cite{187}</td>
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<tr>
<td></td>
<td>S10</td>
<td>H(_{(s)}) → H</td>
<td>\cite{163}</td>
</tr>
<tr>
<td>Adsorbed layer termination</td>
<td>S11</td>
<td>CH(_3)(s) + H → CH(_4)</td>
<td>\cite{187}</td>
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<tr>
<td></td>
<td>S12</td>
<td>C(_2)H(_5)(s) + H → C(_2)H(_6)</td>
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<tr>
<td></td>
<td>S13</td>
<td>CH(_3) + CH(_3)(s) → C(_2)H(_6)</td>
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<tr>
<td></td>
<td>S14</td>
<td>H + H(_{(s)}) → H(_2)</td>
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<td>S15</td>
<td>C + H(<em>{(s)}) → CH(</em>{(b,D)})</td>
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<tr>
<td>Sputtering</td>
<td>S16</td>
<td>CH(<em>3)(^+) + CH(</em>{(b,D)}) → C(_2)H(_4)</td>
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<tr>
<td></td>
<td>S17</td>
<td>CH(<em>4)(^+) + CH(</em>{(b,D)}) → C(_2)H(_5)</td>
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<tr>
<td></td>
<td>S18</td>
<td>CH(<em>5)(^+) + CH(</em>{(b,D)}) → CH(_5)(^+) + CH</td>
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<td>S19</td>
<td>C(_2)H(<em>5)(^+) + CH(</em>{(b,D)}) → C(_2)H(_5)(^+) + CH</td>
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<td>S20</td>
<td>C(_2)H(<em>4)(^+) + CH(</em>{(b,D)}) → C(_2)H(_2) + CH(_3)</td>
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<td>S21</td>
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<td>S22</td>
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140
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<td>$\text{H}<em>3^+ + \text{CH}</em>{(b,D)} \rightarrow \text{H}_3^+ + \text{CH}$</td>
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<td>$\text{CH}<em>3^+ + \text{H}</em>{(s)} \rightarrow \text{CH}_3^+ + \text{H}$</td>
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<td>S25</td>
<td>$\text{CH}<em>4^+ + \text{H}</em>{(s)} \rightarrow \text{CH}_4^+ + \text{H}$</td>
</tr>
<tr>
<td>S26</td>
<td>$\text{CH}<em>5^+ + \text{H}</em>{(s)} \rightarrow \text{CH}<em>5^+ + \text{H}</em>{(s)}$</td>
</tr>
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<td>S27</td>
<td>$\text{C}_2\text{H}<em>5^+ + \text{H}</em>{(s)} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$</td>
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<tr>
<td>S28</td>
<td>$\text{C}_2\text{H}<em>4^+ + \text{H}</em>{(s)} \rightarrow \text{C}_2\text{H}_4^+ + \text{H}$</td>
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<td>S29</td>
<td>$\text{C}_2\text{H}<em>2^+ + \text{H}</em>{(s)} \rightarrow \text{C}_2\text{H}_2 + \text{H}$</td>
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<td>S30</td>
<td>$\text{H}<em>2^+ + \text{H}</em>{(s)} \rightarrow \text{H}_2^+ + \text{H}$</td>
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<td>S31</td>
<td>$\text{H}<em>3^+ + \text{H}</em>{(s)} \rightarrow 2\text{H}_2$</td>
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<td>S32</td>
<td>$\text{CH}<em>3^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_3^+ + \text{H}$</td>
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<td>$\text{CH}<em>4^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_3^+ + \text{H}$</td>
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<td>S34</td>
<td>$\text{CH}<em>5^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_5^+ + \text{H}$</td>
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<td>S35</td>
<td>$\text{C}_2\text{H}<em>5^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_4^+ + \text{H}_2$</td>
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<td>S37</td>
<td>$\text{C}_2\text{H}<em>2^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_2^+ + \text{H}$</td>
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<tr>
<td>S38</td>
<td>$\text{H}<em>2^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{H}_2^+ + \text{H}$</td>
</tr>
<tr>
<td>S39</td>
<td>$\text{H}<em>3^+ + \text{CH}<em>2</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{H}_3^+ + \text{H}$</td>
</tr>
<tr>
<td>S40</td>
<td>$\text{CH}<em>3^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_3^+ + \text{H}_2$</td>
</tr>
<tr>
<td>S41</td>
<td>$\text{CH}<em>4^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_4^+ + \text{H}_2$</td>
</tr>
<tr>
<td>S42</td>
<td>$\text{CH}<em>5^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{CH}_5^+ + \text{H}_2$</td>
</tr>
<tr>
<td>S43</td>
<td>$\text{C}_2\text{H}<em>5^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_5^+ + \text{H}_2$</td>
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<td>S44</td>
<td>$\text{C}_2\text{H}<em>4^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_4^+ + \text{H}_2$</td>
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<tr>
<td>S45</td>
<td>$\text{C}_2\text{H}<em>2^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_2^+ + \text{H}_2$</td>
</tr>
<tr>
<td>S46</td>
<td>$\text{H}<em>2^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{H}_2^+ + \text{H}_2$</td>
</tr>
<tr>
<td>S47</td>
<td>$\text{H}<em>3^+ + \text{CH}<em>3</em>{(s)} \rightarrow \text{CH}</em>{(b,D)}^+ + \text{H}_3^+ + \text{H}_2$</td>
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<tr>
<td>S48</td>
<td>$\text{CH}_3^+ + \text{C}<em>2\text{H}<em>5</em>{(s)} \rightarrow 2\text{CH}</em>{(b,D)}^+ + \text{CH}_3^+ + \text{H}_2 + \text{H}$</td>
</tr>
<tr>
<td>S49</td>
<td>$\text{CH}_4^+ + \text{C}<em>2\text{H}<em>5</em>{(s)} \rightarrow 2\text{CH}</em>{(b,D)}^+ + \text{CH}_4^+ + \text{H}_2 + \text{H}$</td>
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<tr>
<td>S50</td>
<td>$\text{CH}_5^+ + \text{C}<em>2\text{H}<em>5</em>{(s)} \rightarrow 2\text{CH}</em>{(b,D)}^+ + \text{CH}_5^+ + \text{H}_2 + \text{H}$</td>
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<tr>
<td>S51</td>
<td>$\text{C}_2\text{H}_5^+ + \text{C}<em>2\text{H}<em>5</em>{(s)} \rightarrow 2\text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_4^+ + \text{2H}_2$</td>
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<tr>
<td>S52</td>
<td>$\text{C}_2\text{H}_4^+ + \text{C}<em>2\text{H}<em>5</em>{(s)} \rightarrow 2\text{CH}</em>{(b,D)}^+ + \text{C}_2\text{H}_4^+ + \text{H}_2 + \text{H}$</td>
</tr>
<tr>
<td>Step</td>
<td>Reaction</td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>S55</td>
<td>( \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}<em>5(\text{s}) \rightarrow 2\text{CH}</em>{(b,D)} + \text{C}_2\text{H}_2^+ + \text{H}_2 + \text{H} )</td>
</tr>
<tr>
<td>S56</td>
<td>( \text{H}_2^+ + \text{C}_2\text{H}<em>5(\text{s}) \rightarrow 2\text{CH}</em>{(b,D)} + \text{H}_2^+ + \text{H}_2 + \text{H} )</td>
</tr>
<tr>
<td>S57</td>
<td>( \text{H}_3^+ + \text{C}_2\text{H}<em>5(\text{s}) \rightarrow 2\text{CH}</em>{(b,D)} + \text{H}_3^+ + \text{H}_2 + \text{H} )</td>
</tr>
<tr>
<td>S58</td>
<td>( \text{CH}_{(b,D)} + 3\text{H} \rightarrow \text{CH}_4 )</td>
</tr>
<tr>
<td>S59</td>
<td>( \text{Soot} \rightarrow \text{Soot}_{(b)} )</td>
</tr>
</tbody>
</table>

**_radical/neutral adsorbed layer reaction**

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td>( \text{CH}(\text{s}) + \text{H} \rightarrow \text{C}_{(s,R)} + \text{H}_2 )</td>
</tr>
<tr>
<td>Radical recombination</td>
<td>( \text{C}<em>{(s,R)} + \text{H} \rightarrow \text{CH}</em>{(s)} )</td>
</tr>
<tr>
<td>Methyl radical addition</td>
<td>( \text{C}_{(s,R)} + \text{CH}<em>3 \rightarrow \text{C}</em>{(b,D)} + \text{CH}_3(\text{s}) )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{2(s)} + \text{H} \rightarrow \text{CH}</em>{(s,R)} + \text{H}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{3(s)} + \text{H} \rightarrow \text{CH}</em>{2(s,R)} + \text{H}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{2(s,R)} + \text{CH}</em>{(s,R)} \rightarrow \text{CH}<em>{2(s)} + \text{CH}</em>{(s,R)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{2(s)} + \text{CH}</em>{(s,R)} \rightarrow \text{CH}<em>2^* + \text{CH}</em>{(s,R)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>2^* + \text{CH}</em>{(s,R)} + \text{H} \rightarrow 2\text{CH}_{(s)} + \text{H}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}<em>{(s,R)} + \text{C} \rightarrow \text{C}</em>{(b,D)} + \text{C}_{(s,R)} )</td>
</tr>
<tr>
<td>Carbon atom addition</td>
<td>( \text{C}<em>{(s,R)} + \text{CH}</em>{2(s)} \rightarrow \text{CH}<em>{(s,R)} + \text{CH}</em>{(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{(s,R)} + \text{H} \rightarrow \text{CH}</em>{2(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_{(s,R)} + \text{H}<em>2 \rightarrow \text{CH}</em>{2(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}<em>{(s,R)} + \text{H} \rightarrow \text{CH}</em>{(s,R)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{(s,R)} + \text{H} \rightarrow \text{CH}</em>{3(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_{(s,R)} + \text{H}<em>2 \rightarrow \text{CH}</em>{3(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{(s,R)} + \text{CH}<em>3 \rightarrow \text{CH}</em>{4} + \text{C}</em>{(b,D)} + \text{C}_{(s,R)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}<em>{(s,R)} + \text{H} \rightarrow \text{C}</em>{(s,R)} + \text{H}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_{(s,R)} + \text{H}<em>2 \rightarrow \text{CH}</em>{(s,R)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}<em>{(s,R)} + \text{H} \rightarrow \text{CH}</em>{3(s)} )</td>
</tr>
<tr>
<td></td>
<td>( \text{C}<em>{(s,R)} + \text{C} \rightarrow \text{C}</em>{(b,G)} + \text{C}_{(s,R)} )</td>
</tr>
</tbody>
</table>

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\[ \text{S84: } C_{(s,R,G)} + C_2H_2 \rightarrow C_{(b,G)} + C_2H_2(s,R) \]

\( s: \) surface species  
\( b: \) deposited bulk species  
\( D: \) diamond like carbon  
\( G: \) graphitic carbon  
\( Rx: \) surface species with ‘x’ dangling bonds (x = 1 – 3)

### 7.3 Boundary Conditions

Flux boundary conditions are provided for the electrons at the electrodes. The electron flux to the electrode is given by the sum of thermal flux minus the rate of secondary electron release due to ion bombardment. The expression is as follows:

\[
\tilde{\Gamma}_e = \frac{1}{4} n_e u_{th} - \gamma \sum_i q_i \tilde{\Gamma}_i 
\]  

(7.1)

where, \( \gamma \) is the secondary electron emission coefficient and \( u_{th} \) is the electron thermal velocity. A secondary electron emission coefficient of 0.1 was set for our calculations.

The boundary condition for the electron energy \( T_e \) is expressed as:

\[
2T_e \tilde{\Gamma}_e = \frac{5}{2} T_e \tilde{\Gamma}_e - \frac{5}{2} n_e D_e \nabla T_e 
\]  

(7.2)

where, \( n_e \) is the electron number density and \( D_e \) is the electron diffusion coefficient.

For the boundary conditions of different ions, radicals and neutrals a surface chemistry model is implemented (Table 7.3). Details of the surface chemistry have been discussed in the previous section. For species not participating in the surface chemistry a thermal flux boundary condition is implemented. The electrode surfaces are set to be isothermal walls with room
temperature 300 K for solving the gas mixture temperature. No slip boundary condition was maintained at the electrodes to solve the fluid averaged velocity.

### 7.4 Simulation of Methane-Hydrogen Micro Glow Discharges

#### 7.4.1 Discharge Characteristics

Table 7.4: Fixed, variable parameters and resulting discharge current for the atmospheric pressure methane-hydrogen micro discharge simulations.

<table>
<thead>
<tr>
<th>Case</th>
<th>Supply voltage ($V_{pwr}$) (V)</th>
<th>Parasite capacitance ($C$) (pF)</th>
<th>Ballast resistance ($R$) (kΩ)</th>
<th>Methane mass fraction (%)</th>
<th>Discharge current ($I_d$) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>1.0</td>
<td></td>
<td></td>
<td>4.70</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>1.0</td>
<td></td>
<td></td>
<td>2.37</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>1.0</td>
<td></td>
<td></td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>1.0</td>
<td></td>
<td></td>
<td>1.19</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>1.0</td>
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<td></td>
<td>0.96</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>0.1</td>
<td></td>
<td></td>
<td>0.80</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td></td>
<td></td>
<td>0.1</td>
<td>4.69</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td></td>
<td></td>
<td>0.5</td>
<td>4.69</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td></td>
<td></td>
<td>2.0</td>
<td>4.70</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td></td>
<td></td>
<td>5.0</td>
<td>4.71</td>
</tr>
</tbody>
</table>

A total of 10 cases were simulated for an atmospheric pressure methane-hydrogen micro discharge. The 10 cases simulated were for a varying ballast resistance and methane-hydrogen mass fraction. For all the cases the supply voltage and the parasitic capacitance were kept constant. Details of the simulation parameters are listed in Table 7.4. The ballast resistance and methane-hydrogen mass fraction were varied in order to study the effect of the discharge current and the methane concentration on the discharge characteristics and the film deposition.
Figure 7.2: Voltage-current characteristics of the atmospheric pressure methane-hydrogen micro discharge (cases 1 – 6).

The voltage-current (V-I) profile resulting from the varying ballast resistance cases (Cases 1 – 6) is shown in Figure 7.2. The discharge voltage is found to increase almost linearly with an increase in the discharge current. The discharge voltage increases from 241 V at 0.80 mA to 260 V at 4.70 mA, having low positive differential impedance. This indicates the discharge to operate in the ‘abnormal’ glow mode. Since one dimensional simulations were conducted the size of the electrode was limited, and therefore with an increase in the discharge voltage the discharge current was found to increase. The increase in the discharge current occurs with an increase in the current density, which is the characteristic of ‘abnormal’ glow discharge. Plot of discharge current as a function of time for case 1 is shown in Figure 7.3. A very sharp increase of the discharge current is observed during the initial stage which indicates the breakdown stage. Breakdown is found to occur at ~ 0.005 microseconds; the location of the
discharge current spike. The discharge current then decreases and reaches a quasi-steady state once a stable glow discharge is formed. This discharge current evolution is similar to that observed experimentally by Staack et al.\textsuperscript{22}. All the discharge current and voltages obtained from simulations corresponds to values when a quasi-steady state has been reached.

Figure 7.3: Discharge current as a function of time (case 1). Breakdown occurs at ~ 0.005 microseconds.

Figure 7.4 (a) and (b) illustrates the calculated densities of the hydrogen and hydrocarbon ionic species along the axial distance (case 1). It can be seen that H\textsubscript{3}\textsuperscript{+} is the dominant hydrogen ion and it has the maximum value of 5.5 x 10\textsuperscript{19} m\textsuperscript{-3} in the volume of the discharge. The H\textsubscript{2}\textsuperscript{+} ion was found to be one order of magnitude smaller than the H\textsubscript{3}\textsuperscript{+} ions. The decrease in H\textsubscript{3}\textsuperscript{+} density near the cathode is due to the increased H\textsubscript{2}\textsuperscript{+} density in that location. The H\textsubscript{2}\textsuperscript{+} ion had the maximum value at the cathode sheath due to the peak electron temperature in that region (Figure 7.7 (a)). The peak electron temperature results in the formation of H\textsubscript{2}\textsuperscript{+} ions through electron impact ionization (reaction G76). Similarly due to a higher electron temperature in the anode
sheath region (Figure 7.7 (a)) a smaller peak in the \( \text{H}_2^+ \) ions was observed there as well. The decrease of \( \text{H}_2^+ \) ions in the volume of the discharge is due to the formation of \( \text{H}_3^+ \) ions through the ion-neutral collision of \( \text{H}_2^+ \) with hydrogen molecules (reaction G77). Both the \( \text{H}_3^+ \) and \( \text{H}_2^+ \) ions are found to decrease at the electrode surfaces due to there participation in different surface reactions (Table 7.3).

Of the different hydro-carbon ions (Figure 7.4 (b)), \( \text{CH}_5^+ \) was found to be the dominant ion with a peak density of \( 3.9 \times 10^{19} \text{ m}^{-3} \). The \( \text{CH}_5^+ \) number density distribution indicate volumetric production of \( \text{CH}_5^+ \) in the discharge with the peak being in between the cathode sheath and the bulk plasma volume. Comparing to the \( \text{H}_3^+ \) ions, the \( \text{CH}_5^+ \) ions were found to be smaller by a factor of 1.4. The second dominant hydro-carbon ion was \( \text{C}_2\text{H}_5^+ \) having a peak value of \( 7.9 \times 10^{17} \text{ m}^{-3} \). This is smaller by two orders of magnitude than the peak density of \( \text{CH}_5^+ \). \( \text{CH}_3^+ \), \( \text{CH}_4^+ \), \( \text{C}_2\text{H}_4^+ \) and \( \text{C}_2\text{H}_2^+ \) had similar density profiles, with the peak density existing in between the cathode sheath and the bulk plasma. The peak \( \text{CH}_3^+ \) and \( \text{CH}_4^+ \) density predicted was \( 1.3 \times 10^{17} \text{ m}^{-3} \) and \( 4.5 \times 10^{17} \text{ m}^{-3} \) respectively. The threshold energy for dissociative ionization of methane molecule (Table 7.1, G26) forming \( \text{CH}_3^+ \) is 14.3 eV \(^{173}\). On the other hand the formation of \( \text{CH}_4^+ \) through direct impact ionization (Table 7.1, G25) is 12.6 eV \(^{173}\). This results in the lower density of \( \text{CH}_3^+ \) ions. Moreover both \( \text{CH}_3^+ \) and \( \text{CH}_4^+ \) are consumed to produce \( \text{C}_2\text{H}_5^+ \) and \( \text{CH}_5^+ \) respectively, resulting in lowering their number density. Being three orders of magnitude smaller than \( \text{CH}_5^+ \) the \( \text{C}_2\text{H}_4^+ \) ion was found to have the smallest number density to the fact that \( \text{C}_2\text{H}_4 \) was of low density in the discharge (Figure 7.5 (b)).
Figure 7.4: Species density along the axial distance a) hydrogen ionic species ($H_2^+$ and $H_3^+$) and b) hydrocarbon ionic species ($CH_3^+$, $CH_4^+$, $CH_5^+$, $C_2H_2^+$, $C_2H_4^+$ and $C_2H_5^+$). Ballast resistance $200 \, k\Omega$, $V_d = 260 \, V$ and $I_d = 4.70 \, mA$, $CH_4$ mass fraction = 1.0 % (case 1).

The distribution of the different radicals along the axial distance for the same case is shown in Figure 7.5 (a). Atomic H was found to be the dominant radical. A peak H density of $7 \times 10^{22} \, m^{-3}$ was observed in the cathode sheath region, resulting in a dissociation degree of 0.003. The high density of H observed would result in fast relaxation of vibrationally excited hydrogen.
molecules in atmospheric pressure micro discharges. This justifies the assumption of not taking into account vibrationally excited species in the plasma calculations. The radical density distribution indicates the abundance of CH₂ and CH₃, CH₂ and CH₃ being dominant in the volume and in the sheath respectively. The peak densities of these radicals were found to be on the order of $10^{21}$ m⁻³. Both CH₂ and CH₃ are key components for DLC deposition. CH and C₂H₅ were radicals with the lowest density. Their peak density was on the order of $10^{18}$ m⁻³ occurring in the cathode sheath region. Figure 7.5 (b) shows the neutral density distribution along the axial distance (case 1). It can be seen that even for 1 % methane mass fraction the higher order hydrocarbon molecules (C₂H₆, C₂H₄, C₂H₂, C₃H₈) are formed by neutral-neutral reactions (Table 7.1) in significant levels. The peak C₂H₂ and C₂H₄ predicted were on the order of $10^{21}$ m⁻³, smaller by a factor of 10 than that of the peak density of CH₄. The higher C₂H₂ density indicates the possibility of DLC formation through acetylene addition, which was identified to be a dominant mechanism by other researchers. C₂H₆ was observed to have a peak density of $1.0 \times 10^{19}$ m⁻³, in the cathode sheath. Of the different neutral species the heaviest hydrocarbon molecule C₃H₈ had the smallest abundance with a peak density of $1.1 \times 10^{17}$ m⁻³. As collision between C₂H₅ and CH₃ is the main mechanism for C₃H₈ formation, the low density of C₂H₅ in the discharge is responsible for the low density of C₃H₈.
Figure 7.5: Species density along the axial distance a) radical species (H, CH, CH₂, CH₃ and C₂H₅) and b) neutral species (H₂, CH₄, C₂H₂, C₂H₄, C₂H₆ and C₃H₈). Ballast resistance 200 kΩ, V_d = 260 V and I_d = 4.70 mA, CH₄ mass fraction = 1.0 % (case 1).
Figure 7.6: a) Electric field profile and b) electron and ion (H$_2^+$ + H$_3^+$ + CH$_3^+$ + CH$_4^+$ + CH$_5^+$ + C$_2$H$_2^+$ + C$_2$H$_4^+$ + C$_2$H$_5^+$) density distribution along the axial distance. Ballast resistance 200 kΩ, $V_d = 260$ V and $I_d = 4.70$ mA, CH$_4$ mass fraction = 1.0 % (case 1).

A plot of the electric field distribution along the axis of the discharge (case 1) is shown in Figure 7.6 (a). The electric field profile shows the maximum at the cathode having a peak value of $\sim 13200$ kV m$^{-1}$. The high electric field region indicates the edge of the cathode sheath. Within
a distance of 28 μm from the cathode the electric field decreases almost linearly to a very low value. An electric field of ~385 kV m⁻¹ was observed in the bulk of the plasma which is the positive column. A slight increase in the electric field was observed near the cathode, denoting the anode sheath. The electric field increased from ~ 385 to ~1500 kV m⁻¹ at the anode over a distance of 12 μm. The predicted electric field profile is consistent with that observed for glow discharges. The combined ions (H₂⁺ + H₃⁺ + CH₃⁺ + CH₄⁺ + CH₅⁺ + C₂H₂⁺ + C₂H₄⁺ + C₂H₅⁺) and the electron density profile along the axial distance are shown in Figure 7.6 (b) (case 1). As for the bulk, the plasma was found to be quasi neutral, which corresponds to the low electric field observed in the volume. The quasi neutrality did not hold true in the cathode and anode sheaths. In the cathode sheath the ion density was found to be significantly higher than the electron density; larger by two orders of magnitude. Creation of the cathode sheath occurs due to the multiplication of the cathode emitted electrons in the strong electric field near the cathode, leading to an increase in the ion density. On the other hand the electron density in the anode sheath was found to be higher by an order of magnitude than that of the ion density. The anode sheath results from the diffusion current of the electrons exceeding the drift current. At the anode the drift velocity of the electron is small due to the low electric field and the diffusion current dominates. The predicted ion and electron density profiles are consistent with that observed for glow discharges and are also similar to that reported by Shi and Kong.
Figure 7.7: Axial distribution of a) Electron temperature and b) Ion current density. Ballast resistance 200 kΩ, $V_d = 260$ V and $I_d = 4.70$ mA, CH₄ mass fraction = 1.0 % (case 1).

