Computational Investigations of Fundamental Plasma Processes in Semiconductor Industrial Applications

by

Chenhui Qu

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Electrical and Computer Engineering) in the University of Michigan 2020

Doctoral Committee:

Professor Mark J. Kushner, Chair
Professor John Foster
Professor Yogesh B. Gianchandani
Professor Brian Gilchrist
Associate Professor Eric Johnsen
Dedication

This dissertation is dedicated to my mother, Lingyu Wang, and my father, Meng Qu.
Acknowledgments

It was six years ago that I first joined University of Michigan. Looking back and I see an intriguing and exhilarating journey that still brings excitement to me. It is something I will treasure throughout my whole life. Doing research work can be fulfilling at some time but difficult at others. I am extremely lucky to have so many mentors and friends to share my joy and guide me through the hard times. I cannot imagine the past years without their helps.

Firstly, I want to thank my advisor Prof. Mark J. Kushner. I am so honored to be his student and am extremely thankful for all the guidance he offered. He showed me how exciting plasma science is and how a professional scientist should do to perform high-quality research work. He unconditionally shared his valuable experiences, from the proficient coding habit to the efficient communicating tactics with fellow researchers. The lessons I learned from him will indisputably benefit me life-long.

Secondly, I would like to thank my thesis committee members, Prof. John Foster, Associate Prof. Eric Johnsen, Prof. Brian Gilchrist, and Prof. Yogesh B. Gianchandani, for their warmly help and advices on my research. I would like to thank my project collaborators: Sang Ki Nam, (Samsung Electronics); Prof. Steven C. Shannon, Joel Brandon, Kristopher Ford, and Carl Smith (North Carolina State University); David Coumou (MKS Instrument); Prof. Vincent M. Donnelly, Priyanka Arora, Tianyu Ma, and Tyler List (University of Houston); Assitant Professor Abbas Semnani (University of Toledo); Pulkit Agarwal, Yukinori Sakiyama, and Adrien LaVoie (Lam Research Corp.). I want to thank them for their invaluable inputs, and
extreme patience when they offer their helps. They have broadened my view on plasma science and showed me ways to look at it from various aspects. I would also like to thank my friends at Lam Research Corporation: Saravanapriyan Sriraman, Rohini Mishra, Juline Shoeb, Rajesh Dorai, Kapil Sawlani, Alex Paterson, John Holland, and Harmee Singh. They showed me the cutting-edge technology of plasma application in the semiconductor industry and helped me having a good time during my internship there.

Thirdly, I would love to thank the sponsors, the US Department of Energy Office of Fusion Energy Science, National Science Foundation, Lam Research Corporation, and Samsung Electronics for providing the financial support to the projects for my graduate study. It is their supports make everything possible. Their generous help is very much appreciated.

I want to also thank all the group members: Prof. Hae June Lee, Yiting Zhang, Peng Tian, Seth Norberg, Wei Tian, Chad Huard, Michael Logue, Soheila Mohades, Guy Parsey, Aram Markosyan, Juliusz Kruszelnicki, Steven Lanham, Amanda Lietz, Shuo Huang, Xifeng Wang, Jordyn Polito, Mackenzie Meyer, Kseniia Konina, and Florian Krueger. I’ve spent most of my time with them in the past years. They are the friendliest and are always there to offer their help. Discussing with them is indeed a happy experience and an extremely efficient way to learn. I would also like to give my special thanks to Julia Falkovitch-Khain, who has been taken care of all the administrative issues I had in the past years. She made my life much easier so that I can focus on my research work whole-heartedly.

Finally, I would like to thank my family. I would love to thank my parents for raising me and supporting me chasing my dream. Nothing would be possible without them. Also, I would like to thank my girlfriend Yan Zhuang for standing by me and encouraging me to be a better self.
Table of Contents

Dedication ................................................................................................................................. ii
Acknowledgments ................................................................................................................... iii
List of Figures........................................................................................................................ viii
List of Tables ........................................................................................................................ xvii
List of Acronyms ............................................................................................................... xviii
Abstract ............................................................................................................................. xx

Chapter 1: Introduction ............................................................................................................1
  1.1 Low Temperature Plasmas in Semiconductor Processing ...........................................1
  1.2 Plasma Sources ...................................................................................................3
    1.2.1 Inductively Coupled Plasma Source ............................................................. 5
    1.2.2 Capacitively Coupled Plasma Source ......................................................... 9
  1.3 Plasma Enhanced Atomic Layer Deposition of Silicon Dioxide ............................... 12
  1.4 Modeling of Low Temperature Plasmas ................................................................ 14
  1.5 Feature Profile Modeling ..................................................................................... 16
  1.6 Summary ............................................................................................................. 18
  1.7 Figures ............................................................................................................... 24
  1.8 References ........................................................................................................ 34

Chapter 2: Description of the Models .................................................................................... 38
  2.1 Hybrid Plasma Equipment Model ................................................................. 38
  2.1.1 Electromagnetics Module (EMM) ............................................................. 39
  2.1.2 Electron Energy Transport Module (EETM) ............................................ 44
  2.1.3 Fluid Kinetics Poisson Module (FKPM) ................................................... 47
  2.1.4 Plasma Chemistry Monte Carlo Module (PCMCM) ....................... 53
  2.1.5 Surface Kinetics Module (SKM) ............................................................... 54
  2.2 Monte Carlo Feature Profile Model (MCFPM) ........................................... 55
    2.2.1 Co-deposition ....................................................................................... 56
    2.2.2 Energetic Particle Surface Reaction ...................................................... 58
  2.3 Figures ............................................................................................................. 60
  2.4 References ........................................................................................................ 63

Chapter 3: Insights to Plasma Transients in Low-High Pulsed Power Inductively Coupled Plasmas ........................................................ 64
List of Figures

Fig. 1.1 Plasma categorized by electron density ($n_e$) and electron temperature ($T_e$). The low-temperature plasma is shadowed. Reproduced from Ref. [4].................................24

Fig. 1.2 Diagram of the sheath with potential $\Phi_W$. Ion density ($n_i$) is higher than electron density ($n_e$) in the sheath due to the high electron temperature ($T_e$) and small electron mass ($m_e$). $v_i$ is ion velocity on the sheath boundary. Reproduced from Ref. [10].........................25

Fig. 1.3 Potential energy curves of oxygen molecule and ions. Reproduced from Ref. [11].........26

Fig. 1.4 Electron impact O$_2$ cross section. $Q_m$ is momentum transfer, $Q_a$ is attachment, $Q_p$ is ion-pair formation, and $Q_i$ is ionization. vib. exc. represents vibrational excitation states. Reproduced from Ref. [12].........................................................................................27

Fig. 1.5 a) An ICP reactor setup with planar coil configuration and b) one of the early ICP reactor designed at IBM. Reproduced from Ref. [13]. .............................................................28

Fig. 1.6 Spike of the radiation temperature at the beginning of the pulse, representing an electron temperature ($T_e$) spike as high as 90-100 eV. Ar, 300 W, 20 mTorr, PRF = 100 kHz, DC = 50%. Reproduced from Ref. [21]. ...........................................................................29

Fig. 1.7 Schematic of a) heating mechanisms in a CCP reactor and b) a CCP reactor setup in an experiment. Reproduced from Ref. [33].................................................................30

Fig. 1.8 Spatio-temporal evolutions of the electron impact excitation rate from the ground state into Ne2p$_1$ state within two RF cycles at different RF voltages for two driving frequencies, i.e. 8 MHz (first row) and 12 MHz (second row), at 50 Pa. A transition to $\gamma$-mode appears in (a3). Reproduced from Ref. [34]..................................31

Fig. 1.9 The effect of DC-bias on the substrate potential and plasma potential in two RF periods ($\tau_{RF}$).........................................................................................................................32

Fig. 1.10 Schematic of the AB binary sequence of ALD. The self-limiting ensures a maximum deposition rate of one mono-layer per cycle. Reproduced from Ref. [50].................33

Fig. 2.1 The flow chart of the Hybrid Plasma Equipment Model (HPEM) used in this thesis. .....60
Fig. 2.2 a) Schematic of the circuit model and b) the detail of each segment representing 1/100 of an antenna.

Fig. 2.3 Schematic of the fork-join model used in OpenMP for parallel computation.

Fig. 3.1 Geometry and power profile used in the model. a) The geometry is an inductively coupled plasma having a 4-turn antenna. The dots (with dimensions) indicate where plasma properties are shown. b) Pulse power profile for the base case.

Fig. 3.2 Plasma properties for the base case (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W) at 0 μs (end of the low-power) and 100 μs (end of the high power) during the power pulse. a) Electron density, b) electron temperature and c) ionization source by collisions of bulk electrons. Maximum value, range of values plotted and units for contour labels are indicated in each image.

Fig. 3.3 Plasma properties for the base case (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W) at 0 μs (end of the low-power) and 100 μs (end of the high power) during the power pulse. a) Cl₂⁺ density, b) Cl⁻ density and c) gas temperature. Maximum value, range of values plotted and units for contour labels are indicated in each image.

Fig. 3.4 Axial distribution of electron and Cl⁻ densities at mid-radius of wafer at a) end of the low-power pulse (0 μs) and b) end of the high-power pulse (100 μs).

Fig. 3.5 Time dependence of a) electron density and b) electron temperature at different heights above the substrate and mid-radius over 2 pulse periods (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W). These heights are noted in Fig. 3.1. The results for electron temperature have been numerically smoothed.

Fig. 3.6 Electron energy distributions (EEDs) at different heights above the substrate at mid-radius of the wafer at the a) end of the low-power pulse (0 μs) and b) end of the high power pulse (100 μs). (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W.) These heights are noted in Fig. 3.1. The EEDs have been numerically smoothed.

Fig. 3.7 Electron density at the end of the high-power pulse (100 μs) for gas mixtures of Ar/Cl₂ = a) 20/80, b) 40/60, c) 60/40 and d) 80/20. (20 mTorr, 96 W - 160 W.) The contours are plotted on a 2-decade log scale with the maximum value in each frame noted. Contour labels have units of 10¹¹ cm⁻³.

Fig. 3.8 Electron density as a function of time for different values of the Cl₂ mole fraction at a) 11 cm above the substrate and b) 2 cm above the substrate. (20 mTorr, 96 W - 160 W.)

Fig. 3.9 Electron temperature as a function of time for different values of the Cl₂ mole fraction at a) 11 cm above the substrate and b) 2 cm above the substrate. (20 mTorr, 96 W - 160 W.) The values for T_e have been numerically smoothed.
Fig. 3.10 Electron temperature while varying the power ramp-down time. a) Power profiles for ramp-down times from 10 to 80 μs. Electron temperature for different ramp-down times at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W.) These values of Tₑ have been numerically smoothed. 

Fig. 3.11 Electron density while varying the power ramp-down time. a) Power profiles for ramp-down times from 10 to 80 μs. Electron density for different ramp-down times at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W.)

Fig. 3.12 Electron temperature while varying the low power during the cycle. a) Power profiles for low powers of 32 W to 160 W. Electron temperature for different low powers at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.) These values of Tₑ have been numerically smoothed.

Fig. 3.13 Electron density while varying the low power during the cycle. a) Power profiles for low powers of 32 W to 160 W. Electron density for different low powers at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.)

Fig. 3.14 Plasma properties 11 cm above the substrate while varying the low power during the cycle. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.) a) Total cation density, b) Cl⁻ density and c) ratio α = nCl₂ + nCl +. 

Fig. 4.1 Circuit schematic a) The circuit consists of impedances of the power generator, transmission line, matchbox, antenna, plasma, and termination circuit components. The antenna and transformed plasma impedances area represented by a discrete transmission line with each segment having having serial impedance Zₙ and parallel impedance due to capacitive coupling, Zₖn. b) The Zₙ components consist of the physical resistance (Rₙ) and inductance (Lₙ) of the antenna, and the transformed impedance (resistance and inductance) of the plasma, Zₖn. The impedance due to capacitive coupling, Zₖn, has components due to the air gap and dielectric, sheath and bulk resistance of the plasma.

Fig. 4.2 Geometry of the cylindrically symmetric ICP reactor.

Fig. 4.3 Capacitive and inductive power deposition, and electron density when plasma is sustained with at total continuous power of a) 5 W and b) 200 W. (Ar/Cl₂ = 65/35, 25 mTorr.) The match is perfect. The capacitive power is shown as color contours with a line separating positive and negative values. Contour labels are mW/cm³. Electron density is shown as color contours. Inductive power deposition is shown as contour lines with labels in mW/cm³. The contour lines are blanked near the axis to enable clear view of the sheath formed under the powered coil.

Fig. 4.4 Plasma and circuit properties as a function of CW power deposition for perfect matching (Ar/Cl₂ = 65/35, 25 mTorr). a) Electron density and fraction of power deposition due
inductive H-mode, capacitive E-mode and antenna heating. b) Analytical solutions for $C_P$ and $C_S$ for a perfect match and the ionization efficiency. The ionization efficiency is total electron density divided by power deposition in the plasma, and is a relative measure of efficiency.

Fig. 4.5 Ionization efficiency as a function of CW power (Ar/Cl₂ = 65/35, 25 mTorr). Cases are shown for perfect matches for small and large residence time ($\tau_{res}$) and with circuit values for a perfect match at 150 W with small $\tau_{res}$. The ionization efficiency is total electron density divided by power deposition in the plasma, and is a relative measure of efficiency.

Fig. 4.6 Plasma and circuit values for a pulsed ICP with perfect matching. a) Electron and ion densities, and plasma potential, b) modes of power deposition and c) $C_P$ and $C_S$ for perfect match conditions, and reactive and resistive components of the impedance $Z_L$. The pulse repetition frequency is 13.3 kHz, duty cycle of 35% and forward power during the pulse is $P_S=250$ W, shown in c).

Fig. 4.7 Modes of power deposition, total power deposition and power reflection coefficient $\Gamma$ when $C_P$ and $C_S$ are chosen to match at $t_M$ = a) 1.5, b) 3.25, c) 7 and d) 21 µs into the pulse. (Ar/Cl₂=65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250$ W.)

Fig. 4.8 Circuit values and power deposition as a function of matching time. a) Power reflection coefficients through one pulsed period when matching at different $t_M$. b) Inductive and capacitive power at their maximum value and at the end of pulse ($t = 23$ µs) with varying match time $t_M$. (Ar/Cl₂ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250$ W.)

Fig. 4.9 Plasma properties when varying duty cycle (25 to 65%) during a pulsed period. The circuit match values correspond to a duty cycle of 35% with the match time at $t_M = 7$ µs. a) Electron density and b) plasma potential. For clarity, the plots for plasma potential have been shifted by increments of 10 ns. (Ar/Cl₂=65/35, 25 mTorr, PRF = 13.3 kHz, $P_S = 250$ W).

Fig. 4.10 Ion energy distribution (IED) incident onto the dielectric window at different times during the pulse. a) 0-2.0 µs, and b) 2.0-22 µs. The inset shows the plasma potential. The labels A-H are the locations in the pulsed cycle at which the IEDs are plotted. (Ar/Cl₂ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 25%).

Fig. 4.11 Inductive and capacitive power deposition for different gaps, d, between the coils and the top of the dielectric window. Heights range between $d = 0$ to 8.2 mm. a) Power over the entire power-on period and b) power during the first 5 µs. The circuit match values correspond to the match time $t_M = 20$ µs. (Ar/Cl₂ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250$ W.)

Fig. 4.12 Electron density (color contours) and charge density over the first few RF cycles of a pulsed period. a) 2nd, b) 3rd, c) 4th and d) 6th cycles. The circuit match values correspond
to the match time $t_M = 1.5 \, \mu s$. The charge density $\rho$ is shown by labels in units of $q \left(1.6 \times 10^{-19} \, C/cm^3\right)$ with a line denoting $\rho = 0$. (Ar/Cl$_2$ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250 \, W$). The impulsive power deposition launches electrostatic waves.

Fig. 5.1 Geometry of the inductively coupled plasma (ICP) reactor used in this work .................159

Fig. 5.2 Distributions of electron density and power density, and spatially averaged electron density and electron temperature. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%.......160

Fig. 5.3 Diagram of power transmission line with power supply, impedance matching network, and load impedance consisting of the coil, plasma, and termination circuit components. ......................................................................................................................161

Fig. 5.4 Real and imaginary parts of the load impedance ($Z_L$) and the capacitances in the matching network ($C_P$ and $C_S$) required for the impedance match. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%......................................................162

Fig. 5.5 Power deposition ($P_{\text{dep}}$) and reflection ($P_{\text{ref}}$) and load impedance when the impedance matching network is chosen to match a) in the early pulse at $\tau = 10 \, \mu s$ and b) in the late pulse at $\tau = 90 \, \mu s$. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%. ......................163

Fig. 5.6 a) A typical response of power reflection coefficient ($\Gamma$) with radiofrequency, and b) a schematic diagram of frequency tuning in the HPEM. ....................................................164

Fig. 5.7 Power deposition ($P_{\text{dep}}$) and reflection ($P_{\text{ref}}$) with (FT) and without (no FT) frequency tuning when a) b) IMN is chosen to match early in the pulse at $\tau = 10 \, \mu s$ and when c) d) IMN is chosen to match late in the pulse at $\tau = 90 \, \mu s$..............................................................165

Fig. 5.8 Power deposition efficiency with and without frequency tuning with different powers. Ar, 15 mTorr, PRF = 5 kHz, DC = 50%. ..................................................................................166

Fig. 5.9 a) Spatially averaged electron density b) power reflection coefficient without frequency tuning and c) power reflection coefficient in the first 20 $\mu$s with and without frequency tuning. Ar, 15 mTorr, PRF = 5 kHz, DC = 50%..............................................167

Fig. 5.10 a) Power deposition efficiency as a function of power transition time ($\tau_t$) and b) power reflection coefficient when $\tau_t = 4, 40,$ and 80 $\mu$s. Ar, 50 W, 15 mTorr, PRF = 5 kHz, DC = 50%. ..............................................................................168

Fig. 5.11 a) Power deposition efficiency as a function of duty cycle and b) power deposition, power reflection, and frequency with and without frequency tuning when DC = 40%. Ar, 50 W, 15 mTorr, PRF = 5 kHz............................................169
Fig. 6.1 Geometry of the reactor. 80 MHz power (500 W) is applied to the top electrode, 5 and 10 MHz power (400 W each frequency) are applied to the substrate. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr.

Fig. 6.2 Spatially averaged a) ion and b) neutral species’ densities. An acceleration technique was used to help the plasma reach the quasi-steady state faster, causing rapid density changes in the first 250 μs. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.3 2D profile of a) electron density, b) electron temperature, c) ionization source by bulk electrons, d) ionization source by beam electrons, e) Ar$^+$ density, f) F$^-$ density and g) O density in base case. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.4 The a) IEADs averaged over 0° and b) normalized IEDs of CF$_3^+$ and Ar$^+$ at mid-radius of the wafer (r = 7.5 cm). Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.5 a) EEDFs from different axial locations and b) the locations from where the EEDFs are recorded. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.6 a) EEDFs from different radial locations and b) the locations from where the EEDFs are recorded at z = 4.8 cm. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.7 2D profiles of the electron density and ionization source by bulk electrons when the power from 80 MHz power source is 50, 500 and 1000 W. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.8 The EEDFs from a) center (r = 13.5 cm, z = 4.8 cm) and b) upper (r = 13.5 cm, z = 6.0 cm) point when the power from 80 MHz power source is 50, 500 and 1000 W. Inset of a) is the zoom-in on the low energy component of EEDFs at center point and the inset of b) is the spatially averaged electron density and electron temperature with increasing HF power. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.9 IEADs of a) Ar$^+$ and b) CF$_3^+$ and the normalized IEDs of c) Ar$^+$ and d) CF$_3^+$ when the power from 80 MHz power source is 50, 500 and 1000 W. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.10 2D profiles of the electron density and ionization source by bulk electrons when the pressure is 15, 30 and 50 mTorr. Ar/CF$_4$/O$_2$ (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.11 a) EEDFs from the center point \( (r = 13.5 \text{ cm}, \ z = 4.8 \text{ cm}) \) when the pressure is 15, 30 and 50 mTorr. And the b) spatially averaged electron density and electron temperature. Ar/CF\(_4\)/O\(_2\) (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.12 The IEADs of a) Ar\(^+\) and b) CF\(_3\)\(^+\) and the normalized IEDs of c) Ar\(^+\) and d) CF\(_3\)\(^+\) when the pressure is 15, 30 and 50 mTorr. Ar/CF\(_4\)/O\(_2\) (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.13 2D profiles of the electron density and ionization source by bulk electrons when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.14 EEDFs at the center point \( (r = 13.5 \text{ cm}, \ z = 4.8 \text{ cm}) \) when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.15 IEADs of a) Ar\(^+\) and b) CF\(_3\)\(^+\) and the normalized IEDs of c) Ar\(^+\) and d) CF\(_3\)\(^+\) when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.16 2D profiles of the electron density and ionization source by bulk electrons when the gap length is 2.3, 3.3 and 4.3 cm. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.17 EEDFs from the center point \( (r = 13.5 \text{ cm}, \ z = 4.8 \text{ cm}) \) when the gap length is 2.3, 3.3 and 4.3 cm. The inset is the spatially averaged electron density and electron temperature with increasing gap length. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 6.18 IEADs of a) Ar\(^+\) and b) CF\(_3\)\(^+\) and the normalized IEDs of c) Ar\(^+\) and d) CF\(_3\)\(^+\) when the gap length is 2.3, 3.3 and 4.3 cm. Ar/CF\(_4\)/O\(_2\) (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).

Fig. 7.1 Geometry of the reactor. 500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O\(_2\) (4/1), 5 slm; secondary gas inlet: O\(_2\), 6 slm.

Fig. 7.2 O\(_2\) flux, 2-dimensional distribution of electron density, O\(_2^+\) density and O\(^-\) density. 500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O\(_2\) (4/1), 5 slm; secondary gas inlet: O\(_2\), 6 slm.

Fig. 7.3 a) Energy and angular distributions (EADs) of dominant cations Ar\(^+\) and O\(_2^+\), and radical O. b) Fluxes of major species across half-wafer. 500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O\(_2\) (4/1), 5 slm; secondary gas inlet: O\(_2\), 6 slm.
Fig. 7.4 a) Flowchart of SiO$_2$ PE-ALD process and b) impact of ligand remnant on the upper layer of SiO$_2$ film deposition.

Fig. 7.5 a) 2-dimensional film profile of the middle slice at $y = 5$ nm and b) 3-dimensional profile of the SiO$_2$ film at the end of 5$^{th}$ and 10$^{th}$ cycle.

Fig. 7.6 a) O$_2$(s) sites surface coverage ratio, b) concentrations of oxygen, silicon, vacancy and ligand group in entire film and oxygen to silicon ratio and c) time-averaged and instantaneous film growth rate using the default setup. 0.5 nm/cell, 1 nm per SiO$_2$ layer, blanket deposition.

Fig. 7.7 a) 2D film profile at the end of the 10$^{th}$ cycle and b) 3D film profiles at the end of the 5$^{th}$ and 10$^{th}$ cycle when depositing in a trench of 30 nm (W) $\times$ 120 nm (H) $\times$ 10 nm (D).

Fig. 7.8 a) Concentrations of oxygen, silicon, vacancy and ligand group in entire film and oxygen to silicon ratio and c) time-averaged and instantaneous film growth rate at the bottom of the trench. 0.5 nm/cell, 1 nm per SiO$_2$ layer, trench deposition.

Fig. 7.9 a) Energy and angular distributions (EADs) of Ar$^+$ and O when power is 400 W and 1 kW and b) fluxes of major species at mid-radius of wafer. 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm.

Fig. 7.10 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying power. Data are from 5$^{th}$ cycle. 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer.

Fig. 7.11 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying power. Data are from 5$^{th}$ cycle. 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer.

Fig. 7.12 a) Energy and angular distributions (EADs) of Ar$^+$ and O when pressure is 0.5 and 2 Torr, b) energy distribution function of all cations and c) fluxes of major species at mid-radius of wafer. 500 W, 10 MHz, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm.

Fig. 7.13 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying pressure. Data are from 5$^{th}$ cycle. 10 MHz, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer.

