SELF-CONSISTENT MONTE CARLO SIMULATIONS
OF PLASMA PROCESSING REACTORS

BY
YILIN WENG
B.S., Huazhong University of Science and Technology, 1982
M.S., University of Illinois, 1988

THESIS
Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Electrical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1991

Urbana, Illinois
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

THE GRADUATE COLLEGE

SEPTEMBER 1991

WE HEREBY RECOMMEND THAT THE THESIS BY

YILIN WENG

ENTITLED

SELF-CONSISTENT MONTE CARLO SIMULATIONS

OF PLASMA PROCESSING REACTORS

BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

[Signatures]

Director of Thesis Research

Head of Department

Committee on Final Examination:

[Signatures]

Chairperson

†Required for doctor's degree but not for master's.
SELF-CONSISTENT MONTE CARLO SIMULATIONS
OF PLASMA PROCESSING REACTORS

Yilin Weng, Ph.D.
Department of Electrical and Computer Engineering
University of Illinois at Urbana-Champaign, 1991
Mark J. Kushner, Adviser

When the fractional ionization of a plasma exceeds $10^{-5} - 10^{-4}$, electron-electron (e-e) collisions become important. These collisions cause the electron energy distribution (EED) to approach a Maxwellian distribution. Electron cyclotron resonance (ECR) reactors for etching and deposition have a high plasma density and fall into the category of devices for which e-e collisions must be considered. In this thesis, a self-consistent Monte Carlo (MC) simulation for low-temperature partially ionized plasmas is presented. In this simulation, the effects of electron-electron collisions are taken into account. Electron-electron collisions are treated as being functionally equivalent to electron-neutral collisions. That is, instead of having an electron collide with an individual electron, the electrons collide with an energy-resolved electron fluid. The modified null-cross-sectional technique is employed, making the MC simulation computationally tractable. The model is used to study ECR reactors and is a hybrid MC fluid model. The MC simulation generates details of the EED and the fluid model generates the ambipolar fields. The MC and fluid models are iterated to obtain a converged solutions. The model has been utilized to investigate electron swarm parameters in ECR reactors for Ar and N₂ plasmas at different pressures and different input microwave powers. The parameters investigated are the EED, electron impact rate coefficients, average electron energy, plasma potential, and power deposition. The results are in general agreement with experiment.
DEDICATION

To my husband, Jianping Zhang, and
my parents, Peide Weng and Liangzhang Chen
ACKNOWLEDGMENTS

I would like to thank my thesis advisor, Professor Mark Jay Kushner, for his optimism, direction, patience, and discussions during the period of my dissertation research. I appreciate his support, especially during my pregnancy and delivery. Without his help and prodding, this work would not have been finished at this time.

My husband, Jianping Zhang gave me a great deal of help and encouraged me to complete this study. I am also grateful to my parents, Peide Weng and Liangzhang Chen, for their support, help and encouragement, especially after the birth of my daughter, Lorna.

I would also like to thank the members of the optical and discharge physics group, past and present, for their friendship and camaraderie, particularly John DiCarlo, Jeanne Balbach, Hoyoung Pak, Tim Sommerer, Jong Shon, and Phillip Stout. A special thanks is due to Seung Choi for his matrix inversion program. Thanks also go to Randall Bramley for his patient and careful proofreading of my dissertation.

Finally, I would like to acknowledge the National Science Foundation for its support.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>10</td>
</tr>
<tr>
<td>2.2.1</td>
<td>12</td>
</tr>
<tr>
<td>2.2.2</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3</td>
<td>16</td>
</tr>
<tr>
<td>2.2.4</td>
<td>19</td>
</tr>
<tr>
<td>2.2.5</td>
<td>19</td>
</tr>
<tr>
<td>2.2.5.1</td>
<td>20</td>
</tr>
<tr>
<td>2.2.5.2</td>
<td>20</td>
</tr>
<tr>
<td>2.2.6</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
</tr>
<tr>
<td>3.1</td>
<td>30</td>
</tr>
<tr>
<td>3.2</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>38</td>
</tr>
</tbody>
</table>
5 APPLICATIONS OF MC SIMULATION TO ECR REACTORS .......... 43
  5.1 ECR Reactors .............................................. 44
  5.2 The Model System ........................................... 48

6 RESULTS FOR EEDs IN ECR REACTORS ....................... 57
  6.1 Electron Energy Distribution Functions in ECR Reactors .......... 57
      6.1.1 Argon plasma ......................................... 57
      6.1.2 Nitrogen plasma ....................................... 59
  6.2 Rates .......................................................... 60
  6.3 Average Electron Energy ..................................... 62
  6.4 Density ....................................................... 66
  6.5 Potential ..................................................... 66
  6.6 Power Deposition ............................................. 68
  6.7 Flared Geometry ............................................. 69

7 SUMMARY AND FUTURE WORK .................................... 91

REFERENCES ....................................................... 93

VITA ................................................................. 96
CHAPTER 1

INTRODUCTION

The importance of solving electron energy distributions (EEDs) in fully and partially ionized plasmas is well-known. Particle simulations are powerful techniques to simulate rf discharges and electron cyclotron resonance (ECR) reactors, which are commonly used in many electronic device fabrication processes such as semiconductor etching and thin film deposition. These simulations are especially useful for modeling electron transport when the EED is not in equilibrium with the local electric field (either temporally or spatially) or for complex geometries. Particle simulations may be divided into two generic categories: Particle-in-cell simulations (PICS) and Monte Carlo (MC) simulations. The two methods employ many of the same techniques to advance particle trajectories and solve Poisson's equation for changes in the electric field. The major differences lie in how collisions are represented. One does not typically include electron-electron collisions in MC simulations; PICS do, to some degree, include electron-electron collisions but in a manner which is computationally intensive. In this research, we investigate methods for using MC simulations which include electron-electron collisions. In doing so, a new and efficient MC simulation inclusive of electron-electron collisions has been developed.
1.1 Brief History of Using Monte Carlo Simulations for EEDs

Usually, there are two ways to obtain the electron energy distribution function. One is to solve Boltzmann's equation directly. Another is to use Monte Carlo simulations to obtain a statistical result. As early as 1946, Holstein\(^1\) derived the general form for the energy distribution equation which is based upon a first-order approximation of Boltzmann's equation. This form is valid only when the energy exchange between collisions is smaller than the electron energy. This corresponds to a low value of E/N, the electric field to gas density ratio. Twenty years later, the development of digital computers made possible the use of Monte Carlo methods. Itoh and Musha\(^2\) and Thomas and Thomas\(^3\) independently solved Boltzmann's equation for large values of E/N. The Monte Carlo method simulates the motion of an electron by integrating its equations of motion at all stages of its passage across the discharge gap, providing a history of electron collisions. The energy distribution and the related discharge parameters can be calculated by analyzing large numbers of electrons. In 1973, Rockwood\(^4\) presented a practical way to include electron-electron interactions in the dc Boltzmann's equation at low E/N. Bretagne, Godart and Puech\(^5\) later used the Rockwood formalism and calculated the electron distribution function including all of the interactions between electrons and ground or excited states of atomic and molecular argon.

Both Boltzmann analyses and Monte Carlo simulations have been improved as methods for studying the behavior of electrons in gases under the influence of an electric field during the past twenty years. To improve accuracy, researchers have used higher-order approximations to Boltzmann's equation, ranging from two (which is still popular) to six terms.\(^6-10\) Lucas\(^11\) and Penetrante, Bardsley and Pitchford\(^12\) and other researchers\(^13-14\) have also performed comparisons between the two methods. Particle simulations are now widely applied to the analysis of fully and partially ionized plasmas.\(^15-21\) Sophisticated techniques have been developed to self-consistently simulate fully ionized and solid-state plasmas. In comparison, the use of Monte Carlo particle simulations for modeling low-temperature
(0.1 eV \leq T_e \leq 10 eV, where T_e is electron temperature) partially ionized \,(10^{-6} \leq n_e/N \leq 10^{-2},
where n_e and N are electron density and gas density, respectively) collisional plasmas is in an immature state of development. This condition results from the difficulty of self-consistently including the effects of electron-electron collisions in a Monte Carlo simulation under highly collisional conditions.

Although the frequency of electron-electron collision is much lower than that of other collisions, it still plays an important role in determining the electron energy distribution due to the large momentum transfer and energy exchange which may occur. These collisions can thermalize the EED towards a Maxwellian distribution and result in changing transport properties. This effect can be seen from Fig. 1.1 (figures appear at the end of each chapter) which shows the EED for N_2 with E/N = 20 Td. As the fractional ionization \( \delta \) increases, the EED does evolve towards a Maxwellian distribution. Therefore, in low-temperature plasmas, when the fractional ionization exceeds \( 10^{-5}-10^{-4} \), the influence of electron-electron collisions must be taken into account. By doing so, the basic physics of the systems can be better understood, and the optimization of high plasma density devices such as electron cyclotron resonance (ECR) reactors becomes possible.

Particle simulations of partially ionized plasmas, though, do not typically include electron-electron collisions. This exclusion limits the class of plasmas for which these particle simulations may be used. In this research, first of all, we have developed a new and efficient Monte Carlo simulation method which includes electron-electron collisions by using a null-cross-sectional technique.\(^{14}\) In this method, collisions of electrons with electrons are conceptually treated in the same way as collisions of electrons with heavy particles (i.e., atoms and molecules). This is accomplished by having the electron particles in the simulation collide with an energy-resolved electron fluid in the same manner in which electrons collide with the neutral heavy particle fluid. In doing so, the impact Lorentz
approximation may be used for the collisions of electron particles with the electron fluid. The advantages of this method are that the same algorithms are used for all collisions, and the integrating time step may be as large as the time between collisions. To make this technique computationally tractable, a modified null-cross-sectional algorithm is used which eliminates the need for recomputing the probability integrals for electron collisions as the EED evolves. This will be discussed in Chapter 2 in detail. The method can have a response time of less than or equal to tens of nanoseconds, thereby enabling one to simulate transient phenomena having a frequency of tens of megahertz.

1.2 Description of ECR Plasma Processing Reactors

The purpose of developing this MC method is to address design issues of real plasma processing reactors. Plasma processing research is now focused on low-pressure and high-density sources. Important developments in these kinds of sources are electron cyclotron resonance (ECR) excited discharges and magnetron devices, both of which are currently being investigated for use in plasma etching and deposition of semiconductor materials.

The configurations of the ECR reactors being investigated for use in plasma processing are varied, as are the measurements of the electron swarm parameters. A typical plasma process reactor is schematically shown in Fig. 1.2. It consists of a cylindrical discharge region which is called a plasma chamber and expands to a larger diameter downstream, called the process chamber, in which the substrate is placed. A microwave electric field is fed into the plasma chamber through a dielectric window and propagated collinearly to the axis of the reactor. In the chamber, a magnetic field is supplied by one or more coils surrounding the plasma chamber, and an optional coil is placed downstream. The purpose of the two coils upstream is to obtain a more uniform magnetic field in the
plasma chamber. Using the coil downstream results in a magnetic field profile which is somewhat collimated: in the absence of that coil the magnetic field is flared. Variants of this configuration will place the substrate in or near the ECR zone, where the electron cyclotron frequency equals that of the microwave field, or will use a radio frequency (rf) bias on the substrate to increase or control the ion energies striking the substrate. Alternate configurations use a tunable resonant cavity with a multicusp magnetic configuration, or an untuned cavity with a multipole magnetic field. In the latter configurations, permanent magnets placed on the exterior of the chamber significantly reduce the loss of charged particles to the walls and produce a large volume of uniform plasma.

