A study of Direct Current Corona Discharges in Gases and Liquids for Thin Film Deposition

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Dedications

I would like to dedicate this thesis to my family; my dad, mum and sister. Thank-you for your constant and unwavering support.
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# Table of Contents

List of Tables ........................................................................................................................................ viii

List of Figures ......................................................................................................................................... ix

Abstract .................................................................................................................................................. xiii

Chapter 1 : Introduction .......................................................................................................................... 1

1.1. Plasma discharges ........................................................................................................................... 1

1.1.1. Thermal plasma discharges ....................................................................................................... 2

1.1.2. Non-thermal plasma discharges ............................................................................................... 3

1.2. Motivation: Application of atmospheric pressure plasma discharges in material processing ................................................................. 3

Chapter 2 : Background and Literature Review ..................................................................................... 5

2.1. Corona discharges ............................................................................................................................ 5

2.2. DC and pulsed plasma discharges in liquids .................................................................................... 6

Chapter 3 : Atmospheric pressure dc negative corona discharge in gases ............................................. 9

3.1. Experimental setup and procedure ............................................................................................... 9

3.2. Global characterization of the discharge in air .............................................................................. 11

3.2.1. Comparison of the negative corona to the positive corona ................................................... 11

3.2.2. Discharge Visualization .......................................................................................................... 13

3.2.3. Electrical Characterization ..................................................................................................... 16
3.2.4. Spectral characteristics ................................................................. 18

3.3. Spatially resolved characteristics of the discharge in air .................. 21

3.3.1. Spatially resolved temperature measurements .......................... 21

3.3.2. Current density measurements .................................................... 26

3.3.3. Electric field measurements ......................................................... 28

3.4. Global characterization of the discharge in Nitrogen and Helium ........ 32

3.5. Application in thin film deposition .................................................. 35

3.6. Analysis of the diffuse glow ............................................................ 38

3.7. Chapter Summary ........................................................................... 40

Chapter 4 : DC Plasma Discharges in Liquids ........................................... 41

4.1. Experimental setup and procedure .................................................. 41

4.2. Global characterization of the discharge in TEOS ........................... 43

4.2.1. Discharge visualization ............................................................... 43

4.2.2. Electrical characterization .......................................................... 45

4.3. Global characterization of the discharge in transformer oil .............. 47

4.3.1. Discharge visualization ............................................................... 47

4.3.2. Electrical characterization .......................................................... 48

4.4. Application of the discharge in thin film deposition ......................... 49

4.5. Chapter Summary ........................................................................... 52

Chapter 5 : Conclusions and Recommendations for Future Work ........... 53
5.1. Conclusions ................................................................................................................. 53

5.2. Recommendations and Future Work ............................................................................. 55

5.2.1. Preliminary study of pulsed corona discharges in liquids ......... 55

5.2.2. Modelling of atmospheric pressure plasma discharges ............. 62

References ............................................................................................................................ 64
List of Tables

Table 3.1: Cases studied ........................................................................................................ 11
List of Figures

Figure 1.1: A schematic description of the initiation of a plasma discharge between a point and a plate electrode .......................................................... 2

Figure 3.1: External electrical circuit used to characterize the DC negative corona discharge. .......................................................... 10

Figure 3.2: Semi-log plot of V-I characteristics for a negative (case 2) and a positive corona (case 3) discharges in air. The electrode spacing is 5.0 mm for both discharges. 12

Figure 3.3: Positive corona (case 3) in air for a pin to plate configuration. The cathode plate is indicated by a white line. Conditions are 30 μA and 5.0 mm electrode spacing. 13

Figure 3.4: Images of the DC negative corona discharge in air at (a) 6.0 mm, case 1 (b) 5.0 mm, case 2 (c) 3.0 mm, case 5 and (d) 2.0 mm, case 6 electrode spacing. The anode plate is at the bottom of the image................................. 15

Figure 3.5: The height and the radius of the diffuse glow for different electrode spacing, cases 1, 2, 4 and 5 respectively................................. 16

Figure 3.6: Current-voltage characteristics for the negative corona discharge in air at different electrode spacings, cases 1, 2, 5, 6 and 7 respectively. The dashed lines indicate an unstable transition regime with time-averaged current.......................... 17

Figure 3.7: Optical emission spectra from the DC negative corona discharge in air (case 2) between 300.0 and 400.0 nm near (a) anode and (b) cathode.......................... 19

Figure 3.8: Measured optical emission spectra and best fit SPECAIR prediction for a 0.1 mA DC negative corona discharge in air at atmospheric pressure, case 2. ....................... 20
Figure 3.9: Spatially resolved rotational/gas temperature in air for a 5.0 mm electrode spacing, case 2. ................................. 22

Figure 3.10: Spatially resolved vibrational temperature in air for a 5.0 mm electrode spacing, case 2. ................................... 23

Figure 3.11: Ratio of intensities of the N₂ second positive and the N₂ first positive transitions across the discharge gap, case 2. ................................................................. 24

Figure 3.12: Electronic excitation temperature as a function of axial distance from the anode surface, case 2................................. 25

Figure 3.13: Spatially resolved current density measurements across the discharge gap in air for four inter-electrode spacings (cases 1, 2, 4 and 5) at a constant discharge current of 110 μA. ................................................................. 27

Figure 3.14: Spatially resolved current density measurements across a discharge gap of 6.0 mm (case 1) for four different values of discharge current. ............................................. 28

Figure 3.15: An image of the floating potential probe used to make electric field measurements......................................................... 29

Figure 3.16: Floating potential probe measurements for the discharge in air for a 5.0 mm electrode spacing (case 2) in the diffuse glow region. (a) probe voltage and (b) electric field as functions of axial distance from the anode to the cathode. ......................... 31

Figure 3.17: The discharge in (a) nitrogen (case 8) and (b) helium (case 9) at an electrode spacing of 5.0 mm. The cathode in both (a) and (b) is the pin electrode. ......................... 33

Figure 3.18: Current-voltage characteristics for the discharges in nitrogen (case 8) and helium (case 9) at a 5.0 mm electrode spacing. ......................................................... 34
Figure 3.19: Voltage-current characteristics for the DC negative corona discharge in a hydrogen-methane mixture, case 10 .......................................................... 36

Figure 3.20: Images of the anode (substrate) after one hour in H₂-CH₄ discharge for (a) 5% CH₄ (case 10) and (b) 0.1% CH₄ concentrations (case 11) .............................................. 36

Figure 4.1: Schematic of the experimental setup for the study of discharges in liquids. 42

Figure 4.2: Images of the electrode setup in TEOS for a discharge gap of ~ 2.0 mm (cathode is a fabricated tungsten tip) for (a) No-discharge, ambient lights on and (b) Discharge current of 15 μA and an exposure time of 50 msec ............................................. 44

Figure 4.3: Images of the electrode setup in TEOS for a discharge gap of ~ 2.0 mm (cathode is a stainless-steel wire) for (a) No-discharge and (b) Discharge current of 8 μA and an exposure time of 10 sec ........................................................................................................ 45

Figure 4.4: Current-Voltage characteristics for the electrical discharge in TEOS for smaller electrode spacing (100.0 μm – 400.0 μm) .................................................................................. 46

Figure 4.5: Current-Voltage characteristics for the electrical discharge in TEOS for larger electrode spacing (500.0 μm – 3.0 mm) .................................................................................. 47

Figure 4.6: Images of the electrode setup in silicon oil for a discharge gap of ~ 1.0 mm (cathode is a stainless-steel wire) for (a) No-discharge, ambient lights on and (b) Discharge current of 2 μA and an exposure time of 50 msec ............................................. 48

Figure 4.7: Current-Voltage characteristics for the electrical discharge in silicon oil for different electrode spacings (500.0 μm – 3.0 mm) .................................................................................. 49

Figure 4.8: Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a stainless-steel wire of diameter ~ 168 μm (a) Image of the deposit and (b) Zoomed in image of the deposit ................................................................. 50
Figure 4.9: Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a stainless-steel wire of diameter ~ 168 μm (a) Image of the center of the deposit and (b) Image of the circumference of the deposit where non-uniformities are visible ................................................................. 51

Figure 4.10: Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a fabricated tungsten tip (a) Image of the deposit and (b) Zoomed in image of the center of the deposit ................................................................. 51

Figure 5.1: External circuit used to generate pulsed plasma discharges in liquids, S.G. 1 and S.G. 2 represent the two spark gaps and C is the capacitor bank ................................................. 57

Figure 5.2: Variation of the discharge voltage with the length of spark gap 1 (S.G. 1) at a constant length of S.G. 2 = 2.5 mm ........................................................................ 58