Figure 7.7 (a) illustrates the predicted electron temperature along the axial distance of the discharge (case 1). It can be seen that a peak electron temperature of about 10.60 eV occurs near the cathode surface (Figure 7.7 (a)). Joule heating being the main source, the peak electron temperature exists near the location of the maximum electric field (Figure 7.7 (a)). The electron
temperature was thereafter found to decrease to about 2.62 eV. The loss of the electron energy is
due to the collision of electrons with the background neutral molecules, resulting in the
formation of different ionic species (Figure 7.4 (a) and (b)). The space between the cathode and
the location of the minimum electron temperature is where the majority of the gas ionization
takes place. This coincides with the location where the peaks of the different ionic species are
observed (Figure 7.4 (a) and (b)). In the mid region of the discharge the electron temperature was
found to increase to about 2.85 eV. The increase in the electron temperature is due to the energy
gain from the electric field. Near the anode surface the electron temperature increased to about
3.20 eV due to presence of the relatively higher electric field in the anode sheath (Figure 7.6 (a)).
The ion current density distribution along the discharge axis for case 1 is presented in Figure 7.7
(b). The maximum ion current density was \( \sim 24 \, \text{A cm}^{-2} \) for the discharge current of 4.70 mA.

Spatial distribution of the neutral gas temperature along the discharge axis is presented in
Figure 7.8 (a). A peak neutral gas temperature of 1100 K was observed in the central region of
the discharge. At the electrode surfaces the gas temperature was 300 K due to the isothermal
boundary condition imposed. The isothermal electrode which is an idealized condition provides
cooling of the discharge. The contributions of the different source terms (heavy particle
reactions, Frank-Condon heating \(^{142}\) due to dissociation reactions, elastic collisions and ion Joule
heating) to the energy equation are shown in Figure 7.8 (b). The contribution of ion Joule heating
was found to be the dominant gas heating mechanism, which is similar to that observed by Wang
et al. \(^{169}\) and Kushner \(^{99}\) in their atmospheric pressure direct current micro plasma simulations.
The Joule heating peaked at the cathode where the ion current density and the electric field are
the maximum. The Frank-Condon effect was smaller by an order of magnitude than the Joule
heating. However apart from the cathode sheath it was more dominant in the volume of the
discharge. Heat release due to the heavy particle reaction was of the same order of magnitude as that of Frank-Condon heating. It was found to peak in the cathode sheath, where the maximum density of different ions and radicals exists. Heat release due to elastic collisions was found to have the smallest contribution to the neutral gas heating. Compared with the ion Joule heating it was two orders of magnitude lower.

Figure 7.8: Spatial distribution of the a) neutral gas temperature and b) energy source terms along the axial distance of the discharge. Ballast resistance 200 kΩ, \( V_d = 260 \) V and \( I_d = 4.70 \) mA, \( \text{CH}_4 \) mass fraction = 1.0 % (case 1).
Figure 7.9: Soot number density along the axial distance. Ballast resistance 200 kΩ, $V_d = 260$ V and $I_d = 4.70$ mA, CH$_4$ mass fraction = 1.0 % (case 1).

The gas phase chemistry used in the model took into account the formation of soot from C$_2$H$_2$. The reaction rate constant for the soot formation reaction $[C_2H_2 \rightarrow \text{Soot} + H_2, \; k_{\text{soot}} = 1.7 \times 10^{-7548/T_{\text{gas}}} \text{]}$ was taken from the literature. The reaction rate constant has a strong dependence on temperature. Therefore at higher gas temperature and C$_2$H$_2$ density, considerable amount of soot will be produced in the discharge. Figure 7.9 shows the soot number density profile along the axial distance for case 1. A peak soot density of $1.1 \times 10^{12}$ m$^{-3}$ was observed in the central region of the discharge. This existed near the region of maximum neutral gas temperature. The soot density decreased near the electrode surfaces due to the soot deposition surface reaction (Table 7.3, S59).
Figure 7.10: Spatial distribution of a) neutral gas temperature and b) soot number density as a function of discharge current (cases 1 – 6).

The neutral gas temperature profiles for different discharge currents are summarized in Figure 7.10 (a). It can be seen that with an increase in the discharge current there is a rise in the neutral gas temperature. Increase in the discharge current results in an increase in the ion current density at the cathode. Ion Joule heating being the key gas heating mechanism, the resulting
larger ion current density increases the neutral gas temperature significantly. With an increase in the discharge current from 0.80 mA to 4.70 mA, the peak neutral gas temperature increased from 455 K to 1100 K. The effect of discharge current on soot concentration is shown in Figure 7.10 (b). It is observed that with an increase in the gas temperature as a result of increasing discharge current, the soot concentration increases drastically in the discharge. For a discharge current range of 0.80 – 4.70 mA, the peak soot number density increases from $10^6$ to $10^{12}$ m$^{-3}$. A six order magnitude increase is observed for a 645 K increase in the gas temperature. This suggests that the discharge would be more “sooty” at higher power. The predictions indicate that in order to avoid the soot regime it is necessary to operate the micro discharge at lower power.
Figure 7.11: Peak number density of species as a function of discharge current a) ionic species, b) radical species and c) neutral species (cases 1 – 6).
We carried out six simulations in the discharge current range between 0.80 – 4.70 mA, while all the other plasma parameters were kept constant (case 1 – 6). The peak number densities of different ions, radicals and neutrals as function of discharge current are shown in Figure 7.11 (a), (b) and (c) respectively. From Figure 7.11 (a) it can be seen that peak number density of all the ionic species grow with increasing discharge current. Apart from H$_2^+$, C$_2$H$_5^+$, C$_2$H$_4^+$ and C$_2$H$_2^+$ all the other ionic species were found to be slightly increasing (no change in order of magnitude). Over the discharge current range H$_2^+$ increased from $2.3 \times 10^{17}$ m$^{-3}$ to $4.0 \times 10^{18}$ m$^{-3}$ an increase of an order of magnitude. Similar trends were observed for C$_2$H$_5^+$ which increased from $9.4 \times 10^{16}$ m$^{-3}$ to $8.0 \times 10^{18}$ m$^{-3}$. The peak C$_2$H$_4^+$ increased by an order of magnitude as well. As for C$_2$H$_2^+$ the peak density increased from $3.7 \times 10^{14}$ m$^{-3}$ to $1.2 \times 10^{17}$ m$^{-3}$, an increase of three orders of magnitude, which was the maximum among all the ions. The peak radical and neutral density had similar dependence on the discharge current as that of the peak ion density (Figure 7.11 (b) and (c)). Large rise in the peak density of C$_2$H$_3$ and soot were only observed. In the discharge current range the peak C$_2$H$_3$ and soot density increased by two and six orders of magnitude respectively. The increase in ion, radical and neutral density with an increase in the discharge current is due to the ‘abnormal’ glow operating mode of the discharge. In the ‘abnormal’ glow mode an increase in the discharge current is accompanied with an increase in the discharge voltage, which thereby increases the electric field in the discharge and hence the species density. Similar dependence were observed in low pressure methane-hydrogen discharges operating in the ‘abnormal’ glow mode$^{69}$. 
Figure 7.12: Peak number density of species as a function of methane mass fraction a) ionic species, b) radical species and c) neutral species (cases 1, 7, 8, 9 and 10).
To investigate the effect of the gas mixture, the methane mass fraction was varied from 0.1 % to 5.0 % (cases 7, 8, 1, 9 and 10) while the other parameters were kept constant. The hydrogen mass fraction was changed to maintain a 100 % total mass fraction. No external gas feeding mechanism was considered, the simulations were conducted by time marching for a given mass fraction of the hydrogen-methane mixture until a quasi-steady state was reached. The effect of gas mixture on the different peak ion, radicals and neutral densities are summarized in Figure 7.12 (a), (b) and (c) respectively. The H$_2^+$ and H$_3^+$ ion density decreased with an increase in the methane mass fraction. This is due to the decrease in the molecular hydrogen in the discharge. The hydrocarbon ions were found to increase with increasing methane fraction. However a sharp rise in the peak hydrocarbon ion density occurred in the 0.1 – 1.0 % methane fraction range which was followed by a steady increase in between 1.0 – 5.0 % methane fraction. The increase in the hydrocarbon density results due to the occurrence of increased methane chemical kinetics. In particular the CH$_5^+$ and C$_2$H$_5^+$ density rises as a result of the ion – neutral reactions (G31 – G36) increasing with increased methane mass fraction. As a consequence of the higher methane chemical kinetics similar increasing trends were observed for the radicals and neutrals (Figure 7.12 (b) and (c)). It can be seen in Figure 7.12 (c) that the peak soot number density increased by five orders of magnitude over the methane mass fraction range. The drastic rise in the soot density was due to the increase of C$_2$H$_2$ formation in the discharge.

7.4.2 Film Deposition and Characterization

The deposition rate of the different species (DLC, graphitic carbon and soot) at the cathode surface for case 1 is summarized in Figure 7.13. This would provide information regarding the quality of the deposited film. The deposition rate of DLC due to stitching reactions (Table 7.3, S32 – S57) and surface molecule/radical reactions (Table 7.3, S62, S66, S68 and
S71) were tracked separately to determine the contribution from these two different growth mechanisms. The DLC deposition rate due to stitching reaction was found to be the maximum. With a deposition rate of 0.115 micron min$^{-1}$ it comprised 72.69% of the total deposition rate. The deposition rate of DLC due to surface molecule/radical reaction was 0.043 micron min$^{-1}$, contributing 27.18% of the total deposition. The graphitic carbon and the soot had the minimum contribution to the film growth. The deposition rate for graphitic carbon and soot were found to be $2.10 \times 10^{-4}$ and $9.57 \times 10^{-7}$ micron min$^{-1}$. Even though they were of very low rates it indicated that the deposited film was not pristine DLC.

Figure 7.13: Deposition rate of diamond-like-carbon, graphitic carbon and soot. Ballast resistance $200 \, k\Omega$, $V_d = 260 \, V$ and $I_d = 4.70 \, mA$, CH$_4$ mass fraction = 1.0 % (case 1).
The effect of discharge current on the deposition rate of DLC, graphitic carbon and soot at the cathode surface is summarized in Figure 7.14 (a). For lower discharge current the deposited film is more diamond like. In that regime the graphitic and the soot deposition rates are six and 12 orders of magnitude lower than DLC. Even though DLC and graphitic carbon deposition rates do not increase significantly, the soot deposition rate increases drastically with...
an increase in the discharge current. In the discharge current range of 0.80 – 4.70 mA, the soot deposition rate increases from $6.2 \times 10^{-14}$ micron min$^{-1}$ to $9.6 \times 10^{-6}$ micron min$^{-1}$, an increase of seven orders of magnitude. The soot deposition rate increases due to the increase of the soot density in the volume (Figure 7.10 (b)). The deposition rate dependence on discharge current indicates a small window of operation for obtaining pristine DLC thin film deposition. Figure 7.14 (b) shows the DLC/soot ratio as a function of the total deposition rate (diamond like carbon + graphitic carbon + soot) over the discharge current range. It can be seen that for low deposition rate (low discharge current) the film quality is more diamond like. For a total deposition rate of $1.75 \times 10^{-2}$ micron min$^{-1}$ at 0.80 mA discharge current the DLC/soot ratio was $2.9 \times 10^{11}$, indicating a film with very little soot content. The DLC/soot ratio was observed to decrease drastically with increasing deposition rate (increasing discharge current). This results in a reduction of the film quality. A reduction of six orders of magnitude of the DLC/soot ratio occurred for a total deposition rate of $1.58 \times 10^{-1}$ micron min$^{-1}$ at 4.70 mA discharge current.
Figure 7.15: a) Deposition rates at the cathode surface as a function of methane mass fraction and b) DLC/soot ratio as a function of total deposition rate (cases 1, 7, 8, 9 and 10).

Figure 7.15 (a) shows the deposition rate of DLC, graphitic carbon and soot at the cathode surface for different methane mass fraction. For a methane mass fraction of 0.1% the DLC, graphitic carbon and soot depositions were predicted to be $1.1 \times 10^{-2}$ micron min$^{-1}$, $4.6 \times 10^{-5}$ micron min$^{-1}$ and $1.9 \times 10^{-10}$ micron min$^{-1}$. This indicates good quality deposition with very little graphitic carbon and negligible soot. With increasing methane mass fraction the deposition
starts losing its purity as more graphitic carbon and soot contributes to the film growth. Even though the graphitic carbon deposition rate does not increase significantly a drastic increase in the soot deposition rate is observed. The soot deposition rate increases from $1.9 \times 10^{-10}$ micron min$^{-1}$ at 0.1 % methane mass fraction to $5.2 \times 10^{-4}$ micron min$^{-1}$ at 5.0 % methane fraction, an increase of six orders of magnitude. For both DLC and graphitic carbon only an order of magnitude increase was seen. The increase in the methane mass fraction results in an increase in the different radicals, ions and neutrals which take part in the DLC and graphitic carbon mechanism, however the increase in the soot in the volume significantly larger compared to them (Figure 7.12 (c)). This resulted in the higher soot deposition rate. The DLC/soot ratio as function of the total deposition rate over the methane fraction range is shown in Figure 7.15 (b). The DLC/soot ratio was observed to reduce significantly over the range of the deposition rate. The DLC/soot ratio decreased from $4.9 \times 10^{7}$ to $7.2 \times 10^{2}$ over the deposition rate range, which corresponds to deposition rate with increasing methane fraction. This indicates that the quality of the film can be controlled by varying the methane fraction. However the quality of the film at low discharge current (Figure 7.14 (b)) is better than that at lower methane fraction.

7.5 Comparison with Experimental Measurements

7.5.1 Experimental Setup

A schematic diagram of the experimental setup is show in Figure 7.16. The discharge is enclosed in a sealed glass chamber. The discharge chamber has two valves to control the gas inflow and outflow. One of the electrodes is connected to a micro positioner (not shown in the Figure) for setting the inter electrode separation. Two Omega FMA 2600 flow controllers were used to maintain a constant feed gas composition. In addition the discharge chamber was
connected to a mass spectrometer for conducting mass spectrometry of the discharge. A Swagelok needle valve having a vernier handle connected the discharge chamber to the mass spectrometer. The needle valve is essential to maintain the flow rate to the mass spectrometer within the desirable range. In the experiments the needle valve was set to have a flow rate of 0.5 sccm. A HP 5970B quadrupole mass spectrometer was used for sampling the species created in the discharge volume. The experimental setup is similar to that of Stoffels et al. \(^{189}\) and Choi et al. \(^{190}\). The mass spectrometer is equipped with an internal electron source with constant electron energy of 70 eV.

![Diagram of Experimental Setup](image)

Figure 7.16: Schematic of the experimental setup.
7.5.2 **Mass Spectrometer Measurements**

Figure 7.17: Mass spectra a) without the plasma discharge and b) with the plasma discharge ($I_d = 3.8$ mA). For both cases the mass spectrometer ionization source was turned on and kept at 70 eV (Feed gas = 99% H$_2$ + 1% CH$_4$).
Ambient gas composition is determined from the mass spectra at 70 eV without the plasma discharge being turned on. For the experiments the inter electrode separation was set to 200 μm ± 5 μm and 99% H₂, 1% CH₄ mixture fraction (200 sccm of H₂, 2 sccm of CH₄) was used. The response of the different mass signals was monitored for varying discharge current. Figure 7.17 (a) and (b) shows the mass spectra with and without the plasma discharge. The most prominent peak is seen at 16 amu, which corresponds to CH₄. The peaks observed at 18 amu, 28 amu, 32 amu, 40 amu and 44 amu without the plasma discharge (Figure 7.17 (a)) correspond to H₂O, N₂, O₂, Ar and CO₂ respectively and is a result of small leakage of ambient air in the discharge chamber. With the plasma discharge it can be clearly seen that distinct peaks exist in the range of 24 – 50 amu which were not observed without the plasma discharge. The observed peaks suggest significant production of C₂Hₙ, C₃Hₙ and C₄Hₙ species in the discharge volume.

Following Dekempeneer et al. 161 and Herrebout et al. 69 we compare the measured conversion factor of CH₄ with that predicted from the simulations. The conversion factor (cf) is defined as \( cf = 1 - \frac{I}{I_o} \), where \( I \) and \( I_o \) are the CH₄ densities with and without the plasma discharge. For the experimental measurements \( I \) and \( I_o \) represent the intensity of methane with and without the plasma discharge 161. The conversion factor gives information about how many methane molecules have reacted, not only due to dissociation but also due to ionization and neutral-neutral reactions. Since volume averaged measurements of the CH₄ density was conducted, the predicted CH₄ density from the simulations were spatially averaged to conduct a one to one comparison. A comparison between the experimental and predicted values for the conversion factor as a function of discharge current is shown in Figure 7.18. It can be seen that in both the cases the conversion factor increased with increasing discharge current. The predicted
conversion factor increased from 35% to 72% in the discharge current range of 0.80 – 4.70 mA. Even though the general trends appears to be in satisfactory agreement, the simulations under predicted the conversion factor. The possible reason for the discrepancy could be the fixed 70 eV internal electron source of the mass spectrometer, which would result in increased dissociation of methane. In addition, even though very small amount of C₄Hₙ species were observed in the mass spectra (Figure 7.17 (b)), they were not taken into account in the model; this might also contribute to the observed discrepancy.

Figure 7.18: Comparison between the experimental and calculated methane conversion factor as a function of discharge current (99% H₂ and 1% CH₄ feed gas).

Since C₂H₂ was predicted to be the dominant neutral species, we compare the predicted C₂H₂ density with the mass spectrometer measurements. In order to conduct a one to one comparison the measured intensity of C₂H₂ was normalized by the CH₄ intensity, and the predicted C₂H₂ density was spatially averaged and normalized by the spatially averaged CH₄ density prediction. Figure 7.19 shows the measured and predicted C₂H₂ percentage as a function
of discharge current. Both the experimental measurements and numerical prediction show an increase in the C$_2$H$_2$ concentration with an increase in the discharge current. Even though the model under predicts the C$_2$H$_2$ concentration the general trends are in good agreement. The discrepancy could be a result of the fewer chemical pathways of C$_2$H$_2$ formation that was taken into account in the gas phase chemical kinetics.

![Graph showing C$_2$H$_2$ percentage as a function of discharge current](image)

Figure 7.19: Comparison between the measured and predicted C$_2$H$_2$ percentage as a function of discharge current (Feed gas = 99% H$_2$ + 1% CH$_4$).

### 7.6 Conclusions

This chapter presents a numerical study of an atmospheric pressure methane hydrogen micro discharge and the associated deposition characteristics. The spatial distribution of the species densities, electron and neutral gas temperature in these micro discharges were predicted and at the same time we identified the influence of the different plasma parameters on the deposition characteristics. A one dimensional hybrid model together with an external circuit was developed. The model included detailed volume (23 species, 81 reaction steps) and surface (18
species, 84 reaction steps) chemistry to predict the species distribution in the volume and the
growth rate of the deposited film. Sixteen vibrational excitation reactions were taken into
account with different background neutrals, in order to obtain a more accurate EEDF.

Simulations were conducted for a parallel plate electrode geometry with an inter
electrode separation of 200 μm. The V-I characteristics obtained from the simulations showed an
increase in the discharge voltage with an increase in the discharge current, indicating the
discharge to operate in the ‘abnormal’ glow mode. The micro discharge was found to be quasi
neutral in the bulk of the plasma region, apart from the sheaths formed at the electrodes. The
cathode and anode sheaths were identified from the electric field and the electron and ion density
profiles. Distinct cathode and anode sheaths were observed, with the cathode having a larger
sheath than the anode. Compared to low pressure glow discharges where H₂⁺ and CH₅⁺ are the
dominant ions ⁶⁹, heavier ionic species H₃⁺, C₂H₅⁺ and CH₅⁺ were found to be the dominant
hydrogen and hydrocarbon ions in the present simulation; considerable amounts of CH₃⁺ and
CH₄⁺ were also found to be present. In the present simulations, H, CH₂ and CH₃ were found to
be the prominent radicals, while CH₂ and CH₃ are also the key components for DLC deposition.
Substantial amounts of CH and C₂H₅ radicals were found to be present in the atmospheric
pressure micro discharges which are minor products in low pressure macro discharges ⁶⁹, ¹⁶².
Apart from CH₄ the higher order neutral hydrocarbons (C₂H₆, C₂H₄, C₂H₂ and C₃H₈) were found
to be present in abundance, which is not the case for low pressure macroplasmas ⁶³. C₂H₂ had the
maximum density among the neutral hydrocarbons, which is a growth species for DLC
deposition as well. Significant gas heating was observed with the peak gas temperature existing
near the cathode surface. Joule heating was identified to be the dominant gas heating in the

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sheath, whereas Frank-Condon heating and heating due to heavy particle reactions were dominant in the volume.

The ballast resistance of the external circuit and the methane mass fraction was varied to study the effect of discharge current and gas mixture on the plasma characteristics and hence on the deposition. An increase in the gas temperature was observed for an increase in the discharge current because of the ion Joule heating. The gas temperature had significant affect on soot formation and deposition. The model predicted the discharge current to be a key factor to obtain pristine DLC deposition. Even though high power is desirable to raise the deposition rate, it significantly increases the soot deposition rate and hampers the film quality. The methane mass fraction had similar influence. It was found that increasing the methane mass fraction increased the formation of C$_2$H$_2$ in the discharge which resulted in higher soot content in the volume and hence a more sooty deposit. The moderately high temperature and soot formation observed in dc atmospheric pressure micro plasma discharges is not seen in low pressure macro plasmas 69, 160-162, 191.

Mass spectrometry experiments were conducted to measure the conversion factor of CH$_4$ and the C$_2$H$_2$ in the discharge and compare with the numerical predictions. The measured conversion factor showed an increase with an increase in the discharge current, which suggests that more methane under went dissociation, ionization and neutral-neutral reactions at higher discharge current. A similar trend was also observed for the C$_2$H$_2$ density. The general trends of the predicted conversion factor and the C$_2$H$_2$ density agreed satisfactorily with the experimental measurements.
8 TWO DIMENSIONAL SIMULATIONS OF METHANE-HYDROGEN MICRO PLASMA DISCHARGE FOR THIN FILM DEPOSITION

8.1 Introduction

In this chapter we report results from two dimensional axisymmetric simulations of atmospheric pressure methane-hydrogen micro plasma discharge. The simulations were conducted for a pin to plate electrode configuration having a 50 μm anode diameter, 1000 μm cathode diameter and a 400 μm inter-electrode separation. For the simulations a time stepping technique was employed to take into account the different time steps associated with the plasma and fluid transport. Basic plasma properties such as electron and species density, electric field, electron temperature and gas temperature were studied. Special attention was devoted on the deposition characteristics and the effect of discharge current on the spatial profile of the deposition rate.

8.2 Schematic of the Problem Geometry

Figure 8.1 (a) depicts the computational domain for the simulation of atmospheric pressure micro glow discharge in methane-hydrogen for a pin to plate electrode configuration (metal wire tip and a planar metal surface). The inter-electrode separation is set to 400 μm. A cathode radius of 500 μm was chosen so that zero-gradient boundary conditions could be applied along the boundary c-d. The electrodes are coupled to an external circuit. The external circuit contains a resistance $R$ and a capacitance $C$ connected in series and in parallel respectively (Figure 8.1 (b)). The ballast resistance $R$ is required in order to limit the discharge current, preventing the discharge from reaching an ‘abnormal’ (high current) mode. The capacitance $C$ represents the parasitic capacitance which is present in the experiments intrinsically due to the
external cables. The power supply voltage $V_{pwr}$ is fixed at 2400 V, so that it is larger than the required breakdown voltage for an atmospheric pressure pure hydrogen discharge. The capacitance $C$ is fixed at 0.1 pF, corresponding to the estimated value of the experimental setup. In order to obtain different discharge currents the ballast resistance is varied from 2000 kΩ to 500 kΩ.