In the ECR zone, electrons can be accelerated to high energy at low gas pressure (< 1 mTorr) due to the resonance excitation. Therefore, ECR reactors enable us to sustain plasmas at low pressure and achieve uniform processing. Since the workpiece is downstream, out of the plasma zone, the plasma density and ion energy incident on the substrate can be separately controlled. The microwave power is absorbed upstream in the plasma chamber and generates high-energy particles. These particles come downstream by diffusion and advection. Contamination is reduced by the substrate's removal from the ECR area and low gas pressure.

Typical conditions for etching in ECR reactors are an average electron energy of 6 to 8 eV and gas pressure of a few milliTorr. The microwave frequency is usually 2.45 GHz (the corresponding resonance magnetic field is 875 G) resulting in an electron density of $10^{11}-10^{12}$ cm$^{-3}$. Many diagnostic experiments have been performed and models have been developed for ECR sources and etching. But this research is not yet mature particularly from a modeling viewpoint. For example, the physics behind these reactor operations is still poorly understood; therefore, it is hard to make predictions about etching
uniformity or rate. Since few researchers have considered the influence of electron-electron collisions in particle simulations, few kinetic descriptions of electron transport published thus far are applicable to ECR reactors.

1.3 Preview of the Dissertation

This project is divided into two parts. The first is the development of the methodology for MC simulations with electron-electron collisions which is discussed in Chapters 2 and 3. The second considers applications, and ECR reactors are the application of choice. In Chapter 2, we discuss the motivation for developing the new method and describe it in detail. Compared to the solutions of the Boltzmann equation, all of the cases dealt with in Chapter 2 use a spatially uniform and time-independent electric field. In Chapter 3, spatially and time-dependent situations are considered. A hybrid Monte Carlo and fluid model is described in Chapter 4, and ECR reactors are investigated in Chapter 5. The simulation results and discussions about ECR reactors are presented in Chapter 6. Finally, future work is proposed in Chapter 7.
Figure 1.1. Calculated electron energy distribution as a function of fractional ionization for N₂. The effect of electron-electron collisions is clearly shown. The gas pressure is 3.1 Torr and E/N is 20 Td.
Figure 1.2. Schematic of electron cyclotron resonance (ECR) apparatus for etching or deposition.
CHAPTER 2

METHODOLOGY OF THE MONTE CARLO SIMULATION

2.1 Particle Simulations

Particle simulations of highly ionized plasmas usually are based on either the Vlasov equation,\textsuperscript{32} which is collisionless, or the Fokker-Plank equation,\textsuperscript{33} which considers only elastic collisions. Electron-electron collisions can be included in particle simulations of fully ionized plasmas using either the Vlasov or Fokker-Plank equations. In the Vlasov equation, electron-electron interactions are included in Poisson's equation, as follows

\[
\frac{\partial f}{\partial t} = - \mathbf{v} \cdot \nabla f + \frac{q}{m} (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \nabla_v f
\]

\[
\nabla \cdot \mathbf{E} = 4\pi \rho
\]

(2.1)

where \( f \) is the particle distribution function, \( \rho \) is the charge density, \( m \) is the mass, \( q \) is the electronic charge, \( \mathbf{v} \) is the charge particle velocity, and \( \mathbf{E} \) and \( \mathbf{B} \) are the electric and magnetic fields, respectively. By including charge fluctuations on the scale of the Debye length, electron-electron interactions are considered. The Fokker-Plank equation is

\[
\frac{\partial f}{\partial t} = - \mathbf{v} \cdot \nabla f - \mathbf{F} \cdot \nabla_v f + \frac{\partial f}{\partial t}_c
\]

(2.2)

where \( \mathbf{F} \) includes the applied electric and magnetic fields. The collision term includes only elastic collisions, i.e., electron-electron and electron-ion, which have only a small energy
change between collisions. The term explicitly includes the Coulomb interaction between electrons.

In typical high-temperature fully ionized plasmas, the electron temperature and density are approximately 20 keV and $10^{13}$ cm$^{-3}$, respectively. The resulting Debye length and number of electrons in a Debye sphere are $\lambda_D = 0.035$ cm and $n_D = 2 \times 10^8$. Each pseudoparticle in a MC simulation may represent many actual electrons, e.g., $10^5 - 10^9$. In a low-temperature partially ionized plasma, as used for plasma etching, $T_e = 2$ eV and $n_e = 10^9$ cm$^{-3}$. This results in a similar value for $\lambda_D (\approx 0.03$ cm) and $n_D (\approx 2 \times 10^5)$. The computational spatial mesh for a simulation in each case must therefore be very fine (<< millimeters), the integration step quite small (<< picoseconds), and the number of computational particles large. These requirements may be somewhat relaxed by using numerical averaging techniques. One such method is to use finite-sized particles in which the charge density of individual computational particles is averaged over adjacent mesh points.\textsuperscript{17} This technique, however, also smoothes the small changes in charge density, and hence the interparticle forces, which constitute an electron-electron collision. Therefore, when electron-electron collisions compete with inelastic electron-neutral species collisions, as in a partially ionized plasma, there may be a systematic biasing of the relative amount of energy which is exchanged in an electron-electron collision as compared to that exchanged in $e-N$ collisions.

\subsection*{2.2 Monte Carlo Simulation}

The systems of interest are partially ionized quasi-neutral plasmas. That means that the electric field is constant in regions of many Debye lengths, which is typically a few to tens of microns. Although the Fokker-Plank and Vlasov equations are satisfied under these conditions, to resolve the Coulomb force the resolution must be on the order of the Debye length. This scale is too small to practically simulate partially ionized plasmas having scale
lengths of many centimeters. Partially ionized plasmas differ from fully ionized plasmas in that inelastic and non-Coulomb elastic collisions are also important in determining the electron transport coefficients. The distance between these collisions is much larger than the order of Debye length, hence, resolving the problem on the order of microns is obviously not practical. Therefore, neither method is optimal for including electron-electron collisions in Monte Carlo (MC) simulations of these plasmas.

In a low-temperature partially ionized plasma, momentum-transfer collisions and inelastic collisions with heavy neutral particles (atoms and molecules) are usually most important in determining the EED, and hence in determining electron-transport coefficients. These collisions result from short-range forces having spatial extents measured in angstroms. Since the electron thermal velocity is typically larger than $10^7$ cm/s, the duration of $e-N$ collisions is smaller than $10^{-15}$ s. In addition, the temperature of the neutral heavy particle is $10^{-1}-10^{-3}$ that of the electrons, resulting in heavy-particle thermal velocities which are $10^{-2} - 10^{-4}$ that of the electrons. Because of these conditions, $e-N$ collisions are most often simulated using the impact-Lorentz approximation. This approximation states that collisions between electrons and heavy neutral particles occur over a time period ($10^{-15}$ s) and distance ($10^{-8}$ cm) which are insignificantly small compared to other time and spatial scales, such as the Debye length and the time between collisions (the time between collisions scales as 1 ns/p, where p is the gas pressure in Torr). Therefore, one approximates that $e-N$ collisions occur instantaneously, without change in the spatial location of the electron, and that the relative motion of heavy particles is not important in computing the collision integral. Therefore, a MC simulation is the more appropriate vehicle for calculating the EED of a low-temperature partially ionized plasma.
2.2.1 The MC method using a null collision technique

Prior to beginning the MC simulation, a gas mixture is selected and the energy range of interest is divided into bins centered at energy $\varepsilon_i$. The total electron collision frequency in each energy interval $\nu_l$ is determined, and probability arrays are initialized for each energy interval. The probability arrays are denoted $P_{ij}$ for energy range $i$ and collision process $j$. They have the properties that

$$P_{ij} = \frac{\nu_{ij}^c}{\nu_i}, \quad \nu_{ij}^c = \sum_{l=1}^{j} \nu_{il}$$  \hspace{1cm} (2.3)$$

where $\nu_{il}$ is the collision frequency for energy interval $i$ and process $l$, $\nu_{ij}^c$ is the cumulative collision frequency for processes $l \leq j$, and $P_{ij}$ is normalized so that for $m$ processes, $\sum_{j=1}^{m} P_{ij} = 1$. The difference between elements of $P_{ij}$ represents the relative probability of an electron undergoing a particular collision at a specific energy.

The trajectory of an electron having energy $\varepsilon_l$ moving in a uniform electric field may be updated using the average time steps of $1/\nu_i$ if the impact approximation is used, since during this time the electron is accelerated only by the electric field. Using the Monte Carlo method, three random numbers are needed. All of them are in a sequence uniformly distributed in the interval $(0,1)$. The first random number $r_1$ is used to obtain the actual time step chosen for advancing a particular particle which can be presented as $\Delta t = -\ln(r_1)/\nu_i$. Given this time step, the position and velocity of the electron are updated by integrating the equations of motion for $\Delta t$. At the end of this update, a collision occurs. The type of collision that occurs is determined by choosing a second random number $r_2$. The collision, denoted $j$, is that process which satisfies
\[ P_{i,j-1} < r_2 \leq P_{i,j}. \] (2.4)

The energy of the electron is revised to \( e \rightarrow e + \Delta e_{ij} \), where \( \Delta e_{ij} \) is the change in energy associated with process \( j \) at energy \( i \), which can be either positive or negative. A positive change corresponds to gain which comes from superelastic collisions, and a negative change corresponds to a loss from inelastic collisions. The velocity of the electron is updated based on the change in energy and the scattering angle given by the differential cross section.

Obviously, if the acceleration of the electron during its flight between collisions significantly changes its energy, its total collision frequency may also change. In this case, the choice of \( \Delta t \) is ambiguous because \( v_i \) at the beginning of the flight differs from that at the end of the flight. This complication may be avoided by using a null cross section\(^{14} \) or "self-scattering" event.\(^{34} \) In this method, the maximum electron collision frequency, \( v_m \), over the energy interval of interest is determined. An additional fictitious or "null" collision process is added to the real processes at each energy. The null collision process at energy \( e_i \) has a collision frequency \( v_{in} = v_m - v_i \). In doing so, the time between collisions for electrons at all energies can unambiguously be given by \( \Delta t = -ln(r_1)/v_m \). After updating the velocity and location of the particle using this time step, another random number is chosen. If \( r_2 > v_{in}/v_m \), where the energy bin \( i \) is based on the instantaneous energy of the electron, then a real collision has occurred, and the particle's velocity is revised accordingly. The specific collision which occurs is obtained by using \( r_2 \) to search the probability array as shown in Eq. (2.4). If, however, \( r_2 \leq v_{in}/v_m \), then a "null" collision occurs and the particle proceeds to its next "collision" unhindered.
2.2.2 The equivalence method for including electron-electron collisions

The basis of the method to include electron-electron collisions in MC simulations is to treat electron-electron collisions functionally the same as e-\(N\) collisions. That is, instead of having an electron collide with individual electrons, as in a particle-particle technique, the electrons collide with an energy-resolved electron fluid in the same manner as electrons collide with the neutral gas. The implementation then resembles a particle-mesh algorithm. In doing so, we must implicitly assume that changes in the charge densities which may occur on spatial scales of much less than \(\lambda_D\) are not a result of, or do not contribute to, Coulomb collisions between electrons. In the bulk plasma of interest, where quasineutrality holds over dimensions much greater than \(\lambda_D\), this is a good approximation. The change in electric field which results from there being a finite charge density in the sheath regions may be included in this method with no change in the algorithm.