Figure 5.3: Images of the pulsed plasma discharge in DIUF (discharge gap ~ 3.0 mm) during two different external circuit modes (a) Normal pulse mode and (b) Stepped voltage mode .................................................................................................. 58

Figure 5.4: Variation of the pulse duration with the length of spark gap 2 (S.G. 2) at a constant length of S.G. 1 = 6.5 mm ........................................................................ 59

Figure 5.5: Oscilloscope traces (discharge voltage and current) for a single pulse in TEOS, insert shows the traces for a smaller time-scale ......................................................... 60

Figure 5.6: Oscilloscope traces (discharge voltage and current) for a single pulse in PEG, insert shows the traces for a smaller time-scale ......................................................... 61
Abstract

A study of Direct Current Corona Discharges in Gases and Liquids for Thin Film Deposition
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The applicability of DC corona discharges with their lower temperatures and uniformity was investigated for the deposition of thin films. The deposition was done at atmospheric pressure and room temperature, which lowers the facility cost as no vacuum or low pressure facilities are required and also enables continuous processing rather than batch processing. The operating regimes and the structures of DC negative corona discharges for a point to plate electrode configuration for thin film deposition were studied. Traditionally DC coronas have been operated at extremely low currents. By modifying the circuit, the DC corona was operated at higher currents without spark breakdown. The DC negative corona discharge was operated in a new regime where a stable and diffuse glow was observed near the anode surface. This diffuse glow was observed in air and methane discharges. The discharge was characterized by voltage-current diagnostics. Optical emission spectroscopy (OES) was used to obtain spatially resolved temperature measurements and electric field measurements. The DC negative corona discharge was also observed to deposit films on the anode surface. The deposition of films and particles on the anode surface has introduced the possibility of using corona discharges as a novel method of materials deposition or surface modification at atmospheric pressure.

The study of electrical breakdown in both conducting and dielectric liquids has gained interest due to various applications. These discharges in liquids are unsuitable for
many applications due to their thermal nature. Non-thermal discharges in liquids are relatively unexplored. DC plasma discharges in liquids for a negative pin-to-plate electrode configuration were also investigated. The discharge was characterized by voltage-current characteristics and visualization. The corona discharge is observed to deposit films on the anode surface when operated in tetraethyl orthosilicate (TEOS). Deposition on the anode surface by the proposed method has introduced the possibility of using corona discharges as a method of materials deposition or surface modification directly in liquid phase. The proposed plasma enhanced liquid deposition (PELD) technique is encouraging because it is both simple and effective in depositing films without damaging the substrate material.
1.1. Plasma discharges

Matter is usually classified into three categories: solids, liquids and gases. The most simplified definition of plasma is that it is the fourth state of matter. However, a more rigorous definition is that a plasma discharge is an excited state of a gas. This excited gas (plasma) contains charged particles (electrons, positive ions and negative ions) and neutral particles moving in directions described by an external force. The main external force acting on particles in a plasma discharge is the applied electric field. In general plasma discharges are electrically neutral, i.e. the number of positively charged particles equals the number of negatively charged particles. To form a plasma discharge, the process of “breakdown” must occur. This “breakdown” process is shown in the schematic in figure 1.1. Consider two electrodes separated by a small spacing that are connected to the terminals of a power source; the point electrode is connected to the negative terminal and the plate electrode is connected to the positive terminal (or ground). When the electric field at the tip of the point electrode is high enough (depending on the gas and pressure), breakdown occurs. Breakdown is the formation of ions in the discharge gap and is caused by avalanche multiplication of the electrons, i.e., electrons excited/accelerated by the applied electric field gain sufficient energy to ionise neutral atoms or molecules and form new “free” electrons as part of the ionisation process (figure 1.1). The other processes that occur after breakdown are secondary electron emission from the electrodes and photoionisation [1, 2].
Figure 1.1: A schematic description of the initiation of a plasma discharge between a point and a plate electrode

It is well known that energy of an atom or a molecule is quantized [3] and can be partitioned between various modes of internal energy. Atoms typically have translational electronic excitation and electron kinetic modes of energy. In addition to those three, molecules have rotational and vibrational modes of internal energy. Each internal energy mode is associated with a temperature (i.e., $T_{\text{trans}}$, $T_{\text{rot}}$, $T_{\text{vib}}$, $T_{\text{elec}}$ and $T_e$). In general, the various temperatures follow the trend $T_{\text{trans}} < T_{\text{rot}} < T_{\text{vib}} < T_{\text{elec}} < T_e$, with $T_e$ having values close to 1.0 eV or 10000 K. Based on these temperatures/modes of internal energy, plasma discharges can be broadly classified into “thermal” and “non-thermal” discharges. A brief description of each is provided below.

1.1.1. Thermal plasma discharges

When the temperatures of the different modes are in thermal equilibrium (i.e., $T_{\text{trans}} = T_{\text{rot}} = T_{\text{vib}} = T_{\text{elec}} = T_e$), the plasma discharges are termed as equilibrium or thermal
discharges. Typical examples of thermal discharges are arc discharges and spark discharges. A common thermal discharge observed in nature is lightning seen during a thunderstorm. In general, thermal discharges are very hot and fairly non-uniform.

1.1.2. Non-thermal plasma discharges

When the temperatures of the different modes in a plasma discharge follow the trend $T_{\text{trans}} = T_{\text{rot}} < T_{\text{vib}} < T_{\text{elec}} < T_e$, the discharges are called non-thermal or non-equilibrium discharges. In such discharges, $T_{\text{trans}} = T_{\text{rot}}$ have values close to room temperature (cold discharges) or higher than room temperature but below 1000 K (warm discharges). The high reactivity of such non-equilibrium plasma discharges with temperatures near room temperature makes them attractive for material processing applications. Typical examples of non-equilibrium discharges are the corona discharge, the glow discharge and the dielectric barrier discharge (DBD).

1.2. Motivation: Application of atmospheric pressure plasma discharges in material processing

Low pressure plasma discharges have been used for material processing due to the low temperatures of the discharge as well as thin film like deposits the low pressure systems produce. Atmospheric pressure discharges have been known to be thermal/equilibrium discharges as well as unstable and non-uniform. Examples of such atmospheric pressure discharges are the streamer discharges, spark discharges and arc discharges. However, recent advances in stabilizing atmospheric pressure discharges like the micro-glow discharge [4, 5] have shown that thin film deposition is possible. The
added advantage of atmospheric pressure discharges is the fact that expensive and bulky low pressure equipment (low pressure chambers, vacuum pumps, etc.) are not required. Additionally, it is possible to move away from batch processing and increase deposition rates which will increase productivity. Hence there is a need to study the applicability of various atmospheric pressure plasma discharges to materials processing.
Chapter 2: Background and Literature Review

2.1. Corona discharges

Corona discharges are formed on sharp points, edges or on thin wires where the electric field is sufficiently large [2]. They received attention of many past researchers over the last sixty years [6-13]. Corona discharges are spatially non-uniform and the ionization, electric field and luminosity are located near the pin-shaped electrode [1, 2]. The rest of the discharge gap is reported to be dark, with no radiation visible from this outer region. The electric field in this region is also weak. For a negative corona (sharp-tip cathode) in electronegative gases like air, there are no electrons outside the cathode region and the main charge carrying species are negative ions [1].

The corona discharge has been studied for applications in electrostatic precipitation [14, 15], materials treatment [16-18], ozone production [19], odor control and volatile organic compound removal [20], destruction of gaseous contaminants [21] and water treatment [22]. Negative corona discharges have been studied as a method of stabilizing shock waves [23] and as electric actuators used to trip boundary layers [24, 25]. Corona discharges are also responsible for undesirable effects in power transmission like producing radio noise and power loss [26].

There are different modes of dc negative corona discharges that have been studied over the years. In the pulsing mode, also known as Trichel pulse mode [11, 27], the discharge propagates radially and is then chocked off by the accumulated space charges [26] giving rise to the pulses. These pulses depend on the current and the voltage
applied. Near the point of initiation of the discharge, the pulses are random and irregular. Their frequency increases as the applied voltage is increased. The increase in the applied voltage has the opposite effect on the current amplitude [26]. The frequency of the pulses depends on various factors such as electrode geometry and surface conditions which dictates secondary electron emission. Another mode is the *pulseless glow mode* [26]. In this regime, the corona discharge has the structure of a glow discharge. A Faraday dark space, a positive column which is conical in shape and another dark space between the positive column and the anode (plate) surface are observed. This regime occurs mainly when the negative electrode is oval or spherical in shape. The other known mode of the dc negative corona is the *streamer mode*. In this mode, the streamers are initiated from the negative glow sphere. The conical positive column mentioned above then constricts itself to form the streamer stem which has been reported to have little or no branching [26]. The streamer mode is known to form more easily on an oval or spherical electrode as compared to a pointed electrode.