Fig. 7.14 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying pressure. Data are from 5$^{th}$ cycle. 10 MHz, primary
Fig. 7.15 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying co-deposition probability $p_R$. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer. ................................................................................................................................. 261

Fig. 7.16 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying co-deposition probability $p_R$. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer. ........................................................................................................... 262

Fig. 7.17 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate for blanket deposition with and without oxygen replacement reactions. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer. ........................................................................................................... 263

Fig. 7.18 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate in the bottom of a trench with varying aspect ratio from 2-8. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer. ........................................................................................................... 264

Fig. 7.19 a) Geometry of the via and film profile at the end of the 5th cycle and b) concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and c) time-averaged and instantaneous film growth rate in the bottom of this via with varying aspect ratio from 2-8. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer. ........................................................................................................... 265
List of Tables

Table I  List of voltages at each frequency, plasma potential and DC bias with varying conditions in a triple-frequency Ar/CF₄/O₂ CCP.................................................................................................................. 192
Table II List of surface reactions for PE-ALD of SiO₂ using Ar/O₂ plasma as oxidation agent and BTBAS as Si precursor ........................................................................................................................................... 243
### List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-d</td>
<td>0-dimensional</td>
</tr>
<tr>
<td>2-d</td>
<td>2-dimensional</td>
</tr>
<tr>
<td>3-d</td>
<td>3-dimensional</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic Layer Etching</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>CCP</td>
<td>Capacitively Coupled Plasma</td>
</tr>
<tr>
<td>CD</td>
<td>Critical Dimension</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric Barrier Discharge</td>
</tr>
<tr>
<td>dc</td>
<td>direct current</td>
</tr>
<tr>
<td>DC</td>
<td>Duty Cycle</td>
</tr>
<tr>
<td>DF-CCP</td>
<td>Dual-frequency Capacitively Coupled Plasma</td>
</tr>
<tr>
<td>eMCS</td>
<td>electron Monte Carlo Simulation</td>
</tr>
<tr>
<td>EED</td>
<td>Electron Energy Distribution</td>
</tr>
<tr>
<td>EETM</td>
<td>Electron Energy Transport Module</td>
</tr>
<tr>
<td>EMM</td>
<td>Electromagnetic Module</td>
</tr>
<tr>
<td>FKPM</td>
<td>Fluid Kinetics Poisson Module</td>
</tr>
<tr>
<td>GPC</td>
<td>Growth Per Cycle</td>
</tr>
<tr>
<td>HAR</td>
<td>High Aspect Ratio</td>
</tr>
<tr>
<td>HPEM</td>
<td>Hybrid Plasma Equipment Model</td>
</tr>
<tr>
<td>IAD</td>
<td>Ion Angular Distribution</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IEAD</td>
<td>Ion Energy and Angular Distribution</td>
</tr>
<tr>
<td>IED</td>
<td>Ion Energy Distribution</td>
</tr>
<tr>
<td>IMN</td>
<td>Impedance Matching Network</td>
</tr>
<tr>
<td>LTP</td>
<td>Low Temperature Plasma</td>
</tr>
<tr>
<td>MCFPM</td>
<td>Monte Carlo Feature Profile Model</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamic</td>
</tr>
<tr>
<td>MF-CCP</td>
<td>Multi-frequency Capacitively Coupled Plasma</td>
</tr>
<tr>
<td>NEAD</td>
<td>Neutral Energy and Angular Distribution</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary Differential Equation</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------------------------------------------</td>
</tr>
<tr>
<td>PCMCM</td>
<td>Plasma Chemistry Monte Carlo Module</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial Differential Equation</td>
</tr>
<tr>
<td>PRF</td>
<td>Pulse Repetition Frequency</td>
</tr>
<tr>
<td>PSI</td>
<td>Plasma Surface Interaction</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>SF-CCP</td>
<td>Single-frequency Capacitively Coupled Plasma</td>
</tr>
<tr>
<td>S-G</td>
<td>Scharfetter-Gummel</td>
</tr>
<tr>
<td>SKM</td>
<td>Surface Kinetics Module</td>
</tr>
<tr>
<td>SOR</td>
<td>Successive-over-Relaxation</td>
</tr>
<tr>
<td>SSBM</td>
<td>Surface Site Balance Model</td>
</tr>
<tr>
<td>SVR</td>
<td>Surface-to-Volume Ratio</td>
</tr>
<tr>
<td>TF-CCP</td>
<td>Tri-frequency Capacitively Coupled Plasma</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
</tbody>
</table>
Abstract

The continuous downsizing of the critical dimensions (CDs) of semiconductor devices poses challenges to plasma-involved semiconductor fabrication processes. As the CD decreases to sub-ten nanometers (e.g., 6 nm-width fin field-effect transistor [FinFET]), control of plasma properties to provide atomic scale precision becomes necessary. Meanwhile, to ensure high yield, semiconductor fabrication is often deployed on a large scale, on 300 mm wafers. Therefore, it is essential to have a uniform plasma distribution across the reactor for consistent yields.

In this thesis, reactor and feature scale modeling was performed. The research work involves developing computational modules and applying acceleration mechanisms in two simulation platforms: the Hybrid Plasma Equipment Model (HPEM), for reactor scale modeling, and the Monte Carlo Feature Profile Model (MCFPM), for feature scale simulations. Frequency tuning and impedance matching with an impedance matching network (IMN) were implemented in the HPEM to study the electrical dynamics during pulsed-plasma operation. Surface reaction mechanisms of SiO₂ plasma-enhanced atomic layer deposition (PE-ALD) using bis-tertiary-butyl-amino-silane (BTBAS) as the precursor were developed.

In an inductively coupled plasma (ICP) reactor, the power deposition into the plasma is always less than the output from the power source. The power that is not directed into the plasma is lost in the transmission line, reflected at the coil-plasma interface due to the impedance mismatch, or dissipated by the materials in the plasma reactor. The power reflection is
minimized by implementing an IMN between the power source and the coil. By tuning the circuit components used in the IMN, the impedance of the pre-plasma circuit (including coils, IMNs, and power source) is brought close to the impedance of the plasma, thus reducing the power reflection. However, in practice, the components in an IMN have fixed values because tuning the IMN is a mechanical process that takes several milliseconds to even seconds. Frequency tuning is another mechanism for impedance matching, which takes advantage of the high tuning rate with solid state electronics. This technique can be used with an IMN if the plasma has a rapidly changing impedance (e.g., pulsed plasma). The function of analytically calculating the circuit components in IMN to minimize power reflection in an ICP reactor was implemented in the HPEM. An algorithm of frequency tuning in an ICP was also added to enable impedance matching by adjusting RF frequency when the IMN is fixed.

SiO₂ films are widely used in semiconductor devices, and PE-ALD is a preferred method for deposition when a low process temperature is needed. The PE-ALD of SiO₂ has two major steps: precursor dosing and plasma exposure. During precursor dosing, a silicon precursor such as BTBAS is used to treat the target surface and forms a monolayer of Si-H compounds. Subsequently, in the plasma exposure step, the target surface is treated with an oxygen plasma and is oxidized. The reaction is self-limiting for both steps, and a monolayer of SiO₂ is deposited in one cycle. However, in experiments, the growth-per-cycle (GPC) is often less than one monolayer, which partly is caused by steric hindrance. Incomplete reactions during precursor dosing leave alkyl ligand remains on the target surface, which block neighboring sites, and slows the deposition. The impacts of the operating conditions and steric hindrance on SiO₂ films during PE-ALD were studied.
Chapter 1: Introduction

1.1 Low Temperature Plasmas in Semiconductor Processing

Since the mid-1980’s, the use of low-temperature plasmas (LTPs) has become an essential part of the semiconductor industry. In fact, developments in manipulating LTPs have become a driving force for increasing transistor density in computer microchips that keeps pushing the technology to follow Moore’s law [6,7]. Different types of plasmas are often categorized as a function of electron density and electron temperature, as shown in Fig 1.1 [4]. In this thesis, the focus is on a greater understanding of low-temperature plasmas and their application in the semiconductor industry.

Plasma is commonly referred to as the fourth state of matter. It is an electrically quasi-neutral gas consisting of charged and neutral particles with collective behaviors [1]. Generally speaking, as temperatures increase from absolute zero a substance experiences phase changes from solid, to liquid, to gas. Beyond the gas phase, if additional energy is provided, the matter transforms into the plasma state. It is recognized that the majority of the matter in the visible universe is plasma. For example, both the ionosphere of the earth and the photosphere of the sun are plasmas. Because plasma provides highly reactive particles, and its behavior is subject to the surrounding external electrical field (E-field), it is widely used for industrial applications. The most recognizable examples of these are plasmas in visual display panels and in fluorescent lighting. Both of these utilize ultraviolet (UV) light produced in a plasma [2,3]. From
fluorescent lighting to the surface of the sun, plasma parameters cover a vast range of possible uses.

There is no strict definition of low-temperature plasmas (LTPs). However, for plasma processing applications, an LTP often refers to a non-thermal-equilibrium, weakly-ionized plasma with an electron temperature ($T_e$) between several to 10s eV [5]. The electron density ($n_e$) of an LTP is often at $10^8 - 10^{13}$ cm$^{-3}$, and the pressure is from a few mTorr up to atmospheric pressure (100s Torr). The properties of an LTP depend on many factors, including but are not limited to the input power, pressure, and the geometry of the reactor. Therefore, many control knobs can be manipulated to characterize an LTP for specific applications, which is typically not the case for other manufacturing approaches.

The wide range of chemical and electrical properties of an LTP exceed the boundary of normal manufacturing. For example, using LTP enables high aspect ratio (HAR) etching in microchip manufacturing within nanometer-scale critical dimensions (CD) due to the emphasis on physical etching [8]. Before the use of plasmas, wet chemical etching was the mainstream etching technique. However, wet etching is isotropic, and therefore is not suitable for HAR processing. Applying LTP also enables the deposition of dielectric material with nanometer-scale precision in low temperature ($< 300 ^\circ$C) applications [9]. Access to the reactive particles in the LTP moderates otherwise thermally expensive reactions therefore allowing deposition to be performed on temperature-sensitive devices. Examples such as those mentioned above demonstrate that LTPs become indispensable components in semiconductor fabrication. As the technology node hits sub-10 nm, and the design of semiconductor devices shifts from 2-dimensional (2D) to 3-dimensional (3D), it is critical to have precise control over the
manufacturing processes. Producing highly uniform plasmas, with abundant desired reactants and maximum power efficiency, continues to be the goal of industrial related LTP research.

This dissertation focuses on two topics: to survey the possible methods for improving plasma uniformity and stability; and to investigate the impact of operating conditions on a PE-ALD of SiO$_2$. Both topics are studied using computational tools. A brief overview of the fundamentals of LTP and plasma sources is presented in Section 1.2. PE-ALD of SiO$_2$ is briefly explained in Section 1.3 and the modeling of reactor-scale plasma phenomena and feature-scale deposition processes is described in Section 1.4 and 1.5.

1.2 Plasma Sources

To sustain a plasma, an external supply is required to provide the power to ionize and excite the neutral particles. The resulting ions and excited state species are essential components in plasma and are often desired for surface treatment or etching.

LTPs are made up of bulk and sheath regions and make up a quasi-neutral dynamic system with a delicate charge balance in the sheath-bulk plasma interface. The sheath is a thin high-electrical field region above all the surfaces exposed to the plasma. A diagram of the plasma sheath is shown in Fig. 1.2 [10]. In an LTP, $T_e \gg T_i$ and the mass of an electron ($m_e$) is much less than the mass of an ion ($m_i$). Therefore, the thermal velocity of the electron is much faster than that of heavy ions. When a surface is presented in a plasma, electrons are lost at a much faster rate than neighboring ions due to their high velocity. Because the plasma is a quasi-neutral system, the loss of electrons to the surface results in a positively charged region almost exclusively containing only cations and neutrals. This charge provides a plasma potential that leads to the formation of an electrical field (E-field) from the plasma bulk to the surface. This
potential repels the electron flux ($\Gamma_e$) and accelerates cation fluxes ($\Gamma_i$) toward the surface. This high E-field region with $n_i > n_e$ is commonly referred to as the sheath region. If the surface is not grounded, it is referred to as an electrically floating surface. A floating surface can be charged by fast-moving electrons, and this also results in a surface-pointing E-field and the development of the sheath. The sheath formation on a powered electrode is more complicated and will be discussed in detail later.

Most of the plasma chemical reactions occur in the bulk plasma. Charged particles and excited state species are created through ionization and excitation, and they are lost through recombination reactions and diffusion to the wall. Electron impact reactions are the most common types of reactions in an LTP. Electrons accelerated by the E-field gain energy and collide with neutral particles, and this transitions the particle to an excited state. If the electron energy is high enough, ionization occurs. The energy of a species is often plotted on a potential energy curve. For example, the potential energy curve of O$_2$ is shown in Fig. 1.3 [11]. When external energy is applied to the ground state oxygen molecule, it can be pumped to another potential curve and this represents the shifting of its energy states and the occurrence of a reaction. If two potential curves cross, a shift of states may occur. Most of the reactions in LTPs are energy-dependent, meaning the reaction rate varies with the energy of the reactant electrons. This energy-dependence is addressed by using cross section ($\sigma$) in the expression of the reaction rate coefficient. A cross section is an energy-dependent parameter of the unit of area and is specific for each species. The electron impact cross sections for oxygen are shown in Fig. 1.4 [12]. Inelastic collisions such as ionization and excitation have threshold energy requirements, while the momentum transfer reaction (elastic collision) is available across all energy regimes. An averaged reaction rate constant ($k$) is:
\[ k = \int_{\varepsilon}^{\varepsilon'} \sigma(\varepsilon) \left( \frac{2\varepsilon}{m} \right)^{\frac{3}{2}} f(\varepsilon) d\varepsilon, \]  

(1.1)

where \( f(\varepsilon) \) is the electron energy distribution function (EEDF).

Note that plasma is a dynamic system defined by the group behavior of electrons and ions. One of the most important features of a plasma is its plasma frequency. The electrons and ions are constantly oscillating due to the self-restoring force caused by the perturbation of local charge equilibrium. The electrons and ions oscillate at different frequencies \( \omega_{pe} \) and \( \omega_{pi} \):

\[ \omega_{p(e,i)} = \sqrt{\frac{q^2 n_0}{\varepsilon_0 m_{(e,i)}}}, \]  

(1.2)

where \( q \) is the elementary charge, \( n_0 \) is the plasma density, and \( m_{e,i} \) are the electron and ion masses, respectively. Because the electron mass is much smaller than the ion mass, the electron plasma frequency is always much larger than the plasma ion frequency, \( \omega_{pe} \gg \omega_{pi} \). Therefore, in most scenarios, it is safe to consider only the electron plasma frequency and treat ions as stationary particles. The oscillation of the charge species creates a local non-equilibrium of charge density. In an LTP, the scale over which the charge-equilibrium can be violated is the Debye Length (\( \lambda_D \)):

\[ \lambda_D = \frac{\varepsilon_0 T_e}{q^2 n_e}, \]  

(1.3)

where \( T_e \) is the electron temperature. Remember that within the sheath, the plasma is not charge-neutral \((n_i > n_e)\). The thickness of the sheath is often several \( \lambda_D \).

1.2.1 Inductively Coupled Plasma Source

Inductively coupled plasma (ICP) sources are widely deployed in the semiconductor industry. A commonly used ICP has the “stovetop coil” configuration shown in Fig. 1.5 [13]. In this case, radiofrequency (RF) power is fed through the planar coil. The oscillating E-field
generates a time-varying magnetic field in the reactor which then creates an E-field that oscillates in the azimuthal direction. This E-field accelerates electrons back and forth and transmits the power from the coil to the plasma. The plasma potential is often low in an ICP (10s V). This low potential results in a thin sheath and low ion energy onto the surface, thus causing less sputtering and contamination in the plasma. Because the targeted feature size can be 10s or sub-10 nm scale, reducing contamination is critical. Usually, separately controlled power sources are applied to the substrate in an ICP reactor to control the ion energy and angular distributions (IEADs) onto the wafer. Therefore, an almost independent control of the plasma density and IEADs is made possible with the use of ICP.

In an industrial application, the frequency of the RF power is typically at 13.56 MHz, and the pressure is 10s mTorr. The momentum transfer collision frequency \(v_m\) is less than or close to the driving frequency of the coil. Under these conditions, the skin depth of the electromagnetic field (EM-field) into the plasma can be approximated by

\[
\delta = \left( \frac{m_e}{q^2 \mu_0 n_e} \right)^{1/2}
\]

where \(\delta\) represents the skin depth, and \(\mu_0\) is the vacuum permeability. The power is mainly transferred to the plasma within the range of this skin-depth. Power transition is largely carried out through collisionless heating due to the low pressure. In a typical ICP, \(\delta \approx 1\text{-}2\text{ cm}\).

To optimize the power delivery to the plasma, an impedance matching network (IMN) is often implemented between the power source and the coil [14,15]. An IMN is a circuit that contains only inductors and capacitors, so there is no net power consumption. By tuning the circuit components used in the IMN, the input impedance of the IMN is matched to the output impedance of the power source, which usually is 50 \(\Omega\). Using IMN ensures high power delivery.
efficiency by reducing the power reflection. The electric field reflection coefficient ($\Gamma_R$) is calculated as

$$\Gamma_R = \frac{Z_L - Z_0}{Z_L + Z_0},$$

(1.5)

where $Z_L$ is the impedance of the load, including the impedances of IMN, plasma, and the electrical termination components; $Z_0$ is the 50 $\Omega$ impedance of the power source. The power deposition into the plasma is then equaled $P_{tot}(1-|\Gamma_R|^2)$, where $P_{tot}$ is the power output from the power source.

Pulsed power is often used to gain better control of the reactive species fluxes to the substrate. The pulse repetition frequency (PRF) is often between 1-20 kHz, and the duty cycle (the fraction of the power-on time in the whole period) is 10s of percent. Using pulsed power enables higher plasma density while maintaining a moderate average power. Also, unique plasma chemistry is enabled during the power-off period [16-18]. Even better control of the reactive particles fluxes to the wafer can be achieved when combining the pulsed ICP power with a separately controlled powered substrate [19, 20].

A commonly observed behavior in a pulsed plasma is that $T_e$ often spikes over the quasi-steady state value at the leading edge of pulse-on, as shown in Fig. 1.6 [21]. This phenomenon is caused by low $n_e$ during the pulse-off. Without power input, electrons are rapidly lost to the chamber wall and through recombination and attachment reactions. Therefore, at the end of the pulse-off, $n_e$ can be as low as $10^8$ cm$^{-3}$. Consequently, 10s to 100s of Watts of power are distributed in a small number of electrons in the early pulse, which efficiently heat the electrons and causes the spike of $T_e$. With high $T_e$, the ionization reaction rate increases, leading to a boost of $n_e$, and sequentially causes the drop of $T_e$ to the quasi-steady state value. Because the spike of
Another unique dynamic of a pulsed ICP is the E-H mode transition during power ramps when $n_e$ changes abruptly. The ICP operates in H-mode when the plasma density is high. In H-mode, the skin depth ($\delta$) of the electromagnetic wave is smaller than the dimension of the reactor. The power is mainly transferred to the plasma through the azimuthal E-field. However, $\delta \propto 1/n_e$. When $n_e$ is low, such as at the beginning of the pulse-on, $\delta$ can be longer than the dimension of the reactor, meaning power cannot be effectively transferred to the plasma through the azimuthal E-field. However, because the coils are high-voltage metals, according to Poisson’s equation, they produce E-field in the axial direction. This E-field propagates into the plasma and accelerate electrons accordingly. The power coupled to the plasma through this method is the capacitively coupled power. When the power is mainly coupled through capacitive coupling, the plasma operates in the E-mode.

The E-mode occurs when $\delta$ extends further into the plasma, and $n_e$ is low, which is most often the condition at the end of the pulse-off. Therefore, in a pulsed plasma, it is often observed that during the power ramp-up, a plasma begins in E-mode. As $n_e$ increases, the plasma experiences an E-H transition and switches to H-mode dominant. The E-H transition has been observed in various studies, and often shows hysteresis behavior [24-27]. The E-to-H and H-to-E transition can occur at different powers. The pressure, dimension of the reactor, and even the power loss in the transmission line, are all believed to affect the E-H transition, which explains the uniqueness of the phenomenon from case to case [28, 29]. An ionization instability and the modulation of the electron density ($n_e$) are often the outcomes of an E-H transition [30]. Because E-H transition results from the re-ignition of the plasma, one approach to avoid it is to use a $T_e$ depends on the low $n_e$ during pulse-off, it is more significant when the PRF is low and when the plasma is sustained in gases with high electron affinity, such as Cl$_2$ [22, 23].
high-low pulsed power scheme [31]. With a low power input during the low-power period, a minimum plasma density is maintained to ensure the plasma always operates in the H-mode. Another method to minimize the effect of E-H transition is to apply a Faraday shield between the planar coil and the dielectric window, which minimizes capacitive power coupling to the plasma [32].

1.2.2 Capacitively Coupled Plasma Source

Another widely used plasma source is the capacitively coupled plasma (CCP). A conceptual diagram and an experimental CCP reactor are shown in Fig. 1.7 [33]. Comparing with an ICP reactor, the CCP reactor typically is shorter in the axial direction. The smaller dimension allows it to operate under higher pressures. In the semiconductor industry, a CCP reactor is often used in the deposition process when the pressure is up to several Torr.

Unlike an ICP, in a CCP reactor, the power is fed into the plasma through the plate electrodes. As the voltage on the electrode varies at radio frequency, so does the E-field created adjacent to the electrode. The oscillating E-field creates an oscillating sheath that heats electrons and sustains the plasma. This electron heating mechanism with a time-varying sheath is called stochastic heating. In a CCP, the plasma potential is often high due to its capacitive power coupling. This high plasma potential creates a high time-averaged E-field pointing from the plasma bulk to the electrode, which accelerates ions to an energy up to 100s eV. These energetic ions bombard the electrode, leading to the emission of electrons. This process is referred to as a secondary electron emission. However, the secondary electron emission is not uniquely caused by ions. A hot neutral species, that is, a neutral particle with high energy that can be created by charge exchange reactions, can also cause secondary electron emissions. Even so, the ion-induced secondary electron emission usually dominates in a CCP. The probability of the secondary electron emission depends on the energy, mass, states of the heavy particles impacting
on the surface, and the material of the electrode. Note that the secondary electron emission is not a simple kinetic energy transfer process.

If a CCP is primarily sustained by the hot electrons from a secondary electron emission, that is, the secondary electrons cause most of the ionization and excitation reactions, the plasma is regarded as in $\gamma$-mode. Otherwise, if the plasma is sustained by the bulk electrons heated by stochastic heating, the plasma is in $\alpha$-mode. The difference between these two modes has been extensively studied [34-37]. A transition from $\alpha$- to $\gamma$-mode CCP with an increasing applied voltage in a Neon discharge is depicted in Fig. 1.8 [34]. Unlike ICP switching between E- and H-mode in a single process, a CCP mostly does not experience a $\gamma$- and $\alpha$-mode transition. The reason partly is that whether the plasma operates in $\gamma$- or $\alpha$-mode highly depends on the local operating conditions, such as pressure and radio frequency, which are commonly constant in a process.

The sheath plays a critical role in the generation of a CCP. Another important parameter closely related to sheath properties is the self-generated DC-bias voltage. This DC-bias voltage is the key parameter to affect the plasma properties that are most important for a semiconductor fabrication process, such as IEADs. Brief descriptions of the sheath on a powered electrode and the generation of the DC-bias are provided as follows.

As mentioned at the beginning of Chapter 1.2, electrons are much easier lost to a surface than ions in an LTP because of electron temperature is much larger than ion temperature ($T_e \gg T_i$). The thin electron-barren layer formed next to the surface with high E-field generates the plasma potential ($V_p$). This layer is effectively a sheath. A sheath also forms on a powered electrode, but the mechanism is more complicated. Since it is connected to the power source the potential of the electrode is oscillating at the radio frequency, which is often several to 10s MHz.
Therefore, when the potential of the electrode is in the positive half, it attracts nearby electrons and causes the sheath to collapse. When the potential of the electrode is in the negative half, it repels electrons and leads to the sheath expansion. As a result, the sheath in a CCP is constantly oscillating. These sheath dynamics are so important that stochastic heating is one of the main electron heating mechanisms in a CCP.

In a CCP reactor, a blocking capacitor is often connected to the electrode to dominate over the effects of any stray impedance. Upon this capacitor, a DC-bias is generated. The DC-bias is produced due to the geometrical asymmetry, that the surface area of the grounded surface ($A_{\text{ground}}$) is unequal to the surface area of the power surface ($A_{\text{power}}$). This asymmetry results in current inconsistency in the reactor as the current magnitude will be larger on the surface with larger area. Therefore, a DC-bias is built up on the blocking capacitor to maintain the current consistency. In most LTP reactors, $A_{\text{ground}} > A_{\text{power}}$, which produces a negative DC-bias ($-V_{\text{bias}}$) on the powered electrode. With this DC-bias, the superpositioned voltage on the electrode is shifted by the amount $-V_{\text{bias}}$, and the time when the RF potential on the electrode exceeds the floating plasma potential is shortened, as shown in Fig. 1.9. When a DC-bias is generated on the substrate, it is one of the most important parameters that affect the ion energy because ions only react to low-frequency or continuous wave (CW) voltages due to their heavy masses.

One of the shortcomings of the CCP is that most plasma properties are heavily coupled. For example, in an ICP, the plasma density and the ion energy to the wafer can be independently controlled. This disassociation is caused by the negligible heating of electrons by the thin sheath above the substrate. In a CCP, varying the operating conditions often result in the changes of many plasma parameters. In some cases, increasing the power leads to the increase of plasma density, but also causes high ion fluxes to the substrate. In the deposition process, a high plasma
density is desired because it leads to high deposition rates. However, high ion flux can lead to
damage of the deposited film and should be avoided. Such a dilemma is common when using a
conventional single-frequency CCP (SF-CCP). One approach to decoupling the plasma
parameters is to use a dual- or multi-frequency CCP [38-44]. As mentioned above, in a CCP,
power can be transferred predominantly to the plasma electrons through stochastic heating. If so,
the electron power transfer efficiency is proportional to the radio frequency. Therefore, input
power with a high-frequency (10s MHz) affects the heating of electrons more than at low-
frequency (several MHz). At the same time, heavy particles, such as most ions, can barely
follow the fast-changing E-field but will respond well to a low-frequency signal. Therefore,
theoretically, by applying dual-frequency power, the plasma density and ion fluxes and the IEAD
can be independently controlled to some degree. Ideally, high-frequency power is used to
control the plasma density while low-frequency power is used to control the IEAD to the wafer.
Even so, some level of coupling still occurs. Secondary electron emission, which are
proportional to the ion energy and flux, affects the electron density if the plasma and operate in
\( \gamma \)-mode. In these cases, the low-frequency affects the plasma density by influencing ion fluxes,
even though two frequencies are applied [45]. Following this process, multi-frequency power
sources are implemented to have more control options in a CCP-involved process [46, 47].

1.3 Plasma Enhanced Atomic Layer Deposition of Silicon Dioxide

Some sort of dielectric material is one of the most prevalent materials in semiconductor
fabrication. As the complexity of semiconductor devices escalates, the requirements on the
dielectric material deposition become more stringent including high conformality, a low level of
contamination, high deposition rates, and low wet etch rates (WER) of the film [48, 49]. Atomic
layer deposition (ALD) technology for the deposition of many dielectric layers has improved in
the past decades [50-54]. A schematic of the ALD process is shown in Fig. 1.10 [50]. An ALD process often involves two steps, and each step deposits a portion of the desired material on the target surface. Typically, a monolayer of the chemical compound is deposited at the end of each cycle. This ALD process is called the AB binary reaction sequence. A successful ALD strictly depends on the successful self-limiting of surface reactions on each step. That is to say, deposition saturates once the surface is covered with one layer of the target material and self-limitedly prevents any build-up, ensuring nanometer scale control and is the key factor in ALD.

Plasma enhanced atomic layer deposition (PE-ALD) has become more important in the past few years and particularly involves the use of LTP. In fact, one of the most significant advantages of the PE-ALD is its low deposition temperature requirement. The ions in the LTP can activate the surface by transferring kinetic energy to the surface particles during the bombardment. Also, the reactive species in LTP often have a lower energy threshold for their surface reactions. Therefore, less thermal energy is needed in a PE-ALD process. The deposition temperature can be decreased from 100s to 100 or even 10s˚C for some processes [55-57]. Another advantage is that this decrease of deposition temperature broadens the choices of material available for semiconductor fabrication. Materials that break down under high temperature become usable if PE-ALD replaces thermal depositions.