Recall that in Monte Carlo simulations electron-gas collisions are included by computing the collision frequency for process \(i\). The collision frequency \(\nu\) at velocity \(v_e\) for process \(i\) is

\[
\nu_i (v_e) = N \int f(v) |v - v_e| \sigma_i(v, v_e) d^3v
\]

(2.5)

where \(f\) is the velocity distribution of the collision partner, \(N\) is the number density of the collision partner and \(v\) is the collision partner velocity, that is, the target velocity. The subscript "e" corresponds to electron velocity and \(\sigma_i\) is the cross section of process \(i\). For heavy gases, \(f\) can be simplified as a \(\delta\)-function by the Lorentz approximation. Using \(\delta\)-function properties, the integral can easily be evaluated:

\[
\nu_i (v_e) = N |v_e| \sigma_i(v_e).
\]

(2.6)
To treat electron-electron collisions the same as e-N collisions, by specifying a collision frequency for the process, one must be able to calculate the frequency of electron-electron collisions as a function of the relative velocity between the incident electron and the target electron, as shown in Eq. (2.5). This may be accomplished by using an electron fluid having the velocity distribution \( f_e(v) \) with the Coulomb cross section \( \sigma_{ee}(v, v_e) \), and the electron density \( n_e \); the electron-electron collision frequency is

\[
v_{ee}(v_e) = n_e \int f_e(v)|v - v_e| \sigma_{ee}(v, v_e) d^3v.
\]  

(2.7)

Here \( v \) corresponds to the background electron velocity, \( n_e \) is the electron density and \( f_e(v) \) is the electron velocity distribution of the fluid. Since the Lorentz approximation is not valid for this case, the full electron distribution function \( f_e(v) \) is required which is precisely what we are solving for. This problem is handled as follows: an initial estimate for \( f_e(v) \) is used. As the simulation proceeds, the velocity distribution of the electron particles is sampled and \( f_e(v) \) is updated. Electron energy distribution, \( f_e(v) \), will tend to the quasi-steady-state solution as time goes on. In the current research, individual electron-electron collisions are not considered as in the particle-particle basis approach. The method introduced here uses a particle-mesh basis. Discretizing Eq. (2.5) yields

\[
v_{ee}^i = \sum_j v_{ee}^{ij} = n_e \sum_j v_{ij} \sigma_{ee}(v_{ij}) f_j \Delta \varepsilon_j,
\]  

(2.8)

where \( v_{ee}^i \) is the electron-electron collision frequency for an electron having energies in the energy interval \( (\varepsilon_j, \varepsilon_j + \Delta \varepsilon_j) \), \( v_{ee}^{ij} \) is the electron-electron collision frequency between incident electrons in energy intervals \( i \) and the electron fluid in interval \( j \), \( v_{ij} \) is the interaction speed between incident electron and fluid electrons in energy intervals \( i \) and \( j \), respectively, and \( \sigma_{ee} \) is the interaction cross section. By characterizing the electron fluid in terms of
energy, though, the vector information required to solve the collision integral in Eq.(2.7) is lost.

The formulation presented above appears ill-posed since we require prior knowledge of \( f_e(v) \) in the form of \( f_j \) to obtain the EED, which for a self-consistent solution should be mirrored by \( f_e(v) \). In our model, the values of \( f_j \) are obtained during the simulation by sampling the EED of the particles and updating \( f_j \) as the EED evolves. This process is performed by using a modified null-cross-sectional technique. The method eliminates the need to recompute the probability array as the EED evolves, and therefore is computationally efficient. This implementation is described below.

2.2.3 Modified null-cross-sectional technique

By using a null-collision technique, electron-electron collisions are considered as another process identical to gas particle collisions and are placed on top of all of the real processes in the probability array. A subarray is created to deal specifically with electron-electron collision processes. In the usual method, the probability of having null collisions is included in the arrays by searching for the maximum collision frequency \( v_m \), and adding \( v_{in} = v_m - v_i \) to the real collision frequencies. The modified null-cross-sectional technique involves using an additional null-collision frequency, \( v_{in}^{ce} \), when calculating the probability arrays. The additional null-collision probability is conceptually allocated to the space for electron-electron collisions. This hierarchy of a null-collision probability array is illustrated in Fig. 2.1, which presents two arrays. The column on the left side is called the main array and represents the relative probability of electron collisions at a specific energy. The probability may include a portion which is permanently allocated to null collisions. The portion allocated to electron-electron collisions is divided into real collisions and a working null area. As the electron-energy distribution evolves, either spatially or temporally, the
space allocated to real electron-electron collisions expands or contracts at the expense of the working null space.

To minimize the number of null collisions during the simulation, the fraction of the probability array allocated to "working" null space should be kept as small as possible. In practice, this is complicated by the fact that the cross section for electron-electron collisions scales as $1/e^2$ and therefore is largest at lowest energy. This results in a large fraction of null collisions at higher energy. This problem is avoided by dividing the energy range into subranges. In each subrange, the maximum electron collision frequency is determined, and a separate null-collision frequency is used. Collision times and choices of collisions are then made, based on the subrange on which the electron currently "resides." There is some ambiguity when an electron crosses from one subrange to an adjacent subrange during the flight between collisions, but the fraction of flights for which this occurs is small. On the other hand, this small ambiguity is a penalty. It means that while we have developed a more efficient method, the accuracy may suffer slightly by the treatment.

We have already mentioned two of the random numbers in Section 2.2.1; now it is time to choose the last random number $r_3$, which is used to determine the electron-electron collisions. In the subarray, the null collision is still put on top, and this array is also normalized. The only difference between these two arrays is that the subarray needs to be periodically updated according to the evolution of electron distribution, while the main array need not be updated, pending changes in the densities of heavy particles.

The fraction of fluid electrons per unit energy in interval $j$ is $f_j$, having normalization $\Sigma_j f_j \Delta E_j = 1$. In writing Eq. (2.8), we are expressing the rate of e-e collisions for an electron in energy interval $i$ as the sum of collision frequencies with discrete portions of the electron fluid distribution. In doing so, each energy interval of the
electron fluid is treated exactly as we would an atomic species having density $n_e f_j \Delta e_j$. That is, in the calculation of $v_{ij}$, we add the contribution of the $v_{ee}^{ij}$ to the frequencies for the electron-neutral collision just as though they were heavy particle collisions. As the simulation proceeds and the EED evolves, the values of $v_{ee}^{ij}$ are periodically updated based on a sampling of the instantaneous distribution function. In this manner, self-consistency is obtained. Since "working" null space was previously allocated in the original probability arrays, the values of $v_{ee}^{ij}$ do not need to be recalculated. Having enough "working null" space in the subarray, the update requires only taking a ratio between the current value of $f_j$ and that value which was used to construct the original probability array. Therefore, Eq.(2.8) can be rewritten as

$$v_{ee}^i = \sum_j \frac{f_j}{(f_j)_0} (v_{ij})_0,$$

where $(f_j)_0$ is the initial estimate of the electron fluid density in interval $j$, and $(v_{ij})_0$ is the initial collision frequency from interval $i$ to $j$. The real electron-electron collision probability then expands and contracts, at the expense of space allocated for null collisions, as the simulation progresses. From the above equation, the initial estimate of $(f_j)_0$ and periodic updates of $(f_j)$ yield the electron-electron collision rate without recomputing large arrays of collision probabilities. Using this method, the probabilities for $e-N$ collisions do not have to be recalculated either. In practice, we have found that the EED equilibrates with only a few updates of the probability array. For example, in simulating an electron swarm in $N_2$ with $E/N = 20$ Td and $n_e/N_2 = 10^{-4}$, the distribution function equilibrates in only a few tens of nanoseconds when using a few hundred particles. Therefore, this technique allows time-dependent calculations with frequencies exceeding a few tens of megahertz.
2.2.4 Coulomb cross section and energy exchange

The Coulomb cross section and energy exchange during an e-e collision depend on the vector velocities of the projectile and target electrons. Since the method described here is effectively a particle-mesh technique, we have lost the vector information of the target electron. We approximate the interaction speed of the collisions as being the maximum of the speed of the target and projectile. With this approximation for the interaction speed, we use the classical Coulomb cross section

$$\sigma(v) = 4\pi b_0 \left[ 1 + \ln \left( \frac{\lambda_D}{b_0} \right) \right]^{1/2}, \quad b_0 = \frac{e^2/4\pi\varepsilon_0}{\mu v^2},$$

(2.10)

where $\mu$ is reduce mass and $v$ is electron's velocity. Assuming isotropic scattering with the angle $= 2\cos^{-1}(r)$, the energy loss (positive) or energy gain (negative) for the projectile electron $i$ scattering from the electron fluid element having energy $\varepsilon_j$ is approximated as

$$\Delta \varepsilon_i = \begin{cases} \varepsilon_i [1 + \cos(\theta)]/2 & \varepsilon_i > \varepsilon_j \\ -\varepsilon_j [1 + \cos(\theta)]/2 & \varepsilon_i < \varepsilon_j \end{cases}$$

(2.11)

The change in energy is imparted to the projectile electron. The energy imparted to the target electron is implicitly accounted for when the EED is sampled during the next update of the probability arrays.

2.2.5 Comparison with a Boltzmann solution

In order to prove that the new MC simulation is reliable, comparisons with the Boltzmann code will be presented. We have used a spatially uniform and time invariant electric field. This allows us to make comparisons with the results obtained by solving Boltzmann's equation using conventional continuum techniques. The method of solving Boltzmann's equation for this comparison is functionally equivalent to that used by Rockwood. Two important results should be compared. One is electron energy
distribution functions and the other is rate coefficients. We present both results for swarms in N₂ and Ar under conditions where electron-electron collisions are important.

2.2.5.1 Electron energy distribution functions

First of all, EED comparisons obtained for Ar and N₂ are shown in Fig. 2.2. The applied field is \( E/N = 20 \, \text{Td} \) (1 Td = \( 10^{-17} \, \text{Vm}^2 \)). The electron impact cross sections were obtained from Refs. 37 and 38 for Ar, and Refs. 38 and 39 for N₂. Elastic collisions with Ar⁺ and N₂⁺ and dissociative recombination collisions of electrons with N₂⁺ were also included, although no collisions with excited states of Ar or N₂ were accounted for. Two cases are treated: excluding electron-electron collisions and including electron-electron collisions with a fractional ionization \( \delta = 5 \times 10^{-4} \). The EEDs obtained under the same conditions from the continuum solution of Boltzmann's equation are shown in Fig. 2.2 by dashed lines and from the Monte Carlo simulation in Fig. 2.2 by solid lines. One can see that the EEDs obtained from the two methods are essentially the same. The close agreement between MC simulation and Boltzmann's equation implies that the new MC method is reliable. Figure 2.2(a) is for Ar, and Fig. 2.2(b) for N₂. Looking first at the results for Ar, the EED with \( \delta = 0 \) in Fig. 2.2(a) shows the typical cutoffs in the EED at \( e \approx 11 \, \text{eV} \) resulting from the energy loss due to electronic excitation of Ar. The EEDs in N₂ show the cutoff at \( e = 2 \, \text{eV} \) resulting from vibrational excitation. For both gases, the EEDs with \( \delta = 5 \times 10^{-4} \) appear more Maxwellian due to the dominance of thermalizing collisions between electrons. In addition, the EEDs are depressed at intermediate energies and enhanced at lower and higher energies compared to the case without electron-electron collisions.