### 2.2. DC and pulsed plasma discharges in liquids

The study of electrical breakdown in liquids both conducting and dielectric has gained interest due to its various applications. Electrical breakdown in liquids can be classified into two basic groups, thermal discharges and non-thermal discharges. Thermal discharges [28-31] can be broadly classified as macro discharges and non-thermal discharges can be classified as micro and nano discharges. The uses of macro/thermal discharges are mainly in the field of underwater welding and cutting [32] and in
the production of carbon nanotubes [33] and thin film deposition on semi-conductors [34, 35]. The uses of streamer discharges (non-thermal macro discharges) include purification of water containing organic chemical impurities and aerosols and sterilisation of milk and juices [36]. Streamer discharges in liquids produce high electric fields [37] and create high energy electrons, ozone, chemically active species, ultraviolet rays and shock waves [38]. The importance of using non-thermal discharges in purification and sterilisation is that the temperatures are relatively low and the chemical balance of the system (liquid) is not disturbed. This has been applied to treatment of waste water and drinking water as environmentally friendly treatment process [39]. Other important applications involve using electrical discharges as energy storage devices or as switching devices [40, 41] (for nanosecond pulse generation). This is important as the liquid remains insulating after breakdown has occurred [42]. Due to the relatively high dielectric constant of liquids, they exhibit relatively higher breakdown strength as compared to compressed gases [43] and they also have the ability to circulate leading to better thermal management and easier removal of debris after breakdown as compared to solids. Despite the fact that electrical discharges in liquids have been studied with an emphasis of electrical insulation [44-48], there is no final or complete understanding of the processes related to initiation of the discharge, the physics of charge creation in liquids and the plasma dynamics at sub-microsecond time scales. It is widely accepted that bubbles are required for the initiation of a discharge in liquids [41, 49-68]. The origin of the bubble (low density region) required to initiate the discharge is highly debated. Most research groups assume the presence of a pre-existing bubble [51, 52, 56, 57]. It has been proposed that the formation of a gas bubble is due to either thermal effects [69, 70] or electrostatic effects
[71]. The formation of a plasma discharge in a liquid is observed to be much faster [72] than the time required to vaporize the liquid. Hence it can be concluded that the dominant mechanism for initiation of the discharge is most likely due to electrostatic forces which produce regions of low density (bubbles) and help in the propagation of the discharge.
Chapter 3: Atmospheric pressure dc negative corona discharge in gases

3.1. Experimental setup and procedure

Figure 3.1 shows the schematic of the electrical circuit used to generate the discharge. A DC power supply with selectable polarity (Bertan Associates, Inc. model 205B) was connected in series to a ballast resistor and the discharge. The power source was able to supply up to 0.4 mA of current. A current probe (Pearsons, model 2877) was connected to the ground (plate) side of the discharge set-up and an oscilloscope was used to establish the stability of the discharge. A shunt (600 Ω) was connected in series with the plate electrode between the plate and ground and the voltage drop across the shunt was measured. Based on the value of the shunt, the discharge current was obtained. The discharge current was used to calculate the discharge voltage using the following formula: \( V_d = V_{ps} - I \cdot R_b - I \cdot R_s \), where \( V_d \) is the discharge voltage, \( V_{ps} \) is the voltage of the power source, \( I \) is the current and \( R_b \) and \( R_s \) are the values of the ballast and shunt resistors used. A stainless steel wire of diameter 165.0 μm was used as the cathode and a stainless steel plate was used as the anode. Stainless steel was chosen due to its resistance to oxidation. A ballast resistor of 47.5 MΩ was used for all cases. The ballast resistor was connected close to the discharge and the circuit was kept small so as to reduce the stray capacitance in the circuit and thus enable us to operate the discharge in a stable mode.

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1 The results presented in this chapter can be found in, “Antao, D. S., Staack, D. A., Fridman, A. and Farouk, B., "Atmospheric pressure dc corona discharges: Operating regimes and potential applications", Plasma Sources Science and Technology, 2009, vol. 18”
Figure 3.1: External electrical circuit used to characterize the DC negative corona discharge.

The wire electrode is mounted on a 3-dimensional positioning system. The plate electrode is always connected to the ground. The pin electrode was connected to either negative or positive terminal of the power source. Mass-flow controllers were used to regulate the inlet gas flow.

The study of the corona discharge included visualization of the discharge, and the investigation of the current-voltage characteristics. Electric field measurements in the discharge gap were done using a floating potential probe, spatially resolved temperature measurements were obtained using OES and current density approximations were made. Table 3.1 below summarizes the cases that were studied. Air is the medium for cases 1 - 7. In cases 1 - 7, the discharges were characterized globally and also by spatially resolved measurements. The spatial characterization for the discharge in air helped explain the diffuse glow that was observed near the anode surface for a DC negative corona discharge. For all cases except case 3, the pin was the negative electrode.
We considered nitrogen in case 8, helium in case 9 and methane-hydrogen mixtures in cases 10 and 11.

Table 3.1: Cases studied

<table>
<thead>
<tr>
<th>Case Number</th>
<th>Discharge gap (mm)</th>
<th>Range of Discharge Voltage (kV)</th>
<th>Gas medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>0 - 8.8</td>
<td>Air</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>0 - 7.5</td>
<td>Air</td>
</tr>
<tr>
<td>*3</td>
<td>5.0</td>
<td>0 - 7.5</td>
<td>Air</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>0 - 5.6</td>
<td>Air</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>0 - 4.7</td>
<td>Air</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>0 - 3.0</td>
<td>Air</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>0 - 3.5</td>
<td>Air</td>
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<td>0 - 3.1</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>9</td>
<td>5.0</td>
<td>0 - 0.51</td>
<td>Helium</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>0 - 1.5</td>
<td>Hydrogen-Methane (5.0 %)</td>
</tr>
<tr>
<td>11</td>
<td>5.0</td>
<td>0 - 1.5</td>
<td>Hydrogen-Methane (0.10 %)</td>
</tr>
</tbody>
</table>

3.2. Global characterization of the discharge in air

The characteristics of the negative and positive corona discharges in air are presented first. Visualization and current-voltage characteristics of the corona discharges in air are then discussed. The spectral characteristics of the corona discharges in air are also presented in this section.

3.2.1. Comparison of the negative corona to the positive corona

Figure 3.2 shows the V-I characteristics of a positive (case 3) and a negative (case 2) corona in air for an electrode spacing of 5.0 mm. Due to the weak electric field in the vicinity of the negative electrode (cathode-plate) in a positive corona, there is no significant avalanche multiplication [1]. The production of electrons is dependent on
secondary photo processes around the sharp tip. The breakdown voltage for a positive corona in air is slightly higher than that for a negative corona [1]. The dashed lines in Figure 3.2 indicate an unstable transition regime with time-averaged current. At a certain threshold voltage, the corona discharge transitioned from the stable corona mode to an unstable spark discharge regime for each discharge gap.

![Figure 3.2: Semi-log plot of V-I characteristics for a negative (case 2) and a positive corona (case 3) discharges in air. The electrode spacing is 5.0 mm for both discharges.](image)

Figure 3.3 is a photograph of the positive corona (case 3) in air with a 5.0 mm electrode spacing. It is observed that the positive corona generated at the pin electrode is similar in structure to the positive corona discharge observed at low pressure (~100 Torr.) and low discharge currents (~10-20 μA) [73]. This visualization of the discharge of the positive corona shows a homogenous glow and not a filamentary structure. An
oscilloscope was used to ensure that the discharge was not pulsing and that it was in a stable mode.

![Image](image.png)

**Figure 3.3:** Positive corona (case 3) in air for a pin to plate configuration. The cathode plate is indicated by a white line. Conditions are 30 μA and 5.0 mm electrode spacing.

### 3.2.2. Discharge Visualization

The visualization of the discharge was done using a CCD color video camera (DIGITAL, model WDAC-5700C) mounted on a microscope and a Nikon D70 camera with an attached macro lens. The microscope-camera setup enabled variable magnification between a 2.0 mm × 1.5 mm and a 20.0 mm × 15.0 mm fields of view. The images were captured digitally by a personal computer. The sizes of the discharge were estimated with the images obtained. The current measurements were used to estimate the current densities in the diffuse glow region.