Silicon dioxide (SiO₂) is a material frequently used in semiconductor devices. SiO₂ film deposition is common and requires precise control as the size of the feature decreases. In a SiO₂ PE-ALD process, the target surface is first dosed with the silicon precursor and then is exposed to oxidant-containing plasma. Depending on the choice of silicon precursor, and the plasma operating conditions, the plasma exposure time can vary from 100s ms to 10 s [58-60]. The rule of thumb is that the plasma exposure time is long enough for the oxidant to oxidize the surface,
but not so long as to induce significant ion bombardment that damages the film. The variable requirements of SiO₂ film quality, and various plasma operating conditions cause this order of magnitudes difference of plasma exposure time for particular applications. Note that oxygen plasma is mainly used as the oxidant agent in most SiO₂ PE-ALD processes.

One’s choice of silicon precursor is another critical factor that affects the PE-ALD process. Irrespective of the popularity of using silane as the precursor for silicon-based material deposition, it is rarely used in an ALD process due to its low adsorption probability [61]. As an alternative, alkyl- or amine-ligand containing silane precursors are commonly used [62-64]. The asymmetrical structures of these species often lead to lower bonding energy between the silicon core and the ligands, thus increases their adsorption probability. One shortcoming of these organic silicon precursors is that if adsorption is incomplete, and the large ligand groups remain on the surface, other sites on the surface can be physically blocked by these ligands [65]. This results in decreases in the growth per cycle (GPC).

1.4 Modeling of Low Temperature Plasmas

Computational investigation is a critical approach to studying the physics of LTPs. It provides insights into LTPs without the need to conduct experiments. Modeling work is more cost-efficient compared with the experiments, and broader parameters of study can be performed. Therefore, computational modeling of LTP is often performed as the first step of reactor design.

There are three kinds of LTPs models: kinetic, hybrid, and fluid [66]. The main differences between these models are the scale and the equations they are built on. Generally speaking, the fluid model is the most time-efficient, and the kinetic model is the most accurate. A hybrid model is a combination of the fluid and kinetic model, thus can lean towards either high efficiency or high fidelity, based on the chosen setup. There is no definitive superior model.
The choice of the model being used should depend on the particular problem that is being addressed.

The fluid model uses macroscopic properties such as densities, mean velocities, and mean energies to describe LTPs. A fluid model is based on the Boltzmann equation. Nearly all of the governing equations of a fluid model, the continuity, momentum, and energy equations, can be derived from the Boltzmann equation. Then the effect of the electromagnetic field on the plasma is gained by coupling these equations with Maxwell’s equation. Because the fluid model is governed by the fluid equations, the number of variables (densities, energies, and velocities) being tracked is a function of the number of species included in the model, which is often 50 or more. As described, a fluid model is computationally light and is proven useful when conducting a quick study on the LTPs. However, information such as electron energy distribution functions (EEDFs) is missing in a fluid model, which may introduce inaccuracy in the results.

In a kinetic model pseudoparticles that are the computational units used to represent groups of particles of various species. The kinetic model is based on first-principles equations, such as the Newton-Lorentz and Maxwell’s equations. Because of this, the kinetic model often provides highly accurate results [67,68]. However, because the time consumed in executing a kinetic model scales with the number of pseudoparticles used, a kinetic model is often computationally expensive. In most scenarios, only the electrons and ions can be tracked using pseudoparticles, while the neutral species are treated as background gas to save computational time. Another method for accelerating a kinetic model is to apply a high-speed computational unit, such as a graphic processing unit (GPU), for modeling. In any case, it is advantageous to
use the kinetic model when studying plasma with non-Maxwellian EEDFs, statistical properties such as the EEDFs are captured.

The hybrid model is the combination of the fluid and kinetic models. It combines sections that solve the plasma properties in the macroscopic scale as in a fluid approach as well as sections tracking the plasma properties using pseudoparticles as in a kinetic model [69]. A full fluid model provides the quickest result when studying the quasi-steady state of an LTP, however, if EEDFs are the subject of interest, electrons can be treated using the Monte Carlo approach, while ion properties are solved using fluid equations. If ion energy and angular distributions (IEADs) are the key factors that need to be logged, ions can be treated as pseudoparticles. The hybrid model provides high flexibility between accuracy and efficiency and can be customized to a specific task.

Because in a hybrid model both the macro- and micro-scale physics are tracked, it is difficult to choose the proper time step [70]. The time step requirements can vary by orders of magnitude. Microscale physics, such as the oscillation of the E-field at radio frequency occurs at a time scale smaller than 1 ns. On the other hand, to capture some phenomena that occur at the reactor scale (e.g., gas flow), several seconds are needed. This issue is often addressed in a hybrid model by dividing the calculation into different modules. Each module has its own time step for resolving the natural behavior of the corresponding physics, with parameters updated and transferred between the modules in a time-slicing fashion. That is, the parameters are updated hierarchically until the system reaches the quasi-steady state.

1.5 Feature Profile Modeling

The frontline of material processing using LTPs is the plasma-material interface. LTPs provide reactive particles to modify both the chemical (e.g., surface components) and physical
(e.g., topology) properties of the surface material. The products of the surface reactions are released into the plasma, causing modification of the plasma properties. The interaction between LTPs and the material is called a plasma surface interaction (PSI). Modeling the PSI offers physics insight, and provides valuable information for the subsequent process optimization.

There are three major approaches to the PSI modeling: ab initio modeling, molecular dynamic (MD) modeling, and kinetic Monte Carlo (KMC) modeling [71]. The ab initio model is based on quantum mechanics, and uses the densities functional theory (DFT) to calculate the particle potentials. Therefore, this model generally provides the result with the highest accuracy [72]. However, it is challenging to apply the ab initio model on the entire feature with a scale of 1,000s nanometers. The ab initio model is mainly used to study the particle surface reaction without considering the topology of the surface. The bulk surface material defined in an ab initio model often contains up to 100s atoms.

In a molecular dynamic model, unlike the ab initio model, the potentials of the particles are not solved from the time-independent Schrödinger’s equation, but is part of the input. The solution of an MD model therefore depends on the choice of this potential. However, errors can be induced if the potential is chosen improperly. Even so, the MD model is computationally much lighter than the ab initio model due to its use of this semi-empirical potential function. Therefore, the MD model is frequently used to explore the atomic scale reaction mechanisms of a PSI [73, 74]. Despite the fact that an MD model is computationally lighter than an ab initio model, it still is almost impossible to apply the MD model to a large simulation domain that covers the whole structure at, say, 100s nanometer scale.

To have the entire target structure covered in a simulation, kinetic Monte Carlo models are often developed. The prerequisite for using a KMC model is the inclusion of experimental
data or the simulation results from ab initio or MD models. The KMC model takes those surface reaction rates as a known parameter while focusing on the topological development of the feature. Three methods can be used to represent the surface in a KMC model: the string method, level set method, and the cell-based method [75]. The string method uses the straight-line connected nodes (segments) to represent the surface. The movement of the surface is captured by moving segments along with the nodes. Because the slope of the segments remains constant during the simulation, the string method is most suitable for modeling an isotropic procedure such as wet chemical etching. In the level set method, the surface is given an initial profile. This profile is updated by applying a time- and space-dependent force on it. This force is then calculated based on the local conditions on each node. If compared with the string method, the level set method can much more easily capture the anisotropic properties of a process. But updating the driving force is computationally intensive, which is a difficult trade off to make for many applications that require high efficiency.

A cell-based method defines each mesh cell as associated material and the gas phase particles are also tracked. Any surface reactions are addressed as Monte Carlo collisions when gas phase particles hit the solid material. The cell-based method directly tracks the feature profile and the topological evolvement. By choosing the proper cell size, the computational time can be effectively reduced. However, this is proportional to the number of Monte Carlo particles involved. If many particles are tracked, the cell-based method can also be computationally heavy.

1.6 Summary

To continue to pursue Moore’s law, the semiconductor industry is now targeting sub-10 nm scale manufacturing techniques. Plasma-involved processes continue to play an important
role in fulfilling this task, requiring a highly uniform and stable plasma. Applying a multi-frequency power source and modifying the power profile are two widely used techniques for achieving these goals. Properties of a triple-frequency capacitively coupled plasma and an inductively coupled plasma sustained in low-high pulsed power are discussed in this dissertation. Triple-frequency power offers more control options to modify plasma properties, while a low-high pulsed power mitigates the abrupt changes of plasma properties during power transitions.

To enable a fabrication process to benefit from these unique power formats, it is essential to have optimal power delivery to the plasma. The majority of the power delivered to such systems is at radio frequencies, delivered to the plasma reactor by a transmission line. One needs to minimize the power reflection by the reactor so that the power delivered to the plasma has the desired profile. Since the power delivery efficiency is a function of the impedances of the load represented by the reactor, impedance matching circuitry is often used. Using pulsed power, the impedance of the reactor changes significantly, making matching difficult. Set-point matching uses a fixed impedance matching network (IMN) between the power supply and the plasma reactor with the goal of having a matched load at some point during the pulsed cycle. Frequency tuning employs a power supply with having a variable frequency for dynamic impedance matching. The effects of both impedance matching techniques on pulsed ICPs are discussed in this dissertation.

Finally, the ultimate goal for a plasma processing in semiconductor fabrication is to manufacture nm-scale features. In this regard, the use of plasma enhanced atomic layer deposition (PE-ALD) for SiO₂ films is discussed. The impact of macroscopic parameters such as input power and pressure in the reactor on the film deposition are discussed.
To summarize, in this dissertation, both reactor and feature scale simulation results are studied to investigate the effects of operating conditions on an LTP, the proper IMNs setup in a pulsed plasma, and the possible optimization methods of a SiO$_2$ PE-ALD process.

In Chapter 2, the algorithms used for the models applied in this dissertation are described. A 2-dimensional model, the Hybrid Plasma Equipment Model (HPEM), is used for the reactor scale plasma simulation and the basic structure of the HPEM is discussed. The calculation of the IMNs with consideration of power reflection is also described. A 3-dimensional model, the Monte Carlo Feature Profile Model (MCFPM), was used in the investigation of PE-ALD of SiO$_2$ films and a description of this model is also provided in Chapter 2.

In Chapter 3, the transient plasma properties of an ICP driven by high-low pulsed power are discussed. The plasma is sustained in an Ar/Cl$_2$ gas mixture, and the pressure is 10s mTorr. The use of Cl$_2$ enables unique chemistry during the low-power period due to its high electron affinity. The high electron attachment rate to Cl$_2$ leads to low electron density ($n_e$) in the late low-power period. This low $n_e$ causes a spike in the electron temperature ($T_e$) shortly after low-high power transition due to the transitional boost of energy per particle. This overshoot of $T_e$ ends promptly as $n_e$ increases and approaches the quasi-steady state. However, plasma transit states differ from various positions. For example, spikes of $T_e$ disappear 10 cm away from the power source, near the wafer. But the response time of the plasma to the power transition is then longer due to transport delay. Elongating the power ramp and applying higher “low power” can stabilize the plasma near the wafer at the cost of having less low-power chemistry.

In Chapter 4, the power transition from a power source to the plasma is discussed with an impedance matching network (IMN) included. The plasma is an ICP sustained with Ar/Cl$_2$ gas mixture at a pressure of 10s mTorr using pulsed power. At the beginning of the pulse, when the
plasma density is low, the power is mainly capacitively coupled to the plasma, and the plasma is in E-mode. As the $n_e$ increases with the power, plasma switches from E- to H-mode, meaning the power is predominantly inductively coupled to the plasma and no abrupt change of $n_e$ is captured during the mode transition in this work. The IMN used in this work is a set-point matching circuit. That is, the IMN is fixed during the pulsing period. Picking the match point appears to have a significant impact on power delivery. For example, matching the early pulse suppresses the E-mode but causes consistent power reflection through the pulse-on. On the contrary, matching the late pulse increases the averaged power delivery efficiency but emphasizes E-mode in the early pulse.

In Chapter 5, results from a computational investigation regarding power transition with impedance matching network (IMN) and frequency tuning are discussed. This investigation is conducted on a pure Ar plasma sustained in a 5 kHz pulsed power. The reactor used is the ICP reactor ICAROS, designed in North Carolina State University, Dr. Shannon’s group. The values of the circuit components used in the IMN are first analytically calculated to match the impedance of the load to the impedance of the power supply. The IMN is then fixed according to this result to match the impedance at certain point in a pulse referred to as match point. The use of only the IMN for impedance match is referred to as set-point matching. A real-time impedance matching technique, frequency tuning, is applied along with set-point matching to further optimize the impedance matching through the entire pulse and provides optimal power transition. Impedance matching in early pulse is found vital for the plasma ignition, which is difficult if there is severe impedance mismatch in the early stage of a pulse. Frequency tuning becomes necessary when plasma operates away from the match point for long periods of time.

In Chapter 6, the results of a computational investigation on a triple-frequency CCP (TF-
CCP) sustained in Ar/CF$_4$/O$_2$ gas mixture are discussed. The pressure being 10s mTorr, and the gap length between the electrode is 2-5 cm. Three power sources are connected to two electrodes: 80 MHz 500 W on the top electrode, and 10 MHz and 5 MHz power on the bottom electrode with 400 W on each frequency. All the power sources are controlled independently. The 80 MHz power has been found to predominantly control the plasma density. Increasing the power from 80 MHz power source is much more effective in raising the $n_e$ than increasing power on low frequencies. A more lifted high-energy tail of the electron energy distribution function (EEDF) can be observed near the top electrode than near the substrate, even though the power is lower from the 80 MHz power source compared with the total power from the low frequencies. Increasing high frequency signifies the stochastic heating, and this weakens the local electrostatic effect on the edge of the wafer, and improves the plasma uniformity.

In Chapter 7, results are discussed from an integrated investigation from both reactor- and feature-scale simulations on SiO$_2$ atomic layer deposition. The deposition is performed in a CCP reactor and the process consists of two steps: precursor dosing, and plasma exposure. An Ar/O$_2$ plasma is used during the plasma exposure to oxidizing the precursors adsorbed on the surface during precursor dosing. The pressure in the reactor is several Torr in both steps. And the power of 100s W is used to generate the oxygen plasma. Varying pressure has been found to be more effective in affecting SiO$_2$ film properties than varying power. High pressure creates a collisional sheath, therefore reducing ion bombardment damage on the film. When depositing in a trench or a via structure, conduction limit hinders the oxidation in the bottom of the feature, causing slow film growth rate and high vacancy concentration. Because compared to the other unstable oxidants (e.g., excited state O$_2$ and O$_3$), O is less subjected to conduction limit. Therefore, it predominantly determines the oxidation process in the bottom of a high AR feature.
In Chapter 8, a summary of the discussed research work is given. Some interesting future work is suggested.
1.7 Figures

Fig. 1.1 Plasma categorized by electron density \( n_e \) and electron temperature \( T_e \). The low-temperature plasma is shadowed. Reproduced from Ref. [4].
Fig. 1.2 Diagram of the sheath with potential $\Phi_W$. Ion density ($n_i$) is higher than electron density ($n_e$) in the sheath due to the high electron temperature ($T_e$) and small electron mass ($m_e$). $v_i$ is ion velocity on the sheath boundary. Reproduced from Ref. [10].
Fig. 1.3 Potential energy curves of oxygen molecule and ions. Reproduced from Ref. [11].
Fig. 1.4 Electron impact $O_2$ cross section. $Q_m$ is momentum transfer, $Q_a$ is attachment, $Q_p$ is ion-pair formation, and $Q_i$ is ionization. vib. exc. represents vibrational excitation states. Reproduced from Ref. [12].
Fig. 1.5 a) An ICP reactor setup with planar coil configuration and b) one of the early ICP reactor designed at IBM. Reproduced from Ref. [13].
Fig. 1.6 Spike of the radiation temperature at the beginning of the pulse, representing an electron temperature ($T_e$) spike as high as 90-100 eV. Ar, 300 W, 20 mTorr, PRF = 100 kHz, DC = 50%. Reproduced from Ref. [21].
Fig. 1.7 Schematic of a) heating mechanisms in a CCP reactor and b) a CCP reactor setup in an experiment. Reproduced from Ref. [33].
Fig. 1.8 Spatio-temporal evolutions of the electron impact excitation rate from the ground state into Ne2p1 state within two RF cycles at different RF voltages for two driving frequencies, i.e. 8 MHz (first row) and 12 MHz (second row), at 50 Pa. A transition to γ-mode appears in (a3). Reproduced from Ref. [34].
Fig. 1.9 The effect of DC-bias on the substrate potential and plasma potential in two RF periods ($\tau_{RF}$).
Fig. 1.10 Schematic of the AB binary sequence of ALD. The self-limiting ensures a maximum deposition rate of one mono-layer per cycle. Reproduced from Ref. [50].
1.8 References

43. B. B. Sahu, and J. G. Han, Physics of Plasmas 23, 053514 (2016).
Chapter 2: Description of the Models

The modeling of Low Temperature Plasmas provides insight into the minute physics that occurs during material processing. This makes a physics-based plasma model an essential tool in the early stage of reactor and process design. In this thesis, two plasma models were used: the Hybrid Plasma Equipment Model (HPEM), and the Monte Carlo Feature Profile Model (MCFPM). A detailed description of the HPEM is provided in this chapter, followed by a brief overview of the MCFPM.

2.1 Hybrid Plasma Equipment Model

The HPEM hybrid model contains several modules [1]. Each module addresses one area of the LTP physics hierarchically interacting with other modules. The modules that are used for the simulation in this thesis are Electromagnetics Module (EMM), Electron Energy Transport Module (EETM), Fluid Kinetics Poisson Module (FKPM), and Plasma Chemistry Monte Carlo Module (PCMCM). A schematic of the HPEM is given in Fig. 2.1. The simulation starts with an estimation of the densities of various species and their distribution. This provides the initial conductivity of the plasma to the EMM.

The EMM module calculates the electromagnetic fields $\vec{E}(\vec{r}, \phi)$ and $\vec{B}(\vec{r}, \phi)$ produced by antenna in materials and the plasma, where $\vec{r}$ is the spatial dependency and $\phi$ is the time dependency. A circuit model is used to represent the impedance matching network. This circuit model can capture various properties such as power reflection. The EM field calculated in the
EMM is transferred to the Electron Energy Transport Module (EETM). In the EETM, the behavior of the electrons is attained kinetically using a Monte Carlo simulation. The electron impact reaction rates $k(\vec{r},\varphi)$ and the electron impact source terms $S(\vec{r},\varphi)$ are then calculated and transferred to the Fluid Kinetics Poisson Module (FKPM). Within the FKPM, the densities $N(\vec{r})$, velocities $\vec{v}(\vec{r})$, and the temperatures $T(\vec{r})$ of the heavy particles are produced. The heavy particle reaction rate coefficients and source functions are also generated in this module. With the information for charge densities in the plasma and on the materials, Poisson’s equation is solved in the FKPM, and this provides the electrostatic electric field $\vec{E}_s(\vec{r},\varphi)$ and the plasma potential $\Phi_p(\vec{r},\varphi)$. The electrostatic E-field and ionization sources are passed to the Plasma Chemistry Monte Carlo Module (PCMCM), where the pseudoparticles of ions and neutrals are launched and tracked using the Monte Carlo approach. The energy and angular distributions (EADs) of the heavy particles and electrons are logged on certain surfaces in the PCMCM.

In the HPEM, modules are coupled using a time-slicing technique. When performing a simulation, the evolution of the plasma is captured by executing modules with a unit of a global iteration. During each global iteration, modules are called and variables are updated with different time steps. For example, in a $\mu$s global iteration, FKPM is operated once, with several updates of electron impact reaction rates $k(\vec{r},\varphi)$ from EETM. This technique enables simulation in longer time scale without sacrificing much accuracy.

2.1.1 Electromagnetics Module (EMM)

The inductively coupled electromagnetic field is calculated in the EMM using the frequency-domain Maxwell’s equations. The time-varying electric field $\vec{E}$ is obtained by solving the following wave equation using the finite difference method
\[-\nabla \left( \frac{1}{\mu} \nabla \cdot \vec{E} \right) + \nabla \cdot \left( \frac{1}{\mu} \nabla \vec{E} \right) = \omega^2 \varepsilon^2 \vec{E} + i\omega \left( \vec{j}_{\text{coil}} + \vec{\sigma} \cdot \vec{E} \right), \quad (2.1)\]

where \( \mu \) is the permeability, \( \varepsilon \) is the permittivity, \( \omega \) is the radian frequency of the applied power, and \( i \) is the imaginary unit. The last term \( \vec{j}_{\text{coil}} \) represents the conduction current in the coil and \( \vec{\sigma} \cdot \vec{E} \) is the conduction current from the plasma. The \( \vec{\sigma} \) is the conductivity tensor with the form:

\[
\vec{\sigma} = \frac{\sigma_0}{(\alpha^2 + |\vec{B}|^2)} \begin{pmatrix}
\alpha^2 B_r^2 & \alpha B_z + B_r B_\theta & -\alpha B_\theta + B_r B_z \\
-\alpha B_z + B_r B_\theta & \alpha^2 + B_\theta^2 & \alpha B_r + B_\theta B_z \\
\alpha B_\theta + B_r B_z & -\alpha B_z + B_\theta B_z & \alpha^2 + B_z^2
\end{pmatrix}, \quad (2.2)
\]

where

\[
\sigma_0 = \frac{e^2 n_e}{m_e} \frac{1}{\nu_m + i\omega}, \quad (2.3)
\]

\[
\alpha = \frac{m_e}{e} (\nu_m + i\omega), \quad (2.4)
\]

\( B \) is the static magnetic field, \( n_e \) is the electron density, \( m_e \) is the electron mass, \( e \) is the elementary charge, and \( \nu_m \) is the electron momentum collision frequency [2]. For a simulation of the inductively coupled plasma, the electromagnetic field is calculated in the EMM as a function of position and phase in an RF period. Because no static magnetic field is used regarding the work in this thesis, the conductivity is isotropic and equals \( \sigma_0 \). Using the electric field calculated by Eq. (2.1), the magnetic field is derived as:

\[
\vec{B} = (i / \omega) \nabla \times \vec{E}, \quad (2.5)
\]

Assuming the collisional power deposition through the azimuthal electric field, this electric field from Eq. (2.1) is then normalized to provide desired power through \( \vec{j}_e \cdot \vec{E} \).

The EMM also contains a circuit model with which the power supply is interfaced to the plasma reactor. A schematic of the circuit representation of the impedance matching network,
antenna, reactor, and plasma is in Fig. 2.2. The antenna is modeled as a discretized transmission line. The geometry of the antenna determines its inductance. This inductance depends on the overall diameter, height, number of turns, and the thickness of the wire. It is divided into 100 discrete series segments, each of which has an appropriate fraction of the total resistance of the antenna. Each segment contains a series impedance, \( Z_{Sn} \), consisting of the resistance \( R_{An} \) and physical inductance \( L_{An} \) of the antenna. The impedance \( Z_{Sn} \) also contains transformed values of resistance and inductance from the plasma [3]. The transformed impedance of the plasma, \( Z_T \), is [4]

\[
Z_T = \left( \frac{\omega M}{Z_p} \right)^2 \left( i\omega L_p + R_p \left( 1 - i \frac{\omega}{V_m} \right) \right), \quad M^2 = k_A L_A L_p, \tag{2.6}
\]

\[
Z_p^2 = \left( \omega L_p + \frac{\omega}{V_m} R_p \right)^2 + R_p^2, \tag{2.7}
\]

where \( R_p \) is the plasma resistance, \( k_A \) is the antenna transformer coupling coefficient, \( L_A \) and \( L_p \) are the inductance of the coil and plasma, respectively. The effective plasma resistance \( R_p \) was given by

\[
R_p = \frac{\int \vec{j}_\theta \cdot \vec{E}_\theta \, d^3r}{\left( \int \vec{j}_\theta \cdot d\vec{A} \right)^2}, \tag{2.8}
\]

The numerator is the volume integrated inductively coupled power, and the denominator is the area integrated azimuthal current. The consequences of the skin depth and the nonlinearities in the plasma are accounted for by including the spatial dependence and phase differences between the current and the electric field.

From each discrete segment of the transmission line representation of the antenna, an impedance \( Z_{Cn} \) is implemented to represent the capacitance and series resistance directed to the
ground. This impedance is the capacitive coupling from the antenna. The reactance of $Z_{Cn}$ consists dominantly of the series capacitances of the air gap between the antenna and dielectric window of the ICP reactor, the window, and the plasma sheath at the surface of the window. The resistance of $Z_{Cn}$ results from the capacitively coupled conduction current flowing to the ground. The impedance of each element $Z_k$ is calculated during the execution of FKPM. A brief description of the calculation of $Z_k$ is provided as follows.