2.2.5.2 Comparison of electron impact rate coefficients

Electron impact rate coefficients for processes which have high energy thresholds are quite sensitive to fractional ionization. This results from the energy exchange during e-e collisions which repopulate the "tail" of the distribution which was depleted by inelastic
collisions. For example, rate coefficients for electron impact excitation and ionization, as computed with the MC simulation as a function of fractional ionization, are shown in Fig. 2.3, where they are also compared to rate coefficients obtained from the direct solution of Boltzmann’s equation.35

Processes having intermediate threshold energies such as excitation are not significantly affected by the raising of the tail of EED, though the MC simulation shows a somewhat stronger effect. Higher threshold processes such as ionization are more acutely affected, with their rate coefficients increasing with $\delta$. The dependence of the rate coefficients on $\delta$ depends, of course, on the details of their cross sections. This dependence is shown in Fig. 2.4, where cross sections and rate coefficients for electron collisions with N$_2$ are shown as a function of $\delta$. Rate coefficients for the excitation of N$_2$ ($\nu = 1$) and N$_2$ ($\nu = 8$) decrease and increase, respectively, with increasing $\delta$. The rate coefficient for electron impact excitation of N$_2$(A$^3\Sigma$) may, in fact, have a maximum as a function of $\delta$ due to the resonance nature of its cross section which is maximum at $\varepsilon = 11$ eV. As the frequency of electron energy exchange collisions increases, the density of low- and high-energy electrons increases at the expense of intermediate energies at which the cross section is maximum. The coefficient, therefore, first experiences a shallow maximum as the tail of the distribution is lifted, and then decreases as more electrons appear at low energy when the EED thermalizes.

2.2.6 Rate coefficients

Rate coefficients are used to describe the collision processes in rate equations. The derivation of these quantities follows. The collisional processes are usually described by individual cross section $\sigma_{ij}(\nu)$ (for any specific processes $i \rightarrow j$) defined by setting the number of such collisional events per unit path length of an electron of velocity $\nu$ in a
density \( n_i \) of "candidate" atoms equal to \( \sigma_{ij} n_i \). Conversely, the rate at which any atom undergoes these collisions with electrons in the velocity interval \( d^3v \) is

\[
\sigma_{ij} \left| \frac{d}{dv} f(v) \right| d^3v.
\]

(2.12)

The total rate at which the atom undergoes these collisions with all types of electrons is

\[
\int \sigma_{ij} v f(v) d^3v = n_e \langle \sigma_{ij} v \rangle.
\]

(2.13)

where

\[
\langle \sigma_{ij} v \rangle \equiv \int \sigma_{ij} v f d^3v / \int f d^3v
\]

(2.14)

is called the rate coefficient for this process. A rate coefficient exists no matter what the form of \( f(v) \), but it does depend on \( f(v) \). Figure 2.5 presents \( f(v) \) vs. \( E/N \) for \( N_2 \) and \( \delta = 5 \times 10^{-4} \). Higher \( E/N \) enhances the "tail" of the EED. Hence, one can expect that higher threshold events will respond to a greater degree.

Due to the thermalization of \( f(v) \) resulting from electron-electron collisions, rate coefficients for "threshold" processes generally increase. Figure 2.6 presents rate coefficients for excitation of \( N_2(v =1) \) and impact excitation of \( N_2(A^3\Sigma) \) as a function of \( E/N \) at \( \delta = 0 \) and \( \delta = 5 \times 10^{-4} \). Higher threshold processes such as impact excitation of \( N_2(A^3\Sigma) \) are more sensitive to increasing \( E/N \). The differences in rate coefficients for \( N_2(v =1) \) and \( N_2(A^3\Sigma) \) with \( E/N \) shown in Fig. 2.6 are about 6 times and 2 order of magnitude, respectively. Therefore higher \( E/N \) will strongly affect higher threshold processes, whatever the fractional ionization is.
Figure 2.1. Schematic of the hierarchy of collision probabilities and the division between real and null collision frequencies used in the simulation.
Figure 2.2. EEDs for (a) Ar and (b) N$_2$ computed with the MC simulation, with and without electron-electron collisions. The fractional ionizations are 0 and $5 \times 10^{-4}$. The comparison is made to EEDs obtained by solving Boltzmann’s equation.
Figure 2.3. Electron impact rate coefficients for Ar as a function of fractional ionization computed with the MC simulation and Boltzmann's equation for $E/N=20$ Td and pressure=3.1 Torr.
Figure 2.4 The electron impact cross sections (a) and rate coefficients of $N_2(v=1)$, $N_2(A^3\Sigma)$ and ionization states (b), rate coefficients as a function of fractional ionization computed with Monte Carlo simulation for $E/N=20$ Td and 3.1 Torr.
Figure 2.5. The influence of E/N on the electron energy distribution function for a nitrogen plasma at 3.1 Torr, computed with Monte Carlo simulation.
Figure 2.6. The excitation coefficients of \( \text{N}_2(V=1) \) and impact excitation of \( \text{N}_2(A^3\Sigma) \) electron impact rate coefficients at 3.1 Torr as a function of \( E/N \) with and without electron-electron collisions, computed with Monte Carlo simulation.
CHAPTER 3

TIME AND SPATIALLY DEPENDENT MC SIMULATION

The difficulty of self-consistently resolving the spatially and time-dependent electron energy distribution in low-temperature partially ionized plasmas in concert with the electric field is well-known. Under these conditions, Boltzmann's equation becomes seven-dimensional, (3 in position space, 3 in velocity space and 1 in time); therefore, the solution is difficult. The advantage of MC simulation is that it allows us to solve these kinds of systems, which have complex geometries or spatially dependent and time variant electric fields. However, since the results from MC simulation are statistical, they depend on the simulation time and number of particles used. Therefore, choosing a suitable simulation time and number of particles becomes important. The longer the simulation time or the larger the number of particles chosen, the more accurate are the results, but more computer time is required. In fact, the important simulation parameter is the product of the number of particles and the total simulation recording steps. Hence, one must optimize the simulation parameters to achieve the best results.

The typical number of particles used in a simulation is one thousand. The time required for EED to reach equilibrium in Ar is shown in Fig. 3.1 for a step function in E/N. In this situation, the time step used in recording statistics is 1 nanosecond (ns). The time interval between each curve is 100 ns. The result indicates that after 0.5 or 0.6 μs the EED approaches the equilibrium state. For this combination of parameters, excluding the
physical equilibration time, the "response time" is approximately 100 ns. The product of particle times recording step, mentioned before, is on the order of \(10^5\).

3.1 Relaxation to Steady State

In low-pressure plasmas, the losses are dominated by diffusion. Therefore, when including diffusion, the self-sustaining \(E/N\) is obtained by balancing ionization with diffusion losses. The relaxation to the steady state using the Monte Carlo simulation for Ar at 1 Torr is investigated, as shown in Fig. 3.2. The initial \(E/N\) started at 62 Td. The straight line represents a steady-state \(E/N\) for this case, which is 47 Td. The time response of this example is determined by diffusion and is not numerically limited. The time to reach steady state is approximately 1 \(\mu\)s.

The temporal response of the EED to changes in the electric field is investigated for both cases -- with and without electron-electron collisions, as shown in Fig. 3.3, where the EED is plotted for an argon plasma at 1 Torr. The applied electric field was decreased from 50 to 10 Td in 1 \(\mu\)s. The response of the EED to changes in \(E/N\) is faster with electron-electron collisions due to the higher rate of energy exchange between electrons, which rapidly "communicates" the loss of energy due to inelastic collisions from one portion of the EED to another. At high \(E/N\), other collision processes will dominate the EED, and the influence of electron-electron collisions is less since the electron-electron cross section scales as \(1/e^2\). The fractional rate of energy exchange for electrons below the inelastic threshold is limited to \(2m_e/M\) per collision in the absence of electron-electron collisions. This rate is \(2m_e/\left(M\delta\right)\) or 0.03 of the rate in the presence of electron-electron collisions.
3.2 Spatial Dependence

By using the modified null-cross-sectional technique, the extension of this method to multiple spatial dimensions is straightforward. This is accomplished by collecting statistics as a function of position during the simulation to obtain an intermediate value of \( f(\varepsilon, x) \). Those values are then used to scale the probability for electron-electron collisions between real and null processes as a function of position. That is, we obtain the ratio \( \frac{v_{ij}(x)}{v_{ij}^m} \), where \( v_{ij}^m \) is the maximum working null-collision frequency allocated for collisions of incident electron \( i \) with electron fluid \( j \). This treatment effectively handles the electron fluid velocity elements at different spatial mesh points as separate species with which the incident electrons can collide.

Again, only a single probability array is required which has adequate working null space to accommodate differences in the rate of electron-electron collisions as a function of position. A changing electron density can also be accounted for in this manner by including enough working space to cover any increase in the rate of electron-electron collisions resulting from the increase in electron density. One pays the penalty, though, that the number of null collisions will increase when the electron density is small, thereby increasing the total computer time.

The schematic illustration of the idea of spatial dependence is demonstrated in Fig. 3.4. Each individual spatial cell is scaled by local density yielding a local null-collision frequency. In this research, only longitudinal statistic information is collected. Hence, the EED has only one degree of freedom in position space. In the transverse direction, the EED is considered uniform. Actually, by using the same argument, one can easily extend the EED into the other two axes if it is necessary.
Again, in low-pressure electric discharges, losses are dominated by diffusion. The electron density is maximum on the axis and lowest near the walls. Electron impact rate coefficients for high-threshold processes should then be higher on the axis of the discharge, where $\delta$ is the highest, than near the walls. To demonstrate this effect, we simulated an electric discharge in argon sustained between two flat plates. The EED as a function of position for a discharge in argon is presented in Fig. 3.5(a). The gas pressure is 3.1 Torr ($N = 10^{17}$ cm$^{-3}$) and $E/N = 20$ Td. The electron density and electron-impact-rate coefficients for these conditions as a function of position are shown in Fig. 3.5(b). The change in electron density (from wall to center line) results in a change in $f(\varepsilon)$ and electron-impact-rate coefficients. The larger electron density on the axis is sufficient to thermalize the EED by electron-electron collisions. The result is a significant increase in the electron-impact-rate coefficient for ionization near the axis compared to that for the wall. Lower threshold processes (i.e., electronic excitation) and elastic collisions have rate coefficients which are more uniform as a function of position. There is also a diffusion cooling effect, though it is not dominant.
Figure 3.1: Demonstration of the electron energy distribution approaching equilibrium for Ar at fractional ionization of $5 \times 10^{-4}$.
Figure 3.2. E/N as a function of time computed with Monte Carlo simulation including diffusion losses and ionization process for Ar at 1 Torr.
Figure 3.3. The electron energy distributions (EEDs) as a function of time for electron swarms in argon with (top) and without (bottom) electron-electron (e-e) collisions. The fractional ionization is $[e]/N = 5 \times 10^{-4}$. The electric field was ramped from $E/N=50$ Td to 10 Td in 1 μs. The response of the EED to changes in electric field is faster when including e-e collisions due to the rapid rate of energy exchange.
Figure 3.4. The schematic plot of spatial dependence. Each cell has its own collision frequency.
Figure 3.5. Results from the Monte Carlo simulation for a low-temperature partially ionized plasma sustained between two flat plates. The simulation is for argon at 3.1 Torr and 20 Td. (a) Electron energy distributions between the center and the wall. (b) Electron density [e] and electron-impact-rate coefficients as a function of position.
CHAPTER 4

HYBRID MC CONTINUUM MODEL

Monte Carlo simulations have been discussed in the previous chapter, in which we focus only on developing a new and tractable simulation method which includes electron-electron collisions and is suitable for low-temperature partially ionized plasmas. To model high source systems such as ECR reactors, (which will be described in more detail in the following chapter), we use a hybrid model combining a MC simulation, which generates details of the EED, with a simple fluid model generating the plasma potential by solving continuity equations.