![Schematic](image.png)

**Figure 8.1:** Schematic of the a) computational domain and b) external circuit.

The gas phase and surface chemistry model used for simulations is the same as that used in our one-dimensional study (Table 7.2 and 7.3). The species considered include CH$_4$, C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_4$, C$_2$H$_2$, C, H$_2$, H$_3^+$, H$_2^+$, CH$_4^+$, CH$_3^+$, CH$_5^+$, C$_2$H$_5^+$, C$_2$H$_4^+$, C$_2$H$_2^+$, C$_2$H$_3$, C$_2$H$_5$, CH$_3$, etc.
CH₂, CH, H, electrons and soot precursor. A total of 81 reactions were considered which include electron-neutral, electron-ion, ion-neutral and neutral-neutral reactions. An 84 step reaction mechanism consisting of 15 surface species (H₃(s), CH₃(s), CH₂(s), CH₃(s), C₂H₃(s), C₂H₅(s), Cₛ(R), Cₛ(R,G), Cₛ(R,3), CH₄(s), CH₂(s), CH₂(s), C₂H₂(s), CH₂⁺(s) ) and four deposited bulk species (CH₄(b,D) (DLC due to stitching reactions), C₄(b,D) (DLC due to surface molecule radical reactions), C₄(b,G) (graphite like carbon), Soot(b) ) was considered.

In order to determine the inlet velocity the experimental setup and the experimental flow rate were considered. The experimental setup had a 50 μm diameter stainless steel wire as the anode electrode; similar to the simulations. However the cathode electrode in the experiments was a 25 x 25 mm square plate having a thickness of 9.4 mm which is larger than the dimension of the cathode of the simulations. The experimental setup for conducting measurements consisted of a 10 cm cube chamber which has been described in detail in Section 6.4 of Chapter 6. A 100 sccm flow rate for the feed gas was maintained during the experiments. Having a 100 sccm flow rate in the small computational domain would make the problem convection dominated which is not the case in the experiments due to the large volume of the discharge chamber. The flow rate was scaled down by the computational to experimental volume ratio, so that the residence time of the feed gas in the simulations was the same as that of the experiments. Based on the scaled down flow rate the gas velocity at the inlet was set to be 2 μm s⁻¹. The feed gas mixture fraction at the inlet was set to be 99.9% H₂ and 0.1% CH₄. The boundary conditions at the electrodes for the other variables are similar to those used in the one dimensional simulations, with the addition of zero gradient boundary conditions at the far field boundary.
8.3 Numerical Scheme

The numerical scheme for solving the governing equations is based on the finite volume approach. For the convective-diffusive terms in the charged species conservation equation the exponential scheme of Scharfetter and Gummel\textsuperscript{111} is used. For the convective-diffusive terms in the excited and neutral species conservation a second order upwind scheme\textsuperscript{112} is used. A second order upwind scheme is also used for the convective-diffusive terms in the mass-averaged momentum conservation and the neutral energy conservation equation. The Poisson’s equation is solved using a central difference scheme. A non-uniform rectangular grid was used with 80 x 90 cells. The grids were dense near the electrodes in order to accurately resolve the sheaths. The smallest grid resolution near the electrode surface is 0.6 μm. In order to address the different time scales associated with the plasma transport and the fluid transport two different time steps were used. A $5 \times 10^{-11}$ second and $10^{-6}$ second time step was used for the plasma and fluid transport respectively. At the beginning implicit time marching for all the variables with a $5 \times 10^{-11}$ second time step was performed. Time marching was done up to a few micro seconds attaining a quasi-steady plasma condition. Once a quasi-steady plasma condition was reached the plasma transport variables were frozen and $10^{-6}$ second time step was used to continue the fluid transport and gas temperature calculations. Time marching was done up to a millisecond to attain a steady flow and temperature field. The plasma variables were then re-coupled to the fluid transport variables and time marching was done with $5 \times 10^{-11}$ second time step to let the plasma equilibrate to the temperature and flow field. The decoupling and re-coupling were continued until a quasi-steady solution was attained. Figure 8.2 depicts how the different time steps were used and the coupling and decoupling by means of a block diagram.
8.4 Plasma Characteristics of Methane-Hydrogen Micro Glow Discharge

A total of 4 cases were simulated for an atmospheric pressure methane-hydrogen micro discharge. The 4 cases simulated were for a varying ballast resistance. For all the cases the supply voltage, parasitic capacitance, methane fraction and secondary electron emission coefficient were kept constant (Table 8.1). The ballast resistance was varied in order to study the effect of the discharge current on the discharge characteristics and the film deposition.

Table 8.1: Fixed, variable parameters and resulting discharge current for the atmospheric pressure methane-hydrogen micro plasma discharge simulations.

<table>
<thead>
<tr>
<th>Case</th>
<th>Supply Voltage ($V_{pwr}$) (V)</th>
<th>Parasite capacitance (C) (pF)</th>
<th>Hydrogen mass fraction (%)</th>
<th>Methane mass fraction (%)</th>
<th>Secondary electron emission coefficient ($\gamma$)</th>
<th>Ballast resistance ($R$) (kΩ)</th>
<th>Discharge current ($I_d$) (mA)</th>
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<td></td>
<td>500</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Figure 8.2: Flow diagram of the steps involved in the simulations.
The experimentally obtained discharge voltage versus discharge current plot together with the voltage current (V-I) characteristics obtained from the numerical simulations can be seen in Figure 8.3. The error bars in the voltage and current data are the standard deviation from five sets of measurements. A relatively ‘flat’ V-I characteristics was observed similar to that observed by Staack et al. 22. The ‘flat’ V-I characteristics is one of the key signatures of the ‘normal’ glow discharge. In a ‘normal’ glow the voltage remains constant with increasing discharge current. Even though the model under predicted the discharge voltage the trend line from the experimental measurement was found to be in good agreement with the model predictions.

Figure 8.3: Voltage-current characteristics of atmospheric pressure methane-hydrogen micro glow discharge (case 1 – 4).

The radial profiles of the ion current density at the cathode are shown in Figure 8.4 for different discharge currents (Cases 1 – 4). The contribution of electron current is small at the
cathode and the ion transports almost all the discharge current at the cathode. In a ‘normal’ glow the discharge extends laterally only across a limited region called the cathode spot with a constant ‘normal’ current density. Increase of the total discharge current occurs only by the growth of the cathode spot. One can see that for a discharge current of 1.02 mA the ‘normal’ current density $j_n$ is established and it is maintained over the entire discharge current range (1.02 – 4.09 mA). The cathode spot was found to increase from $\sim 6 \mu m$ to $\sim 38 \mu m$ radius in the discharge current range. The predicted ‘normal’ current density is found to be 26.2 A cm$^{-2}$ which is in favorable agreement with experimental measurements of $\sim 22.0$ A cm$^{-2}$ ‘normal’ current density in pure hydrogen$^{27,37}$. In this ‘normal’ mode the discharge current is observed to increase at constant $j_n$.

![Figure 8.4: Ion current density profile along the radial distance at the cathode (x = 0) for different discharge currents (case 1 – 4).](image)

Figure 8.4: Ion current density profile along the radial distance at the cathode ($x = 0$) for different discharge currents (case 1 – 4).
A plot of the electric field distribution along the axis of the discharge (case 1) is shown in Figure 8.5 (a). The electric field profile shows the maximum at the cathode having a peak value of ~14400 kV m$^{-1}$. The high electric field region indicates the edge of the cathode sheath. Within a distance of 28 μm from the cathode the electric field decreases almost linearly to a very low value. An electric field of ~520 kV m$^{-1}$ was observed in the bulk of the plasma which is the positive column. A slight increase in the electric field was observed near the cathode, denoting the anode sheath. The electric field increased from ~ 520 kV m$^{-1}$ to ~1560 kV m$^{-1}$ at the anode over a distance of 12 μm. The predicted electric field profile is consistent with that observed for glow discharges. The combined ions ($\text{H}_2^+ + \text{H}_3^+ + \text{CH}_3^+ + \text{CH}_4^+ + \text{CH}_5^+ + \text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_5^+$) and the electron density profile along the axial distance are shown in Figure 8.5 (b) (case 1). As for the bulk, the plasma was found to be quasi neutral, which corresponds to the low electric field observed in the volume. The quasi neutrality did not hold true in the cathode and anode sheaths. In the cathode sheath the ion density was found to be significantly higher than the electrons; larger by two orders of magnitude. Creation of the cathode sheath occurs due to the multiplication of the cathode emitted electrons in the strong electric field near the cathode, leading to an increase in the ion density. On the other hand the electron density in the anode sheath was found to be higher by an order of magnitude than that of the ion density. The anode sheath results from the diffusion current of the electrons exceeding the drift current. At the anode the drift velocity of the electron is small due to the low electric field and the diffusion current dominates.
Figure 8.5: a) Electric field profile and b) electron and ion \((H_2^+ + H_3^+ + CH_3^+ + CH_4^+ + CH_5^+ + C_2H_2^+ + C_2H_4^+ + C_2H_5^+)^\) density distribution along the axial distance. Ballast resistance 750 k\(\Omega\), \(V_d = 343\) V and \(I_d = 2.74\) mA (case 1).
Figure 8.6: a) Electron temperature contours and b) Electron temperature profile along the axial distance of the discharge (r = 0). Ballast resistance 750 kΩ, $V_d = 343$ V and $I_d = 2.74$ mA (case 1).

Figure 8.6 (a) shows the contour plot and axial distribution of the electron temperature. The axial profile was obtained at the center line (r = 0). It can be seen that a peak electron temperature of about 10.90 eV occurs near the cathode surface (Figure 8.6 (a) and (b)). The extension of the peak electron temperature in the radial direction indicates the extent of the
‘negative glow’ or cathode spot. Joule heating being the main source, the peak electron temperature exists near the location of the maximum electric field (Figure 8.5 (a)). The electron temperature was thereafter found to decrease to about 3.12 eV. The loss of the electron energy is due to the collision of electrons with the background neutrals and radicals, resulting in the formation of different ionic species (Figure 8.6, 8.7 and 8.12 (a)). Near the anode surface the electron temperature increased to about 4.0 eV due to the presence of the relatively high electric field in the anode sheath (Figure 8.5(a)). Due to the small diameter of the anode the electrode edge plays a significant role. The high electric field at the anode edge increases the electron energy there and forms a clearly distinct anode sheath. The anode sheath can be clearly seen as a high electron temperature region in the electron temperature contours (Figure 8.6 (a)). An electron temperature of ~ 4.0 eV existed in the entirety of the anode electrode.

The contour plots of $C_2H_2^+$, $C_2H_4^+$, $CH_3^+$, $CH_5^+$, $C_2H_5^+$, $CH_4^+$ and electron number density for case 1 are shown in Figure 8.7, 8.8 and 8.9, respectively. Peak number density of all the ions and electrons is found to exist at the cathode near the location of the peak electric field. The peak density of ions and electrons near the cathode signifies the presence of the ‘negative glow’. The number density contour plots of $CH_3^+$ (Figure 8.7 (c)), $CH_5^+$ (Figure 8.8 (a)), $CH_4^+$ (Figure 8.9 (a)) and electrons (Figure 8.9 (b)) clearly shows the edge effect of the anode. The presence of high electron temperature at the anode edge due to the high electric field results in ions formation due to ionization. Of the different hydrocarbon ions $CH_5^+$ was found to be the maximum, having a density of $\sim 2.1 \times 10^{19}$ m$^{-3}$ and $C_2H_2^+$ was the least having a density of $\sim 5.7 \times 10^{14}$ m$^{-3}$. The peak electron density was predicted to be $\sim 7.2 \times 10^{19}$ m$^{-3}$.
Figure 8.7: Contour plots of constant a) C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} b) C\textsubscript{2}H\textsubscript{4}\textsuperscript{+} and c) CH\textsubscript{3}\textsuperscript{+} number density. Ballast resistance 750 k\textOmega, V\textsubscript{d} = 343 V and I\textsubscript{d} = 2.74 mA (case 1).
Figure 8.8: Contour plots of constant a) CH$_5^+$ and b) C$_2$H$_5^+$ number density. Ballast resistance $750 \, k\Omega$, $V_d = 343 \, V$ and $I_d = 2.74 \, mA$ (case 1).
Figure 8.9: Contour plots of constant a) CH$_4^+$ and b) electron number density. Ballast resistance $R = 750$ k$\Omega$, $V_d = 343$ V and $I_d = 2.74$ mA (case 1).

Figure 8.10 presents the contour plots of the number density of H, CH and CH$_2$ radicals for the same case. A peak H number density of $\sim 6.3 \times 10^{22}$ m$^{-3}$ was predicted in the cathode sheath region (Figure 8.10 (a)), resulting in a dissociation degree of $\sim 0.0025$. Due to similar reasons as that for the ions, at the anode edge a lesser peak of H radical were observed. The H number density at the anode edge was $\sim 4.5 \times 10^{22}$ m$^{-3}$. Significant volumetric production of CH and CH$_2$ radicals were predicted (Figure 8.10 (b) and (c)). Apart from the electron impact dissociation the radicals CH and CH$_2$ are also produced by neutral-neutral reaction of H with
CH₂ and CH₃ radicals respectively [CH₂ + H → CH + H₂, CH₃ + H → CH₂ + H₂]. The production of CH and CH₂ has a significant contribution from the presence of the high density H radicals in the discharge. Both the radicals were found to have their peak density near the cathode sheath region. The peak density of CH and CH₂ radicals were found to be ~ 7.7 x 10¹⁹ m⁻³ and ~ 4.5 x 10¹⁹ m⁻³ respectively. The contour plot of C₂H₂ and ‘soot’ precursor are shown in Figure 8.11 (a) and (b) respectively (case 1). Considerable amount of C₂H₂ was produced in the volume of the discharge even for a 0.1 % CH₄ mass fraction. The peak C₂H₂ number density predicted was ~ 3.1 x 10¹⁸ m⁻³ in the cathode sheath region. The CH, CH₂ radicals and C₂H₄ neutrals formed in the discharge zone are the main reactants for C₂H₂ formation [CH + CH₂ → C₂H₂ + H, 2CH₂ → C₂H₂ + H₂, C₂H₄ + H₂ → C₂H₂ + H₂]. The moderate C₂H₂ density indicates the possibility of DLC formation through acetylene addition, which was identified to be a dominant mechanism by other researchers¹⁶⁷,¹⁸⁸. The gas phase chemistry used in the model took into account the formation of ‘soot’ precursor from C₂H₂ [C₂H₂ → ‘Soot’ precursor + H₂, k = 1.7 exp(-7548/T_{gas})]²⁹. The reaction rate constant has a strong dependence on temperature. Therefore at higher gas temperature and C₂H₂ density, considerable amount of ‘soot’ precursor will be produced in the discharge. The ‘soot’ precursor number density contours plots (Figure 8.11 (b)) shows a peak density of 4.7 x 10⁷ m⁻³ near the cathode sheath region of the discharge. This existed near the region of maximum neutral gas temperature. The ‘soot’ precursor density decreased near the electrode surfaces due to the soot deposition surface reaction.
Figure 8.10: Contour plots of constant a) H b) CH and c) CH2 number density. Ballast resistance
750 kΩ, Vd = 343 V and Id = 2.74 mA (case 1).
Figure 8.11: Contour plots of constant a) $C_2H_2$ and b) soot precursor number density. Ballast resistance 750 k$\Omega$, $V_d = 343$ V and $I_d = 2.74$ mA (case 1).

Figure 8.12 (a) and (b) illustrates the calculated densities of the hydrocarbon and hydrogen ionic species along the axial distance at the center line ($r = 0$) respectively (case 1). Of the different hydro-carbon ions (Figure 8.12 (a)), $CH_5^+$ was found to be the dominant ion with a peak density of $2.1 \times 10^{19}$ m$^{-3}$. The high density of $H_3^+$ ions in the discharge volume (Figure 8.12 (b)) produces $CH_5^+$ in high density through ion-neutral reactions with $CH_4$ [$H_3^+ + CH_4 \rightarrow CH_5^+$ + ...
H2. The CH3+ number density distribution indicate volumetric production of CH5+ in the discharge with the peak being in between the cathode sheath and the bulk plasma volume. CH3+, CH4+, C2H4+, C2H5+ and C2H2+ had similar density profiles, with the peak density occurring between the cathode sheath and the bulk plasma. The second most prominent ions were found to be C2H5+ and CH4+ having peak densities in the order of 10^{17} m^{-3}, smaller by two orders of magnitude than the peak density of CH5+. The smaller number of C2H5+ ions in the discharge was due to the presence of less CH3+, C2H4 and C2H6 (Figure 8.13 (b)) [CH3+ + CH4 → C2H5+ + H2, CH5+ + C2H6 → C2H5+ + CH4 + H2, H3+ + C2H4 → C2H5+ + H2]. The threshold energy for dissociative ionization of methane molecule forming CH3+ is 14.3 eV 173. On the other hand the formation of CH4+ through direct impact ionization is 12.6 eV 173. This results in the lower density of CH3+ ions. Moreover both CH3+ and CH4+ are consumed to produce C2H5+ and CH5+ respectively [CH3+ + CH4 → C2H5+ + H2, CH4+ + CH4 → CH5+ + CH3], resulting in lowering their number density. Having a peak density of 5.9 × 10^{14} m^{-3}, C2H2+ was the least prominent, due to the fact that C2H2 was produced in the discharge in low concentration (Figure 8.13 (b)). It was found that H3+ was the dominant hydrogen ion and it had a maximum value of 5.2 × 10^{19} m^{-3} in the volume of the discharge (Figure 8.12 (b)). Comparing to the CH5+ ions, the H3+ ions were found to be larger by a factor of 2.5. The H2+ ion was observed to be one order of magnitude smaller than the H3+ ions. The H2+ ion had the maximum value at the cathode sheath due to the peak electron temperature in that region (Figure 8.6). The peak electron temperature results in the formation of H2+ ions through electron impact ionization. Similarly due to the higher electron temperature in the anode sheath region (Figure 8.6) a lesser peak in the H2+ ions was observed there as well. The decrease of H2+ ions in the volume of the discharge is due to the formation of H3+ ions through the ion-neutral collision of H2+ with H2 [H2+ + H2 → H3+ + H]. Both the H3+
and H$_2^+$ ions are found to decrease at the electrode surfaces due to there participation in different surface reactions.

Figure 8.12: Species density along the axial distance (r = 0) of the discharge, a) hydrocarbon ionic species (CH$_3^+$, CH$_4^+$, CH$_5^+$, C$_2$H$_2^+$, C$_2$H$_4^+$ and C$_2$H$_5^+$) and a) hydrogen ionic species (H$_2^+$ and H$_3^+$). Ballast resistance 750 kΩ, V$_d$ = 343 V and I$_d$ = 2.74 mA (case 1).
The distribution of the different radicals along the center line of the discharge \((r = 0)\) is shown in Figure 8.13 (a) (case 1). Atomic H was found to be the dominant radical. A peak H density of \(6.3 \times 10^{22} \text{ m}^{-3}\) was observed in the cathode sheath region. The radical density distribution indicates the abundance of CH\(_2\) and CH\(_3\), CH\(_2\) and CH\(_3\) being dominant in the volume and in the sheath respectively. The formation of CH\(_2\) in the volume by chemical reaction between CH\(_3\) and H \([\text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + \text{H}_2]\) results in the depletion of CH\(_3\) in the volume. The peak densities of these radicals were found to be in the order of \(\sim 10^{20} \text{ m}^{-3}\). Both CH\(_2\) and CH\(_3\) are key components for DLC deposition \(^{159,163}\). C\(_2\)H\(_5\) was the radical with the lowest density. Its peak density was \(2.9 \times 10^{17} \text{ m}^{-3}\) occurring in between the cathode sheath and bulk plasma region.

Figure 8.13 (b) shows the neutral density distribution along the axial distance (case 1). It can be seen that even for 0.1\% methane mass fraction the higher order hydrocarbon molecules (C\(_2\)H\(_6\), C\(_2\)H\(_4\), C\(_2\)H\(_2\), C\(_3\)H\(_8\)) formed by neutral-neutral reactions reach significant concentrations. The peak C\(_2\)H\(_2\) and C\(_2\)H\(_4\) predicted were in the order of \(10^{18} \text{ m}^{-3}\). C\(_2\)H\(_6\) was observed to have a peak density of \(6.5 \times 10^{17} \text{ m}^{-3}\), in the cathode sheath. The reduction of C\(_2\)H\(_6\) in the volume was due to the formation of C\(_2\)H\(_5\) radicals and C\(_2\)H\(_4^+\) ions from C\(_2\)H\(_6\). Of the different neutral species the heaviest hydrocarbon molecule C\(_3\)H\(_8\) had the smallest abundance with a peak density of \(7.6 \times 10^{13} \text{ m}^{-3}\). As collision between C\(_2\)H\(_5\) and CH\(_3\) is the main mechanism for C\(_3\)H\(_8\) formation, the low density of C\(_2\)H\(_5\) in the discharge is responsible for the low density of C\(_3\)H\(_8\).
Figure 8.13: Species density along the axial distance \((r = 0)\) of the discharge, a) radical species \((H, \text{CH}, \text{CH}_2, \text{CH}_3 \text{ and C}_2\text{H}_5)\) and b) neutral species \((\text{H}_2, \text{CH}_4, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \text{ and C}_3\text{H}_8)\).

Ballast resistance 200 k\(\Omega\), \(V_d = 343\) V and \(I_d = 2.74\) mA (case 1).
Spatial distribution of the neutral gas temperature in the entire discharge domain and along the discharge axis \((r = 0)\) for case 1 is presented in Figure 8.14. A peak neutral gas temperature of about 750 K was observed in the ‘negative glow’ region of the discharge existing near the cathode, which was in favorable agreement with experimental temperature
measurements in a pure hydrogen ‘normal’ glow discharge. The temperature prediction suggested the discharge to be operating in the non-thermal regime. The peak gas temperature was higher by 450 K from the room temperature indicating a rarefaction of factor 2.5 near the cathode. In the bulk of the plasma the temperature was found to be about 425 K. The gas temperature decreased at the electrode surfaces as result of the 300 K isothermal boundary condition imposed. The isothermal electrode which is an idealized condition provides cooling of the discharge. The moderately high neutral gas temperature occurred in the discharge due to ion Joule and Frank-Condon gas heating mechanisms. Details on the different gas heating mechanisms for a methane-hydrogen micro glow discharge have been discussed in Section 7.3.1 of Chapter 7.