The luminosity of corona discharges is reported to be located in the vicinity of one electrode only [2]. Figures 3.4 (a) – 3.4 (d) show the negative corona discharges in air for 6.0, 5.0, 3.0 and 2.0 mm electrode spacing that corresponds to cases 1, 2, 5 and 6.
in Table 3.1. The negative electrode is the wire coming from the top of the images and the anode is at the bottom of the image. The current in the discharge for all electrode spacings is 70.0 µA and the voltages across the plasma required to sustain the discharge are 6.98, 5.88, 3.68 and 1.58 kV respectively. All images were taken at the same magnification and exposure time. The discharge can be split into three regions, the corona bright spot near the cathode, the diffuse glow near the anode surface which extends into the discharge gap in a conical shape and the dark region in between the corona and the diffuse glow. The only difference of the present corona discharges with the ‘normal micro-glow discharge’ [74] is that the cathode spot (in this case the corona spot) does not have a noticeable increase in size with an increase in discharge current. Another difference between the corona discharge studied and the micro-glow discharge is that the diffuse glow near the anode surface has a relatively constant height which does not change with the discharge gap unlike the positive column in a normal glow discharge [74]. The diffuse glow grows brighter as the current is increased and is brightest before the onset of the transient sparking regime. The occurrence of luminous and non-luminous regions is one of the major indications that discharge is in the non-thermal regime.
Figure 3.4: Images of the DC negative corona discharge in air at (a) 6.0 mm, case 1 (b) 5.0 mm, case 2 (c) 3.0 mm, case 5 and (d) 2.0 mm, case 6 electrode spacing. The anode plate is at the bottom of the image.

Figure 3.5 shows the radius of the glow as a function of the distance from the anode for a constant current of 110 μA for different electrode spacings (cases 1, 2, 4 and 5). The radius of the diffuse glow at each location was obtained from images of the discharges similar to the images shown in Figures 3.4 (a) – 3.4 (d). An image editing software was used to measure the diameter of the diffuse glow every 0.2 mm along the discharge axis. The radius near/on the cathode pin is taken to be the size of the corona spot. This size has been determined using the camera mounted on the microscope to take images of the discharge. The accuracy in this region is around ± 20 μm. It is observed
that the height of the diffuse glow does not vary much with change in inter-electrode spacing and is generally around 0.16 - 0.18 cm from the anode surface. We can also observe from Figure 3.5 that the radius of the diffuse glow near the anode increases with increasing inter-electrode spacing.

![Graph showing the height and radius of the diffuse glow for different electrode spacing cases](image)

**Figure 3.5:** The height and the radius of the diffuse glow for different electrode spacing, cases 1, 2, 4 and 5 respectively.

### 3.2.3. Electrical Characterization

Figure 3.6 is a plot of discharge voltage versus discharge current for different electrode spacings for cases 1, 2, 5, 6 and 7. The error in the measured current is less than 5.0 μA and the error in the measured voltage is about 50.0 V. The current was varied by changing the DC power supply voltage. Oscilloscope traces indicated that the discharge current was constant with no ac components other than noise.
Figure 3.6: Current-voltage characteristics for the negative corona discharge in air at different electrode spacings, cases 1, 2, 5, 6 and 7 respectively. The dashed lines indicate an unstable transition regime with time-averaged current.

The positive \( dV/dI \) that is visible for all the different electrode spacing (in Figure 3.6) is indicative of a Townsend (dark) discharge regime [2] and the corona discharge regime [75]. Hence from the V-I characteristics it can be concluded that the discharge that is being studied is a corona discharge that operates in a new regime with a diffuse glow near the anode surface. The dashed lines in Figure 3.6 indicate unstable transition regimes with time-averaged current. At a certain threshold voltage, the corona discharge transitioned from the stable corona mode to an unstable spark discharge regime for each discharge gap. Beyond the threshold voltage, repetitive (unstable) spark discharges are observed between the pin and the plate.
3.2.4. Spectral characteristics

For the spectroscopic measurements of the discharge in air the Acton Research SpectraPro 500i scanning monochromator was used. The monochromator has a spectral resolution of 0.3 nm. The discharge was focused on the entrance slit of the spectrometer using a plano-convex lens. This was done to enable spatially resolved temperature measurements. The Optical Emission Spectra (OES) of the discharge was obtained in the wavelength range of 200.0 – 900.0 nm. A 3600 g/mm UV optimized and a 2400 g/mm visible optimized gratings were used for the 200.0 – 550.0 nm and the 550.0 – 900.0 nm wavelength ranges. A long pass optical filter at 550.0 nm was placed in front of the entrance to the spectrometer to ensure that signals from the 2nd order mode from the gratings did not disturb the signals from the 1st order modes at higher wavelengths. The procedure used in the OES measurements was similar to the procedure discussed in [76, 77]. A Roper Scientific, model 7430 CCD camera mounted on the exit of the spectrometer was used to digitally acquire the spectra at 0.6 nm resolutions. Typical exposure times were around 5-10 seconds and the images were integrated over 10-50 accumulations.

OES data was collected for the entire range from 200.0 – 900.0 nm. The conditions for the discharge were, 0.1 mA in air with a 5.0 mm electrode spacing (case 2). The OES data was then resolved into two regions, the diffuse glow region and the corona region. The slit width for the spectrometer was held to 2.0 μm and the light was collected over a height of several microns. Figure 3.7 (a) shows the OES data for the diffuse glow region near the anode for a wavelength range of 300.0 to 400.0 nm and Figure 3.7 (b) shows the OES data for the corona region near the cathode over the same
wavelength range. The brightest peaks were observed around 315, 337, 350 and 380 nm. These peaks are due to the nitrogen 2\textsuperscript{nd} positive electronic transition \((N_2 (C^3\Pi_u-B^3\Pi_g))\) and its family of vibrational and rotational level sub-transitions.

**Figure 3.7:** Optical emission spectra from the DC negative corona discharge in air (case 2) between 300.0 and 400.0 nm near (a) anode and (b) cathode.

The strongest line observed in Figures 3.7 (a) and 3.7 (b) is the \(N_2\) 2\textsuperscript{nd} positive (0-0) around 337 nm. The smaller peaks clustered together to the left of each of the main peaks observed at 315, 337, 357 and 380 nm correspond to the rotational sublevels of the
transition. The relative intensities of these rotational and vibrational transitions are related to the distribution among rotational energies of the nitrogen molecules [74].

A Boltzmann distribution is assumed with a rotational temperature, \( T_{\text{rot}} \). The rotational and translational temperatures, \( T_{\text{trans}} \), are assumed equal. This assumption is valid due to the short times of transfer of rotational energy to translational energy [74]. A Boltzmann distribution is also assumed for the non-equilibrium vibrational energies with a vibrational temperature, \( T_{\text{vib}} \). SPECAIR [78, 79] was used to model the spectra from these transitions. We compare the model spectra obtained from SPECAIR and the experimentally determined spectra to obtain the temperature measurements. Figure 3.8 shows a comparison between the model spectra and the experimental spectra using the software SPECAIR.

![Figure 3.8: Measured optical emission spectra and best fit SPECAIR prediction for a 0.1 mA DC negative corona discharge in air at atmospheric pressure, case 2.](image_url)
3.3. Spatially resolved characteristics of the discharge in air

Now we present spatially resolved temperatures (rotational, vibrational, and electronic excitation) and current density measurements in corona discharges in air. Spatially resolved electric field measurements in the discharge (obtained by a floating potential probe) are also presented.

3.3.1. Spatially resolved temperature measurements

Figure 3.9 shows the spatially resolved rotational temperature profile for the discharge gap of 5.0 mm, case 2. The temperature of the corona itself is less than 750°C and that the rest of the discharge gap is relatively at room temperature. This feature makes the discharge very attractive for applications in thin film deposition. From visualization of the discharge, it was observed that there was a dark region between the corona spot and the diffuse glow. The OES data that was obtained from this region had a very high noise to signal ratio. Hence the data from this region was not used to obtain the temperature measurements.
Figure 3.9: Spatially resolved rotational/gas temperature in air for a 5.0 mm electrode spacing, case 2.

Figure 3.10 shows the spatially resolved vibrational temperature measurements for the same discharge gap of 5.0 mm, case 2. The data was spatially resolved along the vertical axis of the pin electrode. It is interesting to note that there is an increase in the vibrational temperature as we approach the anode surface corresponding to the diffuse glow region. This indicates the possibility of a similar trend in the electronic excitation temperature also.
Figure 3.10: Spatially resolved vibrational temperature in air for a 5.0 mm electrode spacing, case 2.