In this model, the MC simulation is iteratively combined with a fluid model for charge densities in the ECR reactor to provide the electrostatic plasma potential profile for use in the MC simulation. To obtain the EED in ECR reactors, the effects of ambipolar fields must be taken into account in the continuity equations due, at least near the ECR zone, to high gradients in charge densities and temperature. In ECR reactors, electrons are resonantly heated in a thin region by the applied microwave field. These hot electrons enhance the ionization processes and diffuse along the magnetic field into the downstream region of lower density. The longitudinal electron diffusion coefficient, however, is usually considerably greater than the ion diffusion coefficient:

\[
\frac{kT_e}{m_e n} \gg \frac{kT_+}{M n} \quad (4.1)
\]
where $k$ is Boltzmann's constant, $T_e$ and $T_i$ are the electron and ion temperatures respectively, $M$ is the ion mass, $m$ is the electron mass, $\nu_{eN}$ is the electron-neutral collision frequency and $\nu_{iN}$ is the ion-neutral collision frequency. The electrons diffusing more rapidly than the ions generates a space charge separation. As soon as this separation forms, a space-charge field is generated, which tends to retard the electrons and accelerate the ions so that space-charge neutrality is maintained. This space-charge field is called an ambipolar electric field. Sometimes this retarding and accelerating effect is called ambipolar limitation. In low-density plasmas where the Coulomb force is weak, this effect can be neglected. In high-density plasmas, this effect must be considered. Under these conditions, the electrons and ions will diffuse at the same rate as determined by the ambipolar diffusion coefficient. The ambipolar diffusion coefficient is found as\textsuperscript{40}

$$D_a = \frac{\mu^+D^+ + \mu^+D^-}{\mu^- + \mu^+} \quad (4.2)$$

where $\mu^+$ is ion mobility and $\mu^-$ is electron mobility. In our work, the longitudinal electron mobility is easy to calculate using the formula $\mu = \frac{e}{mv_e}$, where $v_e$ is collision frequency, based on results of the MC simulation. The ion mobility can be obtained from published data\textsuperscript{41} by using an interpolation technique.

A computer flowchart for the hybrid MC-fluid model is schematically shown in Fig. 4.1. At initial setup, the ambipolar electric field is considered uniform in the system and the particles are randomly generated. The program goes to the MC code first. After one iteration of MC simulation, the program advances to the fluid code. At this time, electron-impact-rate coefficients obtained from the MC simulations are used in the continuity equation for electrons and ions. The MC simulation and the fluid code alternate, each
running for a predetermined time interval. To obtain the space-charge field, \( E_s \), we construct a simple fluid model for the ion and electron densities in which the continuity equations are solved under the assumption of ambipolar diffusion. This model is admittedly an approximation because a fluid description for charge densities is poor at the low pressures of interest. This model, though, is in surprisingly good agreement with experimentation, as discussed in the next chapter. In the fluid model, we solve the continuity equations for electrons and ions along the axial dimensions of the ECR reactor in the steady state,

\[
\frac{\partial n_e}{\partial t} = n_e N K_i + \nabla \cdot \left( D_a^{L} \nabla n_e - n_e \mu_a E \right) - \frac{D_a^{T} n_e}{\Lambda^2} = 0 \tag{4.3}
\]

\[
\frac{\partial N^+}{\partial t} = n_e N K_i + \nabla \cdot \left( D_a^{L} \nabla N^+ - N^+ \mu_a E \right) - \frac{D_a^{T} N^+}{\Lambda^2} = 0 \tag{4.4}
\]

where \( n_e, N \) and \( N^+ \) are electron, gas and ion densities, respectively, \( K_i \) is the ionization coefficient, \( D_a^{L} \) is the ambipolar longitudinal diffusion coefficient, \( \mu_a \) is the ambipolar mobility, \( E \) is the space-charge field, which will be discussed later, \( D_a^{T} \) is the ambipolar transverse diffusion coefficient, and \( \Lambda \) is the diffusion length in the radial direction. For the cylindrical geometry the diffusion length may be written as

\[
\Lambda = \frac{\text{radius}}{2.045} . \tag{4.5}
\]

The ionization rate coefficients and electron transport coefficients are obtained from the MC simulation as values which are functions of axial position averaged over the radius.

A matrix of coefficients using a finite-difference approximation\(^15\) for Eqs.(4.3) and (4.4) is obtained, and the equations solved by matrix inversion. Since the coefficients are
based on the previous densities, the fluid model must be iterated. After we obtain the new densities, the corresponding ambipolar field is straightforward,

\[ E_a = \left( \frac{D^- - D^+}{\mu^- + \mu^+} \right) \cdot \left( \frac{V_L n_e}{n_e} \right) \quad (4.6) \]

where the subscripts L and e are for the longitudinal value and electrons, respectively, and superscripts "-" and "+" represent electron and ion parameters. These values are placed back in the matrix for another iteration.

After completion of the fluid model, only the final results \( n_e, N^+ \) and the longitudinal space charge field are cycled back to the MC simulation and included in the equations of motion of electrons. Therefore, the charge densities and electric field in the MC simulation can be updated frequently. At this point, the electric field in the longitudinal direction of the system is no longer uniform. Theoretically, this allows the simulation to easily reach a steady state closer to a real system. To obtain more accurate results, several iterations between the MC and fluid code are required. In general, when the system reaches a steady state, the iteration can be stopped. Typically, the iteration between the MC simulation and fluid model is repeated 3 or 4 times, which is sufficient to obtain convergence.
Figure 4.1. Computer flowchart of the hybrid Monte Carlo-continuum model.
CHAPTER 5

APPLICATIONS OF MC SIMULATION TO ECR REACTORS

An important development in low-temperature plasma processing is the microwave electron cyclotron resonance (ECR) discharge. The ECR condition enables plasmas to effectively absorb microwave energy.\textsuperscript{22-24,42-43} Thus, the ionization process is fast, and the fractional ionization $\delta$ can be as high as $10^{-3}$ to $10^{-2}$, which is clearly in the region where electron-electron collisions are important and required for the use of the method discussed in previous chapter. The big advantage of ECR reactors over conventional microwave plasma reactors is that to achieve the same electron energy, the system size required by the ECR reactor is much smaller. The reason is clear. Since electrons in the ECR reactor are magnetized, the gyration motion of electrons makes the physical distance of their motion in the electric field much larger than that in the conventional reactor if the size of both systems is the same. Therefore, the electrons in ECR reactors absorb much more energy from the system than those with dc electric fields. Obviously, it is easier to achieve higher electron energy in the ECR reactor. On the other hand, due to the heavy mass of ions, the ions in the ECR reactor are not magnetized, thus the energy of ions is not high. The highest energy of ions obtainable in ECR reactors is the plasma potential, which is, typically, 10 to 20 V at pressures of interest. Generally, the ion energy in reactive ion etching reactors is around 100 eV, which is much higher than ECR reactors. Therefore, at this point ECR reactors can reduce the wafer surface damage which is caused by ion bombardment. Also, the lack of electrodes in an ECR reactor allows clean conditions, and
its ability to create high densities of charged and excited species at low pressures (less than 10 mTorr) makes it an attractive processing discharge in etching and thin film deposition. In this chapter, the ECR reactors and models used in this research are discussed.

5.1 ECR Reactors

Electron cyclotron resonance reactors, as material processing tools, are commonly thought of as being remote devices. That means, the plasma is sustained upstream and remote from the wafer. In this view, excitation and ionization occur in the upstream resonance zone with products flowing to the wafer downstream as shown in Fig. 1.2, modified from a figure in Ref. 27. The remote location of the substrate, though, does not preclude its being bombarded by energetic particles. As the name ECR suggests, microwave energy is coupled to the natural resonant frequency of the electron gas in the presence of a static magnetic field. This resonant frequency occurs when the electron cyclotron frequency equals the applied microwave frequency. The electron cyclotron frequency \( \omega_c \) is found from

\[
\omega_c = \frac{eB}{m_e}
\]  

(5.1)

where \( m_e \) is electron mass, \( e \) is charge on an electron, and \( B \) is the strength of the static magnetic field. In an actual discharge, this condition can be satisfied in a volume or surface layer within the discharge where the static magnetic field strength is adjusted to resonance, i.e., the microwave frequency \( \omega_\mu \) is equal to this frequency \( \omega_c \), and a component of the electric field is perpendicular to the magnetic field. When this condition is satisfied, resonance occurs. The result is that the electrons in the ECR layer are accelerated continuously, gyrating around the magnetic field line and, in turn, ionizing and exciting the
neutral gas. Therefore, a low-pressure, almost collisionless, plasma can be varied from a weakly to a highly ionized state by changing the discharge pressure, gas flow rate or input microwave power. In these reactors, plasmas sustained by microwaves can also be electrodeless, thereby eliminating process contamination from electrodes and greatly extending the operating lifetime of the reactors in reactive gases. The electrodeless and noncollisional heating nature of the discharge together with the availability of well-established, low-cost microwave power supplies make ECR plasma sources attractive for many plasma processing applications such as deposition and etching, especially in semiconductor fabrication processing.

A diagram of a typical ECR configuration is shown in Fig. 1.2. The microwave power at frequency 2.45 GHz is applied to the reactor through a quartz window, and the magnetic field is generated by annular current coils. The substrate is put downstream far from the ECR zone. The injected microwave power will be absorbed by the plasma during its propagation. Conventional ECR theory states that power deposition in high pressure microwave gas discharges should be scaled as, (based on Ref. 44),

\[
P = \frac{n_e e^2 E^2}{2 m_e v_m} \frac{1}{1 + \left[ \frac{\omega - \omega_c}{v_m} \right]^2} \tag{5.2}
\]

where \( v_m \) is the energy dissipation collision frequency, \( \omega \) is the frequency of the applied electric field having amplitude \( E \), and \( \omega_c \) is the electron cyclotron frequency for magnetic field \( B \), (Eq. (5.1)). As \( v_m \) increases, the width of the resonance increases, while the peak value decreases. This formulation is predicated on \( v_m \) being the frequency at which power is dissipated. Excitation and ionization in gas discharges actually occur in two steps. The input power is transferred to electrons through the electric field by resonance and heats these
electrons. This process is almost limited to the ECR layer. Then, the hot electrons collide with gas atoms and transfer power to the gas. In higher-pressure discharges, the power transfers from electric field to electrons and electrons to gas occur in the same spatial location, and Eq. (5.2) is valid. In low-pressure ECR reactors where the width of the ECR zone is thin compared to the mean-free path of electrons, the locations of the power transfer by electric field to electrons and electrons to gas processes may be quite disparate. For example, the collision frequency for inelastic energy loss for a 50 eV electron in argon at 1 mTorr is $7 \times 10^6$ s$^{-1}$. Assuming that the parallel temperature is as low as 1 eV, the axial distance traveled between collisions is 10 cm. The distance is long compared to the width of the ECR zone (a few millimeters). Therefore, the power absorption is not localized. In this implementation, the power deposition from the microwave field to the electrons is determined by

$$P_{f \rightarrow e} = q \int V \cdot E(v) n_e(v) \, dv, \quad (5.3)$$

where $q$ is the electric charge, $V$ is the electron velocity, $E$ is the local field, $n_e$ is the local electron density and $dv$ is the finite volume. The integral is evaluated in the whole space and for all electrons. The maximum power can be absorbed by an electron when its movement is in the same (anti) direction as the field. Higher electron densities can have larger power absorption. Thus, the power deposition is very sensitive to the electron density. The second power deposition from the electron to the gas is calculated in the following way:

$$P_{e \rightarrow g} = \sum_i q \int N_i n_e K_i e_i \, dv, \quad (5.4)$$

where the sum is over collision processes, $N$ is the gas density, $K_i$ is the rate coefficient, and $e_i$ is the energy loss during the collision. The other symbols have the same meaning as
above, and the integral is evaluated in the space and for all electrons. Obviously, the larger the energy loss during the collision, the more power deposition it contributes to the gas. Low gas density gives lower collision frequency and results in smaller power deposition from electrons to gas.