For each turn $k$ of the antenna, the voltage amplitude $V_{ok}$ and phase $\phi_{vk}$ are determined from the circuit model. The voltage $V_k(t) = \text{Re}(V_{ok} \exp(i(\omega t + \phi_{vk}))) = V_{ok} \cos(\omega t + \phi_{vk})$ is used as the boundary condition for solving Poisson’s equation. The displacement current flowing out of each turn of the coil is logged as

$$I_k(t) = \int \varepsilon_0 \frac{d(\vec{E}(t) \cdot \hat{n})}{dt} dA,$$

(2.9)

where $\hat{n}$ is the normal vector of the coil surface, $\vec{E}(t)$ is the time-varying electric field obtained by solving Poisson’s equation, and $A$ is the surface area of the coil. The current $I_k(t)$ is then Fourier transformed to provide frequency-domain current with an amplitude $I_{ok}$ and phase $\phi_{ik}$. The impedance is then

$$Z_k = \frac{V_{ok}}{I_{ok}} \exp(i(\phi_{vk} - \phi_{ik})), \quad (2.10)$$

For pure H-mode, nearly all the power is coupled to the plasma inductively. The phase difference between the voltage and current, $(\phi_{vk} - \phi_{ik})$, is approaching $90^\circ$. For E-mode, when a finite amount of power is capacitively coupled to the plasma, the phase difference is $(\phi_{vk} - \phi_{ik}) \in (-90^\circ, 0^\circ)$. The value of $Z_k$ is distributed to the transmission line segments in the
circuit model, meaning each $Z_{Cn}$ is a fraction of the total impedance $Z_k$. The cycle-averaged capacitively coupled power is

$$P_c = \sum_k P_k = \sum_k \frac{1}{\tau_{rf}} \int \int \epsilon_0 V_k(t) \frac{d(\vec{E}(t) \cdot \hat{n})}{dt} dA dt,$$  \hspace{1cm} (2.11)

where $\tau_{rf}$ is the RF period. The circuit model also produces $P_A$ (resistive losses in the antenna coils), $P_M$ (resistive losses in the matchbox) and $Z_M$, the input impedance to the impedance matching network. The power dissipated by the inductive power coupling is

$$P_l = \int \sigma(\vec{r}) E_{\theta}^2(\vec{r}) d^3 r,$$ \hspace{1cm} (2.12)

With $Z_M$, the electric field reflection coefficient is calculated as

$$\Gamma = \frac{Z_M - Z_0}{Z_M + Z_0},$$ \hspace{1cm} (2.13)

The total power deposited in the system is

$$P_T = \left(1 - |\Gamma|^2\right) P_S = P_M + P_A + P_l + P_c,$$ \hspace{1cm} (2.14)

where $P_A$ is the resistive power dissipated in the antenna, and $P_M$ is the resistive power dissipated in the impedance matching network. Recognizing that $E_{\theta}$ scales linearly with the antenna current and $P_l$ scales with $E_{\theta}^2$, the current flowing into the impedance matching network is renormalized so that Eq. (2.14) is satisfied. With the renormalized values, the circuit and wave-equations are again solved. This process is iterated several thousand times till convergence. The final values of $V_k$, $E_{\theta}$ and $\phi$ are returned to the FKPM for the next iteration for time integration of the fluid equations for densities, momenta, and energy.

For a perfect match of the $P_S$, $Z_M = Z_0$. In the HPEM, matching is produced by adjusting $C_P$ and $C_S$ such that $\text{Re}(Z_M) = Z_0$ and $\text{Im}(Z_M) = 0$. Typically, $Z_0$ is 50 Ω based on the industrial
standard. From a procedural perspective, $C_P$ and $C_S$ can be repeatedly tested to minimize the value of $\Gamma$. However, one can analytically compute $Z_M$ based on the circuit values and plasma conditions, and solve for the values of $C_P$ and $C_S$ that produce the match. The solutions of $C_P$ and $C_S$ depend on the design of the IMN, details for solving $C_P$ and $C_S$ are provided in the Appendix.

Finding the impedance match can be accomplished through adjusting the matching circuit though it can also be done by varying the operating RF frequency. In the HPEM, this approach is accessible through fixing the IMN and performing a frequency sweep. The impedance of the load is then updated and the reflection coefficient is calculated for each frequency. The frequency that provides the smallest reflection is then chosen as the new operating frequency until the fractional variation of the load impedance is higher than the user defined threshold. Finally, the frequency sweep will be performed again and the operating frequency will be updated.

2.1.2 Electron Energy Transport Module (EETM)

The EETM calculates the rate coefficient from electron impact reactions $k(\vec{r},\varphi)$ and corresponding source function $S(\vec{r},\varphi)$ by using the electromagnetic fields $\vec{E}(\vec{r},\varphi)$, $\vec{B}(\vec{r},\varphi)$ provided by EMM, and the electrostatic electric field $\vec{E}_s(\vec{r},\varphi)$, as well as heavy particle densities $N(\vec{r})$ provided by the FKPM. The EETM then obtains the electron properties by using the electron Monte Carlo Simulation (eMCS) to compute electron energy distribution functions (EEDFs). Another method for attaining the electron properties is by solving the electron energy equation, which is performed in the FKPM. In any case, secondary electron emission caused by
heavy particle bombardments on surfaces exposed to the plasma are always addressed using the eMCS.

The eMCS is a fully kinetic approach to resolving the electron dynamics. The pseudoparticles representing the electrons are initially released with random velocities following a Maxwellian distribution. The positions chosen for the electrons are weighted by the electron densities in different parts of the reactor. The governing equation for the electron dynamics is the Lorentz equation

\[
\frac{d\vec{v}_e}{dt} = \frac{e}{m_e} (\vec{E} + \vec{v}_e \times \vec{B}),
\]

where \( \vec{v}_e \) is the electron velocity and \( \vec{E} \) and \( \vec{B} \) are the total local electric and magnetic fields (electromagnetic and static).

The energy grid technique is applied to collect collision frequencies and the statics of the electrons. The electron energy is divided into several uneven ranges, e.g., 0-5, 5-10, 10-50, 50-300, and 300-1000 eV bearing in mind that bulk electrons typically have energy of less than 50 eV. The high energy range is used to capture the secondary electrons. These electrons are accelerated by the sheath, depending on the bias voltage and plasma potential, secondary electrons can have high energy up to several keV. Each energy section is further divided into energy bins and a collision frequency is calculated for each energy bin

\[
\nu_i = \left( \frac{3e_i}{m_e} \right)^{1/2} \sum_{j,k} \sigma_{ijk} N_j ,
\]

where \( e_i \) is the average energy in bin \( i \), \( \sigma_{ijk} \) is the cross-section of the species \( j \) of process \( k \) at energy \( e_i \), and \( N_j \) is the density of the species \( j \). The concept of a null collision is applied in the eMCS to optimize the calculation of collision frequencies. A null collision frequency is defined
as the difference between the maximum collision rate and the real collision frequency. Because
the maximum collision rate is a known parameter, including the null collision makes the total
collision frequency independent of the electron velocity. Hence, the time intervals between
collisions are governed merely by the probability law \( \Delta t = -\ln(r) / \nu_{mj} \) \[5\]. The \( r \) is a random
number within \((0,1)\), and \( \nu_{mj} \) is the maximum collision frequency within an energy bin \( j \). The
types of the collisions are determined by comparing the series of random numbers with the
normalized collision frequencies. If the collision is found to be a null collision, no properties of
the electrons are changed. Otherwise, the electron properties are updated according to the
reactions that occur \[6\].

In the eMCS, the EEDFs are recorded to each energy bin \( i \) and spatial bin \( l \)

\[
F_{il} = \sum_j w_j \delta\left(\epsilon_i \pm \frac{1}{2} \Delta \epsilon_i \right) - \epsilon_i \delta\left(\vec{r}_i \pm \Delta \vec{r} \right),
\]

(2.17)

The \( w_j \) involves the weighting of particles calculated based on the number of particles each
pseudoparticle represents, the time step for updating particle trajectory, and spatial weighting.
The EEDF \( f_e(\epsilon, \vec{r}) \) is obtained at each spatial bin at the end of the eMCS by using

\[
\sum_i F_{ij} \Delta \epsilon_i = \sum_i f_e(\epsilon_i, \vec{r}) \epsilon_i^{1/2} \Delta \epsilon_i = 1,
\]

(2.18)

Secondary electrons are always tracked in the method described above. Unlike bulk
electrons, the secondary electrons are released perpendicular to the surface. They are no longer
tracked when they strike a surface or when their energy is reduced to a value lower than the
lowest excitation threshold. In the latter case, these secondary electrons are placed into a source
function for bulk electrons.

The eMCS can provide highly accurate electron properties, especially when a large
number of pseudoparticles are used. However, it can be computationally expensive. To ease the
computational burden, the application programming interface (API) OpenMP is used to enable parallel computing. The OpenMP is a multi-threading parallel computational platform implementing the fork-join model, as shown in Fig. 2.3 [7]. At the start of the parallel section, the master thread distributes the job to a number of slave threads. Each slave thread performs a fraction of the work and returns its results to the master thread at the end of parallel computation. Because multiple threads are working simultaneously, the parallel computation can provide up to 10 times in the speed of some simplified examples using ten threads.

The subroutines in the eMCS can be categorized into three sections: initialization subroutines (IS), particle trajectories and collisions subroutines (PS), and diagnostic and post-processing subroutines (DPS). In the eMCS, IS is called first to initialize the particle properties, followed by several repeated calls of PS. Then the DPS is called after each call of PS. Note that pseudoparticles representing electrons have no interactions with each other, making it suitable for parallel computing. The eMCS is reconstructed such that the PS is included in one big loop. In this loop, parallel computing is performed. The arrays storing the particle properties are separated by IS into several thread-aware arrays. Each array is then passed to a slave thread. By doing this, the probability of memory-sharing between the threads is significantly reduced. The properties of the pseudoparticles are then updated in the PS in the individual thread. After each PS, in the call of DPS, the thread-aware arrays are reconstructed back to their initial structure. Parallelizing the entire PS rather than each small loop in PS minimizes the computational overhead. Naturally, the speed-up is especially significant when a large number of pseudoparticles are used.

2.1.3 Fluid Kinetics Poisson Module (FKPM)

The heavy particle densities, electron energy equation and Poisson’s equation are resolved in the FKPM. As an alternative to the eMCS, in the FKPM, the electron energy
distribution \( f_e(\epsilon, \vec{r}, \phi) \) is obtained through solving the Boltzmann equation using the two-term approximation.

\[
\frac{\partial f_e}{\partial t} = -\nabla \cdot f_e - \frac{e}{m_e} \left( \vec{E} + \vec{v} \times \vec{B} \right) \cdot \nabla_v f_e + \left( \frac{\partial f_e}{\partial t} \right)_{\text{collisions}},
\]  

(2.19)

In Eq. (2.19), \( \nabla \) is the spatial gradient, and \( \nabla_v \) is the gradient in the velocity space. The last term on the right-hand side of the equation includes all the collisional terms. \( f_e \) from Eq. (2.19) are compute for a wide range of the normalized electric field \( (E/N) \), where \( E \) is the local electric field, and \( N \) is the gas density. A table of rate coefficients versus \( T_e \) is then created. This table is interpolated during execution of the code. Consequently, the electron temperature \( (T_e) \) is obtained using the equation

\[
\frac{\partial \left( \frac{3}{2} n_e k_B T_e \right)}{\partial t} = \nabla \kappa \nabla T_e + \nabla \cdot (\vec{\phi}_e T_e) = P_e,
\]  

(2.20)

where \( k_B \) is the Boltzmann constant, \( \kappa \) is the thermal conductivity and \( \vec{\phi}_e \) is the electron flux. The total power shunted to electrons is

\[
P_e = j_e \cdot \vec{E} + e \vec{\phi}_e \cdot \vec{E},
\]  

(2.21)

There are two methods to express the electron flux: the simple drift-diffusion, and Scharfetter-Gummel (S-G) expression. The simple drift-diffusion form of the electron flux is

\[
\vec{\phi}_e = e \mu_e n_e \vec{E} - D_e \nabla n_e,
\]  

(2.22)

where \( \mu_e \) is electron mobility, and \( D_e \) is the electron diffusion coefficient. The S-G method is widely used to describe the transport of charged particles in the fluid model [7]. With a S-G expression, the flux between the mesh points \( i \) and \( i+1 \) is

\[
\vec{\phi}_{i+1/2} = \frac{\alpha D \left( n_{i+1} - n_i \exp(\alpha \Delta x) \right)}{1 - \exp(\alpha \Delta x)},
\]  

(2.23)
with

\[ \alpha = -e\bar{\mu}\left(\frac{\Phi_{i+1} - \Phi_i}{\Delta x}\right), \]  

(2.24)

where \( \bar{D} \) is the averaged diffusion coefficient between vertex \( i \) and \( i+1 \), \( \bar{\mu} \) and \( \Delta x \) are the averaged mobility and the length of this interval, and \( \Phi_i \) is the potential on vortex \( i \).

The densities of the heavy particles are attained by solving continuity, momentum, and energy equations. For species \( i \) with a source term \( S_i \)

\[ \frac{\partial N_i}{\partial t} = -\nabla \cdot \bar{\phi}_i + S_i, \]  

(2.25)

\[ \frac{\partial \bar{\phi}_i}{\partial t} = \frac{\partial (N_i \bar{v}_i)}{\partial t} = -\frac{1}{m_i} \nabla (kN_i T_i) - \nabla \cdot (N_i \bar{v}_i \bar{v}_i) + \frac{q_i}{m_i} N_i (\vec{E}_s + \bar{v}_i \times \vec{B}) \]

\[ -\nabla \cdot \bar{\mu}_i - \sum_j \frac{m_j}{m_i + m_j} N_i N_j (\bar{v}_i - \bar{v}_j) w_{ij}, \]  

(2.26)

\[ \frac{\partial N_i \epsilon_i}{\partial t} = -\nabla \cdot \bar{\kappa} \nabla T_i - p_i \nabla \cdot \bar{v}_i - \nabla \cdot (N_i \bar{v}_i \epsilon_i) + q_i \bar{\phi}_i \vec{E} - (\bar{\mu}_i \nabla \cdot \nabla \bar{v}_i) \]

\[ -\sum_{m} k_{mij} N_i N_j \epsilon_i + \sum_{m} k_{mij} N_j N_i \Delta \epsilon_{mij}, \]  

(2.27)

where \( \bar{\phi} \) is the flux, \( N \) is the density, \( \bar{v} \) is the velocity, \( m \) is the mass, \( T \) is the temperature, \( \bar{\mu} \) is the viscosity, \( p \) is the pressure, and \( \epsilon \) is the energy.

Because the charge density directly affects the electrostatic field \( \vec{E}_s \), it is convenient to solve Poisson’s equation in the FKPM along with the update of charged particle densities. In the HPEM, the Poisson’s equation is semiimplicitly solved using linear interpolation of ion charge densities in the time domain

\[ \nabla \cdot [\epsilon \nabla \Phi(t + \Delta t)] = -\rho(t + \Delta t) = -\rho(t) - \Delta t \frac{\partial \rho}{\partial t} \bigg|_{t+\Delta t}, \]  

(2.28)
where $\rho$ is the charge density. Because both the surface of a material and the plasma can hold the spatial charge, $\rho$ is expressed as

$$\rho(t) = \rho_m(t) + \sum_i q_i N_i(t),$$

(2.29)

where the first term is the charge density from the solid material, and the second term is the charge from the plasma. $q_i$ is the charge of ion $i$ and $N_i$ is the ion density. By solving Poisson’s equation semi-implicitly, there is no requirement of time step $\Delta t$ to be smaller than the dielectric relaxation time, which is, on the other hand, required for the explicit method [8]. If Scharfetter-Gummel fluxes are used, the term can be written as

$$\left. \frac{\partial \rho}{\partial t} \right|_{t+\Delta t} = \frac{\partial \rho_m(t')}{\partial t} - q_{e,i} \nabla \cdot \left( \bar{\phi}_e(t) + \frac{\partial \bar{\phi}_i(t)}{\partial \Phi} \left[ \Phi_s(t+\Delta t) - \Phi_s(t) \right] \right)$$

$$- \sum_i q_i \nabla \cdot \left( \bar{\phi}_i(t) + \frac{\Delta t}{2} \frac{\partial \bar{\phi}_i(t)}{\partial t} \right),$$

(2.30)

where $q_{e,i}$ represents the charge of electrons and ions, respectively, $\Phi_s$ is the electrostatic potential. $t'$ means that the charge density is evaluated at the current time step $t$, but the potential is evaluated at the time step $t + \Delta t$.

The Jacobian term $\frac{\partial \bar{\phi}_i}{\partial \Phi}$ from Eq. (2.30) is numerically expressed by applying a small change of the potential, and then divide the corresponding electron flux fluctuation with this potential change. The first two terms of the partial derivative are kept as the value of $\frac{\partial \bar{\phi}_i}{\partial \Phi}$.

Typically, the test variation $\Delta \Phi_{i,j}$ is smaller than 5% of the local potential. The numerical expression of the Jacobian term is
\[
\frac{\partial \Phi_{i,j}}{\partial t} = \frac{\hat{\Phi}_{i,j}(\Phi_{i+1,j} + \Delta \Phi_{i+1,j}) - \hat{\Phi}_{i,j}(\Phi_{i+1,j})}{\Phi_{i+1,j}},
\]
where \(i\) and \(j\) are the coordinates of the mesh in the radial and axial direction. The equations mentioned above are solved using either Successive-Over-Relaxation or direct sparse matrix method [9,10].

The charge density is an essential component of the boundary condition. In the FKPM, the charge density on a surface is collected as the sum of the spatial charge in a dielectric material, the ion and electron fluxes to the surface, the secondary electron emitted from the surface, and the conduction current within the material. The potential on a powered material is the instantaneously applied potential superpositioned with the DC-bias \(V_{dc}\).

\[
\Phi(t + \Delta t) = \Phi_{RF}(t) + V_{dc},
\]
where \(\Phi_{RF}(t)\) is the RF potential at time \(t\). As discussed in the Introduction, the magnitude of \(V_{dc}\) depends on the asymmetry of the reactor. In the HPEM, \(V_{dc}\) is calculated as

\[
V_{dc} = \frac{1}{C} \left[ \sum_i m_i \left( \sum_j \hat{\Phi}_j(q_j + q_{ij}) \cdot \hat{n} + \frac{\partial (e \vec{E} \cdot \hat{n})}{\partial t} \right) \right] dt,
\]
where \(C\) is the magnitude of the blocking capacitance, \(i\) is the index of the materials, and \(j\) is the index of the particles. The first term on the right-hand side is the conduction current carried by ion and secondary electron fluxes. \(q_{ij}\) is the secondary electron emission coefficient of material \(i\) when bombarded with particle \(j\). \(\hat{n}\) is the normal vector of the electrode surface. The second term is the displacement current on the electrode. \(m_i\) can be -1 or +1 depending on which side of the circuit the electrode is located. That is, if the electrode is on the powered end, \(m_i = 1\), else if the electrode is electrically close to the ground, \(m_i = -1\).

The power on the electrode is
\[ \bar{P}_{rf} = \frac{1}{\tau} \iint V(t) \left[ j(\vec{r}, t) + \frac{d(e\vec{E}(\vec{r}, t))}{dt} \right] dtdA, \]  

(2.34)

where \( V(t) \) is the time-dependent voltage, \( j \) is the conduction current density, \( \tau \) is the RF integration time, and \( A \) is the surface area of the electrode. The second term in Eq. (2.34) is the displacement current on the electrode, where \( \varepsilon \) is the electrode permittivity and \( \vec{E} \) is the time-varying electric field.

When more than one frequency is applied to the same electrode, the power deposition is calculated individually for each power source. The current on the electrode is Fourier analyzed to distinguish the frequency components.

\[ I_k = \sum_{n=0}^{N-1} i_n e^{-i 2\pi k n / N}, k = 0, 1, 2, \cdots, N - 1 \]  

(2.35)

where \( N \) is the number of time bins used to resolve the RF cycles. Typically, the RF cycle is divided into \( 10^3 \)-\( 10^4 \) bins. With this current mapping in the frequency domain, the time domain current with a radian frequency of \( \omega \) is expressed as

\[ I(t) = \sum_{j=1}^{m} \sum_{j=1}^{n} I_{j} \cos(j\omega_j t + \phi_j), \]  

(2.36)

where \( m \) is the total number of frequencies, \( n \) is the number of harmonics considered for each frequency, and \( \phi_j \) is the phase of the \( j \)\(^{th} \) harmonic of frequency \( i \). Sequentially, the time domain current is multiplied with the voltage, and the RF period averaged power deposition of frequency \( \omega \) is

\[ \bar{P}_{\omega} = \frac{1}{\tau} \int I_{\omega}(t) \cdot V(t) dt, \]  

(2.37)

Finally, the total power on the electrode is the summation of the power from all frequencies.
2.1.4 Plasma Chemistry Monte Carlo Module (PCMCM)

The PCMCM is usually executed after the plasma reaches a quasi-steady state, though it can also be executed throughout the simulation. It is used to record the energy and angular distributions (EADs) of both charged and neutral species in the plasma or on the plasma-material interface [11]. The electric field, the density of species, and the relevant source functions are used in the PCMCM to move and track the pseudoparticles.

The PCMCM is operated kinetically using the Monte Carlo Simulation technique. Pseudoparticles are launched at targeted locations with densities weighted by the source functions of the corresponding species. The initial velocity of a species is isotropic, with a magnitude that replicates the temperature calculated in the FKPM using the Maxwell-Boltzmann distribution. The electric and magnetic field are linearly interpolated in both space and time domains, and used to advance pseudoparticle trajectories. Same as in the eMCS, collisions in the PCMCM are also handled using the null-collision technique. A series of random numbers are used to determine the collision frequencies and type of reaction from each collision.

The time step used to integrate the trajectory of pseudoparticles is calculated to be the minimum of the time between collisions, the time required for a pseudoparticle to move across a specified fraction of the mesh cell, and a fraction of the smallest RF period. In a bulk plasma, the fraction of a mesh cell a pseudoparticle is allowed to travel in each time step is between 0.2 – 0.5. As the pseudoparticle enters the sheath, it is accelerated to a high velocity by the electric field in a short period of time. Therefore, the fraction of a mesh cell a pseudoparticle is allowed to travel is constrained to ensure an accurate energy and angular distributions (EADs) recording.

Charge exchange collision is a common occurrence in the sheath. During a charge exchange collision, an energetic ion accelerated by the sheath collides with a neutral particle. The ion then loses its charge but preserves its initial kinetic energy. Consequently, a duo of a
hot neutral and a cold (thermal) ion is created. The hot neutrals bring a significant amount of kinetic energy to the surface that can activate the surface sites or cause further damage through subsequent bombardments. Due to the combined importance of ions and neutrals, both the IEADs and neutral energy and angular distributions (NEADs) are recorded in the PCMCM.

### 2.1.5 Surface Kinetics Module (SKM)

Reactions at the interface of plasma with a solid material (e.g., wall, wafer, electrode, etc.) can be addressed using a Surface Site Balance Model (SSBM) within SKM. The SSBM consists of the rates of reactions between fractional surface sites and gas phase fluxes, or between different surface sites. The relative sticking coefficient of the gas phase species in the plasma is updated depending on fractional surface coverage [11]. The incident flux ($\phi_{in}$) to a surface is provided by FKPM. A surface reaction generally has the form

$$A(g) + B(s) \rightarrow C(s) + D(g) + E(g), \quad \text{(2.38)}$$

where $g$ stands for gas phase species, and $s$ denotes the surface sites. The rate of $i^{th}$ reaction between gas phase species $A$ and surface sites $B$ on material $m$ is:

$$R_{im} = \alpha_i \phi_{Am} \theta_{Bm}, \quad \text{(2.39)}$$

where $\alpha_i$ is the reaction rate of $i^{th}$ reaction, $\phi_{Am}$ is the flux of gas phase species $A$ on material $m$, $\theta_{Bm}$ is the fractional coverage of surface site $B$ on material $m$. The fractional coverage of surface sites is updated by summing up the reaction rates.

The surface coverage ratio, of all the surface sites, is attained by integrating the rate equations of the corresponding sites using a third-order Runge-Kutta technique. The fractional surface coverage along with the gas phase fluxes from the surface, $\phi_{out}$, is returned to the FKPM, through which the surface reactions feedback to the plasma. The reaction probability of gas phase species on the surface is the summation of the rates of reactions with it as a reactant.
2.2 Monte Carlo Feature Profile Model (MCFPM)

The Monte Carlo Feature Profile Model (MCFPM) is a voxel-based feature scale simulator used to investigate the physics of topologically evolving targets. It is compatible with both 2-dimensional (2D) and 3-dimensional (3D) simulations, while in this thesis, only the 3D geometry is used. A detailed explanation of the MCFPM is provided in Ref. [12]. Only a brief description of the model is given in the following paragraphs.

In the MCFPM, the feature profile is mapped using cubic voxels. Each voxel preserves its assigned material properties. Pseudoparticles with EADs obtained from the HPEM output are typically introduced at the top of the simulation domain. These pseudoparticles are then tracked until they hit the solid material on the surface. Based on the species of the colliding pair, the incident energy of the gas phase species, and the reaction probability, the outcome of the bombardment is determined. Two processes that lead to surface evolvement are deposition and sputtering. In the deposition process, an additional voxel representing the deposited species is added to the initial mesh. In a sputtering process, the voxel indicating the solid reactant is removed from the mesh, and the gas phase product is either tracked as a pseudoparticle using the Monte Carlo technique or returned as a background species.

The properties of these fluxes are logged at the bottom of the feature in a defined window. The number of bombarding particles within this window is calculated by counting the pseudoparticles hitting the surface, and scaling it with the number of particles each pseudoparticle represents. This value is then normalized by dividing it by the sampling area. The fluxes at the bottom of the feature are attained by multiplying the normalized particle number with the velocity components perpendicular to the solid surface. The height of the bottom solid surface is determined by averaging the heights of the top-most voxel from each
mesh column within the test area. This height of the surface is periodically recorded, and the
deposition or etch rate is obtained by dividing the height change with the time interval between
recordings. The number of particles leaving the feature is measured by the number of
pseudoparticles passing through the top boundary of the simulation domain.

2.2.1 Co-deposition

In a semiconductor fabrication process, sometimes, sterically large molecules are used. For example, when depositing SiO2 film using the PE-ALD technique, organic silicon precursors such as BTBAS ([NH(C4H9)2]2SiH2), TIPS ([CH(CH3)2]3SiH), and BDEAS (SiH2[N(CH2CH3)2]2) are used. All of these compounds are more than twice the size of single silicon radicals. With a complete surface reaction, the silicon is the only particle that is deposited on a surface. However, occasionally, if the surface reaction is incomplete, the ligand group from the precursor remains on the surface, causing a steric hindrance. This phenomenon is addressed in the MCFPM by considering co-deposition sites.

In a co-deposition process, extra voxels are added to the mesh to represent the ligand group along with the deposition of the primary species (silicon). Depending on the dimension of the simulation domain, a search of the mesh region centered with the primary deposited site is performed in a 3 × 3 square (2D) or 3 × 3 × 3 cube (3D) for possible co-deposition locations. A series of random numbers are then used to determine the sequence of this search. The co-deposited ligand groups can occupy up to 2 (2D) or 8 (3D) voxels in the mesh. When the co-deposited sites occupy more than one voxel, the location of each voxel is independently searched. Once added to the mesh, the ligand group is treated the same as other surface materials, with specified physical properties (e.g., mass, charge, mobility, etc.) and reactions with the gas phase particles.
The occurrence of co-deposition is probable only when the tagged surface site is deposited from the specific reactants. For example, in a SiO$_2$ PE-ALD process, the ligand group is introduced to the surface during precursor dosing. When a silicon radical is deposited, the ligand group from the precursor is assumed to react with the hydroxyl group on the target surface, and to volatilize as part of the gas phase product. However, if there are not enough hydroxyl groups on the surface, the ligand group will continue to bond with the silicon and stay on the solid surface. In this example, the primary deposition site is the silicon, and the prerequisite reactant is the silicon precursor. The precursor requirement is necessary because silicon can be deposited through various paths. Other than from the precursor, silicon can also be deposited from gas-phase silicon radicals sputtered by the energetic ions. In this case, the probability of co-deposition of the ligand group should be zero since the ligand group does not exist in the reactant. In the MCFPM, all the reactions are mapped with their corresponding reactants and products enabling use of the reactants as the prerequisite condition in the co-deposition process.