From the results it can be observed that $T_{vib} > T_{rot} = T_{trans}$ indicating the non-equilibrium nature of the discharge. The standard assumption in non-equilibrium plasmas is that $T_e > T_n$ [2, 80], the electron temperatures being of the order of 1 eV and the neutral or gas temperature generally much lower [2]. From the root-mean-square error values, the maximum statistical errors for rotational and vibrational temperatures were determined to be ±12.0 K and ±66.0 K respectively. The fitting errors varied between ±2.0 K and ±12.0 K for the rotational temperature measurements and ±12.0 K and ±66.0 K for the vibrational temperatures. The accuracy of the rotational temperature measurement is suggested to be around ±50K and that of the vibrational temperature measurement is around ±10% [81], which is attributed to both the inaccuracies of the
model and in collecting experimental data. Thus our accuracy is around ±60K for the rotational temperature measurement and over 200K vibrational temperature measurement.

The electronic excitation temperature ($T_{elec}$) was obtained by comparing experimentally obtained ratios of the intensity of the $N_2$ 2nd positive Δ Vib 0 ($C^3Π - B^3Π$) and that of the $N_2$ 1st positive Δ Vib -3 ($B^3Π_u - A^3Π_g$) to the ratios obtained from model spectra for various electronic and vibrational temperatures. Figure 3.11 shows the spatially resolved ratios of the intensities of the $N_2$ (C-B) transition (second positive transition at 337.05 nm) to that of the $N_2$ (B-A) transition (first positive transition at 669.4 nm), for case 2. Using SPECAIR [78], model spectra were plotted for various combinations of vibrational and electronic excitation temperatures.

![Figure 3.11](image)

**Figure 3.11:** Ratio of intensities of the $N_2$ second positive and the $N_2$ first positive transitions across the discharge gap, case 2.
The ratios of the intensities were then calculated and combined to form a look-up-table. Finally the electronic excitation temperature of air in the electrode gap was estimated after comparing the experimentally obtained ratios of intensities to the ratios that were obtained from the look-up-table (ratios calculated from SPECAIR’s model spectra). The spatially resolved electronic excitation temperatures in Figure 3.12 show an increase in the temperature from the beginning of the diffuse glow region to the anode surface (case 2). This increase in the electronic excitation temperature indicates an increase in the electric field as $T_{\text{elec}}$ is directly proportional to the electric field [82]. The implications of this increase in $T_{\text{elec}}$ and subsequently the electric field are discussed later.

![Figure 3.12](image)

**Figure 3.12:** Electronic excitation temperature as a function of axial distance from the anode surface, case 2.
3.3.2. Current density measurements

The current density measurements were made to estimate the electron densities, ion densities and the ion energy that were required to explain the diffuse glow phenomenon discussed in section 3.6. Images such as those shown in Figure 3.4 were used to estimate the size of the diffuse glow. Several images were taken at different currents and different electrode spacings. The cross-sectional area of the diffuse glow was calculated assuming the diffuse glow to be conical in shape. Figure 3.13 shows the current density for different electrode spacings (cases 1, 2, 4 and 5) as a function of the axial distance from the anode surface for a constant current of 110 μA. Figure 3.14 shows the current density measurements for an inter-electrode spacing of 6.0 mm and different values of discharge current (case 1). The current density in the negative corona is estimated to be around 12.0 Acm\(^{-2}\) which is on the order of the current density in the negative glow of a DC micro-glow discharge in air [74]. The current density in the diffuse glow near the anode surface is around three orders of magnitude lower.
Figure 3.13: Spatially resolved current density measurements across the discharge gap in air for four inter-electrode spacings (cases 1, 2, 4 and 5) at a constant discharge current of 110 μA.
Figure 3.14: Spatially resolved current density measurements across a discharge gap of 6.0 mm (case 1) for four different values of discharge current.

3.3.3. Electric field measurements

To measure the electric field in the discharge gap, we constructed a floating potential probe that was connected to a voltage divider. The discharge voltage was then measured across the voltage divider. The probe was constructed from 10.0 μm diameter tungsten wire which was shielded using a quartz tube having an outer diameter of 330.0 μm and an inner diameter of 200.0 μm (Figure 3.15). The materials used were the smallest available so as to ensure that the probe did not disturb the discharge. A 100.0 μm tungsten wire was used to provide electrical contact between the probe wire (10.0 μm wire) and the high voltage wire connected to the divider circuit. The voltage divider had a total resistance of a 12.0 – 15.0 GΩ as compared to the resistance of the discharge gap
that was ~300.0 MΩ. The voltage in the gap was measured across a 1.0 MΩ resistor and was digitally acquired by a National Instruments data acquisitioning card (NI-PCI 6221) connected to the personal computer. Corona discharges are known to have highly non-uniform electric fields, i.e. a very high electric field near the point electrode (cathode) and very low electric fields in the discharge gap. A diffuse glow near the anode surface indicated that it was possible for the electric field in the discharge gap to be different from the traditional corona discharges.

Figure 3.15: An image of the floating potential probe used to make electric field measurements

Figures 3.16 (a) and 3.16 (b) show the voltage and electric field measurements obtained as a function of axial distance respectively for cases 1 and 2. The voltage measurements (Figure 3.16 (a)) using the probe were made in the diffuse glow region between the pin and plate electrodes on axis and at 500 μm and 1000 μm off axis. Measurements were made every 500 μm along the axis from the middle of the discharge gap to the plate anode traversing the region occupied by the diffuse glow. From Figure 3.16 (b) it is observed that as we approach the anode there is an increase in the electric
field. This increase in the electric field is the reason we observe the diffuse glow near the anode plate. As can be seen, the electric field near the anode is about 20 kVcm$^{-1}$. This is well below the electric field required for breakdown in air. Hence we only observe a diffuse glow near the anode surface and there is no transition to a spark. Possible reasons for this diffuse glow will be further explained in section 3.6. The electric field measurement are very different when compared to traditional corona models, however, they are similar to those obtained by Akishev et al. [75, 83] when they modeled the electric field in the gap for the DC negative corona.
Figure 3.16: Floating potential probe measurements for the discharge in air for a 5.0 mm electrode spacing (case 2) in the diffuse glow region. (a) probe voltage and (b) electric field as functions of axial distance from the anode to the cathode.
No measurements are reported near the cathode in the above Figures due to possible probe interference. The use of ‘floating potential probes’ in atmospheric pressure discharges is not common as the size of the probe is relatively large in comparison to the discharge size. In low pressure probe measurements the ratio of the volume of the probe to the volume of the discharge is ~ 10^{-2} whereas in our atmospheric pressure corona discharge this ratio is closer to 2.0 for the glow near the cathode (see Figure 3.4). Other uncertainties arise because the probe used here measures the floating potential of the plasma and not the plasma potential. The difference between these voltages is dependent on the sheath which forms between the plasma and the probe. In this discharge which contains both electrons and negative ions the probe sheath potential is likely to vary along the length of the discharge. Nonetheless within the anode region (see Figure 3.4) the discharge appears to be relatively uniform and the changes in the floating probe voltage with position are likely proportional to the electric field and are not affected by the gradient in negative species densities or temperatures.

3.4. Global characterization of the discharge in Nitrogen and Helium

The DC negative corona was generated at atmospheric pressure in helium and nitrogen. The discharges were visualized and the current-voltage characteristics were studied for an experimental setup similar to that used in air. The discharges were studied for an electrode spacing of 5 mm. Care was taken to operate the discharges in pure nitrogen and helium. The gas flow was controlled by a pair of mass flow controllers, (Omega, FMA-2607A). To ensure that air could not contaminate the reactor volume, the
exit valve from the reactor was partially closed so that the pressure inside the reactor was about 5-10 Torr above atmospheric pressure. A period of around 20.0 – 30.0 minutes was allowed to pass before the experiments were conducted. Figures 3.17 (a) and 3.17 (b) show images of the discharge in nitrogen and helium, cases 8 and 9 respectively. In Figures 3.17 (a) and (b), the cathode is the pin electrode at the top of the image where the brightest emission is observed. Figure 3.18 shows the current-voltage characteristics of the DC negative corona discharges in nitrogen and helium. The V-I characteristics for nitrogen indicate a relatively constant $dV/dI$ which is similar to the $dV/dI$ obtained in a DC normal glow discharge in air. From Figure 3.17 (a), it can be seen that the discharge in nitrogen has the structure of a standard corona discharge with the bright glow near the cathode wire and the rest of the discharge gap being dark.