The experimental data show that the injected microwave electric field decreases rapidly with its propagation distance under ECR conditions due to large power absorption. The resonance zone in which the microwave field is absorbed is usually thin, less than 1 cm typically. Thus, the microwave field is no longer a constant along with the propagation direction. The microwave electric field in this model is based on the power absorption from field to electrons. For example, the change in the amplitude of the microwave field in traversing a particular computational cell is

\[ \Delta E_{\mu\text{wave}}^2(z) = \mu_0 c A \, P_{\mu-e}(z), \]  

(5.5)

where \( P_{\mu-e} \) is the net microwave power exchanged with the electrons (either positive or negative), \( A \) is the cross section of that cell, \( c \) is the speed of light, \( \mu_0 \) is the permittivity in a vacuum. Although the ECR zone is very thin, one can still obtain high-energy particles at the reaction area far away from the ECR zone. The reason may be the following. The thermal conductivity of these plasmas is high; therefore, power deposited in the ECR zone can heat downstream electrons due to the large momentum transfer and energy exchange in electron-electron collisions along magnetic field lines, as well as simple advection of hot electrons.
The magnetic field is not constant in real systems. It depends on several parameters such as the number and location of coils and relative current in the coil. We use the Biot-Savart law to calculate the magnetic field. The integral form of the Biot-Savart law is

\[
\mathbf{B} = \sum \frac{\mu_0}{4\pi} \int \frac{I \, d\mathbf{l} \times \mathbf{r}}{r^3}
\]

(5.6)

where \(\mu\) is permeability, \(d\mathbf{l}\) is an element of the length (pointing in the direction of current flow) of a filamentary wire, \(I\) is the current carried by the wire, and \(\mathbf{r}\) is the coordinate vector from the element of length to an observation point. The line integral is taken along the wire. In this situation, the magnetic field is generated by the coils; therefore the line integral is taken around the loop of the coil. The sum is over individual current loops in each coil. Actually, we consider a two-dimensional field: one is in the longitudinal direction, represented by \(B_z(z,r)\), and the other is in the transverse direction, represented by \(B_r(z,r)\), while assuming azimuthal symmetry.

5.2 The Model System

The geometry used in this investigation is a cylindrical ECR reactor, as shown in Fig. 5.1. The length of the reactor is 30 cm and the diameter is 14 cm. It is terminated by a dielectric window on one side and a floating substrate on the other side. The ECR point is chosen to occur at approximately 5 cm. The gas temperature used here is 300 K. Unless otherwise noted, the microwave frequency used for the model is 2.45 GHz, which has a corresponding magnetic field of 875 G.

The magnetic field is supplied by annular current coils. The number and location of these coils can be specified by the user of the model. In this investigation, we simulate two magnetic field cases. One is called collimated geometry, which has two magnetic coils
around the upstream plasma chamber and one coil downstream near the substrate, as shown in Fig. 5.1(a). Another is called flared geometry, which has no downstream coil, as shown in Fig. 5.1(b). The simulations of the magnetic field are plotted in Fig. 5.2(a) for the collimated geometry, and Fig. 5.2(b) for the flared one. The magnetic field decreased rapidly downstream in the flared geometry. The desired location of the ECR point is selected so that the axial value of the magnetic field, which is $B_z(0,z)$, provides a resonance at that location. From the slot, we see that the magnetic field contour, in fact, is nonplanar. Therefore, with an axial electric field having the "beach" configuration, the resulting resonance surface resembles a shallow dome. Unless noted, all results discussed in the next chapter are collimated geometry.

The circularly polarized electric field is incident from the left side of the cylinder propagating along the axis with the electric field oriented perpendicular to the axis of the cylinder. The microwave electric field as a function of position is handled fairly simply with no attempt to predict any model structure in contrast to Refs. 46 and 47. We assume that the electric field is a polarized plane wave with uniform amplitude in the transverse direction in the reactor. The wave propagates collinearly with the axis of the reactor so that the instantaneous electric field amplitude at any location is

$$E(z,t) = E(z) \sin (\omega t - k z)$$  (5.7)

where $\omega$ is the microwave frequency, $k$ is the wave vector and the rest have their usual meaning. We specify the amplitude of the incident electric field $E_0$ at the window; typically, the $E_0$ we choose is 19.3 V/cm which gives an input microwave power of 150 W. We assume that the subsequent amplitude of the electric field is totally determined by the power absorption. The amplitude of the electric field can be calculated from Eq. (5.5).
The MC simulation used in this research is discussed in the previous chapter and in Ref. 48. The electron trajectories are explicitly integrated as a function of time in the MC simulation throughout the reactor using the local values of the electric and magnetic fields. Considering that the Larmor radius of an electron is 100 μm at resonance and that the cyclotron frequency is $2.45 \times 10^9$ s$^{-1}$, this approach is a considerable computational burden. We typically take time steps of $5 \times 10^{-12}$ s and use a third-order Runge-Kutta integration. This order of integration is sufficient to keep the error in energy to less than 1% over $10^5$ periods. There is an algorithm called guiding center which can be used at resonance, treating the microwave electric field as a dc field, thereby allowing the integrating time step to be as large as the time between collisions. For now, we do not use this algorithm for the following reasons. In the time between collisions ($= 0.1 - 0.2$ μs), an electron with even a moderately parallel component of velocity can move many millimeters. An electron can therefore move into or out of the resonance region in an intercollision period. In addition, both the magnetic and electric fields are functions of position and have multiple vector components. We did not find the above method suitable for dealing with these problems. Therefore, we chose to integrate the equations of motion of the pseudoparticles.

In electron-electron collisions, the net change in momentum and energy is zero, since the exchange is with another electron. One might expect that when fractional ionization is increased, the width of the resonance (in terms of magnetic field) will increase by virtue of the increase in the total collision frequency. The electron temperature, however, should not decrease proportionally, since the collision is not truly dissipative. To investigate this possibility, we simulated an ECR excited plasma with and without electron-electron collisions. The gas pressure was 50 mTorr of Ar and the microwave frequency at resonance was 1 GHz. The electron temperature is plotted in Fig. 5.3 as a function of the detuning of the magnetic field from the resonance. The electron temperature is slightly
ΔB = 0 when including electron-electron collisions. The resonance clearly has a greater width and sustains a higher temperature due to large detuning.

If the amplitude of that component decreases, the power transfer will be reduced. As a result, the electron temperature is decreased. This effect is presented in Fig. 5.4. Electron temperature is plotted as a function of the angle between the electric and magnetic fields. An angle of zero means that the two fields are perpendicular to each other, which is the ideal case. The gas chosen for this simulation was argon, the pressure was 10 mTorr, and the microwave frequency at resonance was 1 GHz. The amplitudes of the electric and magnetic fields were 0.32 V/cm and 357.8 G, respectively. The result shows that in the ECR reactors, keeping the magnetic field convergent is one way of obtaining higher electron energy.
Figure 5.1. The ECR systems used in the simulations. (a) There is an additional coil downstream in the reactor, which makes the magnetic field converge downstream. This geometry is called collimated. (b) Flared geometry and its magnetic field diverges downstream are shown.
Figure 5.2. The profile of axial magnetic field distribution used in the simulations as a function of position. (a) Columnar geometry.
Figure 5.2. (cont.) (b) Flared geometry.
Figure 5.3. Electron temperature as a function of the detuning of the magnetic field in ECR plasma. The case including electron-electron collisions has a wider resonance.
Figure 5.4. Electron temperature as a function of the angle between the electric and magnetic fields. Zero means the two fields are perpendicular.
CHAPTER 6

RESULTS FOR EEDs IN ECR REACTORS

6.1 Electron Energy Distribution Functions in ECR Reactors

Measurements of EED and the electron temperature $T_e$ in ECR discharges have been reported by a number of researchers.\textsuperscript{22-24,28,51-53} The use of the term electron temperature does not imply that the EED is Maxwellian (i.e., proportional to $\exp(-v^2)$). Our definition of $T_e$ will be given in Section 6.3. Common gases that researchers are working on are Ar, N$_2$, H$_2$/CH$_4$ mixtures and CF$_4$ or CF$_4$/O$_2$ mixtures. The simulations we did are for Ar and N$_2$ only.

6.1.1 Argon plasma

The dependence of electron energy distribution functions averaged over the ECR reactors on gas pressures (0.2, 1, and 3 mTorr) is shown in Fig. 6.1. The EEDs are not well-described by a Maxwellian distribution at all of the pressures presented here. More than one electron temperature is present in the distributions. The interesting point is that the pressure influence for the lower energy portion ($\varepsilon < 20$ eV) of the distribution is not obvious, but for the higher energy portion of the distribution, it is clear. Whatever the pressure is, the high-energy tail of EEDs in the ECR reactor is raised and extended beyond 150 eV. This effect is due to the gyration of electrons in the reactor, which makes electrons absorb more energy from the field as described in Chapter 5. The level of enhancement of
the EED tail depends on the pressure. The low pressure corresponds to a low collision frequency; therefore, the energy at which the distribution becomes depleted increases.

Although we know that there is a high-energy tail in ECR reactors from Fig. 6.1, the results do not provide information about which electrons made this high-energy tail possible. This information can be obtained from the plot of the EED as a function of position as shown in Fig. 6.2. Figure 6.2(a) is obtained under the conditions of 0.2 mTorr and power of 150 W for argon plasma; Figure 6.2(b) is obtained under the same conditions as 6.2(a) except for the pressure, which is 3 mTorr. The scales used in (a) and (b) are the same for the purpose of comparison. The EEDs are not uniform in the reactor for both cases. The high-energy tail effect comes primarily from the electrons at or near the ECR zone which is chosen to be 5 cm from the upstream dielectric window. In the ECR zone, low-energy electron groups decrease, though not dramatically, and the high electron group increases. The enhancement of the high-energy electron group is significant. This enhancement in the ECR region is more pronounced at a low pressure (\( \leq 1 \text{ mTorr} \)), as in Fig. 6.2(a), and gradually diminishes with pressure, finally almost disappearing at 3 mTorr (Fig. 6.2(b)) for the scale used in the figure. Although the high-energy tail has not been observed at 3 mTorr from Fig. 6.2(b), the energy at which the distribution becomes depleted is still different between the ECR zone and downstream. The fact that the ECR zone has more high-energy electrons than downstream is confirmed in our simulation.

Hopwood et al.\textsuperscript{51} measured EEDs and plasma densities in a microwave tunable multipolar ECR reactor using Langmuir probes. They found that EEDs are not Maxwellian, but intermediate between a Maxwellian and a Druyvesteyn distribution near and downstream of the ECR zone. A high-energy tail to the EED was not detected in their measurements though the possibility of there being such a tail in the ECR zone is not discounted, and it is observed in our simulation results. The absence of the high-energy tail
downstream may be caused by the local nature of the ECR zone and a depletion of the tail downstream, or a trapping of the high-energy electrons in multipole magnetic cusps. The existence of a high-energy tail to the EED in the ECR zone is generally accepted though not always measured.

Lee et al.\textsuperscript{23} measured the EED in the ECR zone of an Ar plasma (1 mTorr). They also found that the EED was intermediate between a Maxwellian and a Druyvesteyn distribution similar to Ref. 51. They did not, however, detect a high-energy tail to the EED. The high-energy tail can be seen in our simulation results at the same pressure, as shown in Fig. 6.3. One of the curves in Fig. 6.3 is the EED in the ECR zone; another is the EED 15 cm downstream of the ECR zone. The EED 15 cm downstream of the ECR zone differs from that in the ECR zone in that the lower portion of the distribution has cooled to 2.5 - 3.5 eV, a consequence of inelastic collisions and drift against the axial ambipolar potential. The higher energy portion of the distribution can still be characterized by a temperature of 15 - 20 eV; however, its density is smaller by more than an order of magnitude. In the ECR zone, the energy at which the distribution is considered depleted (10\textsuperscript{-5}) exceeded 100 eV and was less than 60 eV downstream. Usually, the measurements are made downstream of the ECR zone and thus it is hard to measure a high-energy tail for the EED.