Because the MCFPM is a voxel-based model, all the materials are discretely treated using an aligned voxel mesh in the space domain. Therefore, the microscopic material structure is not resolved. However, the occurrence of a steric hindrance strongly depends on the microscopic properties of the reactants. The structure of the surface material, the neighboring components near the positions where the reaction occurs, and the orientation of the gas phase reactant during a collision are all vital factors that affect the steric hindrance. In the MCFPM, a probability is assigned to the co-deposition reactions to provide extra control and to accommodate the elements that are not included in the model. A series of random numbers ranging from 0 to 1 is used to
determine whether the co-deposition occurs. The random number is compared with the co-deposition probability and co-deposition occurs when the random number is smaller.

### 2.2.2 Energetic Particle Surface Reaction

In the MCFPM, any reactions between gas-phase species and surface sites are mapped in a probability array. When a pseudoparticle hits the surface, a random number is generated and compared with a given reaction probability, which then determines which reaction is to occur. Most of the reactions used in this thesis have a constant reaction probability although it is important to remember that an energetic particle surface reaction probability is energy and angular dependent \[13, 14\]

\[
p(E_i, \theta) = p_0 \left( \frac{E_i - E_{th}}{E_r - E_{th}} \right)^n f(\theta),
\]

where \( E_i \) is the particle energy, \( \theta \) is the incident angle, \( p_0 \) is the reference probability, \( E_r \) is the reference energy, \( E_{th} \) is the threshold energy, and \( f(\theta) \) is the angular dependent function. The exponential term \( n \) is typically 0.5. When bombarding on the surface, energetic particles can cause physical sputtering or chemical enhanced etching, any of which may have different angular dependence. In this thesis, using a PE-ALD process, physical sputtering dominates the likely energetic particle surface reactions, and a reaction probability is at the maximum value when the incident angle is around 60˚. In our case, this reaction probability decreases with a decreasing incident angle and is zero for glazing collisions.

If the target feature has an aspect ratio greater than 1, an energetic particle can experience several collisions on the sidewall before reaching the bottom of the feature. Through this process, the particle losses its energy. The preserved energy \( E_s \) of a sputtered particle after striking the surface is
\[ E_s(\theta) = E_i \left( \frac{E_i - E_c}{E_{ts} - E_c} \right) \left( \frac{\theta - \theta_c}{90 - \theta_c} \right), \]

where \( E_{ts} \) is the threshold energy for specular scattering, \( E_c \) is the cut off energy of diffusive scattering, and \( \theta_c \) is the lower angular boundary for specular scattering. Particles with \( E_i > E_{ts} \) preserve all the energy, and particles with \( E_i < E_c \), or \( \theta < \theta_c \) are treated as to be diffusively scattered.
2.3 Figures

Fig. 2.1 The flow chart of the Hybrid Plasma Equipment Model (HPEM) used in this thesis.
Fig. 2.2 a) Schematic of the circuit model and b) the detail of each segment representing 1/100 of an antenna.
Fig. 2.3 Schematic of the fork-join model used in OpenMP for parallel computation.
2.4 References

10. SLAP Sparse Matrix Library: https://www.netlib.org/.
Chapter 3: Insights to Plasma Transients in Low-High Pulsed Power Inductively Coupled Plasmas*

3.1 Introduction

Inductively coupled plasmas (ICPs) represent a critical technology for plasma etching for semiconductor fabrication, particularly for the manufacture of conductors and compound materials, and for atomic layer etching [1-5]. Typical operating conditions include rare gas-halogen gas mixtures and pressures of a few to tens of mTorr. Power deposition is up to a few kW in chambers accommodating 300 mm diameter wafers. As the critical dimension (CD) of semiconductor devices continues to decrease and more exotic materials are used, finer control is required over the plasma produced reactive fluxes to the wafer.

An increasingly applied method to control reactive fluxes to the wafer is the use of pulsed-power. Typical pulse repetition frequencies (PRF) are up to 5-10 kHz and duty cycles (DC), which are the fraction of the pulse period power is on, are typically tens of percent. Pulsed power enables high peak power during the power-on portion of the cycle while leveraging unique plasma chemical reactions during the power-off portion of the period [6-8]. When combined with continuous or pulsed biases on the substrate, unique combinations of reactant fluxes and ion energies onto the wafer can be produced to accelerate ions onto the wafer [9,10].

Pulsed ICPs have been particularly effective in minimizing damaging the wafer during processing. For example, Ishikawa found that in an SiO$_2$ etching process carried out in an Ar

---

* The results presented and a portion of the text appearing in this chapter were accepted to be published in the paper “Transients using low-high pulsed power in inductively coupled plasmas”, by Chenhui Qu et al., Plasma Sources Sci. Technol. 103665.R1 (2020).
ICP, there was less UV damage when using pulsed power compared to continuous wave (CW) due to the lower UV dose during the power-off period [11]. Petit-Etienne et al. studied silicon recesses during plasma etching with both CW and pulsed-power using HBr/O2/Ar plasmas [12]. They found that when using synchronous pulsed-power, the recess loss of Si could be better controlled due to a decreased ion flux while maintaining neutral fluxes. They also concluded that using pulsed-power may also minimize chamber wall sputtering due to the lower ion flux, which then reduced contamination of the substrate [13]. Bodart et al. investigated the consequences of PRF and DC on radical densities in Cl2/HBr plasmas [14]. They found that in the high PRF regime, changing DC could effectively control the fragmentation of the feedstock gases, whereas in the low frequency regime the effect of DC on the plasma chemistry was small.

Pulsed ICPs have also been extensively investigated through modeling. In an early work, Ramamurthi et al. developed a two-dimensional continuum model to study pulsed ICPs sustained in Cl2 [15]. A highly electronegative ion-ion plasma core with an electropositive edge was observed in the afterglow of the discharge. A spike in $T_e$ was observed at the beginning of the power pulse, which agreed well with experiments. The authors concluded that some plasma properties, such as negative ion density, are strongly dependent on the spatial distribution of the plasma core, also noting the need to control electric probe positions in experiments to obtain a complete perspective of these complex processes. Due to the strong spatial dependence of plasma properties in an electronegative discharge, the separation of the electronegative core and electropositive periphery was accounted for in a volume-averaged model developed by Kim et al. [16]. That model predicts a decreased ratio of neutral-to-ion flux as the aspect ratio of the discharge increases in an O2 plasma, further demonstrating the importance of geometry and the spatial conditions in electronegative plasmas. To better understand the transient behavior of a
pulsed-power driven electronegative plasma, Thorsteinsson et al. performed a computational investigation of an Ar/Cl₂ plasma using a global model [17]. They concluded that improvements in etch selectivity when using a pulsed-power Cl₂ plasma result from the increase of the radical to ion ratio compared to CW operation. This control can be further refined by varying mole fractions in Ar/Cl₂ mixtures, a practice that provides some limited ability to tune the electron temperature.

A commonly observed behavior of $T_e$ in a pulsed ICPs is that at the beginning of the power pulse $T_e$ spikes to a value above that in the quasi-steady state. For example, in the modeling by Ramamurthi et al., this spike in $T_e$ was observed in a pulsed Cl₂ ICP [15]. $T_e$ peaked to 5 eV at the beginning of the pulse and then rapidly decreased to the quasi-steady value of 2 eV in about 10 µs. This phenomenon was observed in early experiments performed by Ashida et al. [18]. In a pulsed ICP sustained in Ar at 5 mTorr, Langmuir probe measurements indicated a peak in $T_e$ at the leading edge of the pulsed period up to 7 eV, with the quasi-steady state temperature being 3.5 eV. Darnon et al. noted that in their experiments the overshoot of $T_e$ at the beginning of the pulse is more significant when the pulse repetition PRF is low [19]. A low PRF provides a longer afterglow, and thus a lower electron density, $n_e$, at the beginning of the next pulse. This lower $n_e$ then produces the overshoot of $T_e$. With the spike of $T_e$ in a pulsed plasma being well documented, its behavior is used as a test of the accuracy of experimental measurements [20]. However, the spatial dependence of the spike of $T_e$ is not often documented.

Although there are several advantages of using pulsed-power for electronegative ICPs, there are also several challenges. Due to the low electron density at the end of the afterglow and at the beginning of power pulse, E-H (capacitive-to-inductive) transitions can occur at the beginning of each pulse. At the beginning of the pulse when the electron density is low, the
electromagnetic skin depth can be larger than the dimensions of the reactor, and electromagnetic coupling is inefficient. Power is electrostatically and capacitively coupled to the plasma through the voltage drop from the coil to the plasma bulk. This is the E-mode. As the electron density $n_e$ increases, the skin depth decreases and power becomes coupled to the plasma inductively through the electromagnetic field. This is the H-mode. During the onset of the E-mode, large oscillations can occur in the plasma potential and plasma density, and electrostatic waves can be launched from beneath the antenna. When operating close to the transition between the E- and H-modes, ionization instabilities may occur which produce periodic maxima in the plasma density [21].

The E-H transition in ICPs was experimentally investigated by Cunge et al. [22] who observed a hysteresis in the mode transition as a function of power. It was observed that the power absorbed by the plasma has a nonlinear dependence on the electron density. In a later work, Chabert et al. investigated this instability in SF$_6$ and Ar/SF$_6$ plasmas with a combination of experimental and modeling work [21]. They concluded that multistep ionization plays an important role in ionization balance, induces nonlinearity in the plasma and produces hysteresis behavior during the E-H mode transition.

One of the origins of the E-H transition in electronegative ICPs and its associated instabilities is the need to reignite the plasma at the beginning of each period in pulsed plasmas. One strategy to circumvent the E-H transition while also modulating power is to use a high-low power scheme [23]. Using this method, the pulsed power format consists of a high-power portion of the pulsed period followed by a low power portion of the pulsed period - that is, non-zero power. The intent of the non-zero power is to maintain the plasma’s conductivity at a high enough value so that the system remains in H-mode throughout the pulsed period. However,
even high-low power pulsing may have instabilities. List et al. found that in high-low power modulated Cl\textsubscript{2} ICPs, the plasma may extinguish at the beginning of the low-power period and then reignite after 10s of microseconds to a few ms [23]. They called this phenomenon “ignition delay”, the cause of which is believed to be related to the ability of the supply to deliver power to the time varying impedance of the plasma.

In this chapter, we discuss results from a computational investigation of high-low pulse power formats for ICPs sustained in Ar/Cl\textsubscript{2} gas mixtures. We found that in high-low pulsed plasmas, $T_e$ undergoes a transient during both power transitions. For long enough high- and low-power periods, $T_e$ is effectively constant during the pulse. However, $T_e$, has a momentary maximum when power transitions from low-to-high, are similar to the leading edge of conventional pulsed ICP. $T_e$, also has a momentary minimum when power transitions from high-to-low. This response of $T_e$ to power transitions highly depends on location with respect to the electromagnetic skin-depth and the fractional dissociation in the Cl\textsubscript{2}-containing plasma. Within the skin-depth, the transients in plasma properties ($T_e$ and $n_e$) during power transitions are distinctly observed. With increasing distance from the skin-depth, the transients disperse in space and dissipate in magnitude. These responses of the plasma to pulsed power can be controlled through gas mixture and the pulsed power format. Decreasing the Cl\textsubscript{2} mole fraction, lengthening the power ramp time, and increasing the low-power diminish the transients and produce a more spatially uniform plasma.

A brief model description is in Sec. 3.2. Plasma properties as a function of high-low power format and gas mixture are discussed in Sec. 3.3. Concluding remarks are provided in Sec. 3.4.
3.2 Description of the Model

Note: The computational investigation was performed using the HPEM (Hybrid Plasma Equipment Model). Details of this model are discussed in Sec. 2.1 and Ref. [24], while a brief description follows focusing on the options used in this study.

In this work, the model employed uses the Electromagnetics Module (EMM), Fluid Kinetics Poisson Module (FKPM), and Electron Monte Carlo Simulation Module (eMCS) within the Electron Energy Transport Module (EETM). The inductively coupled electric field is produced in the EMM from a frequency domain solution of Maxwell’s equation. The densities, fluxes and temperatures of the heavy particles (neutrals and ions), densities of electrons and electrostatic potential are produced in the FKPM. This information is then transferred to the eMCS for electron energy distributions (EEDs) throughout the reactor. Electron trajectories including electron collisions in the time and spatially varying electric and magnetic fields are computed. Transport of both bulk and secondary electrons from surfaces is addressed. Electron-electron collisions are included such that the Maxwellian nature of the EEDs is captured in regions of high electron density.

The species included in this work are Ar, Ar(1s5), Ar(1s4), Ar(1s3), Ar(1s2), Ar(4p), Ar(4d), Ar+, Ar2+, Ar2*, Cl2, Cl2(v), Cl+, Cl, Cl+, Cl(4s), Cl(4p), Cl(3d), Cl−, and electrons.

3.3 Characteristics of Low-High Pulsed Power ICPs

The geometry of the ICP reactor used in this investigation is shown in Fig. 3.1a. The system is a conventional ICP reactor with a stovetop 4-turn coil located at 0.4 cm above a dielectric window. The cylindrical reactor radius is 7.6 cm and the chamber height is 15.6 cm. A wafer of a radius of 3.7 cm is positioned on a grounded substrate 13 cm below the dielectric Al2O3 window. A 1.8 cm wide Al2O3 focus ring surrounds the substrate. The dielectric constant
of the alumina is 9.8 and that of the wafer is 11.8. The dielectric has a negligible conductivity while the wafer has a conductivity of $10^{-3}/\Omega \cdot \text{cm}$. The substrate supporting the wafer is not powered so that any modulation of the plasma is attributed to power changes from the coil. The gas inlet is in the sidewall at 0.4 cm below the dielectric window and the annular pump is at the bottom of the reactor with a 2.1 cm width. The feedstock gas enters the chamber at ambient temperature (300 K). A pressure sensor is embedded in the sidewall at 3.9 cm above the substrate to monitor the local pressure, and that measurement is used to throttle the output flow rate to maintain the specified pressure. The inner wall of the reactor is coated with the dielectric yttria ($\text{Y}_2\text{O}_3$) to decrease the sticking coefficient of radicals, thus increasing the precursor densities in the plasma bulk. The dielectric constant of yttria is about 13. The actual thickness of the yttria coating of a few microns cannot be resolved by the mesh, and so the dielectric constant of the yttria used in the model was increased to $10^4$ so that the capacitance (F/cm$^2$) of the yttria material would be the same as the thin film. The reactor is surrounded by air with electrical ground planes situated at large enough distances so that the electromagnetic waves produced by the coil are not perturbed by the surrounding ground planes.

The secondary electron emission coefficients of both the alumina window and the $\text{Y}_2\text{O}_3$ sidewall coating were 0.05 for ions and 0.01 for excited state species having energy greater than the work function of the material. (Photoelectron emission was not included.) A parametric study was conducted for varying the secondary electron emission coefficient from one third to three times of these base case values. There was little impact on the plasma density or spatial distribution of the plasma. The ionization by secondary electrons is 1-2 orders of magnitudes smaller than the ionization by bulk electrons.

The applied power profile, shown in Fig. 3.1b, is a high-low pulsed format that modulates
the 13.56 MHz radio frequency current applied to the antenna. For the work in this chapter, all the applied power is inductively coupled to the plasma. That is, we did not include capacitive coupling from the coils and so were able to assume H-mode power deposition. This assumption was validated by performing limited simulations with full electrostatic coupling from the antenna. In the base case, the high-power is 160 W and the low-power is 96 W. (With high power, the power density, W/cm\(^3\), is similar to industrial reactors used for microelectronics fabrication.) The pulse repetition frequency (PRF) is 5 kHz and the duty cycle (DC) is 50%. Note that the power takes 10 μs to ramp from low-to-high or from high-to-low power. The ramp-up and ramp-down times are evenly split between the high- and low-power periods so a 50% DC is strictly enforced. For the base case, the feedstock gas used is an Ar/Cl\(_2\) = 5/95 mixture with a flow rate of 22 sccm. The pressure is held constant at 20 mTorr. The reaction mechanism used for the Ar/Cl\(_2\) plasma investigated here is the same as in Ref. [25]. The recombination coefficient on surfaces for ground state Cl to recombine to form Cl\(_2\) was 0.05. Excited states of Cl and Ar quenched on surfaces to form their ground states with unity probability. Cl\(_2\)(v) quenched on all surfaces to form ground state Cl\(_2\) with 0.5 probability. All charged species recombine on surfaces with no reflection, depositing charge on dielectric surfaces.

The 2D profiles of the electron density (\(n_e\)), electron temperature (\(T_e\)) and ionization source by bulk electrons (\(S_e\)) are shown in Fig. 3.2. The figures shown are at the end of the high- and low-power periods, corresponding to the times of 100 μs and 200 μs shown in Fig. 3.1b. In the base case, the position with the highest power deposition is at mid-radius of the reactor at 1 cm below the dielectric window. As the power changes from 96 W to 160 W, the maximum power density increases from 0.8 to 1.4 W/cm\(^3\), leading to an increase in the maximum electron
density from $6.3 \times 10^{10}$ cm$^{-3}$ to $1.3 \times 10^{11}$ cm$^{-3}$. Using these values of $n_e$ and the momentum transfer collision frequency ($\nu_m$) of 2 to $4 \times 10^7$ s$^{-1}$, the skin depth ($\delta$) of the EM wave in the plasma is 1.5 to 2.0 cm, which is much smaller than the height of the reactor (13 cm). Consequently, the pulsed power has little direct impact on the plasma dynamics in the several cm above the wafer.

For example, the ionization source by bulk electrons ($S_e$) decreases by a factor of 100 within 5.0 cm from the dielectric window, indicating the plasma density above the substrate is not directly sustained by the pulsed power but rather results from transport of charged species from the top of the reactor. The plasma near the substrate can at best be sustained by power that is convected from the top of the reactor by non-local electron transport and by electron thermal conduction, or by Penning ionization due to metastable species that transport from the top of the reactor.

The dominant positive and negative ions in the base case are Cl$_2^+$ and Cl$^-$. Their densities and the gas temperature ($T_{\text{gas}}$) are shown in Fig. 3.3 at the end of the low- and high-power portions of the pulsed cycle. The axial densities of electrons and Cl$^-$ at mid-radius of the wafer are shown in Fig. 3.4 at the end of the low- and high-power periods. The maximum Cl$_2^+$ density has only a small increase, $1.6 \times 10^{11}$ cm$^{-3}$ to $1.8 \times 10^{11}$ cm$^{-3}$, as the input power transitions from low (96 W) to high (160 W). The increase in the negative ion density is also small, $1.5 \times 10^{11}$ cm$^{-3}$ to $1.6 \times 10^{11}$ cm$^{-3}$. The electronegativity of the plasma, the ratio of the negative ion density to electron density, decreases from 2.4 at low power to 1.2 at high power. The Cl$^-$ density is relatively stable through one full period due to the high dissociative attachment rate of Cl$_2$ by thermal electrons which can occur throughout the reactor. Losses of Cl$^-$ are dominated by ion-ion recombination since the negative ion is trapped in the plasma by there being a positive
plasma potential throughout the pulsed period. The peak plasma potential is 13 V during low power and 14 V during high power. Unlike pulsed systems where the power is turned off, the plasma potential does not dissipate during the low-power period which would then allow negative ions to diffuse out of the plasmas. With the Cl$^+$ density also fairly stable through the period, the loss term of the Cl$^-$ is also fairly constant.

The maximum gas temperature is modulated during the pulsed cycle by about 170 K (752 K during low power and 920 K during high power). Heating is nearly instantaneous with the application of power while the dominant gas cooling is by thermal conduction to the walls. (There are small additional contributions due to injection of cool gas and pumping of hot gas.) These thermal heating and cooling time scales are short compared to the gas convective time scale, and so there is less modulation in the gas density. As a result, there are pressure oscillations during the pulsed period [26].

The aspect ratio of the ICP reactor has important implications on the local densities of charged particles. In this work, the reactor has a fairly large aspect ratio (height divided by radius) with the power deposition and electron impact ionization being limited to a few cm at the top of the reactor within the electromagnetic skin depth. Transport processes then convect power and density from the skin depth to the lower portion of the reactor. For example, $n_e$ and $T_e$ are shown at mid-radius of the wafer as a function of time for different heights in Fig. 3.5. Within the electromagnetic skin depth (height = 11 cm), $n_e$ is fairly constant during the high- and low-power periods with a change in density commensurate with the change in power. At locations further from the skin depth, the electron density is smaller while the relative modulation in $n_e$ is also smaller. Moving further from the source, there is an increasing positive slope in $n_e$ as a function of time during the high-power pulse and an increasingly more negative slope in $n_e$ as a
function of time during the low-power pulse. These trends result from the finite transport time for the excess electron density produced during the high-power to translate to the bottom of the reactor. The time for transport of the electrons from the top to the bottom of the reactor is commensurate with the pulsed period. Therefore, the increase and decrease in plasma density that is experienced in real-time with power modulation at the top of the reactor is averaged over the cycle at the bottom of the reactor.

The high- and low-power periods are long enough, 100 µs, that the plasma in the skin depth comes into a quasi-steady state during both the high- and low-power periods. For quasi-steady state conditions, the electron temperature $T_e$ is determined by a balance between sources by electron impact ionization and Penning reactions, and losses by attachment, recombination and transport out of the skin depth. In the skin depth, the fractional dissociation, 47%, is nearly constant during the high- and low-power periods, and the change in gas rarefaction between the high- and low-power, 15%, is not large. As a result, $T_e$ during the low- and high-power periods is similar – the value at which sources and losses balance each other. The power deposition is, to first order, $n_e k_L(T_e) N_g$, where $k_L(T_e)$ is the rate coefficient for power loss (which increases with increasing $T_e$) and $N_g$ is the gas density. With $T_e$ and $N_g$ being similar during the low- and high-power, then a change in power requires a change in $n_e$. The change in $n_e$ is downwards when going from high-to-low power and upwards when going from low-to-high power. These transitions in turn require that $T_e$ momentarily decrease below the self-sustaining value in transitioning from high-to-low power to lower the electron density. Similarly, $T_e$ must momentarily increase above the self-sustaining value when transition from low-to-high power to increase electron density.

A similar interpretation of the need for spikes (up or down) in $T_e$, comes from the
perspective of power dissipation. With an instantaneous, step-function increase in power deposition, there is not sufficient time for the electron density to increase to accommodate the increase in power. To enable the increase in power deposition, $T_e$ must increase, which usually also increases the rate of power dissipation per electron. Similarly, if there is an instantaneous decrease in power, there is insufficient time for the electron density to decrease to accommodate the decrease in power. To enable the decrease in power deposition, $T_e$ must decrease, which usually also decreases the rate of power dissipation per electron. The duration of the spikes in $T_e$ (up or down) is then the time required for the electron density to change from the low-to-high values (and vice-versa).

These spikes in $T_e$ are shown in Fig. 3.5, and occur dominantly in the skin depth where power deposition is maximum – positive spike for low-to-high power and negative spike for high-to-low power. When translating lower in the reactor and further from the skin depth, $T_e$ decreases due to collisional power loss. The local heating sources are superelastic collisions (a small contribution), thermal conduction by bulk electrons or non-local transport in the tail of the EED. The spikes in $T_e$ also dissipate and broaden in time, as thermal conductivity and convection translate the pulse of hotter electrons (low-to-high power) or cooler electrons (high-to-low power) to lower heights. The end result is that $T_e$ appears to have periodic waves close to the wafer.

The EEDs at the end of the high- and low-power periods are shown in Fig. 3.6. At the top of the reactor, the EEDs are almost Maxwellian due to the high e-e collision frequency and higher $T_e$. Moving away from the power source, the EEDs gradually shift to bi-Maxwellian with a lower temperature bulk (1.0 eV) and higher temperature tail (1.9 eV). The bulk $T_e$ decreases in translating lower in the reactor due to the lower frequency of e-e collisions and collisional power
loss. The tail of $T_e$ is relatively constant (or decreases less than the bulk $T_e$) as the tail is sustained by non-local transport of high energy electrons that are accelerated in the skin depth and have longer mean free paths. There are no significant differences between the EEDs at the end of the low- and high-power periods. First, the $T_e$ is essentially the same in the skin depth at the end of the low- and high-power periods, and so the power deposition-per-electron is the same. As a result, the EED in the skin depth is essentially the same. Lower in the reactor, the tail of the EED has a higher temperature at the end of the high-power period compared to the low-power period. This is likely a result of the higher thermal conductivity afforded by the higher electron density.

3.3.1 Gas Mixture

In a pure rare gas mixture at low pressure (without dimer ions), loss of electrons and ions is dominated by diffusion to surfaces where they recombine. If in a pulsed system, the period is shorter than the time for ions to diffuse to surfaces, then the plasma source is effectively averaged over the pulse period. The plasma density will then not directly track the variation in power deposition. When increasing the Cl$_2$ mole fraction in a Ar/Cl$_2$ gas mixture, the rate of electron loss by dissociative attachment increases and the electron density is more modulated during the pulsed period. This increased rate of modulation of the plasma density then requires a larger modulation in $T_e$.

The Cl$_2$ mole fraction in the Ar/Cl$_2$ gas mixture was varied from 20% to 80%, and the resulting electron densities are shown in Fig. 3.7 at the end of the high-power part of the cycle. The electron densities and temperatures at heights of 11 cm and 2 cm above the substrate are shown in Figs. 3.8 and 3.9 during the pulsed cycle. The PRF (5 kHz), duty cycle (50%) and low/high power (96 W/160 W) are the same as in the base case.