As a consequence of the moderately high neutral gas temperature in the discharge ‘soot’ precursor are formed from C2H2 (Figure 8.11). ‘Soot’ deposition on the surface start to occur due to the volumetric production of ‘soot’ precursor in the discharge. ‘Soot’ deposition from ‘soot’ precursors was taken into account in the surface chemistry model. The surface chemistry for ‘soot’ deposition [Soot precursor \(\rightarrow\) Soot(D)] had a sticking coefficient of unity, assuming that all the ‘soot’ precursor in the volume is deposited on the surface. Radial distribution of ‘soot’ precursor and ‘soot’ deposition rate at the cathode surface (x = 0) are shown in Figure 8.15 (a) and (b) respectively. The ‘soot’ precursor distribution profile (Figure 8.15 (a)) shows a high density region in the ‘negative glow’ at central discharge axis. The peak density was found to be 1.7 \(\times\) 10\(^7\) m\(^{-3}\) which coincided with the location of high neutral gas temperature (Figure 8.14) and high C2H2 density (Figure 8.11 (a)). The ‘soot’ precursor density reduced to 1 \(\times\) 10\(^0\) m\(^{-3}\) at a distance of 0.25 mm and to a very low value of 1 \(\times\) 10\(^{-2}\) m\(^{-3}\) at 0.3 mm. The density profile flattens out at the boundary due to the zero gradient boundary conditions. The ‘soot’ deposition
rate had a similar profile as that of the ‘soot’ precursor with a peak of $1 \times 10^{-14}$ μm s$^{-1}$ in the central region.

Figure 8.15: a) Soot precursor number density profile and b) soot deposition rate profile along the radial distance at the cathode (x = 0). Ballast resistance 750 kΩ, $V_d = 343$ V and $I_d = 2.74$ mA (case 1).
The DLC and graphite like carbon (GLC) deposition rate profile at the cathode for case 1 are summarized in Figure 8.16 (a) and (b). The DLC deposition rate had its maximum at the center line where peak ion and radical density existed (Figure 8.7, 8.8, 8.9 and 8.10). The DLC deposition rate had a peak value of $5.7 \times 10^{-4}$ μm s$^{-1}$. Most of the deposition was found to occur within a radial distance of 0.1 mm indicating that the deposition was mostly happening in the ‘negative glow’ or cathode spot region of the discharge. The GLC deposition rate also had its maximum at the central region (Figure 8.16 (b)). Compared to the DLC deposition rate the GLC deposition rate was three orders of magnitude smaller and had a maximum deposition rate of $1.6 \times 10^{-7}$ μm s$^{-1}$. The peak GLC to DLC ratio was found to be $\sim 2.8 \times 10^{-4}$ signifying that good quality film was deposited with very little graphitic carbon content. The deposited film also had very negligible ‘soot’ content with the peak ‘soot’ to DLC ratio being $1.8 \times 10^{-11}$. The predicted deposition rate profiles indicated that the obtained film would be pristine DLC.
Figure 8.16: Deposition rate profile of a) DLC and b) DLC and GLC along the radial distance at the cathode surface (x = 0). Ballast resistance 750 kΩ, $V_d = 343$ V and $I_d = 2.74$ mA (case 1).

The DLC deposition rate profiles at the cathode surface for different discharge currents are represented in Figure 8.17. Over the entire discharge current range (1.02 – 4.09 mA) the DLC
peak deposition rate had a fairly constant value of about $5.5 \times 10^{-4}$ $\mu$m s$^{-1}$. The DLC deposition rate profiles had similar patterns as that of the ion current density profiles (Figure 8.4), which expanded in the lateral direction with a constant value. The majority of the DLC deposition in atmospheric pressure micro glow discharge occurs due to ion induced stitching reactions $^{29}$ therefore with an increase in the discharge current the DLC deposition rate profile was observed to expand in the radial direction. This signifies that the radial size of the deposition feature was governed by the cathode spot. In the ‘normal’ glow regime of operation the radial size of the deposited film can be increased by increasing the discharge current as the cathode spot increases in size with a constant ‘normal’ current density.

Figure 8.17: DLC deposition rate along the radial distance at the cathode surface ($x = 0$) for all cases.
8.5 Conclusions

Plasma and associated deposition characteristics of atmospheric pressure methane-hydrogen DC micro glow discharge have been computationally investigated using a hybrid model together with an external circuit. Simulations were conducted for a pin plate electrode configuration with an inter-electrode separation of 400 μm. The V-I characteristics obtained from the simulations showed a fairly constant discharge voltage with increasing discharge current; a flat V-I characteristics indicating the discharge to operate in the ‘normal’ glow mode. The predicted V-I characteristics were found to be in favorable agreement with experimental measurements. The simulations predicted the existence of the constant ‘normal’ current density at the cathode. Increase in the total discharge current occurred only by the growth of the cathode spot through which the current flows. The ‘normal’ current density was found to be 26.2 A cm\(^{-2}\) which was in favorable agreement with published literature values of ‘normal’ current density in atmospheric pressure pure hydrogen micro glow discharge\(^{27,37}\). The micro glow discharge was found to be quasi neutral in the bulk of the plasma region, apart from the sheaths formed at the electrodes. The cathode and anode sheaths were distinctly identifiable from the electric field, electron temperature and electron and ion density profile. The cathode sheath was found to be larger than that of the anode. The simulations revealed that the edge of the small radius anode affected the electron temperature and also the ion and radical number density. The ion concentration in the discharge was dominated by CH\(_5^+\) and H\(_3^+\) ions. The H, CH\(_2\) and CH\(_3\) radicals were found to be the prominent radicals, while CH\(_2\) and CH\(_3\) are also the key components for DLC deposition. The deposited film was predicted to be comprised of mostly DLC with very little graphite like carbon and negligible soot. The radial profiles of DLC deposition rate showed a maximum at the ‘negative glow’ region. With an increase in the
discharge current the DLC deposition rate profile was found to expand in the lateral direction, signifying that the radial size of the deposition was governed by the cathode spot.
9 RADIO FREQUENCY GLOW DISCHARGE AT ATMOSPHERIC PRESSURE

9.1 Introduction

Atmospheric pressure glow discharges are attractive for materials processing applications due to the operational flexibility afforded by the removal of the vacuum system. The use of atmospheric pressure plasma would therefore expand the current scope of material processing. Of the different atmospheric pressure plasma sources that have been developed in recent years RF CCP discharges are of special interest because of their low neutral gas temperature, large volume and ability to treat large surface areas. Experimental studies have been conducted by various researchers to characterize and understand the physics of these atmospheric pressure RF CCP discharges. Park et al. studied the gas breakdown mechanism in the atmospheric pressure RF CCP discharge for different gas mixtures. They also reported the voltage-current characteristics and gas temperature measurements for a parallel plate RF CCP discharge operating at atmospheric pressure helium. Laimer et al. reported two modes (\(\alpha\) and \(\gamma\)) of operation for a helium discharge operating in a parallel plate configuration with gas flow. They observed a transition from \(\alpha\) to \(\gamma\) mode at high input powers. The sensitivity of pressure on RF CCP discharges was studied by Moravej et al. Their experimental system consisted of a parallel plate configuration with perforated electrodes to allow gas flow through them. They conducted experiments for both argon and helium gases and also reported the effect of gas impurities to the discharge characteristics. Several modeling studies have been conducted to investigate the dominant physical and chemical mechanism and structure of

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the RF CCP discharges. A one dimensional self consistent fluid model was developed by Yuan et al. \(^{73}\) to study atmospheric pressure glow discharges in helium. The model considered a Maxwellian electron energy distribution function (EEDF) and did not solve for the neutral gas temperature. They reported the effect of nitrogen impurities and inter-electrode gap width to the discharge characteristics. Shi and Kong \(^{199}\) developed a one dimensional self consistent hybrid model for a RF helium glow discharge. The model predicted the observance of \(\alpha\) and \(\gamma\) modes \(^{199}\) and identified volumetric and localized gas ionization to be the dominant mechanism for the \(\alpha\) and \(\gamma\) mode respectively \(^{74}\). The effect of plasma excitation frequency on the plasma stability was studied by Shi and Kong \(^{76}\). Their study reported the use of high excitation frequencies for expansion of the stability range of RF atmospheric glow discharges. However the models developed do not take into account the effect of the external matching circuit, which is a key component for the operation of RF CCP discharges \(^2\).

In this chapter we report the results of numerical investigation of atmospheric pressure argon RF glow discharge. The aim of the work was to study the effect of the matching circuit parameters on the plasma characteristics and also to identify the operational regimes for the \(\alpha\) and \(\gamma\) modes. The numerical studies were performed using a one dimensional hybrid model. Discharge simulations were carried out for a parallel plate electrode configuration with an inter-electrode gap of 1.0 mm together with an external matching circuit. The external matching circuit parameters were found to have significant effect on the discharge characteristics. The results indicated that the discharge can operate at either the \(\alpha\) or \(\gamma\) mode depending on the matching circuit parameters. The two modes of operation were found to be distinctively different. The predicted \(Ar^*\) density was considered to provide qualitatively the visual appearance of the \(\alpha\) or \(\gamma\) mode discharge. The \(\alpha\) mode was found to have a luminous region in
the center of the discharge. On the other hand the $\gamma$ mode had luminous regions very close to the electrodes which were followed by alternating dark and bright regions. The appearance of the simulated $\gamma$ mode was found to resemble that of an atmospheric pressure direct current glow discharge. The predicted gas temperature indicated the $\gamma$ mode to have higher gas temperature compared to the $\alpha$ mode. The tuning and the loading capacitors of the matching circuit $C_T$ and $C_L$ had significant effects on the plasma characteristics. For small values of the tuning capacitor the discharge was found to operate in the $\alpha$ mode. Furthermore it was found that better matching occurred when the discharge was operating in the $\gamma$ mode.

9.2  Geometry and Reaction Mechanism

Schematic of the parallel plate radio frequency argon glow discharge is shown in Figure 9.1. The inter-electrode separation and electrode diameter were set to 1.0 mm and 10.0 mm respectively. For the present one dimensional model, the electrode diameter is required only to calculate the current through the external circuit. The discharge is powered by an RF power source which is connected to the electrodes through an external circuit. The external circuit contains a resistance $R$, a matching circuit (showed within dotted lines) and a capacitor $C_P$. The resistance $R$ is the internal resistance of the power supply. The capacitor $C_P$, represents the parasitic capacitance which is present intrinsically because of the external cables. An ‘L’ type matching circuit couples the RF power supply with the plasma discharge for the purpose of impedance matching. The matching circuit consists of a loading capacitor $C_L$, connected in parallel, an inductor, $L$ and tuning capacitor, $C_T$ connected in series to the power supply. The matching circuit is similar to Plasmatherm AMNS–500E circuit used for the PECVD system in our laboratory. In the simulations $R$ was set to 50.0 $\Omega$ which is the internal resistance of the
Plasmatherm HFS–500E RF power supply. The $C_P$ is fixed at 5.0 pF, which corresponds to the estimated value for the experimental setup. Similar to the Plasmatherm AMNS–500E the inductor $L$ was fixed at 1.0 $\mu$H, while the loading and tuning capacitors, $C_L$, and $C_T$ were varied to obtain impedance matching. In this study the power supply voltage amplitude $V_{pwr}$ was fixed at 300 V, the frequency of the power supply was fixed at 13.56 MHz, the resistance $R$ was kept constant at 50.0 $\Omega$, the parasitic capacitor $C_P$ and matching circuit inductor $L$ were fixed at 5.0 pF and 1 $\mu$H respectively. Simulations of the plasma characteristics were obtained for selected values of the loading and tuning capacitors, $C_L$, and $C_T$. Details of the variable external circuit parameters considered in the simulations are given in Table 9.1.

![Figure 9.1: Schematic of the parallel-plate plasma glow discharge circuit. The numbers represent the node in the circuit, ‘0’ indicates grounded nodes.](image)

The plasma-chemistry model used in the study is same as that used in DC argon micro discharge simulations (Table 5.1). The model considers five species: electrons, argon monomer and dimer ions ($\text{Ar}^+$, $\text{Ar}_2^+$), electronically excited argon monomer ($\text{Ar}^*$) and neutral argon (Ar). A total of nine reaction steps were considered, these include elastic scattering, ionization, three-body recombination, molecular ion conversion, excitation, de-excitation and dissociative...
recombination. Surface reactions similar to the DC argon micro discharge simulations (Table 5.2) were also employed.

9.3 **External Circuit Model**

The external circuit model (Figure 9.1) consists of the following coupled equations to obtain the discharge voltage.

\[
\frac{dV_{C_L}}{dt} = \left( \frac{i_{pw}}{-i_{L,C_T}} \right) \quad (9.1)
\]

\[
\frac{dV_d}{dt} = \left( \frac{i_{L,C_T} - i_d}{C_p} \right) \quad (9.2)
\]

\[
\frac{di_{L,C_T}}{dt} = \left( \frac{V_{C_L} - V_{C_T} - V_d}{L} \right) \quad (9.3)
\]

\[
\frac{dV_{C_T}}{dt} = \frac{i_{L,C_T}}{C_T} \quad (9.4)
\]

\[
i_{pw} = \frac{V_{pw} - V_{C_L}}{R} \quad (9.5)
\]

where, \( C_L, C_T \) and \( C_p \) are the loading, tuning and parasitic capacitors, \( L \) is the matching circuit inductor, \( R \) is the internal resistance of the power supply, \( V_{C_L} \) and \( V_{C_T} \) are the voltage drops across the loading and the tuning capacitors respectively, \( V_d \) is the discharge voltage, \( V_{pw} \) is the power supply voltage, \( i_{pw} \) is the power supply current, \( i_d \) is the discharge current and \( i_{L,C_T} \) is the current through the branch having the inductor \( L \) and the tuning capacitor \( C_T \).
The plasma model and the external circuit model are coupled via the discharge current $i_d$ and discharge voltage $V_d$. The plasma model calculates the discharge current,

$$i_d = A \left( \varepsilon \frac{\partial E}{\partial t} + e\Gamma_i - e\Gamma_e \right)$$  \hspace{1cm} (9.6)

for a given potential at the electrodes. In the discharge current expression, $A$ is the surface area of the electrode, $\varepsilon$ is the permittivity of the medium, $E$ is the electric field, $e$ is the elementary charge, $\Gamma_i$ and $\Gamma_e$ is the ion and electron flux respectively. The first term in the right hand side represent the displacement current, the second and third terms represent the ion and electron currents. Based on the discharge current the external circuit model recalculates the voltage at the electrodes.

### 9.4 Boundary Conditions

Flux boundary conditions were imposed for all the species densities at the electrodes. The electron flux $\Gamma_e$ at the electrodes is given as:

$$\Gamma_e = \frac{1}{4} n_e u_{th} - \gamma \sum_i q_i \Gamma_i$$  \hspace{1cm} (9.7)

where, $\gamma$ is the secondary electron emission coefficient and $u_{th}$ is the electron thermal velocity.

The effect of secondary electron emission due to ion bombardment was taken into account through the boundary conditions for the electrons. A secondary electron emission coefficient of 0.01 was set for our calculations.

The boundary conditions for the ions takes into account both the thermal and drift flux and is given as:

209
\[
\bar{\Gamma}_i = \frac{1}{4} n_i \beta u_{th,i} + b \mu_i E n_i \begin{cases} 
    b = 0, \text{ electric field directed away from electrode} \\
    b = 1, \text{ electric field directed towards the electrode}
\end{cases}
\]  

(9.8)

where, \(u_{th,i}\) is the thermal velocity of the ion and \(\beta\) is the surface interaction coefficient. At the electrode surfaces all of the ions and the excited species are quenched to neutral species due to surface reactions. For all the surface reactions the surface interaction coefficient \(\beta\) was set to unity.

The boundary condition for the electron energy \(T_e\) is expressed as:

\[
2T_e \bar{\Gamma}_e = \frac{5}{2} T_e \bar{\Gamma} - \frac{5}{2} n_e D_e \nabla T_e
\]

(9.9)

where, \(n_e\) is the electron number density and \(D_e\) is the electron diffusion coefficient.

The electrode surfaces are set to be isothermal walls with room temperature 300 K for solving the gas mixture temperature. No slip boundary condition was maintained at the electrodes to solve the fluid averaged velocity.

The initial value of the electron density was set to \(10^{10}\) m\(^{-3}\), which is the free electron number density at atmospheric pressure \(^2\). The initial values for \(V_{c_e}, V_{c_r}, V_d, i_{por}\) and \(i_{L,Cr}\) for the external circuit model were set to zero.
9.5 Simulation of Atmospheric Pressure Radio Frequency Glow Discharge

9.5.1 ‘α’ and ‘γ’ Mode of Operation

Table 9.1: Parameters for the atmospheric pressure radio frequency argon plasma discharge simulations with $C_L = 100$ pF.

<table>
<thead>
<tr>
<th>Case</th>
<th>Supply Voltage Amplitude, $V_{pwr}$ (V)</th>
<th>Loading Capacitor, $C_L$ (pF)</th>
<th>Tuning Capacitor, $C_T$ (pF)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2</td>
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<td>6</td>
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<td>15*</td>
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</tr>
<tr>
<td>16*</td>
<td></td>
<td>15.0</td>
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</tr>
<tr>
<td>17*</td>
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</tr>
</tbody>
</table>

*Case 9 was provided as an initial condition.*
Table 9.2: Parameters for the atmospheric pressure radio frequency argon plasma discharge simulations with $C_L = 50$ pF.

<table>
<thead>
<tr>
<th>Case</th>
<th>Supply Voltage Amplitude, $V_{pwr}$ (V)</th>
<th>Loading Capacitor, $C_L$ (pF)</th>
<th>Tuning Capacitor, $C_T$ (pF)</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>23</td>
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</tbody>
</table>

Table 9.3: Parameters for the atmospheric pressure radio frequency argon plasma discharge simulations with $C_L = 75$ pF.

<table>
<thead>
<tr>
<th>Case</th>
<th>Supply Voltage Amplitude, $V_{pwr}$ (V)</th>
<th>Loading Capacitor, $C_L$ (pF)</th>
<th>Tuning Capacitor, $C_T$ (pF)</th>
</tr>
</thead>
<tbody>
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<tr>
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<tr>
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<td>100.0</td>
</tr>
</tbody>
</table>