6.1.2 Nitrogen plasma

Amemiya et al.\textsuperscript{52} measured electron temperatures in N\textsubscript{2} and H\textsubscript{2} discharges in a cylindrical magnetic mirror. They noted a depletion of the high-energy tail of the distribution with respect to a Maxwellian distribution at the same temperature, and a depletion of low-energy electrons. The energy at which the distribution became depleted at high energy increased with decreasing gas pressure, and exceeded 100 eV at low pressures (\leq 1 mTorr). Plasma densities for an input power of 100 W were 10\textsuperscript{10} cm\textsuperscript{-3}. 

\textsuperscript{52} Amemiya, A. et al., J. Appl. Phys., 48 (1977), 3155.
We investigated N₂ at 0.1 mTorr and 2 mTorr with input powers of 150 W. The results are shown in Fig. 6.4. The profile of the EED presented in the figure approaches but does not reach a Maxwellian, especially for the lower pressure (< 1 mTorr). A high-energy tail can be observed from the plot. The influence of pressure on the EED is the same as for argon plasma. The lower pressure case has the higher energy tail.

Figure 6.5 represents the EEDs in the reactor at the ECR zone and downstream at 2 mTorr for N₂. The interesting point here is that the EED at the ECR zone is almost Maxwellian and downstream is not. This is the reason why the EED in Fig. 6.4 is Maxwellian-like. The simulation result obtained at the ECR zone is the same as in Ref. 52. The qualitative features of these EEDs are similar to those in argon. The low-energy component of the distribution has a higher value downstream and a lower value in the ECR zone. The high-energy component of the distribution is the opposite. The cross point of the two distributions is 4 eV. The anomalous low-energy component of the EED, typically found in argon plasmas, is not as pronounced in the N₂ plasmas.

6.2 Rates

The influence of pressure on rate coefficients is investigated for argon plasma, as shown in Fig. 6.6. As pressure increases, the gas density is increased. If the electric field is fixed, the effect is equivalent to decreasing E/N, which was described in Section 2.2.6; thus, one can expect that the rate coefficients will decrease with increased pressure. Since there is a very low "threshold" for momentum transfer, the rate coefficient of momentum transfer is almost independent of pressure. The higher "threshold" processes such as ionization and excitation are strongly dependent on pressure for P less than 20 mTorr.
The electron impact rate coefficients of argon at pressure of 0.2 mTorr, 1 mTorr and 5 mTorr are plotted as a function of position in Fig. 6.7. Figure 6.7(a) presents the variation of the electron impact excitation rate coefficients, and Fig 6.7(b) presents that of the electron impact ionization rate coefficients. Since the threshold energies for both processes are different, the curves are different but the profiles are similar. The lowest pressure has the highest electron impact rate coefficient, and the highest pressure has the lowest one. Figure 6.7(a) shows that the variation of the excitation rate coefficient in the ECR reactor is more pronounced at high pressure (≥ 5 mTorr). The coefficient at the ECR zone is almost the same as downstream for the low pressure. But there is a distinguishable difference between the ECR zone and downstream at high pressure. A peak forms upstream around the resonance zone at high pressure. The coefficient becomes flat at 0.2 mTorr. The low pressure enhances the impact excitation process downstream. This dependence of the impact excitation rate on pressure depends, of course, on the EED distribution in the reactor, which is shown in Fig. 6.2. The energy at which the EED is depleted is higher downstream at low pressure than at high pressure; therefore, the impact excitation rate is more uniform at low pressure than at high pressure.

The variation of the impact ionization rate coefficient is illustrated in Fig. 6.7(b) under the same conditions as in Fig. 6.7(a). The larger value of the impact rate for ionization compared to excitation is due to the respective cross-sections. Although ionization has a higher threshold energy than excitation, when energy is larger than 20 eV, the ionization cross section of argon is larger than that of excitation.38 As a result, in the ECR reactors, the electron impact ionization rate coefficient is larger than that for the excitation rate.

Ionization rates of argon plasma in the ECR zone and downstream, 15 cm away from source range, are plotted in Fig. 6.8 as a function of pressure. They decrease with
increasing pressure at both places. At pressures of less than a few milliTorr, the rate coefficients downstream remain commensurate with those in the ECR zone, decreasing by only a factor of 3, indicating that a substantial amount of ionization occurs adjacent to remotely mounted substrates. But the decrease of the downstream rate with increasing pressure is faster than that at the ECR zone. Thus, the downstream electron impact ionization rate is more sensitive to pressure. Since the wafer is put downstream, choosing suitable pressure in the reactor is still important.

The electron impact rate coefficients for N₂ at 2 mTorr with input powers of 150 W were investigated, as shown in Fig 6.9. Two impact rate coefficients are investigated, the ionization and first vibrational excitation of the ground state (ν = 1). The rate coefficient for ionization has a peak at the ECR zone and falls outside the ECR zone, which has a shape similar to that for argon. The rate coefficient for vibrational excitation has an opposite dependence due to its cross section in a limited low-energy region (ε ≤ 4 eV). The heating of the EED in the ECR zone results in a depletion of the lower energy portion of the EED. Therefore, it causes a depression in the impact rate coefficient for vibrational excitation and an increase in that for ionization. As the distribution cools outside the ECR zone, the impact rate coefficient for vibrational excitation rebounds, while that for ionization decreases.

6.3 Average Electron Energy

When we discuss electron energy, we use the term electron temperature \( T_e \) without implying that the EED is a Maxwellian. In the usual convention, the relation between these two parameters is defined as

\[
T_e = \frac{2}{3} <\varepsilon>,
\]  

(6.1)
where $\langle e \rangle$ is the average electron energy and the unit is electron volt. Figure 6.10 represents electron temperature as a function of position in the ECR reactor for argon plasma at 0.2 mTorr, 1 mTorr and 5 mTorr. The electron temperature increases with decreasing gas pressure from 2-3 eV downstream at a pressure of many milliTorr to 15-20 eV in the ECR zone at pressures less than 1 mTorr. The variations of electron temperature mainly occur several centimeters around the resonance zone; then they keep relatively constant after moving 5-10 cm downstream from the ECR zone. The time required for electrons to move this distance from the ECR zone is 1-2 μs. During that time, the electrons experience 5-10 collisions, of which 15-20% are inelastic (at 30 eV). The electron temperature has the highest value at the ECR zone and decreases immediately when out of the resonance zone. The decrease is a consequence of electrons with moderate energies above the inelastic thresholds (20-40 eV) having a few inelastic collisions which decreases their energy to below the inelastic thresholds. This decrease is faster at lower pressure along the axial location. Once this happens, the energy loss is dominated by elastic collisions, which proceed at a far slower rate.

The electron temperatures in a variety of gases were measured using electric probes as in Ref. 22. The measurements began approximately 15 cm downstream of the ECR zone. They observed that electron temperatures in argon were 2 - 6 eV for pressures of 6 mTorr to 0.2 mTorr. The results obtained from our simulation are 1.9 - 6.2 eV for pressures of 5 mTorr to 0.2 mTorr at the same distance as in Ref. 22. The results are in very good agreement with the experimental results. Similar measurements by Lee et al.23 show that the EED in the ECR zone of an argon plasma (1 mTorr) has as average electron energy of 7 eV. The average electron energy at 1 mTorr in the ECR zone from the simulation is 6.8 eV. This close agreement leads us to believe that the electron temperature distribution in the reactor is exactly like the profile presented in Fig. 6.10. In fact, Ref. 53
stated that the average electron energy was relatively constant over the distance of moving 10 cm downstream of the ECR zone at 5 - 7 eV.

Figure 6.11 represents the average electron temperature and the electron temperature at the ECR zone and downstream as functions of pressure. Temperatures increase rapidly when pressure is less than 1 mTorr. The influence of pressure on electron temperature is stronger at the ECR zone than downstream. The high pressure results in a large collision frequency. This frequency will directly affect the energy absorption by electrons from the applied field, which occurs mainly in the resonance zone. As a result, the decrease of electron temperature with increasing gas pressure is faster there than in any other place. The comparison with experimental data\(^2\) is shown in Fig. 6.12. The experimental data show that the average electron temperature was itself fairly constant between 2 and 13 mTorr, and increased rapidly as the pressure was reduced below 2 mTorr. The simulation result agrees with this. The average temperature is constant when pressure is larger than 2 mTorr.

The influence of input microwave power on electron temperature is shown in Fig. 6.13 for argon plasma at a pressure of 1 mTorr. The sensitivity of electron temperature to microwave power at the resonance zone and downstream of the plasma zone is almost the same. The electron temperatures increase moderately with increasing microwave power. They vary linearly with power. The variation of the electron temperature with power is the same as the experimental results in Amemiya et al.\(^5\) They found that both \(T_e\) and the plasma densities at the ECR point were nearly linear functions of incident power between 100 W and 250 W.

Electron temperatures in N\(_2\) were measured\(^2\) by Popov for the ECR reactor. Within the resonance region, or the region in which the absorption of power from the microwave field occurred, the electron temperature was 10 - 13 eV over a fairly large range
of pressure (0.3 mTorr to 5 mTorr). Differences in electron temperature were found only downstream of the resonance zone. In these cases, the electron temperature decreased to 3 eV at 5 mTorr 10 cm downstream of the ECR zone, but decreased to only 8 eV at a pressure of 0.3 mTorr when the input microwave power was 500 W. The electron temperatures we obtained from the simulation at the ECR zone were 11.3 eV and 5.5 eV at pressures 0.1 and 2 mTorr, respectively, with the input microwave power of 150 W. These results show that the electron temperature downstream of the resonance zone decreased to 5.7 eV and 1.8 eV at pressures of 0.1 and 2 mTorr, respectively. Amemiya et al.\textsuperscript{52} obtained temperatures of approximately 5 eV in N\textsubscript{2}, and 9 eV in H\textsubscript{2} at 1 mTorr with a microwave frequency of 4.4 GHz and an input power of 100 W. The result we obtained was 1.7 eV at the same pressure but with different microwave frequency and input power. They found that these values increase with decreasing pressure to = 12.5 eV and > 15 eV at 0.1 mTorr for N\textsubscript{2} and H\textsubscript{2}, respectively.

The wide range of experimental results for the properties of electron swarms in plasma processing ECR systems reflects the fact that the experimental apparatuses are themselves quite varied, and that the manner of power deposition depends critically on details of the magnetic field profile and electric field modes. One can, however, generalize to some extent. In the ECR systems of interest, the electron temperature in the ECR zone at moderate power deposition (Pr = 100 - 500 W) is in the range of 10 -15 eV for argon. The electron temperatures in the ECR zone and downstream of the plasma zone increase with decreasing gas pressure from 10 mTorr to a few mTorr, though not dramatically. The electron temperature at both locations increases with increasing power deposition and decreasing gas pressure (\(\leq 1\) mTorr).
6.4 Density

Electron density as a function of position in argon at 1 mTorr and input powers of 150 W is shown in Fig. 6.14. Since in the low-pressure limit the diffusion loss to the ends dominates the loss, the electron density profile is somewhat like a sine function with a maximum outside the ECR zone. Although the density at the resonance zone is almost the same as downstream 17 cm below the resonance zone (dash line), the quality of the electrons at those locations is quite different. The electrons at the ECR zone have a higher temperature than downstream, as shown in Fig. 6.10.