With the increase in Cl$_2$ mole fraction, the power deposition per electron increases and so
on this basis alone, for a given power density, the electron density decreases. We see this trend in the electromagnetic skin depth where power deposition is maximum – $n_e$ increases from $1.6 \times 10^{11}$ cm$^{-3}$ for an Ar/Cl$_2$ = 20/80 mixture to $7.9 \times 10^{11}$ cm$^{-3}$ for an Ar/Cl$_2$ = 80/20. As electrons diffuse out of the power deposition region, the $T_e$ of these electrons decrease more rapidly with increasing Cl$_2$ mole fraction. For Cl$_2$, which is a thermally attaching gas, the rate of dissociative attachment increases with decreasing $T_e$, and this lowers the average electron density even further. As a result, there is a more severe gradient in electron density between the top and bottom of the reactor with a larger Cl$_2$ mole fraction. For the Ar/Cl$_2$ = 80/20 mixture, $n_e$ decreases by a factor of 2.2 from the top to the bottom of the reactor. For the Ar/Cl$_2$ = 20/80 mixture, this decrease is by a factor of 7.5.

The electron density at the top of the reactor (height = 11 cm) is essentially in phase during the pulse-period – increasing when the power is high and decreasing when the power is low. With the power deposition being limited to the skin depth, there is a time-delay (phase offset) for the increase in plasma density to propagate from the top of the reactor to the bottom of the reactor. This delay is 10-15 $\mu$s for the Ar/Cl$_2$ = 80/20 mixture and decreases with increasing mole fraction. At the same time, the degree of modulation in the plasma density decreases from the top of the reactor to the bottom of the reactor. In the skin depth, the electron density is modulated by a factor of 2. Above the substrate, the modulation is a factor of 1.5. The phase delay and decrease in modulation in plasma density are both a consequence of the finite propagation time for the pulse of higher electron density during the high-power period to propagate across the reactor.

In transitioning from low-to-high power, which requires an increase in plasma density, $T_e$ must increase at least momentarily above the quasi-state self sustaining values. In transitioning
from high-to-low power, which requires a decrease in plasma density, $T_e$ must at least momentarily decrease below the quasi-state self sustaining values. The magnitudes of these momentary increases and decreases in $T_e$ get larger with increasing Cl$_2$ mole fraction. $T_e$ in the skin depth (height = 11 cm) as a function of Cl$_2$ mole fraction is shown in Fig. 3.9a. The leading positive spike of $T_e$ (low-to-high power) increases by about 0.2 eV between a mole fraction of 20% and 80%. This increase is required to offset the additional electron losses by dissociative attachment.

The initial positive spike in $T_e$ produces excess ionization that persists during the high-power pulse. Based on the additional losses inherent to the more chlorine rich Ar/Cl$_2$=20/80 mixture, one would expect $T_e$ to be higher during the pulse in than in more dilute mixtures. This is not the case, as $T_e$ is marginally lower for the chlorine rich mixtures during the pulse. The excess ionization produced by the positive leading spike in $T_e$ enables a lower $T_e$ in the chlorine rich mixtures during the high-power pulse. During the low-power period, $T_e$ is higher for higher Cl$_2$ mole fractions. In transitioning from high-to-low power, there is no ionization excess and so $T_e$ is higher in the more chlorine rich mixtures to offset the additional electron losses.

$T_e$ for different Cl$_2$ mole fractions at 2 cm above the substrate is shown in Fig. 3.9b. The electron transport time from top-to-bottom of the reactor is 10-20 µs, which is also about the duration of the leading spikes and decreases in $T_e$ in the skin depth. As a result, these spikes and decreases in $T_e$ are dissipated and averaged over the high- and low-power periods by the time the transients reach the substrate. The end result is that there are imperceptible spikes (positive or negative) in $T_e$ above the substrate. However, the low-to-high power positive spike in $T_e$, and the high-to-low power negative spike in $T_e$ in the skin depth, when convected to the substrate, produces a temperature that is 0.1 to 0.2 eV higher during the high-power than during the low-
With there being increasing collisional losses with increasing Cl₂ mole fractions while the electrons transport from the source region to the substrate, \( T_e \) above the substrate decreases by 0.7 eV with increasing mole fraction (20% to 80%). A portion of this decrease can be attributed to the lower electron thermal conductivity due to the lower electron density with a large Cl₂ mole fraction. The lower thermal conductivity reduces the diffusion of thermal energy from the source region to the substrate.

### 3.3.2 Power Ramp-Down Time

For the pressures and gas mixtures investigated in this chapter, the time for the system to respond to step function changes in power deposition is the response time \( \tau_R = 10-30 \mu s \). If the change in power is over times longer than \( \tau_R \), then the plasma will track the change in power in a quasi-steady state manner. That is, the electron density and temperature will be nearly in equilibrium with the instantaneous power. When ramping down in power, there must still be a decrease in \( T_e \) below the self-sustaining value to enable a decrease in plasma density; and there must be increases in \( T_e \) above self-sustaining when ramping up in power. However, for long enough ramp times these changes may be imperceptible. If the power ramping time, \( \tau \), is commensurate or shorter than \( \tau_R \), then the \( T_e \) must undergo significant excursions in order to increase power dissipation while increasing electron density (ramp up) or decrease power dissipation while decreasing electron density (ramp down).

The power ramp-down time, \( \tau \), was varied from 10 \( \mu s \) to 80 \( \mu s \) while the ramp-up time remained at 10 \( \mu s \). The corresponding \( T_e \) at heights of 11 and 2 cm are shown in Fig. 3.10, and the corresponding \( n_e \) are in Fig. 3.11. The low- and high-power periods are long enough that the quasi-steady state electron densities are nearly the same, independent of ramp time \( \tau \). Having
said that, larger values of $\tau$ result in higher average power deposition. (Between a ramp time of 10 and 80 $\mu$s, the average power increases from 128 W to 139 W.) As a result, there is proportionately more dissociation of the Cl$_2$ and more gas heating, which results in the electron density being about 10% higher with the longest ramp time. That aside, the conditions for low-to-high power are nearly the same for all ramp times. As a result, the initial spikes in $T_e$ in the skin depth (height = 11 cm) are also nearly independent of $\tau$.

As $\tau$ increases from 10 to 80 $\mu$s, the length of power-down period begins to exceed the plasma response time $\tau_R$. In doing so, the downward spike in $T_e$ becomes less severe – 0.3 eV for $\tau = 10$ $\mu$s to less than 0.1 eV for $\tau = 80$ $\mu$s. If we extend $\tau$ to 100 $\mu$s, the change in $T_e$ falls within the statistical noise of the simulation. Above the substrate, $T_e$ shows the transit time delay and smoothing of the initial spike for the low-to-high power transition (discussed above). During the low power period, $T_e$ is higher for $\tau = 80$ $\mu$s compared to shorter ramp times due to the lack of the downward spike in $T_e$. However, all of these variations are within 0.15 eV.

With the exception of the aforementioned increase in $n_e$ due to the higher average power for large $\tau$, $n_e$ in the skin depth closely tracks the ramping down of the power. At 2 cm above the substrate, the averaging of power deposition over the electron transit time of 10-30 $\mu$s from the skin depth makes the electron density less well correlated with the ramp-down time.

### 3.3.3 Magnitude of Low Power

For what are otherwise the same conditions, if the lengths of the low- and high-power periods are long enough to achieve the steady state, $T_e$ should be independent of the magnitude of power during the low- and high-power periods. That value of $T_e$ is given by ionization sources being balanced by losses. In practice, there are average power affects that must be considered. For example, consider keeping the high-power constant and varying the low-power.
Increasing low power increases the average power deposition, which results in more dissociation of Cl\textsubscript{2}, more gas heating and higher average plasma density. More dissociation of Cl\textsubscript{2} reduces the rate of electron loss by dissociative attachment. More gas heating produces rarefaction that increases losses by diffusion and reduces ion-ion neutralization rate coefficients. Higher plasma densities increase the rates of dissociative recombination and ion-ion neutralization. The end effect on $T_e$ becomes case specific.

Electron temperatures at heights of 11 cm in the skin depth, and 2 cm above the wafer, are shown in Fig. 3.12 while varying the low-power ($P_L$) from 32 W (20\% of the high-power) to 160 W, which is equal to the high power. The electron densities for these conditions are shown in Fig. 3.13. When increasing $P_L$ from 32 W to 160 W, the average power deposition increases from 96 W to 160 W, the fractional dissociation of Cl\textsubscript{2} increases from 38\% to 44\%, and the gas temperature increases from 568 to 573 K. The increase in fractional dissociation of Cl\textsubscript{2} largely enables the quasi-steady state value of $T_e$ in the skin depth to decrease by 0.13 eV when $P_L$ increases from 32 W to 160 W. With this increase in the fraction dissociation of Cl\textsubscript{2}, the electron density during the constant high-power 160 W increases from $9.4 \times 10^{10} \text{ cm}^{-3}$ for $P_L = 32 \text{ W}$ to $1.4 \times 10^{11} \text{ cm}^{-3}$ for $P_L = 160 \text{ W}$.

The low- to high-power spike in $T_e$ increases from zero for $P_L = 160 \text{ W}$, as this is a continuous plasma, to 0.85 eV for $P_L = 32 \text{ W}$. This increasing overshoot in $T_e$ with decreasing $P_L$ is required to avalanche the plasma from progressively lower plasma densities to that for the high-power. For example, for $P_L = 32 \text{ W}$, the electron density increases by factor of 6.9 from low- to high-power. The magnitude of the high- to low-power decrease in $T_e$ intensifies with $P_L$ decreasing from 160 to 32 W. Reducing $P_L$ requires a larger change in $n_e$ which is produced by a larger negative excursion of $T_e$ below the steady state. The high- to low-power decrease in $T_e$ is
0.9 eV for $P_L = 32$ W and 0.26 eV for $P_L = 96$ W.

$T_e$ also has a small decrease in its steady state value in the skin depth (height = 11 cm) during the high- and low-power periods. There is a 0.13 eV decrease in $T_e$ from $P_L = 160$ W to $P_L = 32$ W. This change is largely a result of the higher average power with $P_L = 160$ W producing more dissociation of Cl$_2$ and therefore fewer attachment losses. However, above the substrate (height = 2 cm) there is significant variation of $T_e$ for different $P_L$. For example, at the end of the high-power period, $T_e$ is 0.1 eV lower for $P_L = 32$ W compared to $P_L = 160$ W. This is the opposite trend compared to the skin depth (height = 11 cm) where $P_L = 160$ W has the lower $T_e$. The net change in $T_e$ from the skin depth to the wafer (from high to low $P_L$) is a decrease of 0.23 eV. With $P_L = 32$ W, the average power is lower, the dissociation of Cl$_2$ is lower, the Cl$_2$ density is higher and the electron density is lower. As a result, there are more collisional losses and less thermal conduction from the skin depth as electrons transport down towards the substrate. The aggregate end result is a lower $T_e$.

During the low-power period above the substrate, the decrease in $T_e$ ($P_L = 32$ W compared to $P_L = 160$ W) is 0.35 eV whereas in the skin depth, $T_e$ for $P_L = 160$ W is lower by 0.13 eV. The net change in $T_e$ is 0.5 eV from the skin depth to the wafer, about twice the change as during the high-power period. Since the fractional dissociation is essentially the same during the high- and low-power periods, the larger decrease in $T_e$ can be attributed to lower thermal conductivity due to the lower electron density with $P_L = 32$ W. This lower thermal conductivity is likely also responsible for the slow increase in $T_e$ during the high-power portion of the pulse.

The densities of all the cations (Cl$_2^+$, Cl$^+$, Ar$^+$, and Ar$_2^+$), density of Cl$^-$ and the ratio of the densities of the dominant cation Cl$_2^+$ and Cl$^+$ ($\alpha = [\text{Cl}_2^+] / [\text{Cl}^+]$) in the skin depth (height = 11 cm) are shown in Fig. 3.14 for different values of $P_L$. Among the cations, the dominant species
are Cl$_2^+$ and Cl$^+$, which have densities 2-3 orders of magnitude higher than the densities of Ar$^+$ and Ar$_2^+$. During the high-power part of the cycle, the cation density is nearly constant whereas the Cl$^-$ density increases by 30% from $P_L = 160$ W to $P_L = 32$ W. The decrease in Cl$^-$ density with increasing $P_L$ is partly due to the increase in fractional dissociation of Cl$_2$ (53% to 73%) with increasing power – low Cl$_2$ density translates to lower rates of dissociative attachment – and increased rarefaction in the skin depth at higher power. $\alpha = [\text{Cl}_2^+] / [\text{Cl}^+]$ is particularly sensitive to the $P_L$ and increases with decreasing $P_L$. Again, this is in part explained by the lower fractional dissociation at low $P_L$. The lower fractional dissociation not only reduces the rate of ionization of atomic Cl but also increases the rate of charge exchange of Cl$^+$ with Cl$_2$ to form Cl$_2^+$.

### 3.4 Concluding Remarks

In this chapter, an inductively coupled plasma, driven by a low-high pulsed power sustained Ar/Cl$_2$ mixtures at 20 mTorr, was computationally investigated. Similar to an on-off pulsed plasma, the electron temperature $T_e$ spikes in the electromagnetic skin depth at the beginning of the high-power portion of the cycle. A downward spike of $T_e$ occurs in the skin depth during power transition from high-to-low power, while $T_e$ is nearly the same value (and constant) during the low- and high-power periods. $T_e$ is largely determined by a balance between electron heating from the electric field, and power losses, which in the skin depth includes both collisions and advection out of the skin depth. With the gas density nearly constant during the pulsed cycle the increase in $T_e$ above the steady-state value is required at the leading edge of the low-to-high power period to increase the ionization rate to reach a higher plasma density required to sustain the high-power portion. Analogously, a decrease in $T_e$ below the steady-state value is required at the leading edge of the high-to-low power period to decrease the rate of ionization and increase the rate of attachment. As the low-to-high (and high-to-low) power
ramping time increases and exceeds the energy relaxation time, the leading edge transients in $T_e$ become less severe. For long ramping times, the transients become nearly indistinguishable.

The response of the plasma to the low-high and high-low power changes is highly spatially dependent. For example, the spikes of $T_e$ are distinct in the skin depth while being elongated transients near the substrate. Similarly, the modulation in electron density in the skin depth closely tracks power deposition while $n_e$ is dispersed in time near the substrate. Both transients in $T_e$ and $n_e$ are delayed near the substrate relative to the skin depth. The electron transport time across the reactor, (10-30 µs) coincides with the time of the power transition, and so produces a delay in the transients in the skin depth. During this transport in density and temperature across the reactor, power is collisionally dissipated while thermal conduction disperses the heat pulse. As a result, the spikes (positive and negative) in temperature, and steps in electron density originating in the skin depth, are dispersed in time and in space upon reaching the substrate.

For pulse repetition rates in ICPs that are high enough that the gas density and mole fractions do not significantly change during the pulses. Spikes of $T_e$ (positive or negative) should be expected during power transitions. However, these spikes are really only required in the skin depth where power deposition occurs. The magnitude, duration and phase of the transients in $T_e$ and $n_e$ are at first functions of distance from the skin-depth, and second, a function of the absolute plasma density that controls the thermal conduction of electron power from the skin depth. A third consideration is the non-local transport of electrons in the tail of the energy distribution function which have a longer mean-free-path than the electrons in the bulk of the distribution. For conditions where non-local effects dominate, the convection of electron power from the skin depth to lower in the reactor will be more rapid and efficient.
The results discussed in this chapter demonstrate the importance of considering spatial-
and time-dependent dynamics when optimizing ICPs sustained with pulsed-power. The
dynamics that are experienced during power transitions at positions within the skin depth of the
electromagnetic wave launched into the plasma can be very different from those at more remote
locations. For plasma processing applications, optimizing the flux of reactants to the substrate is
the ultimate goal. In this regard, it is recommended to directly measure the plasma properties by
the substrate rather than interpret them from the measurements performed near the power source.
This is particularly important when using pulsed power, during which large transients can occur
in the skin depth but these transients do not survive to the substrate. Applying a low-high power
profile, instead of off-on pulsed power, and moderately extending the power transition time can
mitigate the severe oscillations of plasma properties during power transitions.
3.5 Figures

Fig. 3.1 Geometry and power profile used in the model. a) The geometry is an inductively coupled plasma having a 4-turn antenna. The dots (with dimensions) indicate where plasma properties are shown. b) Pulse power profile for the base case.
Fig. 3.2 Plasma properties for the base case (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W) at 0 μs (end of the low-power) and 100 μs (end of the high power) during the power pulse. a) Electron density, b) electron temperature and c) ionization source by collisions of bulk electrons. Maximum value, range of values plotted and units for contour labels are indicated in each image.
Fig. 3.3 Plasma properties for the base case (Ar/Cl₂ = 5/95, 20 mTorr, 96 W – 160 W) at 0 µs (end of the low-power) and 100 µs (end of the high power) during the power pulse. a) Cl₂⁺ density, b) Cl⁻ density and c) gas temperature. Maximum value, range of values plotted and units for contour labels are indicated in each image.
Fig. 3.4 Axial distribution of electron and Cl densities at mid-radius of wafer at a) end of the low-power pulse (0 μs) and b) end of the high-power pulse (100 μs).
Fig. 3.5 Time dependence of a) electron density and b) electron temperature at different heights above the substrate and mid-radius over 2 pulse periods (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W). These heights are noted in Fig. 3.1. The results for electron temperature have been numerically smoothed.
Fig. 3.6 Electron energy distributions (EEDs) at different heights above the substrate at mid-radius of the wafer at the a) end of the low-power pulse (0 μs) and b) end of the high power pulse (100 μs). (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W.) These heights are noted in Fig. 3.1. The EEDs have been numerically smoothed.
Fig. 3.7 Electron density at the end of the high-power pulse (100 μs) for gas mixtures of Ar/Cl₂ = a) 20/80, b) 40/60, c) 60/40 and d) 80/20. (20 mTorr, 96 W - 160 W.) The contours are plotted on a 2-decade log scale with the maximum value in each frame noted. Contour labels have units of $10^{11}$ cm$^{-3}$. 
Fig. 3.8 Electron density as a function of time for different values of the Cl₂ mole fraction at a) 11 cm above the substrate and b) 2 cm above the substrate. (20 mTorr, 96 W - 160 W.)
Fig. 3.9 Electron temperature as a function of time for different values of the Cl₂ mole fraction at a) 11 cm above the substrate and b) 2 cm above the substrate. (20 mTorr, 96 W - 160 W.) The values for $T_e$ have been numerically smoothed.
Fig. 3.10 Electron temperature while varying the power ramp-down time. a) Power profiles for ramp-down times from 10 to 80 μs. Electron temperature for different ramp-down times at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 96 W - 160 W.) These values of $T_e$ have been numerically smoothed.
Fig. 3.11 Electron density while varying the power ramp-down time.  a) Power profiles for ramp-down times from 10 to 80 μs.  Electron density for different ramp-down times at b) 11 cm above the substrate and c) 2 cm above the substrate.  (Ar/Cl2 = 5/95, 20 mTorr, 96 W - 160 W.)
Fig. 3.12 Electron temperature while varying the low power during the cycle. a) Power profiles for low powers of 32 W to 160 W. Electron temperature for different low powers at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.) These values of $T_e$ have been numerically smoothed.
Fig. 3.13 Electron density while varying the low power during the cycle.  a) Power profiles for low powers of 32 W to 160 W. Electron density for different low powers at b) 11 cm above the substrate and c) 2 cm above the substrate. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.)
Fig. 3.14 Plasma properties 11 cm above the substrate while varying the low power during the cycle. (Ar/Cl₂ = 5/95, 20 mTorr, 160 W high power.) a) Total cation density, b) Cl⁻ density and c) ratio $\alpha = n_{Cl_2^+}/n_{Cl^+}$. 
3.6 References

4.1 Introduction

The combined impedance of the plasma reactor and the plasma in low pressure plasma processing for microelectronics fabrication, using both capacitively and inductively coupled plasmas (ICPs), is typically non-linear [1-2]. Common combined impedances can range from 100’s of mΩ to 100’s of Ω and up to kilo-ohms of reactance. These conditions make it difficult to deliver power to the plasma from conventional power supplies and transmission lines that typically have fixed impedances of 50-75 Ω. The electric field reflection coefficient, $\Gamma_R$, is the electric field reflected from the plasma reactor relative to the electric field delivered by the power supply through a transmission line (typically a coaxial cable) to the plasma reactor. The reflection results from the output impedance of the power supply and transmission line differing from that of the plasma reactor,

$$\Gamma_R = \frac{Z_L - Z_o}{Z_L + Z_o},$$

where $Z_L$ is the impedance of the load (in this case, the combined impedance of the plasma reactor and the plasma) and $Z_o$ is the output impedance of the power supply and transmission line [3]. Since $Z_L$ has reactive contributions, $\Gamma_R$ typically has both real and imaginary components from which both the magnitude and relative phase of the forward and reflected waves can be

\footnote{The results discussed and portion of the text appearing in this chapter were previously published in the paper by Chenhui Qu et al., “Power matching to pulsed inductively coupled plasmas”, J. Appl. Phys. 127, 133302 (2020).}
determined. Typically only the magnitude of reflection $|\Gamma_R|$ is used to characterize matching efficiency.

The usual remedy to maximize power transfer to a plasma processing reactor (and minimize reflection) is to employ an impedance matching network (IMN) between the transmission line and plasma reactor [4-6]. The IMN usually contains reactance (capacitors and inductors) both in series and parallel to the load with the goal of making the input impedance to the IMN be the same as the power supply termination impedance and transmission line impedance. In doing so, the reflection coefficient is minimized. In practice impedance matching is complicated by both the non-linear characteristics of the plasma and the increasingly common use of multiple frequencies and pulsed power. Even if driven with a single frequency, the non-linear response of the plasma to that single frequency power will produce higher harmonics in current, thereby making reproducible impedance matching more challenging [7,8].

The use of pulsed power further complicates matching as the plasma contribution to $Z_L$ can change by orders of magnitude during the pulsed cycle. For example, pulsed ICPs as used in microelectronics fabrication operate at pressures of tens of mTorr in attaching gas mixtures such as Ar/Cl$_2$ powered with radio frequency (RF) supplies of a few to tens of MHz. The pulsed repetition frequency (PRF), pulses per second, can be hundreds of Hz to tens of kHz. Duty cycle (DC), the fraction of time the power is applied per cycle, can be 10-50%. The end result is that the electron density at the time the power is applied at the leading edge of the pulse can be as low as $10^8$ cm$^3$ whereas later during the pulse, the electron density can exceed $10^{11}$ cm$^3$ [9,10]. These densities can increase across these three decades during a few to 10s or 100s of $\mu$s depending on the power delivery system and reactor design. The reactor contribution to $Z_L$ for an ICP is typically dominated by the positive reactance of the inductance of the antenna, though
the antenna will also have resistance.

$Z_L$ for a pulsed ICP has additional dynamics due to the E-to-H (capacitive-to-inductive) transition that occurs during the transient in plasma density at the beginning of a pulsed period [11-15]. If the electron density at the beginning of a power pulse is too low, the electromagnetic skin depth, $\delta_P$, may exceed the dimensions of the reactor which then makes inductive coupling of power from the antenna problematic. For these conditions, the antenna simply acts as an electrode which electrostatically and capacitively couples power into the plasma through the dielectric window between the antenna and the plasma [11]. This is the E-mode during which power can be dominantly coupled into the plasma by sheath oscillation (much like a capacitively coupled plasma) with power mainly deposited by ion acceleration from the plasma into the dielectric window under the antenna [15]. During the capacitive E-mode, the reactance of the plasma is negative. As the electron density increases, $\delta$ decreases which increases the fraction of power that is inductively coupled until the power is dominantly delivered by electron acceleration in the electromagnetic field within $\delta$ of the antenna. This is the H-mode during which the reactance of the plasma is positive. In practice there may be mixed-mode coupling, both E-mode and H-mode during quasi-steady state operation of the ICP [11,12]. The degree of E- and H-mode coupling depends on factors such as the voltage across the antenna, the proximity of antenna to the plasma, the shape of the antenna, gas pressure and composition, and the use of a Faraday shield between the antenna and plasma [16].

The E-H transition in ICPs has been addressed both experimentally and theoretically [17-25]. When measuring the electron energy distribution (EED), Chung et.al. found that during E-mode, the EED evolves from bi-Maxwellian to Druyvestein-like structure when increasing pressure [26]. During the H-mode, having a significantly larger electron density with a higher
rate of e-e collisions, the EED remains essentially as a Maxwellian. To smoothen the severity of the E-H transition, Singh et al. investigated use of a Faraday shield to minimize capacitive coupling from the antenna [16]. When using the Faraday shield, the plasma potential at low power was lower, indicating lower capacitive coupling while the electron density was lower. During H-mode, the antenna current and voltage decreased when using the Faraday shield. Had the plasma been operating purely in H-mode, there would not have been a decrease in current when using the Faraday shield, which then implies that even in H-mode, there was mixed E- and H-mode coupling.

Kempkes et al. investigate the effect of the power modulation on the E-H transition using rectangular and triangular power waveforms [27]. They found that even with smoothly varying power (triangular waveform) abrupt E-H transitions occurred. Kawamura et al. performed 2-dimensional (2D) simulations of E-H transitions in ICPs sustained in Cl₂ [28]. They found ionization instabilities and modulations in electron density attributed to rapid transitions between E- and H-modes.

The E-H transition often displays hysteresis behavior. The transition between the low E-mode electron density to the high H-mode electron density occurs at different powers if increasing power (occurs at a higher power) or decreasing power (occurs at a low power). The power deposition from both inductive and capacitive coupling was theoretically analyzed by Lee et al. [29], who found that the pressure and the dimensions of the reactor affected the power for the E-H transition. The combined effects of electron density, collision frequency and skin depth of the electromagnetic wave contributes to nonlinear dependence of mode transition on operating conditions. The hysteresis of the E-H transition was experimentally investigated by Daltrini et al. [30]. They suggest that rather than being an intrinsic characteristic of the plasma, the
hysteresis behavior can be affected by the power loss in the matching system, suggesting the need to include circuit analysis when investigating these transitions.

The E-to-H transition is another complicating factor in matching pulsed power to the ICP reactor. The change in $Z_L$ due to the E-to-H transition in addition to the reduction in the resistance of the plasma is typically over shorter times than the components in the match box can be changed. The end result is that power delivery cannot be efficiently matched to the plasma reactor during the entire pulsed cycle. The values of components in the match box are typically chosen to match at a particular time during the pulsed cycle – this is called set-point matching. If the match is chosen early in the pulsed period, the E-mode may be emphasized while there is a mismatch during the latter part of the pulsed cycle. If the set-point is late during the pulse period, the E-mode may be suppressed but there is also a longer time to ramp up the plasma density when power is mismatched early in the pulse.