Simulations were carried out for the RF atmospheric pressure argon discharge (Figure 9.1) by varying the external circuit parameters (Table 9.1, 9.2 and 9.3). The loading ($C_L$) and tuning ($C_T$) capacitors of the matching circuit were varied for this purpose, while the resistance $R$, inductance $L$, parasitic capacitor $C_P$ and the supply voltage amplitude $V_{pwr}$ were kept constant. The frequency of the power supply was maintained at 13.56 MHz for all the cases.
Since the discharge operates in two different modes we analyze two cases (1 and 12) in detail to determine the different plasma characteristics. Figure 9.3 shows the simulated waveforms of the discharge voltage, discharge current (Figure 9.2 (a)), supply current (Figure 9.2 (b)) and the Lissajous plot of discharge voltage – discharge current (Figure 9.2 (c)) for case 1 (α mode). In the α mode, both the discharge voltage and current waveforms are smooth and sinusoidal, indicating a mostly linear response of the discharge (Figure 9.2 (a)). The RMS discharge voltage, current and discharge power are found to be 105.20 V, 0.0538 A and 4.03 W respectively. The capacitive nature of the discharge can be clearly seen as the current waveform is found to lag the voltage waveform by 83º. Comparing the discharge and supply current waveforms (Figure 9.2 (b)) it is seen that in the α mode the discharge is poorly matched due to low ratio of discharge to supply current. The ratio of RMS discharge to supply current was found to be 0.03. Lissajous plot of the discharge voltage – discharge current is presented in Figure 9.2(c). The phase difference between two signals governs the Lissajous patterns and provides a better understanding of the capacitive/resistive nature of the discharge. For the present case 1, the Lissajous plot has a smooth elliptic shape, due to about 83º phase shift between the discharge voltage and current (as indicated in Figure 9.2(a) and 2(b)). This indicates the discharge to be more capacitive, which is one of the key features of a α mode discharge. 199.
Figure 9.2: a) Simulated wave forms of the discharge voltage (dotted line) and the discharge current b) Simulated waveforms of the supply and discharge current c) Lissajous plot of voltage – current for a argon radio frequency atmospheric pressure glow discharge operating in the $\gamma$ mode. $I_{d\text{RMS}} = 0.0538$ A, $V_{d\text{RMS}} = 105.20$ V, $P_{d\text{RMS}} = 4.03$ W (case 1).
Figure 9.3: Time averaged spatial profile of a) electric field and b) electron temperature for a discharge operating in the $\alpha$ mode. $I_{d\text{ RMS}} = 0.0538$ A, $V_{d\text{ RMS}} = 105.20$ V, $P_{d\text{ RMS}} = 4.03$ W (case 1).
Spatial profiles of the time averaged electric field and electron temperature for the \( \alpha \) mode (case 1) are shown in Figure 9.3 to provide insight into mechanisms responsible for the two different glow modes. The maximum electric field is found to exist at the electrode surfaces (Figure 9.3(a)). The electric field has a magnitude of 820 kV m\(^{-1}\) at the electrode surfaces and decreases almost linearly to a very low value in the central region. The sheath region is characterized by a region of almost linear fall of the electric field. A total sheath thickness of about 450 \( \mu \)m is observed having a discharge current of 0.0538 A. A peak electron temperature of about 2.37 eV occurs near the electrode surface (Figure 9.3(b)). Joule heating being the main source, the peak electron temperature exists near the location of the maximum electric field (Figure 9.3(a)). The electron temperature was thereafter found to decrease to about 2.24 eV. The loss of the electron energy is due to the collision of electrons with background neutral argons, resulting in the formation of argon ions and argon excited species (Figure 9.4(a)). The space between an electrode and the location of the minimum electron temperature is where the majority of the gas ionization takes place. In the mid region of the discharge the electron temperature was found to increase to about 2.32 eV. The increase in the electron temperature is due to the energy gain from the electric field.
Figure 9.4: Time averaged spatial profile of a) $\text{Ar}_2^+$, $\text{Ar}$ and $\text{Ar}^+$ number density and b) ions ($\text{Ar}_2^+$ + $\text{Ar}^+$) and electron number density for a discharge operating in the $\alpha$ mode. $I_{d\text{RMS}} = 0.0538$ A, $V_{d\text{RMS}} = 105.20$ V, $P_{d\text{RMS}} = 4.03$ W (case 1).
Figure 9.4 (a) shows the spatial profile of the time averaged species densities of Ar$_2^+$, Ar and Ar$^*$ for case 1. It can be seen that the maximum density of the ionic and electronically excited species are located at the central region of the discharge, indicating significant volumetric production of these species. In the $\alpha$ mode, the electrons have the maximum energy outside the sheath region, in the volume of the discharge. As a result most of the ionization and excitation processes occur outside the sheath region, within which the ionic and the electronically excited species are trapped by the rapidly oscillatory field of the applied voltage. The density of Ar$^+$ and Ar$_2^+$ ions and electronically excited Ar$^*$ monomer drops near the electrode surfaces due to the surface quenching processes. Ar$_2^+$ is found to be the dominant ionic species which is two orders of magnitude larger than that of Ar$^+$. Since the electronically excited Ar$^*$ monomer is responsible for the brightness of the discharge, the Ar$^*$ distribution profile indicate two luminous zones in the volume of the discharge. These luminous zones are found to exist close to the electrodes. Time averaged spatial distribution of the combined ion (Ar$^+$ + Ar$_2^+$) and the electron density for the same case are presented in Figure 9.4(b). In the present $\alpha$ mode, the discharge is found to be quasi-neutral over a distance of about 550 $\mu$m in the central region. Large sheaths were observed having dimensions of about 225 $\mu$m.
Figure 9.5 shows the time averaged ion current density for the case 1. The maximum ion current density was 0.63 mA cm$^{-2}$ for the discharge current of 0.0538 A. The small ion current density also implies the smallest effect of secondary electron emission from the electrode surfaces. The maximum electron current density due to secondary electron emission is 0.0063 mA cm$^{-2}$, for a secondary emission coefficient of 0.01. This small value of secondary electron emission due to ion bombardment indicates the discharge to be volume dominated. The temperature profile in the $\alpha$ mode (case 1) shows a peak gas temperature at the central region of the discharge (Figure 9.6). The peak gas temperature obtained is 370 K which is 70 K above the ambient temperature. The contributions of different neutral gas heating mechanisms are summarized in Figure 9.6 (b). The time averaged spatial profiles of ion joule heating, heating due to elastic collisions and heavy particle reactions are shown. It can be seen that in the $\alpha$ mode the
The dominant gas heating mechanism in the bulk plasma is due to elastic collisions. The ion joule heating has the maximum value at the electrodes. The peak magnitudes of both ion joule heating and heating due to elastic collisions are of the order of $10^7$ W m$^{-3}$. The contribution of ion joule heating in the central region of the discharge is small and is comparable to the maximum value of heating due to heavy particle reactions. The maximum value of heating due to heavy particle reaction was found to be $\sim 6 \times 10^4$ W m$^{-3}$. 
Figure 9.6: Spatial distribution of the a) neutral gas temperature and b) time averaged energy source terms for a discharge operating in the $\gamma$ mode. $I_{d\text{RMS}} = 0.0538$ A, $V_{d\text{RMS}} = 105.20$ V, $P_{d\text{RMS}} = 4.03$ W (case 1).
The simulated wave forms of the discharge voltage and discharge current, and supply and discharge currents are shown in Figures 9.7(a), and 9.7(b) for a γ mode discharge (case 12). The Lissajous plot (discharge voltage vs. discharge current) for the above case is shown in Figure 9.7(c). Both the discharge voltage and current are observed to be sinusoidal but with significant distortion in the peaks. The RMS discharge current and voltage are 0.5220 A and 169.78 V respectively. The current lagged the voltage by 40º, which is 43º smaller than that observed in the α mode (case 1). The decrease in the phase difference is due to the conductive nature of the discharge. In the γ mode, the discharge operates at a significantly higher power, having a RMS value of 95.88 W. Furthermore the discharge is also found to be better matched having RMS discharge to supply current ratio of 0.29 (Figure 9.7(b)). The Lissajous plot of voltage – current (Figure 9.7(c)) in the present case (γ mode) is skewed due to the decrease in the phase angle between the current and the voltage signals. The plot is also observed to have distortions, instead of the smooth profile seen in case 1 (α mode) (Figure 9.2(c)). The skewed, distorted Lissajous pattern is due to the higher conductivity of the discharge. At higher power the discharge transitions from being capacitive to conductive. The γ mode of operation of a RF CCP is identified through this conductive nature of the discharge.\textsuperscript{199}
Figure 9.7: a) Simulated wave forms of the discharge voltage (dotted line) and the discharge current b) Simulated waveforms of the supply and discharge current c) Lissajous plot of voltage – current for a argon radio frequency atmospheric pressure glow discharge operating in the $\gamma$ mode. $I_{d\text{RMS}} = 0.5220$ A, $V_{d\text{RMS}} = 169.78$ V, $P_{d\text{RMS}} = 95.88$ W (case 12).
Figure 9.8: Time averaged spatial profile of a) electric field and b) electron temperature for a discharge operating in the $\gamma$ mode. $I_{d\text{ RMS}} = 0.5220$ A, $V_{d\text{ RMS}} = 169.78$ V, $P_{d\text{ RMS}} = 95.88$ W (case 12).
The time averaged spatial profiles of the electric field and the electron temperature in the \( \gamma \) mode (case 12) are shown in Figure 9.8(a) and (b). Compared to the \( \alpha \) mode (Figure 9.3), the electric field has a maximum value of 5270 kV m\(^{-1}\) at the electrode surfaces, an order of magnitude higher. The sheath thickness is found to decrease significantly. It has a total thickness of about 90 \( \mu \)m. In the \( \gamma \) mode of operation, a peak electron temperature of about 3.0 eV is observed (Figure 9.8(b)). The higher electron temperature results due to the higher electric field in this mode (Figure 9.8(a)). The higher electron temperature in the \( \gamma \) mode suggests that the electrons are substantially accelerated in the sheath and thereby is capable of inducing gas ionization in the sheath region. The electron temperature reaches a minimum value of about 1.75 eV in between the sheath and the bulk plasma. This indicates the location of the maximum ions (Figure 9.9(a)), since the electrons lose most of their energy during the ionization process while colliding with the neutral argon atoms. In the bulk plasma region the electron temperature has a constant value of about 1.83 eV.
Figure 9.9: Time averaged spatial profile of a) $\text{Ar}_2^+$, Ar and $\text{Ar}^+$ number density and b) ions ($\text{Ar}_2^+$ + Ar$^+$) and electron number density for a discharge operating in the $\gamma$ mode. $I_{d\text{RMS}} = 0.5220$ A, $V_{d\text{RMS}} = 169.78$ V, $P_{d\text{RMS}} = 95.88$ W (case 12).
Figure 9.9(a) shows the spatial profiles of the time averaged species density for case 12. It can be seen that in the $\gamma$ mode, the maximum density of the ionic and electronically excited species are located near the electrode surfaces. The $\gamma$ mode operates at higher discharge currents and has a higher electric field in the sheath region (Figure 9.8(a)). As a result, the electrons have higher energy at the sheath region and therefore can perform the ionization and the excitation processes. The peak species density is observed in the location of the minimum electron energy as most of the electron energy is lost during the ionization and excitation processes. The decrease in the species density in between the sheath and the bulk is the consequence of the low electron energy in that region (Figure 9.8(b)). As the electrons start acquiring energy in the bulk plasma, the species density increases in the bulk region which is reflected in the species profiles. Similar to the $\alpha$ mode the $\text{Ar}_2^+$ is found to be the dominant ionic species. However it is one order of magnitude larger than that of $\text{Ar}^+$, compared to the two orders of magnitude difference observed in the $\alpha$ mode. The $\text{Ar}^*$ spatial profile indicates that the discharge has two thin luminous regions immediately adjacent to the electrodes. This is followed by a dark and bright region. The luminosity of the discharge in the $\gamma$ mode is similar to the ‘negative glow’, ‘Faraday dark space’ and ‘positive column’ observed in direct current (DC) atmospheric glow discharges. Comparing the number density of the electronically excited $\text{Ar}^*$ monomer the $\gamma$ mode has a higher luminosity. The peak $\text{Ar}^*$ density in the $\gamma$ mode is larger by two orders of magnitude. The density distribution of the $\text{Ar}^*$ monomers for both the $\alpha$ and $\gamma$ mode match the visualization studies of RF CCP discharges reported in the literature. In Figure 9.9(b) the spatial profiles of the time averaged combined ions ($\text{Ar}^+ + \text{Ar}_2^+$) and electron densities are shown. In the $\gamma$ mode of operation, the discharge is quasi-neutral in most of the volume apart from the sheaths. Small sheaths having thickness of about 45 $\mu$m were observed. The sheath thickness is similar to that
observed for a DC atmospheric pressure argon discharge. Comparing the sheath thicknesses between the two modes, the $\gamma$ mode sheath was smaller by a factor of 5. The time averaged ion current density for the same case is shown in Figure 9.10. The discharge has a peak ion current density of 385.60 mA cm$^{-2}$ for a discharge current of 0.5220 A. This is three orders of magnitude larger than that observed in the $\alpha$ mode (case 1). The electron current density due to secondary electron emission is 3.856 mA cm$^{-2}$, which is also larger by three orders of magnitude. The higher value of the secondary electron emission current indicates the discharge to be surface dominated.

Figure 9.10: Spatial profile of the time averaged ion current density for a discharge operating in the $\gamma$ mode. $I_{d,\text{RMS}} = 0.5220$ A, $V_{d,\text{RMS}} = 169.78$ V, $P_{d,\text{RMS}} = 95.88$ W (case 12).
Figure 9.11: Spatial distribution of the a) neutral gas temperature and b) time averaged energy source terms for a discharge operating in the \( \gamma \) mode. I_{d\text{RMS}} = 0.5220 \, \text{A}, V_{d\text{RMS}} = 169.78 \, \text{V}, P_{d\text{RMS}} = 95.88 \, \text{W} \) (case 12).
In Figure 9.11 (a) and (b) the spatial distribution of the neutral gas temperature and the time averaged energy source terms are shown for case 12. Significant change in the temperature profile can be seen when the discharge operates in the $\gamma$ mode. The peak gas temperature was found to be 650 K, 280 K higher than the $\alpha$ mode. The peak gas temperature is seen to exist adjacent to the electrodes, at the location of the peak ion and electron density. This resembles the maximum temperature observed in the ‘negative glow’ of an atmospheric pressure DC glow discharge. The contributions of different gas heating mechanisms indicate ion joule heating to be the dominant gas heating mechanism in the sheaths. The higher ion joule heating in the $\gamma$ mode results due to the high electric field and ion current density (Figures 9.8(a), 9.10). The maximum ion joule heating was found to be $\sim 4 \times 10^{10}$ W m$^{-3}$ in the sheaths, which is three orders of magnitude higher than that observed for the $\alpha$ mode (case 1). In the central region of the discharge, heating due to elastic collision has a more dominant effect. The heating due to elastic collision in the central region of the discharge is found to be $\sim 4 \times 10^{8}$ W m$^{-3}$, which is larger by one and three orders of magnitude than the heating due to heavy particle reactions and ion joule heating respectively.

To observe the evolution of the sheath thickness with increasing discharge current the spatial profiles of the time averaged electric field for different RMS discharge currents are shown in Figure 9.12 (case 1, 3, 5, 7 and 12). These cases are chosen so that a gradual evolution in the $\alpha$ mode to a transition to the $\gamma$ mode can be observed. For all the cases the maximum electric field is at the electrode surface and it increases with an increase in the discharge. The maximum electric field changed from 820 kV m$^{-1}$ at 0.0538 A to 5270 kV m$^{-1}$ at 0.5220 A. At 0.1321 A discharge current (case 7), just before an onset to $\gamma$ mode, the peak electric field was found to be 2662 kV m$^{-1}$. The sheath thickness of the discharge is found to decrease with an increase in the
discharge current. The sheath region is characterized by a region of almost linear fall of the electric field. The total sheath thickness decreased from $450 \mu m$ to $90 \mu m$ for a discharge current increase from $0.0538 \text{ A}$ to $0.5220 \text{ A}$. Just before the onset to the $\gamma$ mode the total sheath thickness reduced to about $220 \mu m$ (case 7). Due to the small sheath thickness and high electric field, the secondary electron emission due to ion bombardment starts to become significant. The discharge starts becoming surface dominated rather than being volume dominated.

Figure 9.12: Spatial profile of the time averaged electric field for different discharge currents (Cases 1, 3, 5, 7 and 12).

Time averaged spatial profiles of $\text{Ar}_2^+$, $\text{Ar}^+$ and electrons for different RMS discharge currents (case 1, 3, 5, 7 and 12) is shown in Figures 9.13, 9.14 and 9.15 respectively. It can be seen that with an increasing discharge current $\text{Ar}_2^+$, $\text{Ar}^+$ and electron density increases and starts expanding in the axial direction. At low discharge currents the $\text{Ar}^+$ and electron density profiles are bell-shaped and similar to that observed in low pressures $^{202}$. The density profiles of $\text{Ar}_2^+$ and
\(\text{Ar}^+\) suggests volumetric production outside the sheath when operating at low discharge current. As the discharge current increases the peak density of \(\text{Ar}_2^+\), \(\text{Ar}^+\) and electrons starts shifting towards the electrodes. For a discharge current of 0.1321 A peak ions (\(\text{Ar}_2^+\) and \(\text{Ar}^+\)) and electron density is observed to shift towards the electrodes (Figures 9.13, 9.14 and 9.15). This indicates the initiation of gas ionizations in the sheath region of the discharge. The secondary electron emission due to ion bombardment would also start to play a significant role, because of the presence of the peak ion density near the electrodes. The change in the spatial density profile indicates a transition in the mode of operation of the discharge. The discharge is found to change from \(\alpha\) mode (volume dominated) to \(\gamma\) mode (surface dominated) with an increase in the discharge current.

![Spatial profile of the time averaged \(\text{Ar}_2^+\) number density for different discharge currents (Cases 1, 3, 5, 7 and 12).](image)

Figure 9.13: Spatial profile of the time averaged \(\text{Ar}_2^+\) number density for different discharge currents (Cases 1, 3, 5, 7 and 12).
Figure 9.14: Spatial profile of the time averaged $\text{Ar}^+$ number density for different discharge currents (Cases 1, 3, 5, 7 and 12).

Figure 9.15: Spatial profile of the time averaged electron number density for different discharge currents (Cases 1, 3, 5, 7 and 12).
The voltage–current (V–I) characteristics resulting from the simulations (Cases 1-17) is shown in Figure 9.16. Two distinct mode of operation can be clearly seen, which are the $\alpha$ and the $\gamma$ mode. In the $\alpha$ mode of operation the discharge voltage sharply increases with an increase in the discharge current resulting in large positive impedance in this regime. This is the ‘abnormal’ glow operating regime that has also been observed in other studies of atmospheric pressure RF plasma discharges $^{73, 194, 201, 203}$. As the current increases above 0.1083 A, the discharge voltage increases less for a given increment in the discharge current. For a 21.9 % increase in the discharge current ($I_{d\text{RMS}, \, 0.1083 \text{ A}–0.1321 \text{ A}}$), a 1.1 % increase in the discharge voltage ($V_{d\text{RMS}, \, 186.37–188.25}$) is observed. At a discharge current of 0.1552 A (point C) a transition is observed (showed in dotted line). The discharge voltage decreases from 188.25 V at 0.1321 A to 164 V at 0.1552 A, a decrease of ~ 24 V. The decrease in the discharge voltage with an increasing discharge current indicates the existence of negative differential impedance in this region. This evolution is consistent with the experimental observation of $\alpha – \gamma$ transitions in atmospheric pressure RF glow discharges $^{201, 203}$. Once the discharge evolves to a $\gamma$ mode the discharge voltage is once again observed to increase with discharge current. However the positive differential impedance of the discharge in the $\gamma$ mode is smaller compared to that of the $\alpha$ mode. While in the $\gamma$ mode, the discharge is also found to be operating as an ‘abnormal’ glow. Once in the $\gamma$ mode, the discharge remains in the same mode of operation even with decreasing discharge current (Case 15). For these cases a $\gamma$ mode discharge (case 9) was given as an initial condition. In Figure 9.2 these points are shown in red squares. A second transition is observed at point D for a discharge current of 0.0652 A, where the discharge evolves back into the $\alpha$ mode (point A). The hysteresis loop ‘ABCD’ is similar to those observed in atmospheric pressure RF
discharges\textsuperscript{201}. The simulated V–I characteristics are found to match the general trends of experimental studies\textsuperscript{201,203}.

Figure 9.16: RMS voltage current characteristics of the radio frequency argon discharge at 760 Torr (Cases 1 – 17). The ‘solid square’ denotes solution where a $\gamma$ mode discharge was provided as an initial condition.

Figure 9.17 represents the time averaged peak Ar$^+_2$, Ar$^+$ density as a function of the RMS discharge current for cases 1-17 (Table 9.1). Over the range of discharge current the Ar$^+_2$ is found to be the dominant ionic species. At lower discharge current the peak Ar$^+_2$ density is larger by a two orders of magnitude from that of the Ar$^+$ density. The peak Ar$^+_2$ density is found to be one order of magnitude higher than that of Ar$^+$ in the higher discharge current range. Over the high discharge range the increase in the peak ion density is significantly lower compared to that observed in the low discharge current range. The peak Ar$^+_2$ density increased from 3.49 x 10\textsuperscript{18} m\textsuperscript{-3} at 0.1321 A to 6.21 x 10\textsuperscript{18} m\textsuperscript{-3} at 0.1552 A when the $\alpha$ – $\gamma$ transition occurred. Once in the $\gamma$ mode the discharge remains in the same mode of operation even with decreasing current. For a
discharge current of 0.1069 A, the peak Ar$_2^+$ is 3.62 x 10$^{18}$ m$^{-3}$ while still operating in the γ mode (showed with ‘solid square’, case 15). A γ − α transition is observed when the discharge current is reduced to 0.0813 A. The time averaged peak electron density as function of the RMS discharge current and voltage are shown in Figures 9.18(a) and (b) for cases 1-17. The dependence of the peak electron number density on the discharge current has similar trends as the peak ion density. The peak electron density increased from 3.35 x 10$^{18}$ m$^{-3}$ at 0.1321 A to 5.97 x 10$^{18}$ m$^{-3}$ at 0.1552 A. Both the peak ion and electron density show a gradual increase when the discharge evolves into the γ mode. The dependence of peak electron density on RMS discharge voltage (Figure 9.18(b)) shows an increase in the electron density with the discharge voltage until the α − γ transition. The peak electron density increases sharply just before the transition, in the discharge current range of 0.1083 – 0.1321 A. As the discharge transitions from the α to the γ mode the peak electron density increased with a decrease in the discharge voltage. This is due to the secondary electrons being emitted from the electrode surfaces, which dominates in the γ mode. Once in the γ mode, the peak electron density starts increasing with an increase in the discharge voltage. In the γ mode the discharge remains in the same mode of operation even with decreasing current. For a discharge current and voltage of 0.1069 A and 152.66 V respectively, the peak electron density was found to be 3.43 x 10$^{18}$ m$^{-3}$. Raizer et al. 204 have established that in moderate pressure RF plasmas, the α − γ transition occurs if the plasma density exceeds a critical value for sheath breakdown. The critical electron density is given by Raizer et al. 204:

$$n_{crucial} = \frac{B_p}{e A} \left[ \ln \left( \frac{A}{\ln(1 + \gamma^{-1})} \right) + \ln(2 \rho A) \right]$$  \hspace{1cm} (9.10)
where, $A$ and $B$ are constants for argon gas (12 cm$^{-1}$ Torr$^{-1}$ and 180 V cm$^{-1}$ Torr$^{-1}$ $^2$), $p$ is the pressure (Torr), $\gamma$ is the secondary electron emission coefficient of the electrodes, $e$ is the electron charge, $\epsilon_0$ is the permittivity and $A$ is oscillation amplitude of the plasma boundary. The $\alpha - \gamma$ transition occurs when the oscillation amplitude $A$ of the plasma boundary exceeds the total sheath thickness $d_s$, i.e. $2A = d_s$. For a total sheath thickness of 220 $\mu$m, just before the transition, one obtains a critical electron density of $1.82 \times 10^{18}$ m$^{-3}$. This compares favorably to the predicted peak electron density of $3.35 \times 10^{18}$ m$^{-3}$ (Figure 9.18 (a)) just before the transition.

![Figure 9.17: Time averaged peak Ar$_2^+$ and Ar$^+$ number density as a function of RMS discharge current (Cases 1 – 17). The ‘solid square’ and ‘solid circle’ denotes peak Ar$_2^+$ and Ar$^+$ respectively, where a $\gamma$ mode discharge was provided as an initial condition.](image-url)
Figure 9.18: Time averaged peak electron number density as a function of a) RMS discharge current and b) RMS discharge voltage (Cases 1 – 17). The ‘solid square’ denotes peak electron density where a $\gamma$ mode discharge was provided as an initial condition.
The time averaged peak ion current density for different discharge current is shown in Figure 9.19 (for cases 1-14). A sharp increase in the ion current density is seen in the low discharge current range. The maximum ion current density increases from 0.63 mA cm\(^{-2}\) at 0.0538 A to 18.44 mA cm\(^{-2}\) at 0.1321 A. The transition to the $\gamma$ mode occurs for a peak ion current density of 32.25 mA cm\(^{-2}\). In the $\gamma$ mode, gradual increase of the peak ion current density is observed over the discharge current range of 0.1552 – 0.6370 A. The ion current density ranges 32.25 – 448.53 mA cm\(^{-2}\) in the $\gamma$ mode operation regime. Compared to the $\alpha$ mode the $\gamma$ mode has significantly higher ion current density. The higher ion current density indicates higher flux of ions coming to the electrode surface. With higher ion flux, the role of secondary electron emission starts to play a significant role. Similar to the peak ions and electron density, while in the $\gamma$ mode of operation the peak ion current density took a different route with a decreasing discharge current (showed with ‘solid squares’). For a discharge current of 0.1069 A ($\gamma$ mode) the peak ion current density was found to be 19.17 mA cm\(^{-2}\).
Figure 9.19: Time averaged peak ion current density as a function of RMS discharge current (Cases 1 – 17). The ‘solid square’ denotes peak ion current density where a $\gamma$ mode discharge was provided as an initial condition.

9.5.2 Effect of External Circuit Parameters

The effect of the loading and tuning capacitors on the discharge power is shown in Figure 9.20 for all the cases listed in Tables 9.1 and 9.2. For a fixed loading capacitance of 100.0 pF, it can be seen that for small tuning capacitance value the RMS discharge power to supply power ratio is low. This indicates a poor matching of impedance between the discharge and the power supply since very little of the applied power is going into the discharge itself and most of it is being lost in the resistive element of the circuit. For a tuning capacitor of 5.0 pF the power ratio is 0.01. The power ratio increases from 0.01 for a tuning capacitor of 5.0 pF to 0.06 for a tuning capacitor of 100.0 pF. In the entire $\alpha$ mode the discharge is found to be poorly matched. The discharge to supply power ratio starts to increase when the discharge evolves to the $\gamma$ mode. A
sharp increase in the ratio is seen in the tuning capacitance range 102.5 – 107.5 pF. In the γ mode small changes in the tuning capacitance had significant effect on the discharge power. The RMS discharge to supply power ratio increased from 0.08 to 0.33 in the γ regime. This better matching is due to the low differential impedance of the discharge in this region (Figure 9.16). By reducing the loading capacitance to 50.0 pF, it was found that better matching could be obtained. However the discharge was still poorly matched in the α mode. For a fixed loading capacitance of 50.0 pF the discharge to supply power ratio ranged from 0.13 – 0.47 for a tuning capacitor range of 60.0 – 100.0 pF.

Figure 9.20: \( \frac{P_{d \text{ RMS}}}{P_{s \text{ RMS}}} \) (RMS discharge power to supply power ratio), as a function of tuning capacitor \( C_T \) for fixed value of loading capacitor.
Figure 9.21: a) Contours of RMS discharge current and b) mode of operation of the discharge as a function of tuning and loading capacitor.
RMS discharge current contours and mode of operation of the discharge as a function of loading and tuning capacitors $C_L$ and $C_T$ respectively is shown in Figure 9.21 (a) and (b). It can be seen that for a low value of $C_L$ a large increase in the RMS discharge occurs for small incremental change in $C_T$ value, resulting in transition to $\gamma$ mode from the $\alpha$ mode. Only a small region of $\alpha$ mode operation exists for a small $C_L$ (Figure 9.21 (b)). The $\alpha$ mode exists only in the $C_T$ range of 50.0 – 57.0 pF for a $C_L$ value of 50.0 pF. For larger $C_L$ values the discharge current steadily increases with increase of $C_T$ (Figure 9.21 (a)). The $\alpha$ mode discharge is observed to exist over a wider range of $C_T$ (Figure 9.21 (b)) for larger $C_L$ values. A larger $C_L$ suppressed the transition to $\gamma$ mode, therefore providing more control to the mode of operation, which was not observed for small values of $C_L$.