![Images of discharges](image)

**Figure 3.17:** The discharge in (a) nitrogen (case 8) and (b) helium (case 9) at an electrode spacing of 5.0 mm. The cathode in both (a) and (b) is the pin electrode.
The V-I characteristics for helium (Figure 3.18) also indicate a relatively flat $dV/dI$ which is similar to that obtained for a DC normal glow discharge. From the discharge, it was observed that a diffuse glow appeared in the region near the anode. As seen in Figure 3.17 (b), the corona spot was wider in size due to a higher discharge current and it appears to ‘spill’ over the edges of the cathode (wire) and occupy the sides of the wire too. This is similar to the observation by Staack et al. [74] for the micro-glow discharge, where it is observed that the negative glow ‘spills over’ the edge of the cathode at higher currents and is stated to be similar to a transition from a normal glow to an abnormal glow discharge at low pressures.
3.5. Application in thin film deposition

During the experiments conducted in air, a change in the colour of the surface of the anode that was under the diffuse glow was observed. Most likely this was oxidation of the anode material used. The spatially resolved temperature measurements indicated that the temperature of the discharge near the anode surface was almost at room temperature. As the measured temperatures are low, oxidation of the anode material is possible at room temperature due only to the creation of highly oxidative species like $O$ and $O_3$.

The diffuse glow near the anode was observed in discharges operated in methane too. Since in general an observed glow corresponds to a high electron density and more reactive plasma discharges this observation raised the possibility of depositing carbon films on the anode surface. Hence we studied the discharge in a hydrogen-methane mixture for two different concentrations of methane precursor, cases 10 and 11 in Table 1. Figure 3.19 shows the $V$-$I$ characteristics for the discharge in a hydrogen-methane mixture (case 10). From the $V$-$I$ characteristics, the positive $dV/dI$ indicates the operation of the discharge in the corona regime.
Figure 3.19: Voltage-current characteristics for the DC negative corona discharge in a hydrogen-methane mixture, case 10

Figure 3.20: Images of the anode (substrate) after one hour in H₂-CH₄ discharge for (a) 5\% CH₄ (case 10) and (b) 0.1\% CH₄ concentrations (case 11)

Figures 3.20 (a) and 3.20 (b) are images of the silicon anode substrate on which the carbon films were deposited. Figure 3.20 (a) shows the deposits formed for a 5.0 \% CH₄ concentration and Figure 3.20 (b) shows the deposited film for a 0.1 \% CH₄
concentration. Figure 3.20 (a) corresponds to case 10 and 20 (b) corresponds to case 11. The images were captured using a microscope at 50x and after running the discharge for approximately one hour. The deposits formed are hard and bonded well to the substrate resistant to wiping and even after the cleaning the substrate with ethanol, there is no visible change in the deposit layer formed. From Figure 3.20 (a) and 3.20 (b) it can be observed that for different concentrations of methane it is possible to obtain either soot or film like layers on the anode surface. At higher concentrations of methane, soot is formed on the anode surface. Based upon the diffractive properties of the film and the colour the thickness of the film is estimated to be between 40 and 50 nm. The deposition rate was thus on the order of 0.66 - 0.83 nm/min. This rate though quite low is comparable to rate achieved in low pressure deposition systems which is around 0.5 - 1.0 nm/min, however these results are preliminary and show promise with further optimization of the discharge and deposition process. Structures and patterns are observed on the deposited surface (Figure 3.20 (b)). These structures are due to non-uniformities left from the initial cleaning of the substrate. This is an encouraging result as the deposition is done at relatively low gas temperatures (~70 – 80 °C) near the surface of the substrate. Further studies will be required to fully characterize the applicability of this discharge to plasma enhanced chemical vapor deposition of thin films. The reason that this method would be important to thin film deposition is that the deposition is done at atmospheric pressure and room temperature, which lowers the facility cost as no vacuum or low pressure facilities are required and also enables continuous processing rather than batch processing.
3.6. Analysis of the diffuse glow

The diffuse glow observed near the anode surface in a negative corona discharge has not been reported earlier. The diffuse glow was observed to form only in negative corona discharges in air and hydrogen-methane which suggests that the electronegativity of a gas plays a role in the formation of the diffuse glow [84].

In this section a hypothesis is presented to explain the formation of the diffuse glow near the anode surface in air. For discharges in air, \( O_2^- \) is the main negative charge carrying species near the anode and from our current density measurements; we estimated the density of \( O_2^- \) ions to be about \( 10^{17} \, \text{m}^{-3} \). As compared to free electrons entering the anode to complete the circuit, it is relatively difficult for the electron attached to \( O_2^- \) to detach itself and enter the anode material. This is because the \( O_2^- \) molecules do not possess the required energy to initiate electron detachment. Since not every negative ion striking the anode gives up its electron this leads to a collection of \( O_2^- \) near the anode surface. This collection of charges creates a voltage sheath near the anode surface, thus leading to an increase in the electric field between the anode and the charged layer. This increase in the electric field is observed both from the floating potential probe measurements and the electric field estimations from the electronic excitation temperature measurements.

The main light emitting species near the anode surface is observed from the OES to be the \( N_2 \) (C-B) transition. The excitation of an atom or a molecule requires the presence of an electron with sufficient energy to excite the atom or molecule. The increased electric field due to the sheath may provide the required energy. The other
requirement is a free electron. Typically in a negative corona discharge, attachment processes occur which bind all the free electrons to form $O_2^-$. With the increased electric field near the anode, it is possible that if a few free electrons were available there would be electron avalanche formation. Although for these conditions the attachment rates are still higher than detachment rates and additional sources of the free electrons required may come from photoionization. Estimations of ion energy indicate that ion kinetic detachment (equation 3.1) may also be an active detachment mechanism required to produce the initial free electrons.

\[
(O_2^-)^* + M \rightarrow O_2 + M + e^- \quad (3.1)
\]

Ion kinetic detachment refers to the detachment of electrons from $O_2^-$ due to collisions in which the ions (say $(O_2^-)^*$) have kinetic energy in excess to the binding energy of the electron (0.44 eV). Due to the electric field the average kinetic energy of the $O_2^-$ ion is estimated to be about 0.2 eV. This value is calculated as the product of the energy gained by an $O_2^-$ ion between collisions and the mean free path [2]. This is roughly an average energy and there will exist a portion of $O_2^-$ ions with energy approaching ~0.44 eV [2] which is the bond energy between the electron and the $O_2$ molecule. From the above calculations of the kinetic energy of $O_2^-$ ions and the electric field estimations, field detachment is another possible source of free electrons in the diffuse glow region. The initial free electrons may participate in some subsequent electron avalanche multiplication by electron impact detachment (equation 3.2) thus giving the level of electron density necessary to create the luminous region observed.

\[
e^- + O_2^- \rightarrow O_2 + 2e^- \quad (3.2)
\]
3.7. Chapter Summary

A dc corona discharge was investigated in atmospheric pressure gases. The dc corona discharge was operated in a new regime in a stable mode and at higher discharge current. Operation of the discharge in this new regime was made possible by modifying the external circuit (reducing the size of the external circuit thereby reducing the stray/parasitic capacitance and increasing the ballast resistance). Electrical measurements of the discharge indicated operation in the corona/Townsend dark discharge regime. The structure of the dc corona discharge operated in this new regime differed from traditional dc corona discharges. Visualisation of the discharge showed a diffuse glow near the anode surface. The diffuse glow was conical in shape and was observed to be relatively constant in height and did not vary with the discharge gap size. The temperature of the corona discharge was estimated from spectra of the discharge obtained using OES. The electric field near the anode surface was estimated by OES and from floating potential probe measurements. The dc corona discharge in this new stable regime was operated in a hydrogen-methane environment to deposit thin films on the surface of the plate anode.
Chapter 4: DC Plasma Discharges in Liquids

4.1. Experimental setup and procedure

Figure 4.1 shows the schematic of the generalized experimental setup used in the experimental study of dc electrical discharges in liquids. A DC power supply with selectable polarity (Bertan Associates, Inc. model 205B) was connected in series to a ballast resistor and the discharge. The power source was able to supply up to 0.4 mA of current. A shunt (200 – 600 Ω) was connected in series with the plate electrode between the plate and ground and the voltage drop across the shunt was measured. Based on the value of the shunt, the discharge current was obtained. The discharge current was used to calculate the discharge voltage using the following formula: $V_d = V_{ps} - I \cdot R_b - I \cdot R_s$, where $V_d$ is the discharge voltage, $V_{ps}$ is the voltage of the power source, $I$ is the current and $R_b$ and $R_s$ are the values of the ballast and shunt resistors used.