In this chapter, some results from a computational investigation of the dynamics of power matching to pulsed ICPs of the type used in microelectronics processing (etching, deposition) are discussed. A model for the circuit and match box has been employed in a 2-dimensional simulation of the ICP. It was found that under perfect matching conditions, there is a smooth transition between the E- and H-modes, in contrast to several experimental results. This suggests that a sharp transition between modes is not a fundamental plasma transport issue, but rather may be related to power delivery. It was found that when using pulsed power, the power delivery is highly dependent on the time during the pulse at which the set-point is matched. Matching early in the pulsed period leads to a faster re-ignition of the plasma, while emphasizing E-mode characteristics during the onset of the pulse. There is also poor matching during the H-mode. Matching later in the pulsed period leads to better power delivery overall, at the cost of longer
ignition delay. The rapid application of power when operating in E-mode can launch electrostatic waves due to the need to establish a sheath to dissipate the applied voltage. The pulsed duty-cycle, matchbox parameters, and antenna shape play key roles in power matching inductively coupled plasmas.

A brief model description is provided in Sec. 4.2. Matching to pulsed ICPs with E-H transitions is discussed in Sec. 4.3. Concluding remarks are in Sec. 4.4.

4.2 Description of the Model

This computational investigation was performed using the Hybrid Plasma Equipment Model (HPEM) complemented by a model for the matchbox. The HPEM is discussed in detail in Chapter 2 and Ref. [31], thereby only a brief description will be provided here. In this case we utilize three modules – the Electromagnetics Module (EMM), Electron Energy Transport Module (EETM) and the Fluid-Kinetics Poisson Module (FKPM). The frequency domain wave equation for inductively coupled electric field is solved in the EMM. In this 2-dimensional simulation, the current flowing in the antenna is in the azimuthal direction $\theta$, producing components at the fundamental frequency of the magnetic field in the $(r,z)$ [radius, height] directions and of the electric field, $E_\theta$, in the $\theta$ direction. The conduction currents are provided by a circuit model. The Poisson’s equation is solved in the FKPM coincident with the update of all charged and neutral species densities. Complex conductivities are transferred back to the EMM to solve the wave equation.

The schematic of the circuit representation for the matchbox, reactor and plasma is shown in Fig. 4.1. As described in Sec. 2.1.1, the antenna is represented as a discretized transmission line in the circuit model. Its inductance is calculated based on its geometry, and divided into 100
segments. Each of these segments has a fraction of the total inductance of the antenna. In this work, four paths of power flow are considered: power loss in the matchbox \((P_M)\), power loss on the antenna \((P_A)\), inductively coupled power \((P_I)\), and capacitively coupled power \((P_C)\).

An ideal matching condition is represented when the power reflection coefficient, \(\Gamma\), is zero. The circuit components for such a condition are solved as \(Z_M = Z_0\), where \(Z_M\) is the input impedance of the matchbox and \(Z_0\) is the intrinsic impedance of the power source. The choices of the circuit components in the matchbox are circuit dependent. That is, the solutions of the circuit components are subject to the architecture chosen for the matchbox. For the matchbox used in this chapter as shown in Fig. 4.1, the capacitors \(C_P\) and \(C_S\) are adjusted to approach the perfect matching, and the solutions are:

\[
C_p = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}, \quad (4.1)
\]

\[
C_s = \frac{\text{Re}(Z_L)^2 \left(1 - \omega^2 L_p C_p \right)^2 + \left[ \omega C_p |Z_L|^2 - \text{Im}(Z_L) \left(1 - \omega^2 L_p C_p \right) \right]^2}{\omega \left(1 - \omega^2 L_p C_p \right) |Z_L|^2 \left[ \omega C_p |Z_L|^2 - \text{Im}(Z_L) \left(1 - \omega^2 L_p C_p \right) \right]}, \quad (4.2)
\]

where

\[
A = [\text{Re}(Z_0) - R_M] \left\{ |Z_L|^2 \omega^4 L_p^2 + \omega^2 |Z_L|^4 + 2 \omega^3 L_p \text{Im}(Z_L) |Z_L|^2 \right\} - \text{Re}(Z_L) \omega^2 L_p^2 |Z_L|^2, \quad (4.3)
\]

\[
B = 2 \omega^2 L_p \text{Re}(Z_L) |Z_L|^2 - 2 \omega |Z_L|^2 \left[ \text{Re}(Z_0) - R_M \right] \left[ \omega L_p + \text{Im}(Z_L) \right], \quad (4.4)
\]

\[
C = \left\{ \left[ \text{Re}(Z_0) - R_M \right] - \text{Re}(Z_L) \right\} |Z_L|^2, \quad (4.5)
\]

### 4.3 Matching to Pulsed ICPs with E-H Transitions

For computationally investigating the fundamental phenomena of E-H matching, we chose a simple ICP geometry and a relatively small chamber. This layout for an ICP reactor
powered by a spiral planar antenna is a standard design used for plasma assisted semiconductor fabrication [35-37]. Industrial systems are typically larger to accommodate wafers up to 30 cm in diameter. Our choice of a smaller chamber for this investigation was based on wanting a fine enough mesh to capture the dynamics of the E-H transitions while also enabling computation of a sufficient number of pulsed periods to reach the quasi-steady state. The details of our investigation are sensitive to the size and topology of the reactor. For example, antenna and chamber impedance are both functions of size and layout, which would affect the specific values of match box parameters, and necessitate a different termination impedance. The spacing of the antenna from the dielectric window affects capacitive coupling, as discussed below. Having said that, the systematic trends we discuss apply to more complex and larger reactors. For example, we have performed limited studies on industrial size ICP reactors [38] and the systematic trends we discuss here are essentially the same.

A schematic of the reactor is shown in Fig. 4.2. The chamber has an internal diameter of 22.5 cm, height (substrate to window) of 12 cm and is powered by a 3-turn antenna having radii of 2.5, 5.3 and 8.0 cm. The coils have thickness of 0.45 cm and height of 1.15 cm, and sit above the 0.8 cm thick quartz window ($\varepsilon/\varepsilon_0 = 4$) with an air gap of 0.4 cm. The total inductance of the antenna is $L_C = 0.95 \ \mu\text{H}$. The antenna-plasma coupling coefficient is $k_C = 0.75$. The entire inner surface of the window serves as gas inlet showerhead with the pump port occupying an annulus between 6.9 and 11.1 cm on the bottom of the chamber. A pressure sensor is located in the outer wall 2 cm above the pump port. All other surfaces are grounded metal.

Unless otherwise noted, the gas mixture is Ar/Cl$_2 = 65/35$ at a pressure of 25 mTorr. Ar/Cl$_2$ gas mixtures are commonly used for conductor etching. The gas inlet flowrate is 200 sccm. The outlet flow rate is adjusted so that the pressure at the sensor is 25 mTorr. As
discussed below, our results are sensitive to the conductivity of the plasma at the start of the power pulse, and that conductivity is sensitive to gas mixture. When using pure Cl₂ plasmas, a thermal electron attaching gas, the system can transition to an ion-ion plasma during the afterglow with a negligible electron density. These conditions then require “re-ignition” of the plasma on every power pulse. Although this may in fact be the case for many industrial systems, the re-ignition requirement adds another constraint and complexity. We therefore chose a gas mixture for which there would be significant change in conductivity during the afterglow but not to the degree that re-ignition is required.

The reaction mechanism is the same as discussed in Ref. 32. An important point for the study in this chapter is that Cl₂ is a thermal electron attaching gas for which the rate coefficient for dissociative electron attachment increases with decreasing electron temperature, \( T_e \). So for otherwise the same conditions, rates of attachment are small when power is applied during a pulse and \( T_e \) is large. Rates of attachment are large when the power is off and \( T_e \) is small.

The fixed circuit elements are coil resistance \( R_C = 0.1 \Omega \), termination impedances \( C_T = 100 \text{ nF} \) and \( L_T = 5 \text{ nH} \), and inductance on match box \( L_P = 100 \text{ nH} \). The internal resistance of the match box was neglected by setting \( R_M = 10^{-6} \Omega \) so that \( P_M \) is negligible. This allows for the independent study of impedance matching impact on plasma transients. In practice, matching network impedances can have 100s to 1000s of mΩ of real resistance, and consume a significant amount of power delivered by the supply. Typically, these dissipative losses are accounted for in the series elements, where the larger dissipative components tend to reside, and where the current through the elements tends to be higher, as opposed to the shunt components. The inner coil of the antenna was connected to the match box, and the outer coil of the antenna was connected to ground through the series termination components \( C_T \) and \( L_T \).
4.3.1 Continuous Power Baseline

With the base case values for circuit and operating conditions, the continuous wave (CW) characteristics of the ICP reactor were first investigated as a function of power delivered from the supply. Using perfect match values for $C_P$ and $C_S$, $\Gamma = 0$, and $P_S = P_T$. The electron density, inductive power and capacitive power are shown in Fig. 4.3 for a total power deposition of 5 W and 200 W. Note that the capacitive power deposition plotted is actually the time average of the capacitive and resistive (bulk) power deposition. The calculation of local power deposition of $p = \vec{j} \cdot \vec{E}$ is unable to distinguish between the capacitive and resistive heating. Given the spatial distribution and the negative sign of the reactance of $Z_k$, the capacitive power is clearly dominated by sheath heating at higher total power.

For 5 W, the voltages on the coils (inner to outer) are 147 V, 112 V and 44 V. The total capacitive power is 3.19 W (63.8% of the total), inductive power is 0.86 W (17.2 %), and resistive antenna losses 0.95 W (19%), a power division that indicates E-mode operation. On a relative basis, antenna losses are larger at lower total power due to the higher relative antenna current required to sustain the plasma. The capacitive component includes contributions from both ion and electron acceleration by the sheath and bulk Joule heating. With the largest voltage and capacitive current from the inner coil, the capacitive heating is maximum under that coil (3.8 mW/cm$^3$) adjacent to the dielectric with resistive current flowing through the plasma to produce Joule heating of 0.7 mW/cm$^3$ in the center of the plasma. Sheath heating also occurs along the metal boundaries. With the peak electron density of $6 \times 10^8$ cm$^3$, inductive power deposition extends to the middle of the reactor (electric field skin depth $\delta = 7.4$ cm) with a maximum value of 3 mW/cm$^3$. The voltages on the 3 coils of the antenna are nearly in phase. However, with different voltage amplitudes and different adjacent sheath thickness, particularly with respect to
ground, there is some recirculation of current between the antenna coils that produces a net negative power deposition in the upper outer radius of the reactor.

For 200 W total power, the voltages on the coils (inner to outer) are 334 V, 276 V and 112 V. The total capacitive power is 9.7 W (4.8% of the total), inductive power is 188.2 W (94.1%), and resistive antenna losses 2.1 W (1.1%), a power division that indicates H-mode. With a higher electron density (peak $6.8 \times 10^{10} \text{ cm}^{-3}$) the plasma is more conductive and capacitive heating is largely limited to the periphery of the reactor. The higher plasma density also reduces the electric field skin depth to $\delta = 0.7 \text{ cm}$.

The capacitive power has a cycled averaged layer of negative power deposition parallel to the dielectric window, in addition to that in the upper right corner, that was not observed at lower power. At the high power, the electron flux directed towards the dielectric is dominated by the ambipolar flux originating from the electron sources produced by inductive coupling. The electron ambipolar flux is retarded by the ambipolar electric field that points from the center of the plasma towards boundaries. This is the same direction as the electric field that produces electron heating due to expansion of the capacitive sheath under the window. During expansion of the capacitive sheath, power is expended in slowing the ambipolar driven electron flux in addition to accelerating electrons out of the sheath region. This negative power deposition is not observed at the lower power in the absence of the large ambipolar electron flux produced by inductive coupling.

The division of power deposition between capacitive and inductive; and average electron density are shown in Fig. 4.4a for $P_T = 5$-200 W for perfect match conditions and continuous power. The values of $C_P$ and $C_S$ to obtain perfect matches and ionization efficiency are shown in Fig. 4.4b. (Ionization efficiency is average plasma density divided by power deposition in the
plasma, and is a relative measure of efficiency.) These results are typical of the E-H transition. At low power deposition, the electron density is low, the skin depth is large and sheath is thick. The low electron density and large skin depth reduces (on a relative basis) the inductive power deposition and the thick sheath (on a relative basis) increases the capacitive power deposition. The thicker sheaths produce a larger sheath velocity, and capacitive power deposition scales with the square of the sheath speed. As noted above, for $P_T = 5$ W, 77% of the power is capacitive and 11% is inductive. The power dissipation by the coil is about 12%. With increasing power deposition, the electron density increases, skin depth decreases and sheath thickness shrinks, all of which contribute to lower capacitive power deposition and higher inductive power deposition.

We do not observe a sharp, step-function increase in electron density that can be identified as the E-H transition. The power at which the E-H transition occurs is then somewhat a qualitative judgement. The fraction of power dissipated by inductive coupling exceeds 50% at $P_T = 25$ W, and exceed 90% at $P_T = 140$ W. To achieve the perfect match, the values of the matching elements $C_P$ decreases by about 20% and $C_S$ increases by a factor of 2.5.

Over the range of $P_T = 5$-200 W, the average electron density increases from $2.8 \times 10^8$ cm$^{-3}$ to $2.3 \times 10^{10}$ cm$^{-3}$, a factor of nearly 100 increase, for $P_T$ increasing by a factor of 40. A portion of the increase in electron density results from an increase in ionization efficiency, plotted here as the total electron density divided by the total power deposition in the plasma. This efficiency increases by a factor of nearly 3. At low $P_T$, the fraction of power dissipated by resistive coil and capacitive heating is large. No ionization occurs from coil heating, and the efficiency of ionization by capacitive coupling is low due to ion acceleration in the sheaths, characteristic of the E-mode. The efficiency remains relatively constant until the H-mode begins, at which time the efficiency increases. At high power deposition, a true H-mode occurs,
as the majority of power is dissipated by electron heating in the bulk which is intrinsically more efficient at producing ionization.

With there always being a perfect match when changing $P_S$, there is a relatively smooth transition from dominantly E-mode to dominantly H-mode with increasing power. To obtain this perfect match with increasing power, the value of $C_S$ smoothly increases (33 pF to 155 pF) and $C_P$ smoothly decreases (267 pF to 168 pF). Experimentally, it is often observed that there is a rapid, almost impulsive, increase in electron density with a rapid switch between E-mode and H-mode when a critical power is delivered from the supply. Based on fundamental plasma transport, there is no requirement for such a sharp transition to occur.

In practice, the transition in apparent ionization efficiency may be exacerbated by the difficulty in matching between the E-mode and H-mode. If the circuit is better able to match to the H-mode (positive reactance) than E-mode (negative reactance), then the ionization efficiency will make a rapid and impulsive increase when the H-mode begins to dominate. There may also be heating of electrical components that can change their impedance. Another factor that may influence the apparent ionization efficiency is changes in plasma conditions due to the power deposition. For example, when operating at constant pressure, higher power deposition produces more gas heating which reduces the gas density and so reduces the electron collision frequency. In chemically active mixtures, more power deposition produces more dissociation and so there are different species with which electrons collide.

To demonstrate these possibilities, two parameterizations were performed. In the first, a parameterization over power ($P_T = 5$-$200$ W) was conducted with the match box settings chosen to provide a perfect match at 150 W ($C_P = 162$ pF, $C_S = 135$ pF) which then produces mismatches at other powers. The resulting ionization efficiency is shown in Fig. 4.5. For these
conditions the circuit is mismatched at lower powers, producing a large reflection coefficient, and a corresponding low ionization efficiency. With power increasing towards 150 W, the reflection coefficient decreases, H-mode begins to dominate and so the ionization efficiency increases.

In the results shown in Fig. 4.4, the length of time for the simulation was deliberately chosen to be long enough so that the plasma properties came into a quasi-steady state; while being short enough that there was no significant dissociation of the feedstock gases and gas temperature excursions were not significantly different. These conditions correspond to a short residence time of the gas in the plasma, \( \tau_{\text{res}} \). In this way, a side-by-side comparison of different powers could be performed without the complication of the impact of changing gas temperatures, gas densities and gas compositions on matching. In actual practice, when changing power one does have these complications of gas heating producing rarefaction and different degrees of dissociation of the gas.

The parameterization in Fig. 4.4 was repeated when computing for a sufficient time that all plasma properties including gas temperature and composition come into a steady state. This would correspond to at large \( \tau_{\text{res}} \). With the large \( \tau_{\text{res}} \), for \( P_T = 5 \) W, the average gas temperature was \( T_g = 330 \) K (for a wall temperature of 325 K) and fractional dissociation of Cl\(_2\) was 1.3%. For \( P_T = 200 \) W, \( T_g = 635 \) K and fractional dissociation was 27%. The resulting ionization efficiency, also shown in Fig. 4.5, increases by a factor of 4.5 from low to high power. The majority of this increase in efficiency results from the decrease in Cl\(_2\) mole fraction (due to dissociation) and decreases in gas density (gas heating), which then decreases the rate of attachment. These results emphasize the difficulty of performing side-by-side comparisons of E-H behavior when changes in power deposition also change fundamental properties of the plasma.
in addition to electron density.

### 4.3.2 Set Point Matching to ICPs

In this section, we discuss matching of a pulsed ICP for the same operating conditions as the CW studies (Ar/Cl₂ = 65/35, 25 mTorr). The standard conditions for pulsed ICP operation were a pulse repetition rate (PRF) of 13.3 kHz (period of 75 µs), duty cycle 35% and forward power delivered from the supply during the power on period of \( P_S = 250 \) W. As a base case, we used perfect match conditions by instantly adjusting \( C_P \) and \( C_S \) to produce \( \Gamma = 0 \) throughout the pulse period. The maximum in the plasma potential, the electron density, Cl⁻ density and positive ion densities are shown in Fig. 4.6a during the power pulse and immediate afterglow. The modes of power dissipation are shown in Fig. 4.6b. The resistive and reactive components of the impedance \( Z_L \), and perfect matching values of \( C_P \) and \( C_S \) are shown in Fig. 4.6c.

At the beginning of the power pulse, the plasma conditions are essentially an ion-ion plasma where the positive ion density is nearly equal to the negative ion density, \([M^+] = [Cl^-] = 4.5 \times 10^{10} \) cm⁻³. The small electron density at the beginning of the pulse, \( n_e = 2 \times 10^8 \) cm⁻³ results from Cl₂ being a thermally attaching gas, which reduces the electron density during the afterglow through dissociative electron attachment producing Cl⁻. During the power pulse the negative ion density \([Cl^-]\) is relatively constant. With the electron temperature \( T_e \approx 2.5 - 3.5 \) eV during the power pulse, the thermal dissociative attachments rates are small compared to ionization rates. The increase in electron density is nearly matched by the increase in positive ion density.

With this low initial electron density, power is initially capacitively coupled. During the first 3 µs, the capacitive power exceeds that of the inductive power and the plasma operates in E-mode. The E-mode is additionally indicated by the oscillation in the plasma potential, \( \Phi_P \), with an amplitude as large as 450 V in the same manner as a capacitively coupled plasma. The
maximum antenna voltage amplitude (inner turn) is 1080 V. There is some oscillation in the voltage amplitude on the antenna, which is due to the rapid increase in electron density, which changes the plasma impedance sufficiently to lower the antenna voltage, which lowers the electron density which induces an increase antenna voltage. This oscillation is likely magnified by the iterative numerical technique used to link the plasma portion of the simulation with the circuit.

As the electron density increases, the electromagnetic skin depth decreases and sheath under the coils thins, the fraction of capacitive power dissipation decreases. By 5 µs, the electron density is high enough, \(1 \times 10^{10} \text{ cm}^{-3}\), and skin depth short enough that power is dominantly inductively coupled and the plasma operates dominantly in H-mode. Due to the proximity of the antenna to the dielectric window, approximately 5% of the total power continues to be capacitively coupled even during H-mode. This is similar to CW operation. In the quasi-steady state during the pulse, the proportion of capacitively coupled power decreases by a few watts but is otherwise nearly constant. Upon termination of the power, both the capacitive and inductive power decrease in nearly the same proportion while remaining in H-mode. The power decreases quickly enough that the electron density does not appreciably change, and so the skin depth remains short enough to allow H-mode operation. This represents a hysteresis-type of behavior. The plasma remains in H-mode during decreasing power at the same power deposition that corresponded to E-mode during the beginning of the pulse.

As the plasma density increases at the leading edge of the power pulse and operation transitions to H-mode, the oscillation in \(\Phi_P\) decreases to an amplitude of 10-20 V. This modulation of \(\Phi_P\) is on top of the quasi-dc plasma potential of about 20 V. This dc value of plasma potential results from the ambipolar nature of the plasma transport \((T_e > T_{ion}, m_e < m_{ion})\).
An indication of purely H-mode operation without capacitive coupling would be quasi-dc plasma potential without significant oscillation. Since the power deposition resulting from $E_\theta$ and electron heating are harmonic, there can be harmonic oscillation in $T_e$ and so there would be some small oscillation in $\Phi_P$ even in purely H-mode. However, in this case, the majority of oscillation in $\Phi_P$ is due to capacitive coupling.

With perfect match conditions, $C_P$ decreases during the power pulse from 290 pF to 160 pF, accompanied by an increase in $C_S$ from 50 pF to 160 pF. The combined load impedance, $Z_L$ (which includes the antenna coil and plasma) has a positive reactance due to the inductance of the antenna. This reactance decreases during the plasma pulse in response to the capacitive component of the antenna current through the plasma. The resistive component increases in response to the power deposition in the plasma.

The impedance of the variable capacitors in RF matching networks is typically changed by a mechanical process (e.g., changing the overlap area between two plates). The speed of the mechanical movement of these variable capacitor systems is largely determined by the driving motors, with end-to-end movement typically on the order of hundreds to thousands of milliseconds. Impedance control algorithms working in conjunction with these mechanical limits will typically produce a tuning transient with a comparable characteristic time. With plasma-induced impedance transients having time scales that are orders of magnitude shorter than what can be achieved by these mechanically driven systems, it is typically not possible to change the values of $C_S$ and $C_P$ rapidly enough to achieve a perfect match throughout the power pulse. Typically set-point matching is employed in which values of $C_S$ and $C_P$ are chosen to minimize $\Gamma$ at a particular instant during the power pulse. We investigated the consequences of set-point matching. Computationally, this was achieved by selecting values at given times for $C_S$ and $C_P$
from the perfect-match case. For example, plasma reactor properties are shown in Fig. 4.7 when values for $C_S$ and $C_P$ were chosen for set-point matches from early to late in the pulse. These times, relative to the start of the power pulse, were 1.5, 3.25, 7 and 21 μs. Since the progression of the plasma prior to the time of the matching point is not exactly the same as for the case with perfect matching, the reflection coefficient at the match point may not be exactly zero.

For a matching point of $t_M = 1.5$ μs, the reactor properties at the match point are a forward power of 82.7 W and $\Gamma = 0.013$. The maximum capacitive power of 62.2 W occurs at the match point. The resistive power is 9.6 W and inductive power is 8.5 W, indicating operation in the E-mode. (Note that $\Gamma$ is finite due to the plasma properties being different than for the perfect match that provided the values of $C_S$ and $C_P$.) As the plasma density begins to increase, the E-mode dissipates and H-mode begins. With this increase in plasma density, the values of $C_S$ and $C_P$ required to achieve a match deviate from the set-point values. The reflection coefficient then monotonically increases until the H-mode is fully established at $t = 6-7$ μs, after which $\Gamma$ is relative constant at 0.5. At the end of the pulse, the electron density is $1.15 \times 10^{10}$ cm$^{-3}$ compared to the perfect match value of $2.4 \times 10^{10}$ cm$^{-3}$. This decrease in electron density is due to the reduction in power deposition following that $\Gamma = 0.5$.

As $t_M$ increases, the peak capacitive power decreases, there is a larger delay in the onset of inductive power deposition and the maximum inductive power increases, as shown in Fig. 4.8. The delay in onset of the H-mode results from there being less ionization produced during the E-mode. With a larger $t_M$, there is a larger mismatch that produces a larger $\Gamma$ early in the pulse, which reduces power deposition and ionization. For example, for $t_M = 2.5$ μs, the peak capacitive power of $P_C = 70$ W occurs at 2 μs when the inductive power is $P_I = 41$ W and $\Gamma = 0.03$. Just prior to the end of the maximum delivered power at 23 μs, $P_C = 9.3$ W, $P_I = 108$
and \( \Gamma = 0.46 \). For \( t_M = 21 \mu s \), the peak capacitive power of \( P_C = 21 \text{ W} \) occurs at 2.6 \( \mu s \) when the inductive power is \( P_I < 1 \text{ W} \) and \( \Gamma = 0.76 \). At 23 \( \mu s \), \( P_C = 12 \text{ W} \), \( P_I = 235 \text{ W} \) and \( \Gamma < 0.001 \). For \( t_M > 7 \mu s \), the set-point values of \( C_S \) and \( C_P \) are well matched to the H-mode, and so \( \Gamma < 0.01 \) for \( t > 10-15 \mu s \) for the remainder of the power pulse. The electron density at the end of the power pulse is nearly that of the perfect match.

### 4.3.3 Matching for Different Duty Cycles

Matching early during the power pulse is sensitive to the electron density at the onset of power, and this is particularly problematic in thermally attaching gas mixtures such as \( \text{Ar/Cl}_2 \). During the inter-pulse period, the electron temperature decreases, which increases the rate of attachment and increases electron loss. The lower electron density at the onset of power for the next pulse makes the system appear to be more capacitive to the matching network. This sensitivity can be demonstrated by varying the duty cycle of the pulsed power.

For the same peak power during the power pulse, a shorter duty cycle translates to lower average power deposition and less fractional dissociation of \( \text{Cl}_2 \). The larger density of \( \text{Cl}_2 \) results in more attachment during a longer inter-pulse period, resulting in a lower initial electron density at the beginning of the next pulse. For example, the electron density and plasma potential \( \Phi_P \) during the pulsed period are shown in Fig. 4.9 for different duty cycles (25% to 65%). Note that the time scales are shifted in Fig. 4.9b by increments of 10 ns in order to show the plasma potentials more clearly. The electron density at the beginning of the pulsed cycle is \( 1 \times 10^8 \text{ cm}^{-3} \) for a duty cycle of 25% and \( 1 \times 10^9 \text{ cm}^{-3} \) for a duty cycle of 65%. The magnitude of oscillation of \( \Phi_P \) indicates the severity of capacitive coupling.