9.6 Conclusions

Atmospheric pressure radio frequency argon glow discharge together with an external matching circuit has been studied numerically. The simulations were conducted for parallel plate geometry with an inter-electrode separation of 1.0 mm. The loading and tuning capacitors of the external circuit were varied to study the effect of the matching network on the plasma characteristics. The predicted voltage – current characteristics predicted two modes of operation of the discharge. In the low discharge current range the discharge operates in the $\alpha$ mode and evolves to a $\gamma$ mode at high discharge currents. In the V-I characteristics a sharp linear increase of the discharge voltage is observed in the $\alpha$ mode. This indicates large positive differential impedance in this regime. In the $\alpha$ – $\gamma$ transition the discharge voltage is found to decrease with increasing discharge current. Once the discharge evolves to the $\gamma$ mode the discharge voltage increases with discharge current. However the differential impedance of the discharge in the $\gamma$
mode is found to be less than that in the \( \alpha \) mode. Furthermore a hysteresis in the V-I characteristics was observed in the \( \alpha - \gamma \) and \( \gamma - \alpha \) transitions. The critical electron number density for \( \alpha - \gamma \) transition was predicted to be \( 3.35 \times 10^{18} \text{ m}^{-3} \) which agreed favorably to the literature values\(^{204}\).

The model predicts the discharge to evolve from being capacitive at low discharge current to being conductive at higher discharge current. The tuning and the loading capacitors of the matching circuit \( C_T \) and \( C_L \) have significant effects on the plasma characteristics. For small values of the tuning capacitor the discharge is found to operate in the \( \alpha \) mode. Furthermore the discharge is found to be better matched when operating in the \( \gamma \) mode. The model predicts volume and surface dominant ionization for the \( \alpha \) and \( \gamma \) mode respectively. Higher gas temperature is observed in the \( \gamma \) mode of operation due to the high electric field and high ion current density. The peak gas temperature predicted in the \( \gamma \) mode was 650 K which was 250 K higher than that of the \( \alpha \) mode. The calculated gas temperature suggests the discharge to be a non-thermal non-equilibrium discharge. The different species density predicted by the model provides insight into the physico-chemical processes. The simulations indicate the molecular argon ion to be dominant for an atmospheric pressure RF glow discharge. The profiles of the electronically excited species density provided insight into the visual appearance of the discharge. In the \( \alpha \) mode luminous region in the central region of the discharge and in the \( \gamma \) mode luminous region adjacent to the electrode followed by dark and bright region were observed. The alternating bright and dark regions predicted in the \( \gamma \) mode resemble the ‘negative glow’, ‘Faraday dark space’ and ‘positive column’ observed in DC glow discharges.
10 ATMOSPHERIC PRESSURE RADIO FREQUENCY PLASMA JET FOR SURFACE DECONTAMINATION

10.1 Introduction

Over the past two decades, there has been considerable interest in applying non-thermal plasmas to hazardous chemical destruction, pollution control, surface decontamination and sterilization. Several different kinds of atmospheric pressure plasma sources have been employed for this purpose which include gliding arc, pulsed negative and positive corona, pulsed dielectric barrier discharges (DBD), resistive barrier discharges and atmospheric pressure plasma jet. Operating in atmospheric pressure provides operation flexibility due to the removal of the vacuum systems. Furthermore, higher reaction rate and continuous process makes it more advantageous than its low pressure counterpart.

Experimental studies of decontamination using atmospheric pressure non-thermal plasmas have been conducted by several researchers. The experimental studies involved in identifying the key dominant species in the plasma discharge and hypothesizing the mechanism responsible for decontamination. Thiyagrajan et al. developed an atmospheric pressure resistive barrier discharge to be used for biological decontamination. They carried out detailed electrical, chemical, optical and biological studies of the discharge. Their experimental studies indicated overwhelming production of ozone and negligible quantities of NO$_2$ and ultra violet (UV) light present in the discharge. A pulsed DBD with coaxial electrode configuration was developed by Laroussi and Lu. Copper ring electrodes attached to a cylindrical glass tube

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were used as their electrode configuration and helium was used as the carrier gas. Their measurements identified the presence of excited nitrogen and helium, nitrogen ions, atomic oxygen and hydroxyl radicals. Hermann et al. used an atmospheric pressure plasma jet (APPJ) and conducted experiments on decontamination of chemical and biological warfare agents. They used a helium-oxygen mixture as the carrier gas and treated Bacillus globigii as a surrogate for Bacillus anthracis. Their experiments showed a 4.5 s decimal reduction value of the spore population with plasma exposure. They drew a comparison of the decontamination efficiency of APPJ with other plasma sources and concluded that APPJ was more efficient because of its high power. Despite all the experimental works there has not been any detailed modeling of plasma surface decontamination. Numerical simulations can provide insight into the physico-chemical processes occurring in the discharge and thereby help identify the dominant species responsible for the decontamination.

In this chapter we present results from simulation of a RF atmospheric pressure plasma jet in helium-oxygen mixture. The numerical simulations were carried out for the plasma generated between an annulus electrode configuration with gas flow in between the electrodes and a surface to be decontaminated in front of the plasma afterglow. The detailed volume chemistry of the model provided insight into the parameters that affect the decontamination process. Basic plasma properties such as electron number density, radical, ion and excited species number densities, gas temperature, electric field and electron temperature are studied. The simulations indicated the discharge to operate in the $\alpha$ mode at low power. In the $\alpha$ mode the discharge was found to be uniform and volume dominated. At high power the discharge was found to transition to $\gamma$ mode, with peak ionic species near the electrode surfaces. The discharge was also found to pinch down in the axial direction. In both the modes He$_2^*$, O, O$_2$ ($^1\Delta_g$) and O$_3$
were the dominant species in the afterglow of the discharge. \( \text{O}, \text{O}_2 \ (^1\Delta_g) \) and \( \text{O}_3 \) are key species for surface decontamination. Peak gas temperature predictions indicate the discharge to be a non-thermal non-equilibrium discharge. However the peak temperature of the discharge while in the \( \gamma \) mode was \( \sim 150 \text{ K} \) higher than that at the \( \alpha \) mode.

10.2 Geometry and Reaction Mechanism

10.2.1 Schematic of the Problem Geometry

Figure 10.1: Schematic of the a) computational domain (all dimensions are in cm) and b) external circuit.
A schematic of the atmospheric pressure plasma jet is shown in Figure 10.1 (a). The computational domain has an annulus electrode configuration. The inner and outer electrode have a radius of 0.5 cm and 0.6 cm respectively; an inter-electrode separation of 0.1 cm. The substrate to be treated is located 0.5 cm away from the electrodes. The length of the substrate was chosen to be 2.0 cm. The inner electrode was powered and the outer electrode was grounded and they were coupled to an external circuit (Figure 10.1 (b)). The external circuit contains a ballast resistance $R$ and a capacitance $C_P$. The ballast resistance and the capacitance are connected to the power supply in series and in parallel respectively. The ballast resistance is necessary to limit the discharge current. The capacitance $C_P$ is present intrinsically due to the external cables, which is known as the parasitic capacitance.

### 10.2.2 Chemical Kinetics

The species considered in the kinetic model include 4 neutral species (He, O$_2$, O and O$_3$), 6 ionic species He$^+$, He$_2^+$, O$^+$, O$_2^+$, O$^-$ and O$_2^-$, consisting of both positive and negative ions, 3 electronically excited species He$^*$, He$_2^*$ and O$_2$(¹Δg) and electrons. These species were identified from the dominant reaction chemistry of helium-oxygen plasma in atmospheric pressure and the reaction rates were obtained from the literature. Table 10.1 summarizes the different species considered in the simulations. The total set of gas phase reactions taken into account is presented in Table 10.2. The gas phase kinetics can be grouped into three broad categories 1) Helium reactions 2) Oxygen reactions and 3) Helium-oxygen reactions. Both the helium and oxygen reaction set contained momentum transfer, dissociation, electron impact ionization, recombination, excitation, de-excitation and molecular ion conversion. Since molecular oxygen is highly electronegative, electron attachment, detachment reactions together with dissociative attachment, associative detachment and ion-ion recombination reactions were also taken into
account. The helium-oxygen reactions contained neutral-neutral, three body attachment and charge transfer reactions.

Table 10.1: Different species taken into account in the helium-oxygen plasma model.

<table>
<thead>
<tr>
<th>Neutrals</th>
<th>Ions</th>
<th>Electronically Excited</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>He^+</td>
<td>O'</td>
<td>He^*</td>
</tr>
<tr>
<td>O_2</td>
<td>He_2^+</td>
<td>O_2^-</td>
<td>He_2^*</td>
</tr>
<tr>
<td>O</td>
<td>O^+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O_3</td>
<td>O_2^+</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10.2: Kinetic processes taken into account in the modeling.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction No</th>
<th>Reaction</th>
<th>Reaction Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Helium Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Momentum transfer</td>
<td>R1</td>
<td>He + e → He + e</td>
<td>E</td>
<td>211</td>
</tr>
<tr>
<td>Ionization</td>
<td>R2</td>
<td>e + He → 2e + He^+</td>
<td>E</td>
<td>211</td>
</tr>
<tr>
<td>Recombination</td>
<td>R3</td>
<td>He_2^+ + 2e → 2He + e</td>
<td>A</td>
<td>77</td>
</tr>
<tr>
<td>Excitation</td>
<td>R4</td>
<td>He + e → He^* + e</td>
<td>E</td>
<td>211</td>
</tr>
<tr>
<td>De-excitation</td>
<td>R5</td>
<td>He^* + e → He + e</td>
<td>A</td>
<td>77</td>
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<tr>
<td>Stepwise ionization</td>
<td>R6</td>
<td>He^* + He^* → He^+ + He + e</td>
<td>A</td>
<td>77</td>
</tr>
<tr>
<td>Molecular ion conversion</td>
<td>R7</td>
<td>He^* + e → He^+ + 2e</td>
<td>A</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>R8</td>
<td>He_2^* + e → He_2^+ + 2e</td>
<td>A</td>
<td>73</td>
</tr>
<tr>
<td>Heavy particle reactions</td>
<td>R9</td>
<td>He^+ + 2He → He_2^+ + He</td>
<td>A</td>
<td>73</td>
</tr>
<tr>
<td><strong>Oxygen Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Momentum transfer</td>
<td>R11</td>
<td>O + e → O + e</td>
<td>E</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>R12</td>
<td>O_2 + e → O_2 + e</td>
<td>E</td>
<td>212</td>
</tr>
<tr>
<td>Ionization</td>
<td>R13</td>
<td>O_2 + e → O_2^+ + 2e</td>
<td>E</td>
<td>212</td>
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<tr>
<td>Recombination</td>
<td>R14</td>
<td>O_2^+ + 2e → O_2 + e</td>
<td>A</td>
<td>213</td>
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<tr>
<td>Reaction Type</td>
<td>Reaction Equation</td>
<td>Energy</td>
<td>States</td>
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<td>--------------------------</td>
<td>---------------------------</td>
<td>--------</td>
<td>--------</td>
<td></td>
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<tr>
<td>Recombination</td>
<td>$\text{R}_{15} \quad \text{O}_2^+ + e \rightarrow 2\text{O}$</td>
<td>A</td>
<td>213</td>
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<tr>
<td>Dissociation</td>
<td>$\text{R}_{16} \quad \text{O}_2 + e \rightarrow 2\text{O} + e$</td>
<td>E</td>
<td>212</td>
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<tr>
<td>Ionization</td>
<td>$\text{R}_{17} \quad \text{O} + e \rightarrow \text{O}^+ + 2e$</td>
<td>E</td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>Attachment</td>
<td>$\text{R}_{18} \quad \text{O}_2 + e \rightarrow \text{O} + \text{O}^-$</td>
<td>E</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Excitation</td>
<td>$\text{R}_{19} \quad \text{O}_2 + e \rightarrow \text{O}_2(^1\Delta_g) + e$</td>
<td>E</td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>De-excitation</td>
<td>$\text{R}_{20} \quad \text{O}_2(^1\Delta_g) + e \rightarrow \text{O}_2 + e$</td>
<td>A</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Detachment</td>
<td>$\text{R}_{21} \quad \text{O}^- + e \rightarrow \text{O} + 2e$</td>
<td>A</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>$\text{R}_{22} \quad \text{O}_2 + e \rightarrow \text{O}^- + \text{O}^+ + e$</td>
<td>A</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Ion-ion recombination</td>
<td>$\text{R}_{23} \quad \text{O}_2^+ + \text{O}^- \rightarrow \text{O}_2 + \text{O}$</td>
<td>A</td>
<td>213</td>
<td></td>
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<tr>
<td>Ion-ion recombination</td>
<td>$\text{R}_{24} \quad \text{O}^- + \text{O} \rightarrow \text{O}_2 + e$</td>
<td>A</td>
<td>214</td>
<td></td>
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<tr>
<td>Associative detachment</td>
<td>$\text{R}_{25} \quad 2\text{O}_2 + e \rightarrow \text{O}_2^- + \text{O}_2$</td>
<td>A</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Ion-ion recombination</td>
<td>$\text{R}_{26} \quad \text{O}_3 + e \rightarrow \text{O}_2^- + \text{O}$</td>
<td>A</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>Associateive detachment</td>
<td>$\text{R}_{27} \quad \text{O}^- + \text{O}_2^+ \rightarrow 3\text{O}$</td>
<td>A</td>
<td>214</td>
<td></td>
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<tr>
<td>Charge transfer</td>
<td>$\text{R}_{28} \quad \text{O}^- + \text{O}_2(^1\Delta_g) \rightarrow \text{O}_3 + e$</td>
<td>A</td>
<td>214</td>
<td></td>
</tr>
<tr>
<td>Three body ion-ion recombination</td>
<td>$\text{R}_{29} \quad \text{O}^- + \text{O}_2(^1\Delta_g) \rightarrow \text{O}_2^- + \text{O}$</td>
<td>A</td>
<td>214</td>
<td></td>
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<tr>
<td>Heavy particle reaction</td>
<td>$\text{R}_{30} \quad \text{O}^- + \text{O}_2^+ + \text{O} \rightarrow \text{O}_3 + \text{O}_2$</td>
<td>A</td>
<td>214</td>
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<tr>
<td>Ion-ion recombination</td>
<td>$\text{R}_{31} \quad \text{O} + 2\text{O}_2 \rightarrow \text{O}_3 + \text{O}_2$</td>
<td>A</td>
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<td>Ion-ion recombination</td>
<td>$\text{R}_{32} \quad \text{O}_2^- + \text{O}_2^+ \rightarrow 2\text{O}_2$</td>
<td>A</td>
<td>214</td>
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<tr>
<td>Three body ion-ion recombination</td>
<td>$\text{R}_{33} \quad \text{O}_2^- + \text{O}_2^+ + \text{O}_2 \rightarrow 2\text{O}_2$</td>
<td>A</td>
<td>214</td>
<td></td>
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<tr>
<td>R34</td>
<td>$\text{O}_3 + \text{O}_2 \rightarrow 2\text{O}_2 + \text{O}$</td>
<td>A</td>
<td>214</td>
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<tr>
<td>R35</td>
<td>$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$</td>
<td>A</td>
<td>210</td>
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<tr>
<td>R36</td>
<td>$2\text{O} + \text{O}_2 \rightarrow 2\text{O}_2$</td>
<td>A</td>
<td>210</td>
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<tr>
<td>Neutral-neutral</td>
<td>$\text{R}_{37} \quad \text{O}_2(^1\Delta_g) + \text{O}_3 \rightarrow 2\text{O}_2 + \text{O}$</td>
<td>A</td>
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<tr>
<td>R38</td>
<td>$\text{O}_2(^1\Delta_g) + \text{O}_2 \rightarrow 2\text{O}_2$</td>
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</table>
### Helium-Oxygen Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Rate Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral-neutral</td>
<td>R39 ( \text{O} + \text{O}_2 + \text{He} \rightarrow \text{O}_3 + \text{He} )</td>
<td>( A )</td>
</tr>
<tr>
<td>Neutral-neutral</td>
<td>R40 ( \text{He} + \text{O}_2(\text{^1} \Delta_g) \rightarrow \text{He} + \text{O}_2 )</td>
<td>( A )</td>
</tr>
<tr>
<td>Neutral-neutral</td>
<td>R41 ( \text{O}_3 + \text{He} \rightarrow \text{O} + \text{O}_2 + \text{He} )</td>
<td>( A )</td>
</tr>
<tr>
<td>Three body attachment</td>
<td>R42 ( \text{O}_2 + \text{He} + \text{e} \rightarrow \text{He} + \text{O}_2^- )</td>
<td>( A )</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>R43 ( \text{He}^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + \text{He} )</td>
<td>( A )</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>R44 ( \text{He}^+ + \text{O}_2 \rightarrow \text{He} + \text{O}_2^+ )</td>
<td>( A )</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>R45 ( \text{He}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{He} )</td>
<td>( A )</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>R46 ( \text{He}_2^+ + \text{O}_2 \rightarrow \text{O}^+ + \text{O} + 2\text{He} )</td>
<td>( A )</td>
</tr>
</tbody>
</table>

A: reaction rate in Arrhenius form  
E: reaction rate dependent on EEDF (electron energy distribution function)

### Table 10.3: Surface reactions.

- \( \text{He}^+ \rightarrow \text{He} \)
- \( \text{He}_2^+ \rightarrow \text{He}_2 \)
- \( \text{He}^* \rightarrow \text{He} \)
- \( \text{He}_2^* \rightarrow \text{He}_2 \)
- \( \text{O}^+ \rightarrow \text{O} \)
- \( \text{O}_2^+ \rightarrow \text{O}_2 \)
- \( \text{O}^- \rightarrow \text{O} \)
- \( \text{O}_2^- \rightarrow \text{O}_2 \)
- \( \text{O}_2(\text{^1} \Delta_g) \rightarrow \text{O}_2 \)
- \( \text{O} \rightarrow \text{O}_{(s)} \)

The surface reactions used in the model are summarized in Table 10.3. The surface reactions employed were mostly surface quenching reactions, where the positive, negative ions and excited species are quenched to neutral species at the surface. An artificial destruction term of O having a sticking coefficient of unity was implemented at the substrate. This would simulate an idealized case of O being used for surface decontamination. This was necessary since no
surface reaction rate constant for atomic oxygen O and surface interaction was available in the literature. For the O\textsubscript{3} species an insulated boundary condition was provided.

10.3 ‘α’ –’γ’ Transition

In the simulations the supply voltage amplitude was fixed at 1000 V, the driving frequency was held constant at 13.56 MHz, the capacitance was fixed at 0.1 pF and the ballast resistance was varied from 5 kΩ to 2 kΩ. For the gas mixture the inlet velocity was fixed at 5.0 m s\textsuperscript{-1} and the oxygen mass fraction was fixed at 1%. We report the results for two cases having ballast resistance of 5 kΩ and 2 kΩ respectively with 1% oxygen mass fraction. For a ballast resistance of 5 kΩ a RMS discharge voltage 221.91 V, RMS discharge current of 96.89 mA and RMS power of 17.79 W were obtained. Figure 10.2 shows the velocity vector plot in the entire domain for a ballast resistance of 5 kΩ. It can be seen that the gas mixture attains a fully developed flow within a very short distance. Once fully developed the velocity has a Poiseuille like profile, with a maximum velocity at the center (Figure 10.4 (a)). The gas flow attains a peak gas velocity of ~ 8 m s\textsuperscript{-1} once it leaves the inter-electrode spacing (Figure 10.4 (b)). The Reynolds number for the low power case was ~ 60, satisfying the assumption of laminar flow. The gas mixture leaves the domain through the sides, which is clear in the streamline patterns (Figure 10.3). In Figure 10.3 it is shown that the flow creates two counter rotating vortices. One vortex is found to form at the end of the inner powered electrode, creating a recirculation zone. This would result in a decrease in the effluent species in that region, creating a non-uniform distribution of the active species. The other vortex is formed near the top exit. These vortices are formed due to the annulus inter-electrode configuration.
Figure 10.2: Velocity vector plot (5 kΩ ballast resistance, 1% O₂, $V_{d \text{RMS}} = 221.91$ V, $I_{d \text{RMS}} = 96.89$ mA, $P_{\text{RMS}} = 17.79$ W, Current density = 30.84 mA cm⁻² (RMS), Power density = 5.66 W cm⁻² (RMS)).

Figure 10.3: Streamline patterns (5 kΩ ballast resistance, 1% O₂, $V_{d \text{RMS}} = 221.91$ V, $I_{d \text{RMS}} = 96.89$ mA, $P_{\text{RMS}} = 17.79$ W, Current density = 30.84 mA cm⁻² (RMS), Power density = 5.66 W cm⁻² (RMS)).
Figure 10.4: U velocity profile along a) the radial distance (inter-electrode separation) at $x = 5.0$ mm and b) the axial distance at $r = 5.5$ mm (5 kΩ ballast resistance, 1% $O_2$, $V_{d\text{ RMS}} = 221.91$ V, $I_{d\text{ RMS}} = 96.89$ mA, $P_{\text{RMS}} = 17.79$ W, Current density = 30.84 mA cm$^{-2}$ (RMS), Power density = 5.66 W cm$^{-2}$ (RMS)).
Neutral gas temperature for the same case is shown in Figure 10.5. A peak gas temperature of 352 K was obtained, an increase of 52 K from the ambient. The presence of helium which has high thermal conductivity and high gas flow rate provides cooling of the discharge. The predicted gas temperature indicates the discharge to be non-thermal. Near the substrate a peak gas temperature of ~ 318 K was found. This cancels out the possibility of having thermal damage to the substrate. The rise in the gas temperature also explains the fact of increased gas velocity at the end of the inter-electrode spacing.

Figure 10.5: Neutral gas temperature contours (5 kΩ ballast resistance, 1% O₂, \(V_{d\text{ RMS}} = 221.91\) V, \(I_{d\text{ RMS}} = 96.89\) mA, \(P_{\text{RMS}} = 17.79\) W, Current density = 30.84 mA cm\(^{-2}\) (RMS), Power density = 5.66 W cm\(^{-2}\) (RMS)).

Figure 10.6, and 10.7 show the time averaged O and O\(_3\) number density contours for a 5 kΩ ballast resistance. A peak O number density of ~ 9 \(\times 10^{20}\) m\(^{-3}\) and ~ 2 \(\times 10^{20}\) is predicted in the plasma volume and in the plasma after glow respectively. Similar trends were observed for O\(_3\). In the after glow of the discharge a peak O\(_3\) of ~ 1.1 \(\times 10^{19}\) m\(^{-3}\) is predicted. The decrease of O at the substrate is due to the surface quenching reactions. These long lived active species (O and O\(_3\)) are the key components for surface decontamination \(^{207, 208}\). The predicted number
density indicated sufficient amount of these species available for surface decontamination purpose. It is clearly evident that the central region of the substrate (opposite to the powered electrode) has very little active species due to the recirculation zone present there. This is more clearly depicted in Figure 10.9 (a) where the distribution of these long lived active species along the substrate length is shown.

Figure 10.6: Time averaged O number density contours (5 kΩ ballast resistance, 1% O₂, \( V_{d\text{ RMS}} = 221.91 \) V, \( I_{d\text{ RMS}} = 96.89 \) mA, \( P_{\text{RMS}} = 17.79 \) W, Current density = 30.84 mA cm\(^{-2}\) (RMS), Power density = 5.66 W cm\(^{-2}\) (RMS)).