Hopwood et al.\textsuperscript{51} measured the plasma density. They found that at pressures of 0.1 - 10 mTorr in argon, plasma densities were 3 - 10 x 10\textsuperscript{11} cm\textsuperscript{-3} at powers of 250 W. The plasma density decreased by a factor of nearly 5 in moving 10 cm downstream of the ECR zone. At pressures of 0.2 - 8 mTorr, the plasma densities we found were 1.3 x 10\textsuperscript{10} to 4.8 x 10\textsuperscript{12} at powers of 150 W as shown in Fig. 6.15. We obtained a lower density at low pressure and a higher density at high pressure than those found in the Hopwood experiment. The difference may be from the ambipolar loss, the only loss mechanism assumed in the model.

6.5 Potential

Hopwood et al.\textsuperscript{51} reported that the plasma potentials varied from 18 V at high pressures (5 - 13 mTorr) to 28 V at low pressure (0.5 mTorr). The plasma potential decreases somewhat linearly below the ECR zone, netting a steady-state space-charge field of 1.3 V/cm. That range of plasma potential has been confirmed by the measurement of ion energy distributions.\textsuperscript{28} The plasma potential, in this research, is generated by the ambipolar diffusion; thus, it is named ambipolar potential. The ambipolar potential plotted in Fig. 6.16 is for argon at 1 mTorr in the ECR reactor. At the boundary, the potential goes to zero.
and becomes very flat in the reactor center. In our model, the ambipolar potential is determined by electron transport along the axis parallel to the magnetic field. The reduction in electron mobility transverse to the magnetic field (in the radial direction) implies that the ambipolar electric field in that direction should be small, and should make a correspondingly small contribution to the total ambipolar potential. These features have been seen in the results of the 2-dimensional simulations of Porteous and Graves for ECR discharges. The maximum in the ambipolar potential is displaced towards the ECR zone, an indication of the higher electron temperature in the ECR zone generating a larger ambipolar electric field.

A prediction for the ambipolar potential as a function of gas pressure appears in Fig. 6.17. The ambipolar potential increases with decreasing gas pressure moderately above 1 mTorr and more rapidly below 1 mTorr, in agreement with experiments. The potentials we observed were 10 V at high pressures from 3 to 8 mTorr. The plasma potential reported by Popov at intermediate pressure (0.6 mTorr) was approximately 25 V. At 0.5 mTorr, Hopwood et al. measured the plasma potential as 28 V; the ambipolar potential calculated here was 25 V which is close to their measurement. Our results predict a somewhat higher ambipolar potential at low pressure (< 0.5 mTorr) than was experimentally observed. This may result from our use of a fluid approximation which underpredicts the ion drift velocity for a given E/N, and therefore results in a larger ambipolar electric field.

The ambipolar potential as a function of microwave power was investigated at 1 mTorr for argon plasma, as shown in Fig. 6.18. Ambipolar potential is in the range of 12 - 24 V at the power of interest. This is the maximum energy ions can obtain from the ECR reactors. Obviously, this maximum energy is much smaller than the amount of energy ions obtain from conventional reactors. The ambipolar potential generally increases with
increasing microwave power, also in agreement with experiment, and commensurate with the increase in electron temperature as shown in Fig. 6.13. This increase with increasing microwave power for ambipolar potential is in a manner somewhat more sensitive than that for electron temperature.

6.6 Power Deposition

As mentioned before, the power deposition to the gas in ECR reactors is not localized at low pressure. The two-step assumption (field to electron and electron to gas) discussed in Chapter 5 must be used. The spatial distributions of these two processes in the reactor (argon plasma) were investigated, as shown in Fig. 6.19. Figure 6.19(a) represents the first step of power deposition, that is, power absorbed by electrons from the microwave field applied at pressures 0.2 and 5 mTorr. Figure 6.19(b) represents the next step, that is, power transferred to the gas from electrons by collisions at the same pressures as in Fig. 6.19(a).

The profile of absorption by electrons is δ-function-like. The dominant power transfer from the microwave field to electrons logically occurs at the discharge region. The highest value of absorption is at the resonance zone; it is zero downstream. The low pressure corresponds to large absorption and results in a high electron temperature. The width of the power deposition from field to electrons results dominantly from the dome-like structure of the ECR surface since the full width of the ECR zone corresponds to ΔB=1 G. The peak of the power transfer from electrons to the gas is broadened compared with the transfer from the electric field to electrons. The profiles shown in Fig. 6.19(b) are slightly different at the different pressures investigated. They occur dominantly outside of the ECR zone where the maximum in the electron density occurs. The low pressure has a narrow peak while the high pressure has a broader one. The reason is that the power transfer from
electron to gas is by collisions. The low pressure has a smaller collision frequency; therefore, the resonance condition corresponds to a smaller $\Delta B$, which corresponds to a smaller $\Delta Z$.

6.7 Flared Geometry

All of the results discussed in the previous sections are based on a collimated geometry configuration. The comparison of EED in columnar and flared geometries is shown in Fig. 6.20. There is only a slight difference in the EED between these two geometries. Therefore, it can be said that the above discussions for collimated geometry are suitable for the flared one. This implies that the downstream magnetic field profile is not that important with respect to the EED; however, other plasma swarm parameters may differ between the two configurations.
Figure 6.1. Electron energy distributions in ECR reactors at pressures 0.2, 1 and 3 mTorr for argon plasma. The input microwave power is 150 W. The lowest pressure has the highest energy tail.
Figure 6.2. The variation of electron energy distributions (EEDs) with distance in the ECR reactor for argon. The input power is 150 W. EED as a function of position shows lifting in the ECR zone. (a) Pressure is 0.2 mTorr
Figure 6.2. (cont.) (b) Pressure is 3 mTorr.
Figure 6.3. Electron energy distributions in ECR zone and 15 cm downstream for argon at 1 mTorr. The input microwave power is 150 W.
Figure 6.4. Electron energy distributions in ECR reactors at pressure 0.1 mTorr, and 2 mTorr for a nitrogen plasma. The input power is 150 W.
Figure 6.5. Electron energy distributions in ECR zone and 15 cm downstream for nitrogen at 2 mTorr with input power of 150 W.
Figure 6.6. The rate coefficients of argon at E/N=20 Td as a function of pressure computed with Monte Carlo simulation.
Figure 6.7. The electron impact rate coefficients of an argon plasma as a function of position at pressure 0.2, 1 and 5 mTorr. The rate coefficients are nearly independent of position at low pressure, and generally become position-dependent with increasing pressure. (a) Impact excitation rate coefficients. (b) Impact ionization rate coefficients.
Figure 6.8. Ionization rate coefficients of argon in the ECR zone and 15 cm downstream as a function of pressure. The coefficients persist downstream with nearly their value in the ECR zone at low pressure, and generally decrease with increasing pressure.
Figure 6.9. The electron impact rate coefficients for N$_2$ at V=1 and ionization state in the ECR reactor at 2 mTorr with input power of 150 W. The rate coefficient for vibrational excitation is depressed in the ECR zone due to depletion of the low-energy portion of the EED.
Figure 6.10. Electron temperature as a function of axial location in the ECR reactor for argon plasma at 0.2 mTorr, 1 mTorr and 5 mTorr with input power of 150 W.
Figure 6.11. Electron temperature at ECR zone, downstream and volume averaged as functions of pressure for argon with input microwave power of 150 W. The electron temperature increases with decreasing pressure approaching 20 eV in the ECR zone at pressures < 1 mTorr.
Figure 6.12. Comparison with experimental results from Ref. 51 for average electron temperature in argon.
Figure 6.13. Electron temperature $T_e$ at ECR zone, downstream and volume average as functions of input microwave power for argon at 1 mTorr. $T_e$ increases moderately with increasing microwave power.
Figure 6.14. Plasma density as a function of position in the ECR reactor for argon at 1 mTorr with input power of 150 W. The maximum density is out of the ECR zone due to diffusion loss to the ends.
Figure 6.15. Plasma density as a function of pressure in argon with input power of 150 W.
Figure 6.16. Ambipolar potential as a function of position in argon at 1 mTorr with input power of 150 W.
Figure 6.17. Ambipolar potential as a function of pressure in argon with input power of 150 W. At pressure < 1 mTorr, the potential increases to many tens of volts.
Figure 6.18. Ambipolar potential as a function of input microwave power in argon at 1 mTorr. The maximum potential increases moderately with increasing microwave power.
Figure 6.19. Power deposition in the ECR reactor. The input microwave power is 150 W. The pressures investigated are 0.2 and 5 mTorr. (a) Power transfer from electrical field to electrons. (b) Power transfer from electrons to gas.
Figure 6.20. Comparison of EED in collimated geometry and flared geometry.
CHAPTER 7

SUMMARY AND FUTURE WORK

We have developed a hybrid Monte Carlo fluid model to simulate partially ionized plasmas in which energy loss is dominated by inelastic collisions of electrons with neutral species and energy exchange is dominated by electron-electron collisions, and have successfully simulated ECR reactors using this model. The basis of the MC simulation is that electron-electron collisions are treated equivalently to electron-neutral-species collisions. This method is made tractable by using a modified null-cross-sectional technique. The assumption of isotropic scattering during electron-electron collisions limits the application of this model as presented to plasmas having low average energies where only a minority of the collisions are forward-scattered. The algorithms can be modified to account for these effects.

We carefully investigated the influences of pressure and input microwave power to electron swarm parameters in the reactors. The results obtained using this model are in good agreement with experiments. We found that the EED is not typically a Maxwellian distribution and often is composed of two or more groups: a fairly low-temperature component (a few eV) and a high-energy tail which can extend for hundreds of eV. The spatial distribution of the EED has two modes. At lower pressure (≤ 1 mTorr), the tail of the EED extends from the ECR region to the substrate (25 or more cm away). At pressures of a few mTorr and above, the tail of the EED is cut off as one typically sees in low-temperature, partially ionized plasmas. We found that, in the ECR reactors, electron swarm
parameters upstream of plasma range such as electron temperature and electron impact rate coefficients vary in a manner which is much more sensitive to gas pressure in the interesting pressure region. We also found that electron cooling, impact rates and even electron energy distributions are distance dependent. Hence, choosing a suitable place for the substrate should be a manufacturer's primary consideration.

The utility of this model is in large part determined by practical considerations such as the amount of computer time required to implement it. The computer time required for the model is spent primarily on MC simulation. We have experienced increases in computer time by a factor of 8 to 10 when a magnetic field exists due to gyration motions. Improvement could result by using a guiding-center technique. The method we used in this research was to follow electron trajectories in the reactor. The guiding-center technique allows us to move particles directly from one place to another between two collisions. The problem is that the critical radius of gyration motion, at which the guiding center technique is valid, is hard to determine. If this problem is solved, it will save computer time and make the simulation more efficient.
REFERENCES


VITA

Yilin Weng was born in Peijing, China. She attended Huazhong University of Science and Technology in Wuhan, People's Republic of China, where she received her Bachelor of Science degree in semiconductor physics and devices in January 1982. After graduation she worked at the Wuhan Radio Research Institute as an engineer. In the summer of 1983, she began her graduate studies in solid state devices at the Huazhong University of Science and Technology. Two years later, she came to the United States to join her husband. In January 1986, she began her graduate studies again in Statistics at the University of Illinois at Urbana-Champaign, transferring to the Department of Electrical and Computer Engineering in the summer of 1986. She was a research assistant in the Department of Electrical and Computer Engineering at the University of Illinois at Urbana-Champaign from September 1986 to August 1991. Her Ph.D. was conferred in October 1991.