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2 The results discussed in this chapter were presented at the “American Physical Society, 62nd Annual Gaseous Electronics Conference, October 20-23, 2009”
Various electrodes were used as the cathode in the experiment. Initially stainless steel wires of varying diameter (~ 70.0 - 200.0 μm) were used as the cathode but at high voltages a change in the electrode spacing was observed because the cathode would start oscillating. Next, tips fabricated by electrolytic etching [85-87] were used as the cathode. These tips had ~ 50.0 - 100.0 μm diameters. Finally, pre-fabricated tungsten tips (GGB Industries) were used. These tips are ~ 1.0 μm in diameter. For the electrical and visual characterization a stainless steel or copper plate was used as the anode. For the deposition studies, silicon wafers were used as the anode. A ballast resistor of 47.5 MΩ was used for all cases. The ballast resistor was connected close to the discharge and the circuit was kept small so as to reduce the stray capacitance in the circuit and thus enable us to operate the discharge in a stable mode. The wire electrode is mounted on a 3-dimensional positioning system. The plate electrode is always connected to the ground.
The pin electrode was connected to the negative terminal of the power source (positive discharges have yet to be characterized). The liquids studied were TEOS and silicon oil.

The visualization of the discharge was done using an ICCD camera (Princeton Instruments, PI-MAX-Gen II) with an attached macro lens (Sigma) and a Nikon D70 digital SLR camera with the same attached macro lens. The images from the ICCD camera were captured digitally by a personal computer. The use of the ICCD camera allowed very low exposure (~ 10 – 50 msec.) images to be captured even though the luminosity of the discharge was extremely low (barely visible to the naked eye). The discharge was generated within a square quartz tube. The use of a quartz tube enables possible optical emission spectroscopy (OES) studies in the ultra-violet and visible regions (UV-Vis).

### 4.2. Global characterization of the discharge in TEOS

The study of the corona discharge included visualization of the discharge, and the investigation of the current-voltage characteristics. In this present study only negative discharges have been investigated.

#### 4.2.1. Discharge visualization

Figure 4.2 shows an image that was taken using the ICCD camera for an exposure time of 50 msec. The tungsten tip visible in the image was fabricated by electrolytic etching and had a tip diameter of ~ 50 – 70 μm. The image in figure 4.3 was taken using the ICCD camera, but the exposure time in this image is relatively high ~10 sec. The cathode pin in figure 21 is a 168.0 μm SS wire. As can be seen in both images, a
homogenous glow is visible near the cathode tip. This homogenous glow is indicative of a corona discharge. Below the threshold voltage (4.0 – 5.0 kV), no discharge is visible. At intermediate voltages, pulsing of the discharge is observed and at higher voltages, a stable discharge is observed.

Figure 4.2: Images of the electrode setup in TEOS for a discharge gap of ~ 2.0 mm (cathode is a fabricated tungsten tip) for (a) No-discharge, ambient lights on and (b) Discharge current of 15 μA and an exposure time of 50 msec
4.2.2. Electrical characterization

The electrical characterization of the discharge was performed in TEOS for different cathode pin diameters and for various inter-electrode distances. The electrical characteristics for different diameter cathodes indicated that we were operating in the discharge regime and not observing a form of electrolysis. Figures 4.4 and 4.5 show the electrical characteristics of the discharge in TEOS at different values of electrode spacing. As can be seen from the figures, beyond a certain threshold of ~ 4.0 – 5.0 kV, the electrical characteristics indicate a trend similar to corona discharges in gases. It is important to clarify here that fluctuations were observed in the current (~ 0.1 – 0.2 μA). These fluctuations were small and the discharge can be stabilized by employing methods similar to those used for atmospheric pressure discharges [74, 88].
Figure 4.4: Current-Voltage characteristics for the electrical discharge in TEOS for smaller electrode spacing (100.0 μm – 400.0 μm)
Figure 4.5: Current-Voltage characteristics for the electrical discharge in TEOS for larger electrode spacing (500.0 μm – 3.0 mm)

4.3. Global characterization of the discharge in transformer oil

The study of the corona discharge in silicon oil included visualization of the discharge, and the investigation of the current-voltage characteristics. Only negative discharges have been investigated.

4.3.1. Discharge visualization

Figure 4.6 shows an image that was taken using the ICCD camera for an exposure time of 50 msec. The cathode tip (made of copper) visible in the image was fabricated by electrolytic etching and had a tip diameter of < 50.0 μm. As can be seen in figure 4.6, a homogenous glow is visible near the tip of the cathode. Unlike the discharge in TEOS, after breakdown, a stable discharge is visible.
Figure 4.6: Images of the electrode setup in silicon oil for a discharge gap of ~ 1.0 mm (cathode is a stainless-steel wire) for (a) No-discharge, ambient lights on and (b) Discharge current of 2 μA and an exposure time of 50 msec

4.3.2. Electrical characterization

The electrical characterization of the discharge was also performed in silicon oil for various inter-electrode distances. Figure 4.7 shows the electrical characteristics for the discharge operated in silicon oil. As can be seen in figure 4.7, the V-I characteristics are comparable to the electrical characteristics of corona discharges in gases. A distinct breakdown voltage is observed after which the discharge has an V-I characteristic similar to the corona discharge in air [89]. Even though a corona discharge is observed in silicon oil, the discharge currents are extremely small (1.0 – 2.0 μA). If this discharge is to be harnessed in to any application, the discharge current will need to be increased for it to be effective.
4.4. Application of the discharge in thin film deposition

For the study of film deposition, silicon wafers were used as the anode. As can be seen from figures 4.8, 4.9 and 4.10, deposits are formed when operating the discharge in TEOS. The deposition times were less than 2 minutes for each of the cases. The deposits formed when the SS wire was used as the cathode (figures 4.8 and 4.9) were uniform in the center and non-uniform at the edges. This is possible due to the oscillations of the cathode wire. It is important to note here that care was taken to ensure that the voltage was not too high to produce oscillations. However, it is possible that due to the flexibility of the wire and the electro hydro-dynamic (EHD) motion of the liquid, oscillations were induced which were not visible to the naked eye. Figure 4.10 shows the deposit formed
when the cathode used was a fabricated tungsten tip. Here, a more uniform deposit is visible.

Though the deposits are formed, it is also important to note that they are not smooth film-like layers, but films formed by particle deposition (particle sizes ~ 1.0 – 5.0 μm). An important task would be to reduce the particle like deposition and increase the thin film deposition which is more attractive for applications.

**Figure 4.8:** Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a stainless-steel wire of diameter ~ 168 μm (a) Image of the deposit and (b) Zoomed in image of the deposit
Figure 4.9: Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a stainless-steel wire of diameter ~ 168 μm (a) Image of the center of the deposit and (b) Image of the circumference of the deposit where non-uniformities are visible.

Figure 4.10: Image of the deposit formed on a silicon substrate by the corona discharge operated in TEOS using a fabricated tungsten tip (a) Image of the deposit and (b) Zoomed in image of the center of the deposit.
4.5. Chapter Summary

A dc corona discharge was studied in liquids. The discharge was generated in transformer oil and TEOS and was seen to be stable. Similar to the experiments in gases, the stability of the discharge was ensured by decreasing the stray capacitance of the external circuit and increasing the ballast resistance. Electrical measurements of the discharge indicated operation in the corona discharge regime and visualisation of the discharge showed the structure of a typical corona discharge with a homogenous glow near the pin cathode. The dc corona discharge in TEOS was shown to deposit films on the anode surface, however further studies are required to ensure better deposits.
Chapter 5: Conclusions and Recommendations for Future Work

5.1. Conclusions

DC corona discharges were operated at atmospheric pressure for a pin-to-plate electrode configuration. The DC negative corona discharge was characterized for a stable regime at higher currents where a diffuse glow was observed near the anode surface. The characterization was done using current-voltage characteristics and visualization. The diffuse glow was observed only in air and hydrogen-methane discharges which suggest that the electronegativity of a gas plays a role in the formation of the diffuse glow. Temperature was measured by comparing emission spectra from the discharge to model emission spectra for the N\textsubscript{2} second positive system. The SPECAIR code was used for this purpose. The temperature measurements indicated that the discharge was non-thermal and a comparison of the rotational and vibrational temperatures confirmed the non-equilibrium nature of the discharge. Spatially resolved temperature measurements were made over the discharge gap and it was observed that the highest temperature was near the cathode (pin) and the temperature near the anode surface was close to room temperature. The electronic excitation temperature measurements and the floating potential probe measurements near the anode (plate) surface indicated an increase in the electric field near the anode surface. We propose that the glow observed in that region is caused due to the formation of free electrons due to the increased electric field and the subsequent excitation of nitrogen by the free electrons that gained energy from the electric field.
The area on the anode surface covered by the diffuse glow underwent modification depending on the gas the corona discharge was operated in. In air, we observed the oxidization of the anode surface and in hydrogen-methane mixtures, deposition of carbon film was observed. The relatively low temperatures of the discharge even at atmospheric pressure and low current density prevents the formation of soot and the agglomeration of carbon particles, thus generating a smooth film-like layer. The presence of surface chemistry was confirmed with measured increased vibrational temperatures near the anode surface. Further studies would be needed to characterize the deposits formed and the applicability of the DC negative corona to thin film deposition.