Figure 10.7: Time averaged O\(_3\) number density contours (5 kΩ ballast resistance, 1% O₂, \( V_{d\text{ RMS}} = 221.91 \) V, \( I_{d\text{ RMS}} = 96.89 \) mA, \( P_{\text{RMS}} = 17.79 \) W, Current density = 30.84 mA cm\(^{-2}\) (RMS), Power density = 5.66 W cm\(^{-2}\) (RMS)).
Time averaged ion and electron number density profiles along the radial distance at $x = 5.5$ mm are represented in Figure 10.8. It was found that of the different ionic species $O_2^+$ is the major positive ion with a peak number density of $\sim 4 \times 10^{17}$ m$^{-3}$. The major negative ion was found to be $O_2^-$ with a peak number density of $\sim 3 \times 10^{17}$ m$^{-3}$. The predicted peak $He_2^+$ and $He^+$ number density were $\sim 3 \times 10^{16}$ m$^{-3}$ and $4 \times 10^{12}$ m$^{-3}$ respectively. These are smaller by one and five orders of magnitude than that of $O_2^+$. The smaller $He^+$ and $He_2^+$ number density is because of the high ionization potential of helium compared to that of oxygen. All the ionic species density profile show a dome like shape with the peaks located in the central region of the discharge, indicating a volume dominated discharge phenomenon. This characteristics is typical of a $\alpha$ mode discharge $^{201}$. However the profiles show a shift in the peak towards the inner electrode because of the self bias initiated due to size difference in the electrode surfaces. The total positive ions, negative ions and electron number density profile are shown in Figure 10.8 (b). The discharge is found to be dominated by negative ions instead of electrons. The peak electron number density is smaller by an order of magnitude than that of the negative ions. The existence of higher negative ions is due to higher attachment rates of electrons with $O_2$ and O.
Figure 10.8: Time averaged a) ion number density b) positive ions ($\text{He}^+ + \text{He}_2^+ + \text{O}^+ + \text{O}_2^+$), negative ions ($\text{O}^- + \text{O}_2^-$) and electron number density along the radial distance (inter-electrode separation) at $x = 5.5$ mm. (5 kΩ ballast resistance, 1% $\text{O}_2$, $\text{V}_{\text{d RMS}} = 221.91$ V, $\text{I}_{\text{d RMS}} = 96.89$ mA, $\text{P}_{\text{RMS}} = 17.79$ W, Current density = 30.84 mA cm$^{-2}$ (RMS), Power density = 5.66 W cm$^{-2}$ (RMS)).
Figure 10.9: a) Time averaged He$_2^+$, O$_2$ ($^1\Delta_g$) and O number density along the radial distance at x = 15 mm. b) Time averaged He$_2^+$, O$_2$ ($^1\Delta_g$) and O number density along the axial distance at r = 5.5 mm. (5 kΩ ballast resistance, 1% O$_2$, $V_{d\text{ RMS}} = 221.91$ V, $I_{d\text{ RMS}} = 96.89$ mA, $P_{\text{RMS}} = 17.79$ W, Current density = 30.84 mA cm$^{-2}$ (RMS), Power density = 5.66 W cm$^{-2}$ (RMS)).
Figure 10.9 (a) represents the long lived active species $\text{He}_2^*$, $\text{O}_2 \left(1\Delta_g\right)$ and $\text{O}$ along the length of the substrate. The central region of the substrate is found to have significantly fewer active species. This is due to the presence of the vortex in that region. The species have a peak number density at a distance of 6 mm from the center which is the location of the jet impingement. $\text{He}_2^*$, $\text{O}_2 \left(1\Delta_g\right)$ and $\text{O}$ number density profile along the axial distance at a fixed radial distance of 5.5 mm is shown in Figure 10.8 (b). All the long lived active species are observed to reach a peak value at 10 mm (end of the plasma domain). In the afterglow the species number density are found to decrease. A sharp decrease near the surface is due to the surface quenching reactions.

![Temperature Contours](image)

Figure 10.10: Neutral gas temperature contours (2 kΩ ballast resistance, 1% $\text{O}_2$. $V_{\text{d RMS}} = 272.1 \text{ V}$, $I_{\text{d RMS}} = 234.32 \text{ mA}$, $P_{\text{RMS}} = 52.1 \text{ W}$, Current density = 74.58 mA cm$^{-2}$ (RMS), Power density = 16.58 W cm$^{-2}$ (RMS)).

Neutral gas temperature contours for a 2 kΩ ballast resistance and 1% oxygen mass fraction is presented in Figure 10.10. For a ballast resistance of 2 kΩ the simulation predicted a RMS voltage, current and power of 272.1 V, 234.2 mA and 52.1 W respectively. The discharge power was found to increase by a factor of 2.9 compared to the high ballast resistance case. The
peak neutral gas temperature for this high power was predicted to be ~ 524 K, higher by 224 K from the ambient. This indicates significant gas heating even with the presence of helium and fast gas flow. The peak gas temperature was located near the edge of the electrodes. Compared to the low power $\alpha$ mode discharge the peak gas temperature was higher by 172 K. Near the substrate surface the gas temperature was observed to be ~ 410 K.

Comparing with the low power $\alpha$ mode discharge the time averaged peak O number density at high power was found to be ~ $9.5 \times 10^{21}$ m$^{-3}$ (Figure 10.11). The peak O was larger by an order of magnitude than that of the $\alpha$ mode discharge. In Figure 10.11 it can be further seen that the O number density distribution is not uniform across the entire inter-electrode separation, rather the high density region exists at the end of the plasma domain close to the electrode edge. The high temperature and non-uniformity of the species and temperature distribution within the inter-electrode separation indicates some change in the mode of operation ($\alpha - \gamma$ transition).

Figure 10.12 shows the time averaged O$_3$ number density contours at high power. At high power
the O₃ number density was found to decrease significantly. The peak O₃ was found to be ~ \(2.7 \times 10^{17}\) m\(^{-3}\), which is smaller by two orders of magnitude compared to that in the low power α mode. The decrease in the O₃ number density is due to high gas temperature observed. Since the high power discharge is significantly hotter and the major O₃ production mechanism (\(O + 2O₂ \rightarrow O₃ + O₂\)) having a very high sensitivity on gas temperature \(^{210}\), the O₃ concentration is found to decrease.

Figure 10.12: Time averaged O₃ number density contours (2 kΩ ballast resistance, 1% O₂. \(V_{d\text{RMS}} = 272.1\) V, \(I_{d\text{RMS}} = 234.32\) mA, \(P_{\text{RMS}} = 52.1\) W, Current density = 74.58 mA cm\(^{-2}\) (RMS), Power density = 16.58 W cm\(^{-2}\) (RMS)).
Figure 10.13: Time averaged He* number density contours a) 5 kΩ ballast resistance ($V_{d\text{ RMS}} = 221.91$ V, $I_{d\text{ RMS}} = 96.89$ mA, $P_{\text{RMS}} = 17.79$ W) $\alpha$ mode, b) 2 kΩ ($V_{d\text{ RMS}} = 272.1$ V, $I_{d\text{ RMS}} = 234.32$ mA, $P_{\text{RMS}} = 52.1$ W) $\gamma$ mode.
The time averaged He\textsuperscript{*} monomer number density for both the cases (5 k\(\Omega\) and 2 k\(\Omega\) ballast resistance) are shown in Figure 10.13. Since the electronically excited He\textsuperscript{*} monomer is responsible for the brightness of the discharge, the He\textsuperscript{*} number density contours describe the visual appearance of the discharge. At low power He\textsuperscript{*} number density contours indicate a luminous zone in the central region of the discharge. This appearance is similar to an \(\alpha\) mode discharge\textsuperscript{201}, where the discharge is volume dominated. At high power a constriction of the discharge is observed. The distribution of He\textsuperscript{*} further predicts two bright luminous regions near the electrode surface and a lesser bright region in the center. The discharge transitions from being volume dominated to surface dominated. The bright region near the electrode surfaces is typical of a \(\gamma\) mode discharge\textsuperscript{201}. The transition to the \(\gamma\) mode at high power occurs due to the sheath breakdown mechanism which has been discussed in details in Section 9.4.1.
Figure 10.14: Time averaged a) ion number density b) positive ions (\(\text{He}^+ + \text{He}_2^+ + \text{O}^+ + \text{O}_2^+\)),
negative ions (\(\text{O}^- + \text{O}_2^-\)) and electron number density along the radial distance (inter-electrode
separation) at \(x = 9.4\) mm. (2 kΩ ballast resistance, 1% \(\text{O}_2\). \(V_{d\ RMS} = 272.1\) V, \(I_{d\ RMS} = 234.32\)
\text{mA}, \(P_{RMS} = 52.1\) W, Current density = 74.58 mA cm\(^{-2}\) (RMS), Power density = 16.58 W cm\(^{-2}\)
(RMS)).
The ion density profiles (Figure 10.14 (a)) show high production rates of the ions near the electrode surfaces in the sheath region. The dominant positive ion was found to be $\text{O}_2^+$ with a peak number density of $\sim 10^{19} \text{ m}^{-3}$, larger by two orders of magnitude than the $\alpha$ mode discharge. A significant increase in the $\text{He}_2^+$ and $\text{He}^+$ number density were also observed. The peak $\text{He}_2^+$ and $\text{He}^+$ number density were larger by 3 and 4 orders of magnitude than that of the $\alpha$ mode. The higher $\text{He}_2^+$ and $\text{He}^+$ number density is a result of the high electric field. The peak electric field in the $\gamma$ mode was found to be $\sim 25 \text{ kV cm}^{-1}$ (Figure 10.16 (d)). The ion density profiles also indicate a transition from a volume dominated ($\alpha$ mode) to a surface dominated discharge ($\gamma$ mode). In the $\gamma$ mode the electron number density was found to be significantly higher than that of the negative ions. Smaller sheath sizes of $\sim 68 \mu\text{m}$ (Figure 10.16 (c) and (d)) and higher current density ($74.58 \text{ mA cm}^{-2}$ (rms)) in the $\gamma$ mode makes secondary electron emission due to ion bombardment important. The electron number density increase in the $\gamma$ mode is an effect of the secondary electron emission.
Figure 10.15: a) Time averaged electric field and b) He* number density distribution along the radial distance (inter-electrode separation) at different axial location (2 kΩ ballast resistance, 1% O₂. \( V_{d\,\text{RMS}} = 272.1 \) V, \( I_{d\,\text{RMS}} = 234.32 \) mA, \( P_{\text{RMS}} = 52.1 \) W, Current density = 74.58 mA cm\(^{-2}\) (RMS), Power density = 16.58 W cm\(^{-2}\) (RMS)).

Electric field and He* number density profile along the inter-electrode separation at different axial location (\( x = 5.5 \) mm and 9.4 mm) is shown in Figure 10.15 (a) and (b).
respectively. Both the distribution profiles indicate that the constriction of the discharge does not occur in a uniform pattern throughout the inter-electrode separation. Towards the end of the plasma domain (towards the electrode edge) the discharge is most constricted. At an axial distance of 5.5 mm the peak time averaged electric field was found to be \( \sim 12 \text{ kV cm}^{-1} \) (Figure 10.15 (a)). The peak time averaged electric field increased to a value of \( \sim 25 \text{ kV cm}^{-1} \) at \( x = 9.4 \), an increase by a factor of two. The sheath is also observed to reduce in size at that location. It reduces from \( \sim 140 \mu\text{m} \) at \( x = 5.5 \text{ mm} \) to \( \sim 68 \mu\text{m} \) at \( x = 9.4 \text{ mm} \). The peak electric field increases and the sheath decreases towards the edge of the electrode. As a result the transition to the \( \gamma \) mode at high power is observed to occur close to the electrode edge. The high electric field at the end of the electrodes is due to the effect of the electrode edges. The high electric field and small sheaths close to the electrode edge initiates the sheath break down phenomena and a transition from \( \alpha - \gamma \) mode is observed. The He\(^*\) number density profile along the inter-electrode separation at different axial location (Figure 10.15 (b)) shows that in the mid region of the discharge the peaks are less sharp and are more spread out, suggesting that in this specific region the discharge maintains \( \alpha \) mode like characteristics. The luminous He\(^*\) peaks get sharper towards the electrode edge. The peak He\(^*\) number density changes by an order of magnitude from \( x = 5.5 \text{ mm} \) to \( x = 9.4 \text{ mm} \). The higher density of He\(^*\) in that region is a consequence of the high electric acting there.
Figure 10.16: Time averaged a) positive and negative ion distribution b) electric field distribution at x = 5.5 mm for 5 kΩ ballast resistance (α mode) c) positive and negative ion distribution d) electric field distribution at x = 9.4 mm for 2 kΩ ballast resistance (γ mode) along the radial distance (inter-electrode separation).

Figure 10.16 summarizes the quasi-neutrality and the electric field in both the α and γ mode and compares them with each other. In the α mode the discharge is found to be quasi-neutral spanning a region of 360 μm in the central volume of the discharge (Figure 10.16 (a)). Large sheaths having a total thickness of 640 μm are observed. The large sheaths near the electrodes are also readily observed in the time averaged electric field distribution profile shown.
in Figure 10.16 (b). The central region having the minimum electric field corresponds to the area of quasi-neutrality. The peak electric field at the electrode surface was predicted to be \( \sim 5 \text{ kV cm}^{-1} \). In the \( \gamma \) mode the region of quasi-neutrality is found to expand laterally; reducing the size of the sheaths (Figure 10.16 (c)). The total sheath thickness in the \( \gamma \) mode was found to be 136 \( \mu \text{m} \), indicating a reduction factor of 2.6. The time averaged electric field distribution in the \( \gamma \) mode presented in Figure 10.16 (d), shows that the peak electric field significantly increases when the discharge operates in the \( \gamma \) mode. The peak electric field was found to be \( \sim 25 \text{ kV cm}^{-1} \), which is larger by a factor of 5 than that of the \( \alpha \) mode. For both the \( \alpha \) and \( \gamma \) mode case the inner electrode was found to have a slightly higher electric field than that at the outer grounded electrode. This higher electric field at the inner electrode was a result of self bias created due to the difference in sizes between the two electrodes. The comparison clearly shows that while operating in the \( \gamma \) mode the electric field gets higher and the sheath thickness becomes smaller. This indicates that the transition from \( \alpha – \gamma \) mode occurs due to a breakdown of the sheath.

### 10.4 Experimental Setup and Discharge Visualization Studies

Schematic diagram and photographs of the experimental setup used for conducting discharge visualization studies in presented in Figure 10.17. The inter-electrode separation was set to 0.145 cm and the length of the inter-electrode separation was 2.2 cm. The inner electrode was powered and the outer electrode was grounded. The powered electrode was connected to the Plasmatherm HFS – 500E RF power supply. Both the electrodes were places concentrically inside a plastic arrangement (shown in Figure 10.17 (c)). This maintained a fixed inter-electrode separation and also insulated the grounded electrode from the powered one. Gas entered the inter-electrode spacing through the periphery. Two Omega FMA 2600 flow controllers were
used to maintain a constant feed gas composition. For the discharge visualization studies the helium and oxygen flow rates were kept constant at 16 slpm and 160 sccm, respectively. The flow rates were chosen to maintain an inlet oxygen fraction of 1%. The 16 slpm helium flow rate also maintained a gas velocity of 5 m s\(^{-1}\) in the inter-electrode separation, which is consistent with the inlet gas velocity used in the simulations.

![Experimental setup](image)

**Figure 10.17:** Experimental setup a) front view b) bottom view and c) schematic diagram.

Figure 10.18 shows front and top view of the discharge with increasing RMS discharge current. A glass plate was placed in front of the plasma jet as a working substrate. The front view shows the length of the plasma afterglow and the top view shows the structure of the discharge in between the inter-electrode spacing. The visualization studies clearly show a transition in the
mode of operation at high discharge currents. At low currents it can be seen that the discharge does not cover the entire electrode separation referring to a ‘normal’ $\alpha$ mode discharge. With increasing discharge current the discharge is seen to fill the entire the electrode separation indicating the formation of $\alpha$ mode discharge operating in the ‘abnormal’ regime. At high discharge currents the discharge is found to pinch and transit to a $\gamma$ mode of operation. In the $\gamma$ mode the discharge occupied a small region in the inter-electrode spacing. The RMS discharge current in the $\gamma$ mode of operation was measured to be 310 mA. The $\alpha – \gamma$ transition predicted by the simulations occurred at similar RMS discharge current of 234.32 mA.

Figure 10.18: Visualization studies of the plasma jet for increasing discharge current. Front and top view with the glass substrate in front of the jet.

10.5 Conclusions

Simulation of atmospheric pressure plasma jet for surface decontamination applications was performed using a hybrid model. The model has an extensive volume chemistry involving 46 reaction step and 14 species. The predicted dominant species in the after glow of the
discharge were O, O$_2$ ($^1\Delta_g$), O$_3$ and He$_2^*$ which are the key species responsible for surface decontamination. A non uniform distribution of the active species on the substrate surface was predicted. It was identified that the vortex formed due to the gas flow created this non uniformity. At low power the simulations indicated the discharge to operate in the $\alpha$ mode (volume dominated). At high power a transition was observed in the operation mode. The discharge was found to transition from $\alpha$ – $\gamma$ mode due to sheath breakdown mechanism. While operating in the $\gamma$ mode the discharge constricted in the axial direction and lost its uniformity. The He$^*$ monomer number density distribution depicted the discharge to have bright luminous regions near the electrode surfaces. The gas temperature in the $\gamma$ mode was also found to be sufficiently higher, making it unsuitable for bio-sterilization and bio-decontamination applications. Visualization studies compared favorably to the $\alpha$ – $\gamma$ transition predicted by the simulations.
11 Summary Conclusions and Recommendations

11.1 Summary

Hybrid models together with external circuit model have been developed to simulate atmospheric pressure, non-thermal micro plasma discharge powered by both DC and RF power sources. The discharge models include: discharge physics, discharge chemistry, surface processes and external circuit effects. The model was found to accurately characterize experimental measurements of the discharge. The simulation of multi dimensional, multi species, non-thermal plasma discharge is very complex which involves the interaction among different species, transport of the species due to electric field and also fluid flow, increase in neutral gas temperature through energy cascading, interaction of species on the surface and also the influence of external circuit elements on the discharge characteristics. The simulations using the hybrid model were able to provide detailed insight into physico-chemical processes that are difficult to obtain through direct measurements in these small scale systems. In addition detailed analysis was conducted through the simulations in determining the discharge characteristics, regime of operation and also in determining potential applications. In a broader aspect the simulation has been used as a tool to understand and analyze the discharge characteristics and study the effect of different operating parameters on the discharge that can lead to the design of novel atmospheric pressure micro plasma reactors.

As the first step of simulations, a multi-dimensional DC argon micro plasma discharge operating in a pin-plate electrode configuration was studied. Monatomic argon micro plasma discharge was chosen due to the simpler gas phase chemical kinetics (no vibrational, rotational levels of excitation). The effect of ballast resistance on the discharge characteristics was
investigated. Experimental measurements of voltage-current characteristics, gas temperature and current density were conducted for model validation purpose. Comparison between the model predictions and experimental measurements were in favorable agreement which validated the developed model. The model was further extended to study atmospheric pressure DC micro plasma discharges operating in hydrogen. Diatomic hydrogen requires addition of vibration; excitation which is one of the most dominant sinks of the electron energy. Vibrational excitation and de-excitation mechanisms were included in the gas phase chemical kinetics model. In addition gas heating due to vibrational to translation relaxation (Frank-Condon effect) was taken into account. The self-consistent hybrid model was used to solve for the temporal and spatial distributions of electrons, ionic species, electronically and vibrationally excited species, electron energy, electric field and electrostatic potential in the discharge. Simulations were performed under the design and operating conditions achieved by the experimental setup to validate the model. The effect of secondary electron emission coefficient and ballast resistance on the discharge characteristics was studied. The simulation predictions compared favorably to the measured voltage-current characteristics, current density and discharge visualization.

A one dimensional hybrid model for simulating DC methane-hydrogen micro plasma discharge operating in atmospheric pressure was developed. The model contained a detailed gas phase chemical kinetics and a surface kinetics model for predicting diamond like carbon (DLC) thin film deposition. The gas phase chemical kinetics model included different levels of vibrational excitation reactions to determine the electron energy distribution function accurately. The gas phase chemistry model was used to determine the dominant radical and ionic species that are responsible for thin film deposition. DLC, graphite like carbon (GLC) and soot deposits were tracked separately in the surface chemistry model to predict the quality of the deposited
film. In addition different chemical pathways responsible for DLC deposition were (stitching vs molecule/radical reactions) also explored. Parametric studies were performed to investigate the effects of operating parameters that are important in obtaining pristine diamond like carbon thin film deposits. The model was validated by comparing the predicted stable neutral species density and methane conversion factor to mass spectrometry measurements. The discharge model was extended to two dimensional cylindrical coordinates to apply for real reactor configurations. The multi dimensional simulations provided insight into the deposition profile and its uniformity; a key issue for applications.

To investigate the effect of the external matching circuit on atmospheric pressure RF glow discharge a one dimensional hybrid model with a detailed external circuit was employed. To simplify chemical kinetics argon as the feed gas was selected. The simulations provided spatial-temporal evolution of electron density, ionic and electronically excited species density, electric field, electrostatic potential, electron and gas temperature distribution within the inter-electrode separation distance. Parametric studies were performed for the RF discharge under different matching circuit conditions. The matching circuit parameters, such as loading and tuning circuit were varied to study their effects on the internal process variables. The internal process variables determine the characteristics and operation mode of the discharge. The predicted voltage-current characteristics were compared with published experimental results and were found to compare favorably.

To study potential applications of atmospheric pressure RF powered non-thermal plasma discharges, an atmospheric pressure plasma jet (APPJ) operating in helium-oxygen feed gas was simulated using the hybrid model for surface decontamination applications. The effect of discharge current (power) on the discharge characteristics was studied. Depending on the
discharge current the discharge evolved from a room temperature, uniform, volume dominated (α mode) to a moderately high temperature, constricted, surface dominated (γ mode) discharge. This prediction was found to agree favorably to the experimental visualization studies.

11.2 General Conclusions

The most significant conclusions that can be drawn from the present study is that hybrid model with ‘local field’ approximation can accurately simulate the discharge characteristics of atmospheric pressure micro glow discharges. In order to conduct accurate predictions however the external circuit parameters were found to be crucial; especially in the ‘normal’ glow regime due to multi-valued solution for the same discharge voltage (i.e. increasing discharge current with a constant discharge voltage). In addition the breakdown phenomena could also be simulated, which is not possible without explicitly considering the external circuit.

The present study further showed that atmospheric pressure micro glow discharges are not essentially ‘cold’ type rather they are ‘warm’ (500 – 1000 K) discharges. Ion joule heating (high power density) and vibrational to translational relaxation are the key mechanisms that results in the moderate gas temperature. By controlling the gas temperature, uniform, good quality DLC thin film can be deposited using DC atmospheric pressure micro glow discharge. Unlike its low pressure counterpart, atmospheric pressure RF glow discharge was found to lose their uniformity and low temperature characteristics and transformed to a non-uniform, moderately high temperature discharge at high power. The more specific conclusions of the research projects are discussed in the following sections.
11.2.1 Simulation of Atmospheric Pressure DC Argon Micro Plasma Discharge

- Simulations were performed for DC argon micro plasma discharge with a pin-plate electrode configuration. The inter-electrode separation for the simulation cases were 200 μm. The ballast resistance was varied to change the discharge current and obtain voltage-current characteristics.

- The flat voltage-current characteristics predicted indicated that the discharge operated as a ‘normal’ glow discharge. An onset to the ‘abnormal’ glow discharge was observed as well. The development of the constant ‘normal’ current density was predicted and had a value of ~ 1.1 A cm⁻². Increase of the total discharge occurred only by the growth of the cathode spot through which the current flow. The onset to the ‘abnormal’ glow discharge occurred when the entire cathode area showed increased current density.

- The electronically excited species Ar⁺ distribution showed high and low intensity regions, corresponding to the ‘negative glow’, ‘Faraday dark space’ and ‘positive column’ observed in low pressure DC glow discharges.

- The peak gas temperature was found to be ~ 550 K in the ‘normal’ glow operating regime, indicating a non-thermal discharge.

- Predicted voltage-current characteristics, ‘normal’ current density, gas temperature compared favorably to the experimental measurements and validated the developed model.
11.2.2 Simulation of Atmospheric Pressure DC Hydrogen Micro Glow Discharge

- Multi dimensional simulation of DC hydrogen micro plasma discharge operating with a pin-plate electrode and having an inter-electrode separation of 400 μm was conducted. The simulations indicated that the discharge had the general characteristics of a non-thermal ‘normal’ glow discharge, which included moderate gas temperature, a flat voltage-current characteristics and a constant ‘normal’ current density of ~ 22 A cm\(^{-2}\).

- The maximum vibrational temperature was found to be 1560 K, significantly larger than the neutral gas temperature. Ion joule heating and Frank-Condon (vibrational – translation relaxation) heating were found to be the dominant gas heating mechanism. Ion joule heating was dominant in the cathode sheath region where as Frank-Condon heating was dominant in the bulk.

- The electronically excited species profiles (\(H_2^* (C^1Π_u 2p\pi) + H^*(2p)\)) indicated two high concentration regions near the cathode and the anode. These correspond to the cathode and anode glow existing due to the presence of the high electric fields in the sheath regions. With an increase in the discharge current (decrease in the ballast resistance) these luminous regions were predicted to increase in size in the lateral direction, covering more areas of the electrode; a key feature of ‘normal’ glow discharge.

- Dependence on the secondary electron emission coefficient showed that with an increase in secondary electron emission coefficient a decrease in the discharge voltage was observed. With a fairly constant voltage drop in the positive column most of the changes were found to occur at the cathode voltage drop.
The general plasma characteristics (voltage-current characteristics, current density measurements and luminous regions) were compared with experimental measurements and were found to be in favorable agreement.

11.2.3 One Dimensional Simulation of Micro Glow Discharge in Methane-Hydrogen

Simulations were conducted for parallel plate electrode geometry with an inter-electrode separation of 200 μm. The spatial distribution of the species densities, electron and neutral gas temperatures in these micro-discharges were predicted and the influence of the different plasma parameters on the deposition characteristics was identified.

The heavy ionic species H$_3^+$, C$_2$H$_5^+$ and CH$_5^+$ were found to be the dominant ions in atmospheric pressure methane-hydrogen micro discharge in contrast to the predominant H$_2^+$ and CH$_5^+$ of the low pressure glow discharge. Considerable amounts of CH$_3^+$ and CH$_4^+$ were also found to be present. All the ion densities were found to have the maximum near the cathode in the sheath region.

Among the different radicals H, CH$_2$ and CH$_3$ were found to be the prominent radicals, while CH$_2$ and CH$_3$ are also key components for DLC deposition. Substantial amounts of CH and C$_2$H$_5$ radicals were found to be present in atmospheric pressure micro discharges which are minor products in low pressure macro discharges. Higher order neutral hydrocarbons C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$ and C$_3$H$_8$ were found to be present in abundance which is not the case for low pressure macro plasmas.
• The effect of discharge current showed that the gas temperature increased with increasing discharge current due to ion Joule heating. The gas temperature had a significant effect on soot formation and deposition. Even though high power is desirable to raise the deposition rate, it increases the soot deposition and significantly degrades the film quality.

• The effect of increased methane fraction was found to increase the C$_2$H$_2$ formation in the discharge, resulting in higher soot content and hence a sooty deposit.

• Mass spectrometry measurements were conducted to determine the methane conversion factor and the C$_2$H$_2$ concentration in the discharge. The numerical predictions were found to be in favorable agreement with the measurements.

11.2.4 Two Dimensional Simulation of Methane-Hydrogen Micro Glow Discharge

• Two dimensional simulations of methane-hydrogen micro glow discharges provided detailed insight into the plasma and the associated deposition characteristics. Simulations were conducted for a pin plate electrode configuration with an inter-electrode separation of 400 μm. A time stepping technique was developed to address the disparate time scales associated with the plasma and fluid transport.

• The obtained voltage-current characteristic was similar to the two dimensional argon and hydrogen micro discharge simulation predictions. The voltage-current characteristics obtained from the simulations showed a fairly constant discharge voltage with increasing discharge current; a ‘normal’ glow discharge characteristics.
• The discharge was found to be quasi-neutral in the bulk of the plasma region, apart from the sheaths formed at the electrode. The cathode sheath was found to be larger than that of the anode. The simulations revealed that the edge of the small radius anode affected the electron temperature and also the ion and radical number density.

• The deposited film was predicted to be comprised of mostly DLC with very little graphite like carbon and negligible soot. The radial profiles of deposition rate showed a maximum at the negative glow region. With an increase in the discharge current the DLC deposition rate profile was found to expand in the lateral direction, signifying that the radial size of the deposition was governed by the cathode spot.

### 11.2.5 One Dimensional Simulation of Argon RF Discharge in Atmospheric Pressure

• The simulations were conducted for parallel plate geometry with an inter-electrode separation of 1.0 mm. The loading and tuning capacitors of the external circuit were varied to study the effect of the matching network on the plasma characteristics.

• The predicted voltage-current characteristics indicated two modes of operation. In the low discharge current range the discharge operates in the $\alpha$ mode and evolves to a $\gamma$ mode at high discharge currents. The model predicted that the discharge remained capacitive while operating in the $\alpha$ mode and evolved to being conductive in the $\gamma$ mode of operation. Higher temperature was observed in the $\gamma$ mode of operation due to the high electric field and high current density.

• The tuning and loading capacitors of the matching circuit were found to have significant effects on the discharge characteristics. For small values of the tuning
capacitor the discharge was found to operate in the $\alpha$ mode. Furthermore the discharge was found to be better matched when operating in the $\gamma$ mode.

### 11.2.6 Simulation of Atmospheric Pressure Plasma Jet (APPJ)

- An atmospheric pressure helium-oxygen plasma jet having an annulus electrode configuration was simulated. The inter-electrode separation was 1 mm with the inner electrode being powered.

- Large concentrations of O and O$_3$ were found to be present, which are key species for decontamination applications. These species however did not have a uniform distribution on the target substrate. This was due to the formation of two counter rotating vortices as a consequence of the electrode configuration.

- The predictions indicated a $\alpha$ – $\gamma$ transition with an increase in the discharge power. In the $\gamma$ mode the discharge lost its uniformity and was found to be constricted to a very small region. Higher gas temperature in the $\gamma$ mode makes it unsuitable for bio-sterilization and bio-decontamination applications.

- Discharge visualization studies were found to compare favorably to the $\alpha$ – $\gamma$ transition predictions.
11.3 Recommendations for Future Work

To further advance the knowledge in developing novel plasma discharges and plasma processing in atmospheric and/or higher pressure the following research tasks are recommended.

11.3.1 Gas Phase Chemical Kinetics Model for Air Micro Plasma Discharge Simulations

Atmospheric pressure micro plasma discharges have been extensively studied in air without the addition of any exotic feed gas. Our present research effort resulted in the development of gas phase chemical kinetics for argon, hydrogen, methane-hydrogen and helium-oxygen. The development of reduced air kinetic model is still an open field. The main complication for air chemistry arises due to fact that both nitrogen and oxygen, major constituents of air, are diatomic. As a result various levels of vibrational and rotational levels of excitation and de-excitation have to be considered to accurately determine the electron energy distribution function and hence the reaction rates and electron transport properties. An accurate database of cross section data is required for that purpose. In addition sensitivity study is also necessary to develop reduced mechanisms from very detailed chemical kinetics.

11.3.2 Extension of Model to Incorporate Surface Evolution

The present models can be extended to incorporate surface evolution in order to predict the shape of the surface. One important application of the simulation of surface evolution in semiconductor industries is the planarization of silicon dioxide inter-level dielectric layers that can be modeled as the outcome of simultaneous sputter, etching and deposition.
11.3.3 Extension of Model to Predict Physical Properties of Deposited Films

In the present model, the deposition rate, uniformity and quality of the diamond like carbon film was calculated. The model can be further extended to predict other film properties such as refractive index, extinction coefficient, thermal conductivity etc.

11.3.4 Ionic Species Concentration Measurements

Most of the model validation in the present research was done by conducting comparison with basic plasma characteristics (voltage-current characteristics, current density, and neutral gas temperature). Even though mass spectrometry measurements were conducted to determine stable neutral density, no measurements for ionic species concentration and their distribution within the inter-electrode separation was done. The measurement of ionic species distribution within the inter-electrode separation would enable a better comparison with the model predictions that would help to validate the gas phase kinetics part of the model. A mass spectrometer having the capability of measuring ionic species in atmospheric pressure condition has to be used for that purpose. In addition, a mass spectrometer having a variable ionization energy source can also be used to conduct threshold mass spectrometry that would enable one to determine the threshold electron energy requirement in different electron induced reactions.

11.3.5 Modeling Non-thermal Plasma Discharge in Liquid Phase

For many years, underwater welding gas required the use of thermal discharges. In this type of plasma, the discharge occurs inside a gas bubble, which forms due to the intense heat produced in the discharge. Current development of water treatment applications has caused a renewed interest in non-thermal plasma discharges in liquid phase \(^{216}\). Even though various experimental studies have been conducted, the discharge formation mechanism is still unclear.
Having a discharge in liquid phase is similar to having a discharge in higher pressure (due to the higher density of species). The present model can be extended to model non-thermal plasma discharge formation in liquid phase.

11.3.6 Code Improvements

All the simulations conducted were run on a serial machine. The code can be parallelized so that the simulations can be run in cluster machines, which would reduce the computation time significantly. In cluster machines multi dimensional simulations having very detailed chemical kinetics can also be easily simulated. In the present study, isothermal boundary conditions for the neutral gas temperature were employed; this is an idealized case. The code can be further improved so that it can handle conjugate heat transfer problems.


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Z. Huang, Z. Pan, Y. Wang, and A. Du, "Deposition of hydrocarbon molecules on diamond surfaces (001) surfaces: atomic scale modeling" *Surface and Coatings Technology* 158-159, p. 94-98 (2002).


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APPENDIX

A.1 Implicit Formulation of Poisson’s Equation

Implicit formulation of electron conservation equation:

\[ n_e^{(t+\Delta t)} = n_e^{(t)} + \Delta t [\nabla \cdot (\mu_e n_e^{(t+\Delta t)} \nabla \phi^{(t+\Delta t)}) + D_e \nabla n_e^{(t+\Delta t)}] + \dot{n}_e \]  \hspace{1cm} (A.1)

The Poisson’s equation at \((t + \Delta t)\) is expressed as:

\[ \nabla \cdot \nabla \phi^{(t+\Delta t)} = \frac{\varepsilon}{\varepsilon} [\sum_{i=ions} q_i n_i^{(t+\Delta t)} - n_e^{(t+\Delta t)}] \]  \hspace{1cm} (A.2)

Combining both equations we get

\[ \nabla \cdot \nabla \phi^{(t+\Delta t)} = \frac{\varepsilon}{\varepsilon} [\sum_{i=ions} q_i n_i^{(t+\Delta t)} - n_e^{(t+\Delta t)}] - \Delta t [\nabla \cdot (\mu_e n_e^{(t+\Delta t)} \nabla \phi^{(t+\Delta t)}) + D_e \nabla n_e^{(t+\Delta t)}] + \dot{n}_e \]  \hspace{1cm} (A.3)
A.2 Scharfetter-Gummel Exponential Discretization Scheme

Fluxes for the charged species are formulated using the optimum exponential scheme of Scharfetter-Gummel, which is robust and provides stable solutions even in the presence of steep gradients. In this method, the flux between node $i$ and neighbour $j$ is given by:

$$\Gamma_{i,j} = \alpha \overline{D} \left( n_j - n_i \exp(\alpha_j \Delta x_j) \right) \left( 1 - \exp(\alpha_j \Delta x_j) \right)$$

(A.4)

where, $\alpha$ is given by:

$$\alpha_{ij} = \frac{q}{|q|} \bar{\mu} \left( \frac{\Phi_j - \Phi_i}{\Delta x_{ij}} \right)$$

(A.5)

where, $q$ is the elementary charge, $\Phi$ is the electrostatic potential, $\Delta x_{ij}$ is the distance between the nodes and $\bar{\mu}$, $\overline{D}$ are the average mobility and diffusion coefficient in the interval.

$$\Delta x_{ij} = \overline{x}_j - \overline{x}_i, \quad \overline{D} = \left( \frac{D_i + D_j}{2} \right), \quad \bar{\mu} = \left( \frac{\mu_i + \mu_j}{2} \right)$$

(A.6)
A.3 Sample Input File for Lookup Table Generation

The input file used for the generation of lookup tables for atmospheric pressure argon glow discharge from the solution of the zero dimensional Boltzmann equation is given below. The electron range is set $1 \times 10^{12}$ m$^{-3}$ to $2 \times 10^{20}$ m$^{-3}$. The upper limit corresponds to normal glow discharge conditions. The lower limit is set to a low value at which electron density (namely electron-electron collisions) does not affect the electron energy distribution function. The electric field values ranges from $10^4$ V m$^{-1}$ to $10^7$ V m$^{-1}$, typical of the electric field in the positive column and negative glow at atmospheric pressure.

```plaintext
# species relaxation parameters (to freeze reactions in 1 cell geometry)
relax_pos_charged_species double 1 0.
relax_neutral_species double 1 0.
# flag to include SQRT(u) in FP equation: default = 0
# always 1 if plasma is on
Energy int 1 1
# determines when to start calculating macro parameters from kinetics:
# default = 0 (never)
N_TIMES_MACRO_BOLTZ int 1 1
# Wall Potential for 0D Boltzmann calculations (e.g. in global model)
# default = 0 (no wall losses)
Phi_Wall_Glob double 1 0.0
# minimum energy on face in kinetic module: default = 0.
MIN_ENERGY_EDF double 1 0
# flag for local Boltzmann calculations
Local_Boltz int 1 1
# flag for lookup table generation (default = 0)
# works only for 0D cell
Lookup_Table_Calc int 1 1
# number of electron density points in lookup table (LUT) (default = 10)
No_Ne_LUT int 1 10
# number of electric field points in lookup table (default = 12)
No_E0_LUT int 1 100
# min and max values of electron density (m-3) for LUT, log-scale
# (defaults = 1.D+16 and 1.D+18)
Ne_LUT_MIN double 1 0E+12
Ne_LUT_MAX double 2 0E+20
# min and max values of electric field E0 (V/m) for LUT, log-scale
# (defaults = 1.D+01 and 1.D+03)
E0_LUT_MIN double 1 0E+04
```

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E0_LUT_MAX double 1 0E+07
# tolerance for LUT calculations
# default = 0 => no tolerance check
TOL_LUT double 1 1E-05
# set how quickly to ramp down time step dt for LUT
# when ramping up E0, dt ~ dt/E0^RAMP_DT_POW_LUT
# default = 0 => do not change dt
RAMP_DT_POW_LUT double 1 1
A.4 Sample Circuit File for DC Discharge Calculations

An example of a SPICE circuit file having an extension of ‘.cir’, for DC simulations corresponding to the RC circuit in Figure 5.2 is shown below:

Atmospheric Pressure DC Discharge

```
.model ccp ACE
+ model="Argon.DC.DTF"
+ pin1="electric:grounded"
+ pin2="electric:anode"
+ tol=1e-2 zero=1e-12
+ minTimeStep=10ps
+ maxvoltchg=50.0
+ trace=2 minIter=2 maxIter=5
+ noCurrentUntil=50ns
+options RELTOL=0.01 VNTOL=0.5V ABSTOL=0.01A ITL4=20
Vsrc 1 0 500V
R1 2 1 100 kOhm
C1 2 0 1pF
Accp 0 2 ccp
.IC V(1)=500 V(2)=0
.TRAN 10 ps 5ms 0 ps 10 ps UIC
```

The complete documentation of the SPICE code can be found in the SPICE code manual. Here we describe some import necessary parameters for the link with CFD-ACE+. The file which controls SPICE execution is called a circuit file (.cir extension). The model parameter sets the name of model.DTF file. The pin1 and pin2 parameters set the names of the boundary patches specified in CFD-GUI (surface patch names in CFD-GUI and .cir file must match). For the example case, one of the electrodes is powered and is named as “anode”, and the other electrode is grounded and is named “grounded”. Vsrc, R1 and C1 designates the power source voltage, ballast resistance and parasitic capacitance respectively. The numbers with the circuit elements corresponds to the nodes in the circuit, with ‘0’ being ground.
The time steps are set by three parameters: minTimeStep, .TRAN(1) and .TRAN(4). These three parameters should be set to the same value (here, 10 ps), which should also be set in CFD-GUI (flow time step and plasma time step). The calculation of the admittance term \(dI/dV\) is switched off for plasma simulations by setting deriv=(0,0) – these gives better convergence and control of the solution. It is useful to set zero current for first several time steps, which is done by setting noCurrentUntil=50 ps. The initial conditions at nodes 1 and 2 are set by .IC V(1)=500 V(2)= 0. The minimum and maximum number of iterations per pin is set by minIter=2 maxIter=5 – these parameters will overwrite the Max. Iterations parameter specified in GUI: Solver Control: Iterations. The output verbosity level is set by trace=2 (it may be set to 3 to get more output information, but the .log file will grow larger). See SPICE code manual for the detailed list of other control parameters.
A.5 Sample Circuit File for RF Discharge Calculations

An example of a SPICE circuit file, for RF simulations corresponding to the RLC circuit in Figure 9.1 is shown below:

```
RF discharge
.model ccp ACE
+ model="1d.argon.rf.DTF"
+ pin1="electric:grounded"
+ pin2="electric:powered"
+ tol=1e-2 zero=1e-12
+ minTimeStep=100ps
+ deriv=(0,0)
+ maxvolchgl=50.0
+ trace=1 minlter=2 maxlter=5
+ noCurrentUntil=1000ps

.options RELTOL=0.01 VNTOL=0.5V ABSTOL=0.01A ITL4=20
Vsrc 1 0 SIN(0V 300V 13.56MegHz 0)
R1 1 2 50 ohm
C1 2 0 50pF
L1 2 3 1uH
C2 3 4 100pF
C3 4 0 5pF

Accp 0 4 ccp
.TRAN 100ps 0.1ms 0ps 100ps UIC
.END
```
A.6 Measurement of NO and NO$_2$ concentration in Atmospheric Pressure Micro Glow Discharge in Air$^6$

A schematic diagram of the experimental setup for conducting mass spectrometry of the discharge is shown in Fig. A.1. The discharge was enclosed in a sealed glass chamber. The discharge chamber had two valves to control the gas inflow and outflow from the chamber. When room air was used as the feed gas both the valves were kept fully open. A Swagelok needle valve having a vernier handle connected the discharge chamber to the mass spectrometer. The needle valve is essential in maintaining the flow rate to the mass spectrometer within the desirable range. In the experiments the needle valve was set to have a flow rate of 0.5 sccm. A HP 5970B quadrupole mass spectrometer was used for sampling the species created in the discharge volume. The mass spectrometer is equipped with an internal electron source with constant electron energy of 70 eV. Although this sampling system is simple volume averaged concentrations of stable species could be measured.

Figure A.1: Schematic diagram of the experimental setup for the mass spectrometry experiments in air micro glow discharge.

Ambient gas composition was determined from the mass spectra at 70 eV without the plasma discharge. The response of the different mass signals especially 30 amu – NO and 46 amu – NO₂ were monitored to varying discharge current. Fig. A.2 shows the mass spectra with and without the plasma discharge. It can be clearly seen that with the plasma discharge two distinct peaks exist at 30 amu and 46 amu, which were not observed without the plasma discharge. The observed peaks suggest significant production of NO and NO₂ in the discharge volume.

![Mass spectra with and without the discharge. The discharge current was 4.44 mA.
For both cases the mass spectrometer ionization source was turned on and kept at 70 eV.](image)

Since the mass spectrometer electron source had constant electron energy of 70 eV additional fragmentation of the stable species occurred within the mass spectrometer. This made it difficult to quantify the species being produced in the plasma discharge. This was overcome by
generating theoretical mass spectra using available fragmentation data of N₂, O₂, NO, NO₂, N₂O and H₂O in a 70 eV ionization source and comparing it with the experimentally obtained mass spectra. The fragmentation data were collected from the NIST database. MATLAB software was used to obtain the best fit between the theoretical and experimental spectra, with N₂, O₂, NO, NO₂, N₂O and H₂O percentage being the fitting parameters. The obtained percentage of N₂, O₂, NO, NO₂, N₂O and H₂O are considered as the species concentration in the discharge volume.

![Figure A.3: NO and NO₂ percentage as a function of discharge current.](image)

Figure A.3 shows the percentage of NO and NO₂ as a function of discharge current for an inter-electrode separation of ~ 1mm. The NO percentage varied in the range of 0.5 – 2.0 %, with a peak of 1.82 % at higher discharge currents. The NO₂ concentration varied in the range of 0.03 – 0.05 % in the discharge current range of 2.83 mA – 5.28 mA. For discharge currents lower than 2.83 mA the NO₂ signals could not be unambiguously distinguished from the noise levels.
The MATLAB code used to obtain the best fit between the theoretical and experimental mass spectra is given below:

function out=fminimize(pct,Param)
    X = Param(2);
    Y = Param(2);

    pctN2=pct(1);
    pctO2=pct(2);
    pctH2O=pct(3);
    pctNO=pct(4);
    pctNO2=pct(5);
    noise = pct(6);

    % mass 14 N
    mt(1,1)=(0.120314*pctN2)+(0.066963*pctNO)+(0.056844*pctNO2);
    % mass 15 N isotope
    mt(2,1)=(0.021419*pctNO);
    % mass 16 O
    mt(3,1)=(0.178307*pctO2)+(0.007359*pctH2O)+(0.013419*pctNO)+(0.132202*pctNO2);
    % mass 17 OH
    mt(4,1)=(0.17498*pctH2O);
    % mass 18 H2O
    mt(5,1)=(0.817661*pctH2O);
    % mass 28 N2
    mt(6,1)=(0.87184*pctN2);
    % mass 29 isotope
    mt(7,1)=(0.007847*pctN2);
    % mass 30 NO
    mt(8,1)=(0.878688*pctNO)+(0.591506*pctNO2);
    % mass 31
    mt(9,1)=(0.003571*pctNO);
    % mass 32 O2
    mt(10,1)=(0.821693*pctO2);
    % mass 44
    mt(11,1)=0.0;
    % mass 45
    mt(12,1)=0.0;
    % mass 46
    mt(13,1)=(0.219449*pctNO2);

    intp=((mt+ noise)/(max(mt)+ noise));
    semilogy(1:13,Y,1:13,intp)
    pause(.01)
DIFF = Y - (intp);

if (sign(pctNO2)) ==(sign(pctN2))
    summ = 1e6
else
    summ = 0.0
end

SQ_DIFF = (DIFF.^2)+summ;
out = sum(SQ_DIFF)
VITA

Tanvir Farouk was born in Dhaka, Bangladesh on January, 1977. He received his Bachelor’s in Mechanical Engineering from Bangladesh University of Engineering and Technology (BUET) in 2001 with concentrations on thermal-fluid science. He then joined BUET as a lecture and worked for almost a year in the department of Mechanical Engineering. He received his Master’s of Applied Science (M.A.Sc.) in Mechanical Engineering from University of Toronto, Canada, where his research work was related to stable fluid configuration under microgravity condition; supported by the Canadian Space Agency. He joined the doctoral program in the department of Mechanical Engineering and Mechanics at Drexel University, Philadelphia, in January 2005. He has received the George Hill Jr. Fellowship, George Law Scholarship, and Graduate Research Excellence Award. He has also received several travel grant fellowship from National Science Foundation and Gordon Research Conference. He has worked both as a Research and Teaching Assistant throughout his years at Drexel University. His research interests include computational and experimental investigations of non-thermal plasma discharges and fluid dynamics problems.

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