A non-thermal discharge was generated in dielectric and conducting liquids using a DC power source. The results indicate the possibility of DC discharges in dielectric liquids. The discharge produced was a corona like discharge. This was confirmed by both electrical characterization of the discharge as well as visualization of the discharge. The DC discharge in TEOS was not very stable and self pulsing of the discharge was observed. This can be corrected by controlling the external circuit parameters (decreasing circuit size- parasitic capacitance and increasing the ballast resistance). Deposition was also demonstrated in TEOS, but the deposits formed were non-uniform and particle like. Despite the particle-like nature of the deposits, the results are encouraging as the study has indicated the possibility of deposition directly in liquids phase.
5.2. Recommendations and Future Work

The study of dc corona discharges in atmospheric pressure gases and in liquids has demonstrated the possibility of applying corona discharges for materials processing. However, these studies for discharges in liquids were preliminary and further optimization of the discharge is required to fully understand the breakdown mechanisms and apply the plasma discharge to materials processing. Another avenue of research is the investigation of pulse plasma discharges in liquids. The use of pulses will enable higher power discharges (and possibly higher deposition rates) without transitioning into thermal and non-uniform discharges. Some preliminary work was performed in this area of pulse plasma discharges in liquids and is briefly discussed in the section. Recommendations are also made to develop accurate numerical models to computationally study the corona discharge in atmospheric pressure. These computational studies will provide further insight into the new “diffuse glow” stable corona discharge mode observed in experiments and can be used to validate the hypothesis for diffuse glow presented in this thesis.

5.2.1. Preliminary study of pulsed corona discharges in liquids

A preliminary study was performed to investigate the applicability of pulsed plasma discharges in liquids. To this purpose, a novel external circuit was developed to generate a pulsed plasma discharge in liquids and the circuit was characterized. The external circuit allowed the variation of the pulsed discharge characteristics (i.e., discharge voltage, mode and duration). Figure 5.1 shows the external circuit used to
generate pulsed discharges in liquids. A DC power supply is connected in series with a ballast resistance and the plasma discharge. A capacitor is placed in parallel with the power source and the discharge. The external pulse generating circuit is a simple two spark gap circuit. This circuit is similar to pulse generating circuit reported by Mankowski et al. [90] and used by Staack et al. [72]. The spark gaps act as switches which control the applied voltage and the pulse duration. The first spark gap breaks down when the electric field is higher than the breakdown electric field for the gas it is operating in (~ 31 kV/cm in air). This first spark gap delivers the voltage to the load (plasma discharge) and the second spark gap removes the voltage from the load (extinguishing the discharge). The lengths of the spark gaps are controlled by micro-positioners. Controlling the length of the spark gaps allows variable values of discharge voltage and pulse duration. The power source voltage, the value of the ballast resistance and the capacitor determine the repetition rate of the pulse. Figure 29 shows an image of the external circuit fabricated in the lab. A pin-to-plate configuration is used for the spark gaps. The pins are fabricated from solid brass rods and the plates are copper plates. The circuit is kept as compact as possible and has as few connections as possible to prevent unwanted parasitic capacitance which leads to ringing in the pulse signal. The final circuit still produced ringing in the output voltage traces, but the ringing was reduced as much as possible.
Figure 5.1: External circuit used to generate pulsed plasma discharges in liquids, S.G. 1 and S.G. 2 represent the two spark gaps and C is the capacitor bank.

The external circuit developed and assembled was capable of variable pulse duration and discharge voltage. In order to fully understand the capability of the external spark gap circuit, it was characterized at different lengths of the two spark gaps with the discharges generated in de-ionised ultra filtered (DIUF) water. To study the effect of spark gap 1 (S.G. 1), the length of spark gap 2 (S.G. 2) was kept constant at 2.5 mm and the length of S.G. 1 was varied along with the power source voltage. The results of this characterization are plotted in figure 5.2. As can be seen, at values of S.G. 1 > S.G. 2, the power source voltage (i.e., the voltage across S.G. 1) and the discharge voltage (across the discharge gap) are the same. This mode is called the “normal pulse mode” (see figure 5.3 (a)) and the discharge appears like a corona discharge in gases with a homogenous glow near the sharp electrode tip. However, at values of S.G. 1 < S.G. 2, the discharge voltage is higher than the voltage across the spark gap S.G. 1. This mode is called the “stepped voltage mode” and is characterized by a brighter and more non-uniform discharge appearance (see figure 5.3 (b)).
Figure 5.2: Variation of the discharge voltage with the length of spark gap 1 (S.G. 1) at a constant length of S.G. 2 = 2.5 mm

Figure 5.3: Images of the pulsed plasma discharge in DIUF (discharge gap ~ 3.0 mm) during two different external circuit modes (a) Normal pulse mode and (b) Stepped voltage mode
The effect of S.G. 2 on the discharge was also characterized. To study this effect, the length of S.G. 1 was maintained constant at 6.5 mm and the length of S.G. 2 was varied. As can be seen in figure 5.4, as the length of S.G. 2 is increased, the duration of the pulsed discharge increased from a minimum of ~ 80 ns to ~ 170 ns. A typical oscillogram of the discharges in conductive fluids like DIUF and TEOS is shown in figure 5.5 below. The duration of the pulses and the peak discharge voltages plotted in figures 5.4 and 5.2 respectively were obtained from such oscillograms.

![Graph showing the variation of pulse duration with the length of S.G. 2](image)

**Figure 5.4:** Variation of the pulse duration with the length of spark gap 2 (S.G. 2) at a constant length of S.G. 1 = 6.5 mm

The plots in figures 5.5 and 5.6 show the oscillograms for conductive (DIUF and TEOS) and non-conductive (polyethylene glycol (PEG) and transformed oil) fluids. The main difference in the two plots is the duration of the pulse. The conductive fluids have much longer pulse durations (~ 100 – 200 ns) compared to the non-conductive fluids (~
10 – 50 ns) for similar spark gap configurations. However, both oscillograms show “ringing” in the signal traces which is indicative of high parasitic capacitance and impedance mismatches in the external circuit.

**Figure 5.5:** Oscilloscope traces (discharge voltage and current) for a single pulse in TEOS, insert shows the traces for a smaller time-scale
These preliminary results for pulse plasma discharges in liquids are encouraging. They demonstrate the possibility of dissipating higher power through pulsed plasma discharges in liquids than the corresponding dc discharges. This will lead to higher deposition rates and possibly more uniform deposits on the electrode surface. Further research is required to optimize the external circuit (reduce the ringing observed, etc.) and make better use of the material processing capabilities of pulsed plasma discharges in liquids. Additional future research may be pursued to study the types of deposits made on the electrodes for discharges in liquids (both dc and pulsed discharges) and optimize the setup to generate high quality conformal deposits.
5.2.2. Modelling of atmospheric pressure plasma discharges

The corona discharge discussed in this thesis is operating in a new regime at relatively low discharge voltages and appears to have a structure similar to a normal glow discharge with a cathode spot and a diffused positive column. Proposed future work may include studying the corona discharges in atmospheric pressure gases computationally. A hybrid model similar to that used by Farouk et al. [91] is proposed to simulate the discharge. The hybrid model combines a fluid model that solves the transport equations of the electrons, ions, excited species and neutrals and a kinetic model that solves a zero-dimensional Boltzmann equation to obtain the reaction rates of the various kinetic processes. The fluid model assumes reaction rates that are described by the Arrhenius form and the coefficients are calculated assuming a Maxwellian distribution of the electron energy distribution function (EEDF) which is a debatable assumption. On the other hand, kinetic model by itself is extremely expensive computationally. In the hybrid model, a Boltzmann equation solver is used to calculate the EEDF thus accounting for the non-equilibrium nature of the discharge. This is accomplished by solving a two term spherical harmonic expansion of the Boltzmann equation for the electron energy distribution. The computationally expensive aspect of the kinetic solver is avoided by solving a simple zero-dimensional Boltzmann solve in advance to generate the required look-up-tables.

It is proposed to begin the computational studies with modeling monatomic gases like helium and argon. The experiments performed with helium (and reported in this thesis) show interesting structures for a corona discharge and hence may be used as the first simulation test case. The advantage of the modeling a helium discharge is two-fold.
Firstly, given the chemistry for a helium discharge is relatively simple, the simulations are computationally inexpensive and secondly, it has been shown experimentally [4, 5, 88] that adding helium to a discharge not only helps stabilize the discharge but also lowers the gas temperature and thus leads to more uniform film deposition. This aspect of the simulating a helium discharge is interesting from a scientific point of view as well as it will be an important tool in plasma enhanced chemical vapour deposition (PECVD).
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