When varying duty cycle, the same set-point match is used corresponding to \( t_M = 7 \mu s \) and a duty cycle of 35%. Duty cycles shorter than 35% produce smaller initial electron densities.
However, the system already starts in the E-mode, and so there is little change in the oscillation of the $\Phi_P$. Increasing duty cycle increases the initial electron density, which enables some H-mode coupling early during the pulse. This H-mode coupled power reduces the power coupled into the E-mode which then reduces the oscillation in $\Phi_P$. This reduction in capacitive power does come at a cost of increasing the reflection coefficient. At the time of the nominal match conditions for a duty cycle of 35%, the reflection coefficient at $t = 7 \, \mu$s is $\Gamma = 0.01$. For a 25% duty cycle, $\Gamma = 0.02$ (still small) whereas for a duty cycle of 65%, the reflection coefficient is $\Gamma = 0.08$.

### 4.3.4 Ion Energy Distribution on Dielectric Window During E-mode

A consequence of early matches that allow significant power into the E-mode is large ion fluxes incident onto the dielectric window while there is still significant oscillation in the plasma potential. These conditions produce energetic ions onto the window which can result in sputtering and erosion. For example, the ion energy distributions (IEDs) incident onto the window with a duty cycle of 25% are shown in Fig. 4.10. At the beginning of the pulse, the plasma potential rises from about 10 V when the sheath beneath the window is thick. The resulting IED is largely thermal with an extended tail. As the plasma density increases, which thins the sheath, and plasma potential increases with the capacitive coupling, the IED extends to as high as 200 eV, for a plasma potential peaking at 375 V during the E-mode. The maximum in the IED does not directly correspond to the maximum in plasma potential due to the locations within the thick sheath that ions are produced and due to the transient charging of the dielectric. As the H-mode is established and the plasma potential decreases, the maximum energy of the IEDs also begins to decrease. By the end of the power pulse, the peak of the IED occurs at 18 eV. In the afterglow where the plasma potential decreases below 10 V, the peak in the IED
occurs at 5 eV.

When matching early in the pulse, capacitive coupling is emphasized, there is more power dissipated in ion acceleration and there are more energetic of ions incident on all inside surfaces of the reactor, and on the window in particular. These energetic ions could be potentially damaging to the window and other surfaces. These energetic fluxes are then another consideration in choosing an early match. Having said that, even with $t_M$ being small, the E-mode dissipates before the plasma density reaches its maximum value. As such, the flux of energetic ions produced by capacitive coupling may not be large, thereby reducing the likelihood for damage.

4.3.5 Antenna Placement

The capacitance between the antenna and the plasma consists of at least three series components – the capacitance of the air gap between the antenna and window, the capacitance of the window and the capacitance of the sheath. In practice, the capacitance of the antenna-window gap is more variable than that of the window. For example, placement of the antenna after maintenance must be extremely precise to replicate the capacitance of the antenna-window gap. The variable capacitance of the antenna-window gap then translates into variability in the plasma.

To demonstrate the sensitivity of matching pulsed ICPs to the placement of the antenna, the following procedure was followed. The gap between the bottom of the flat antenna and the window was varied from $d = 0$ (in contact with the window) to 8.2 mm. For each gap, calculations were first performed with perfect matching. The values of $C_P$ and $C_S$ for each gap size were then chosen as the perfect match values at $t_M = 20 \mu s$. The simulations for gaps sizes of $d = 0 - 8.2$ mm were then repeated with these fixed values $C_P$ and $C_S$. The resulting
capacitive power $P_C$ and inductive power $P_I$ during the power pulse are shown in Fig. 4.11.

With increasing values of the gap, $d$, the series capacitance of the gap-window pair decreases. With $d = 0$ (maximum capacitance), E-mode power is dissipated at the leading edge of the power pulse. This capacitive power produces ionization, which then enables the inductive power to begin earlier leading to an onset of the H-mode. As the gap size $d$ increases, the series capacitance also decreases. This decrease in capacitance of the gap limits current, then decreases the E-mode power at the leading edge of the power pulse and increases the reflection coefficient. With lower E-mode power deposition, the increase in electron density is slower. This slow rate of increase in electron density means that more time is required for the electron density to increase to the point that inductive power dominates and the H-mode begins. During the quasi-steady state portion of the pulse where the circuit is well matched to the plasma, the small values of $d$ allow for larger capacitive power deposition, which then reduces the inductive power deposition.

For all values of the antenna-window gap, there is nearly a perfect match late in the pulse – all forward power is dissipated either in the plasma or in the antenna. However, the manner of deposition, fraction of power dissipated as $P_C$ and $P_I$, is sensitive to the height of the antenna above the window. In results not shown here, there is a similar dependence on the flatness of the antenna. An antenna that may be mounted at a small angle with respect to the window can be perfectly matched, however the fractions of power dissipated as $P_C$ and $P_I$ are a function of the orientation of the antenna. Reproducing performance when replacing an antenna requires both ensuring a match and also reproducing the fraction of power separately dissipated as $P_C$ and $P_I$. In the case of pulsed plasmas, the power waveforms should also be reproduced.

**4.3.6 Electrostatic Waves at Onset of E-mode**

For thermally attaching gas mixtures, as in the Ar/Cl₂ mixture used in this investigation,
the onset of the E-mode at the leading edge of the power pulse produces an impulsive perturbation to the plasma that generates electrostatic waves. At the beginning of the power pulse, the plasma is essentially an ion-ion plasma with the positive and negative ion densities greatly exceeding the electron density. For example, for the base-case at the end of the afterglow, the positive and negative ion densities adjacent to the window are essentially equal at $3.4 \times 10^{10} \text{ cm}^{-3}$ whereas the electron density is $2 \times 10^8 \text{ cm}^{-3}$. The charge density (units of elementary charge, $q = 1.6 \times 10^{-19} \text{ C}$) is $-2.5 \times 10^4 \text{ cm}^{-3}$. There essentially is no sheath as both positive ions have largely thermalized to the same temperature during the afterglow and the ions have nearly the same mobilities.

When the power is applied, a large voltage is generated across the antenna and capacitive coupling to the plasma occurs. The response of the plasma is to attempt to form a sheath to dissipate the capacitive voltage drop. During the first few RF cycles, the sheath is most easily formed by accelerating electrons adjacent to the dielectric into the plasma to produce a positive space charge region. During these first few cycles, the far more numerous positive and negative ions are nearly immobile and do not significantly separate to produce the charge density needed to create the sheath. With each half cycle, electrons are expelled from and attracted to the dielectric. The end result is launching of electrostatic waves into the ion-ion plasma.

The electron and charge density are shown in Fig. 4.12 during the first 6 cycles of the power pulse for the base-case with a match point of $t_M = 1.5 \mu\text{s}$. These conditions were chosen to emphasize the initial E-mode coupling for demonstration purposes. The electron density is shown as color-contours. The charge density $\rho$ (units of elementary charge/cm$^3$) is shown with numerical labels with a line for $\rho = 0$ indicating a sign change in local charge density. As the power increases at the beginning of the pulse, the voltage on the coils increases with each
successive RF cycle. Electrons adjacent to all surfaces in contact with the plasma are expelled into the plasma in an attempt to form a sheath. This expulsion is most pronounced under the window adjacent to the coils but also occurs along the side walls and substrate. The expulsion first produces an electrostatic wave having $\rho < 0$. Since the electron density is 2-orders of magnitude less than the positive and negative ions, this wave can propagate through the plasma without significantly perturbing the overall charge balance. The anodic half of the cycle launches a positive electrostatic wave. With each cycle, a new wave is launched, producing layers of alternating charge propagating into the plasma. The waves appear to emanate from under the inner and middle coils where the voltage is the largest and the largest amount of charge must be expelled to form the sheath.

In time, the electron density increases and positive space charge sheath is formed under the dielectric while the initial electrostatic waves collisionally dissipate. The waves soon become chaotic (not shown) due to the disparity in coil voltages, each with slightly different phases. The oscillating voltage on each coil launches what appears to be a cylindrically expanding electrostatic wave of different magnitude. These individually expanding waves are close enough in phase that their sum appears to have only a slight curvature. However, on successive pulses, the disparity in voltage between the coils increases, producing expanding waves which intersect and become chaotic before dissipating.

These electrostatic waves will occur in any highly electronegative system in which a sharply rising negative voltage is applied to a surface. For example, in pulsed plasma doping (P$^2$LAD) systems, a multi-kV negative, nearly step-function pulse is applied to the substrate to accelerate ions into the wafer for shallow junction implantation [39]. Simulations of P$^2$LAD systems predict similar electrostatic waves, albeit more soliton-like due to the single transient
voltage [40]. In the ICP systems discussed here, the amplitude and duration of the waves are small, and so the effects on processing (e.g., etch rate or uniformity) are likely not large. Their effects on diagnostics and sensors could be problematic, particularly if the waves are not reproducible pulse-to-pulse.

4.4 Concluding Remarks

Power dissipation in CW and pulsed electronegative inductively coupled plasmas sustained in Ar/Cl₂ mixtures and the consequences of impedance matching were computationally investigated. During a pulsed cycle, the modulation in electron density determines the mode of power deposition – capacitive (E-mode) at low electron density where the electromagnetic skin depth is large and inductive (H-mode) at high electron density where the electromagnetic skin is small. Even with perfect power transfer from the supply to the plasma, there is a natural E-H mode that occurs at the beginning of the pulsed period.

When considering matching, the increase in plasma density and spatial distribution of the plasma changes the impedance of the plasma reactor during pulsing, which then changes the matching requirements to deliver power from the supply. Since components in the match box are typically fixed during the pulsed period, components in the match box are set to match the plasma at particular time during the pulsed period. If the match box is chosen to match the impedance at the onset of the power pulse, E-mode is emphasized and a fast plasma ignition is expected due to efficient power deposition during power ramp-up. However, the tradeoff is a high power reflection coefficient during the majority of the power-on period as a consequence of the impedance mismatch to the H-mode plasma. In contrast, matching the higher power H-mode produces more net power transfer from the supply to the plasma, but delays the onset of the H-mode due to the mismatch of power in the E-mode.
Duty cycle during pulsing has important implications on power matching. In general, the shorter the duty cycle, the lower the electron density at the beginning of the next power pulse. This is particularly the case for mixtures using gases that attach thermal electrons, such as Cl₂. The lower electron density with a shorter duty cycle promotes E-mode operation at the start of the next power pulse.

In highly electronegative gases, the plasma at the beginning of the power pulse is essentially an ion-ion plasma. The impulsive application of power in a purely an E-mode results in launching of electrostatic waves during the leading RF cycles. The response of the plasma to the high voltage on the antenna during the E-mode is to form a sheath. The electrostatic waves result from the expulsion of the remaining electrons from nearby surfaces in an attempt to form a sheath. These waves are more severe when the afterglow is long and electronegativity is high.

Capacitance is largely a function of geometry and so the capacitance between the antenna and the plasma is a function of the gap length between the coil and dielectric window. A big gap produces a small capacitance and decreases the capacitive power that can be deposited during the E-mode. That decrease in power reduces the initial increase in electron density which then delays the onset of the H-mode.

The results discussed in this chapter demonstrate that impedance matching to a plasma, especially when using pulsed power, is a complex process. Changes in both operating conditions (duty cycle) and geometry (distance between the antenna and dielectric window) were found to impact the formation of the plasma and the power dissipation, which then affect plasma properties such as plasma density and collision frequency that determine the impedance of the plasma. Therefore, impedance matching networks with fixed components are not able to achieve a match over the entire pulsed period. Even when matching can be achieved, reset of the IMN
may be necessary for even slight modifications of the operating conditions or the setup of the reactor. For example, after preventative maintenance, a slight change in the arrangement of reactor components such as the antenna may produce a change in matching requirements.

Different match box setups lead to distinctive plasma behavior. In a pulsed power sustained plasma, choosing the circuit components in the match box to match the plasma impedance early in the pulse may produce faster ignition but risks impedance mismatch during the latter part of the pulse. Matching during the latter part of the pulse optimizes power delivery during the quasi-steady state with the tradeoff of delayed plasma formation. Matching the early part of the pulse benefits plasmas sustained by pulsed power with small duty cycles, while matching the late part of the pulse is suitable for plasmas sustained by power with long duty cycles or if the power supply is not able to accommodate higher levels of reflected power.

Power matching to transient systems will be challenging as long as the matching requires mechanical changes in components. These mechanical changes simply cannot be made rapidly enough to track the change in plasma impedance. As pulsed plasmas become even more prevalent in semiconductor manufacturing, advanced matching techniques, such as frequency tuning, will be required to minimize mode transitions and instabilities.
4.5 Figures

Fig. 4.1 Circuit schematic a) The circuit consists of impedances of the power generator, transmission line, matchbox, antenna, plasma, and termination circuit components. The antenna and transformed plasma impedances area represented by a discrete transmission line with each segment have having serial impedance $Z_{sn}$ and parallel impedance due to capacitive coupling, $Z_{cn}$. b) The $Z_{sn}$ components consist of the physical resistance ($R_{An}$) and inductance ($L_{An}$) of the antenna, and the transformed impedance (resistance and inductance) of the plasma, $Z_{Tn}$. The impedance due to capacitive coupling, $Z_{cn}$, has components due to the air gap and dielectric, sheath and bulk resistance of the plasma.
Fig. 4.2 Geometry of the cylindrically symmetric ICP reactor.
Fig. 4.3 Capacitive and inductive power deposition, and electron density when plasma is sustained with a total continuous power of a) 5 W and b) 200 W. (Ar/Cl₂ = 65/35, 25 mTorr.) The match is perfect. The capacitive power is shown as color contours with a line separating positive and negative values. Contour labels are mW/cm³. Electron density is shown as color contours. Inductive power deposition is shown as contour lines with labels in mW/cm³. The contour lines are blanked near the axis to enable clear view of the sheath formed under the powered coil.
Fig. 4.4 Plasma and circuit properties as a function of CW power deposition for perfect matching (Ar/Cl₂ = 65/35, 25 mTorr). a) Electron density and fraction of power deposition due inductive H-mode, capacitive E-mode and antenna heating. b) Analytical solutions for $C_p$ and $C_s$ for a perfect match and the ionization efficiency. The ionization efficiency is total electron density divided by power deposition in the plasma, and is a relative measure of efficiency.
Fig. 4.5 Ionization efficiency as a function of CW power (Ar/Cl\textsubscript{2} = 65/35, 25 mTorr). Cases are shown for perfect matches for small and large residence time (τ\textsubscript{res}) and with circuit values for a perfect match at 150 W with small τ\textsubscript{res}. The ionization efficiency is total electron density divided by power deposition in the plasma, and is a relative measure of efficiency.
Fig. 4.6 Plasma and circuit values for a pulsed ICP with perfect matching.  a) Electron and ion densities, and plasma potential, b) modes of power deposition and c) $C_P$ and $C_S$ for perfect match conditions, and reactive and resistive components of the impedance $Z_L$.  The pulse repetition frequency is 13.3 kHz, duty cycle of 35% and forward power during the pulse is $P_S$=250 W, shown in c).
Fig. 4.7 Modes of power deposition, total power deposition and power reflection coefficient $\Gamma$ when $C_p$ and $C_s$ are chosen to match at $t_M = a) 1.5$, b) 3.25, c) 7 and d) 21 $\mu$s into the pulse. (Ar/Cl$_2$=65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S$ = 250 W.)
Fig. 4.8 Circuit values and power deposition as a function of matching time. a) Power reflection coefficients through one pulsed period when matching at different $t_M$. b) Inductive and capacitive power at their maximum value and at the end of pulse ($t = 23 \mu s$) with varying match time $t_M$. (Ar/Cl$_2$ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250$ W.)
Fig. 4.9 Plasma properties when varying duty cycle (25 to 65%) during a pulsed period. The circuit match values correspond to a duty cycle of 35% with the match time at $t_M = 7 \, \mu s$. a) Electron density and b) plasma potential. For clarity, the plots for plasma potential have been shifted by increments of 10 ns. (Ar/Cl₂=65/35, 25 mTorr, PRF = 13.3 kHz, $P_S = 250$ W).
Fig. 4.10 Ion energy distribution (IED) incident onto the dielectric window at different times during the pulse. a) 0-2.0 μs, and b) 2.0-22 μs. The inset shows the plasma potential. The labels A-H are the locations in the pulsed cycle at which the IEDs are plotted. (Ar/Cl₂ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 25%).
Fig. 4.11 Inductive and capacitive power deposition for different gaps, $d$, between the coils and the top of the dielectric window. Heights range between $d = 0$ to $8.2$ mm. a) Power over the entire power-on period and b) power during the first 5 µs. The circuit match values correspond to the match time $t_M = 20$ µs. (Ar/Cl₂ = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35%, $P_S = 250$ W.)
Fig. 4.12 Electron density (color contours) and charge density over the first few RF cycles of a pulsed period. a) 2\(^{nd}\), b) 3\(^{rd}\), c) 4\(^{th}\) and d) 6\(^{th}\) cycles. The circuit match values correspond to the match time \(t_M = 1.5 \mu s\). The charge density \(\rho\) is shown by labels in units of \(q (1.6 \times 10^{-19} \text{ C})/\text{cm}^3\) with a line denoting \(\rho = 0\). (Ar/Cl\(_2\) = 65/35, 25 mTorr, PRF = 13.3 kHz, DC = 35\%, \(P_S = 250\) W). The impulsive power deposition launches electrostatic waves.
4.6 References


5.1 Introduction

Low pressure plasmas are widely used in industrial applications for microscale device fabrication. Efficiently applying sufficient power to the plasma is necessary to produce high plasma densities, which requires a low power reflection coefficient (\(\Gamma\)). The power reflection coefficient is,

\[
\Gamma = \left| \frac{Z_L - Z_0}{Z_L + Z_0} \right|^2, \quad (5.1)
\]

where \(Z_L\) is the combined impedance of plasma, antenna/electrodes, and any circuit components used in the power transmission line, and \(Z_0\) is the output impedance of the power supply, which typically is 50 \(\Omega\). In an inductively coupled plasma (ICP) reactor, to reduce \(\Gamma\), an impedance matching network (IMN) ideally consisting of non-resistive passive circuit components is often implemented between the power supply and plasma reactor. By changing the impedance of the IMN, \(Z_L\) can be tuned to minimize \(\Gamma\). The power delivery to the plasma is then,

\[
P = P_0(1 - \Gamma), \quad (5.2)
\]

where \(P_0\) is the output power from the power supply. The maximum power delivery is attained when \(Z_L = Z_0\). Employing an IMN is a commonly used and effective method to maximize the power delivery to a plasma [3-7].

However, certain challenges emerge when the plasma switches between multiple states
during operation, for example, when the plasma is sustained with pulsed power [8-12]. In
consider a plasma pulsed with 100s W at 10s mTorr pressure at 10s of kHz, both the real and
imaginary parts of the plasma impedance can experience severe oscillations up to 10s Ω to 100s
Ω during power transitions. These oscillations result from the significant difference between
electron densities ($n_e$) between when power is on and off. At the leading edge of the power
pulse, the electron density can increase from lower than $10^8$ cm$^{-3}$ to more than $10^{11}$ cm$^{-3}$ within
several μs. This increase of electron density produces high electron plasma frequency ($\omega_{pe}$) and
plasma conductivity ($\sigma_p$), and low plasma impedance,

$$\omega_{pe} = \left( \frac{e^2 n_e}{\varepsilon_0 m_e} \right)^{1/2},$$  \hspace{1cm} (5.3)

$$\sigma_p = \frac{\varepsilon_0 \omega_{pe}^2}{j \omega + \nu_m},$$  \hspace{1cm} (5.4)

where $e$ is the elementary charge, $\varepsilon_0$ is the permittivity of free space, $m_e$ is the electron mass, $\omega$ is
the radiofrequency (RF) of the input power, and $\nu_m$ is the electron-neutral collision frequency
[13]. If the duty-cycle (DC) of a pulse (the fraction of a period power is on) is small, or the
period is short, it is likely that electron and ion densities will fail to reach the quasi-steady state
before power is turned off again [11-12]. Consequently, the plasma impedance will continuously
change during power-on, making it difficult for an IMN with fixed components to
instantaneously match the impedance. If the power has a high-low pulsing profile—wherein
instead of having zero power input during power-off, a low-power is applied to maintain the
plasma—the different plasma impedances during the high- and low-power periods will pose even
more challenges to the IMN [10]. To that end, real-time impedance matching techniques with an
agile impedance adjustment rate is needed to optimize power delivery.

One approach to improve the impedance matching to a plasma load with a changing
impedance is to use multiple IMNs that match different $Z_L$ [14]. For example, in a high-low pulsed power ICP reactor, two IMNs can be used to match the impedances of the plasma during high- and low-power periods. The IMN is switched between two architectures at each power transition. Using this technique, the power reflection will be greatly reduced compared to when the IMN is fixed. However, switching circuit components in the IMN is often a mechanical process that cannot be performed rapidly (often 100s to 1000s ms). Meaning matching the impedance by modifying the IMN is difficult if the plasma load is pulsed at high pulse repetition frequency (PRF). If the IMN fails to synchronize with the impedance of the plasma, unpredictable instabilities in the plasma can occur.

Another method of impedance matching to a plasma in near real-time is to fix the components of the IMN but modify the frequency of the power delivered from the power supply [15-16]. Both the impedance of the plasma and the circuitry have fairly significant reactive components, making it reasonably efficient to impedance match by frequency tuning. The advantage of using frequency tuning is the high tuning speed. The frequency tuning itself can be done in a time as short as 10s μs as the tuning can be performed electronically without any mechanically moving parts. Additionally, the fractional change of frequency that is required is usually small. For a plasma operating at 10s MHz, without orders of magnitude variation in operating conditions (power, pressure, gas flow rate etc.), the required frequency change to obtain matching during a pulse is often less than several MHz.

In this chapter, we discuss results from computational investigations of impedance matching with both a fixed IMN and with frequency tuning performed on a 15 mTorr Ar ICP. The plasma is produced in the ICP reactor ICAROS, and sustained by a pulsed power having PRF = 5 kHz, DC = 50%, and power of 50 W. Employing a fixed IMN was found to produce a
reasonable impedance matching result, but mismatch occurs when the impedance of the load shifts away from the target impedance of the IMN. This issue is then addressed by applying frequency tuning for a real-time impedance match. The power profile was varied to test the capability of frequency tuning to correct an impedance mismatch. Specifically, the pulsed power ranges from 30-80 W, power ramp time during power transition is varied from 4-80 μs, and DC is adjusted from 40-60%. In all cases, frequency tuning was found to help maintain a low power reflection coefficient. A brief description of the model is provided in Sec. 5.2. Results of the investigation of power deposition with only IMN and a combination of IMN and frequency tuning with varying pulse profiles are provided in Sec. 5.3. Concluding remarks are in Sec. 5.4.

5.2 Description of the Model

The computational platform used in this work is the Hybrid Plasma Equipment Model (HPEM). The details of this model are discussed in Chapter 2 and Ref [17]. Only a brief description is provided here.

The modules from the HPEM that are used in this work are the Fluid Kinetics Poisson Module (FKPM), Electromagnetics Module (EMM), and Electron Energy Transport Module (EETM). The inductively coupled electromagnetic field is obtained by solving the frequency-domain Maxwell’s equation in the EMM. The continuity, momentum, and energy equations for the heavy particles are solved in the FKPM to update the heavy particle densities. With the charge density provided, Poisson’s equation is also addressed in this module to provide the electrostatic potential. Boltzmann’s equation is solved in the EETM for the electron energy distribution function (EEDF). Cross sections are averaged over the EEDF to provide impact rate coefficients. Electron energy equation is solved for the electron temperature.

A circuit model in the EMM is used to represent the IMN in the power transmission line
from the power supply to the ICP reactor. The impedances of the plasma downstream of the antenna are calculated having both inductive and capacitive components. A user-specified IMN is implemented between the antenna and power supply. The values of circuit components in the IMN are analytically calculated to produce a perfect impedance matching condition ($Z_L = Z_0$). This is accomplished by matching both the real and imaginary parts of $Z_L$ and $Z_0$. When using frequency tuning, circuit components in the IMN are fixed, while the frequency of the radiofrequency (RF) provides minimum reflection coefficient is obtained by a minimization search. Both the test range ($f_{\text{range}}$) and step ($\Delta f$) are user-defined values. Frequency tuning is only performed when the fractional change of load impedance exceeds a threshold $\varepsilon$, which is by default 0.01.

The plasma species included in this model are Ar, Ar(1s$^5$), Ar(1s$^4$), Ar(1s$^3$), Ar(1s$^2$), Ar(4p), Ar(4d), Ar$_2^*$, Ar$^+$, Ar$_2^+$ and electrons, where Ar$_2^*$ is a lumped excited state of the argon dimer.

5.3 Plasma Characteristics with Set-Point Matching and Frequency Tuning

The geometry of the ICP reactor used in this work is shown in Fig. 5.1. and represents the ICAROS reactor designed by Prof. Steven Shannon at North Carolina State University. This cylindrically symmetric reactor is relatively small, with the plasma chamber having a radius $r = 4.8$ cm and height $z = 14.3$ cm. Pure Ar is used at a flow rate of 10 sccm at a pressure of 15 mTorr. Gas is injected from the top of the reactor and is pumped out at the bottom. The speed of the pump is adjusted to maintain constant pressure. The wall of this reactor is alumina, with a dielectric constant $\varepsilon_r = 9.8$. A 4-turn solenoidal coil provides power to the plasma. Here, the top coil is connected to the power supply, such that the voltage on the coil decreases from top to bottom. The bottom coil is connected to ground through a 0.35 nF capacitor. Pulsed power with
a pulse repetition frequency (PRF) of 5 kHz and duty cycle (DC) of 50% is applied to the plasma. The default power transition time ($\tau_t$) is 4 $\mu$s, meaning that the power takes 4 $\mu$s to ramp from zero to full power, and from full power to zero. By default, the radiofrequency (RF) is 13.56 MHz. The reactor is surrounded by air. The outer-most boundary of the computational domain is metal, which provides boundary conditions for solutions of Poisson’s equation and the wave equation.

The 2-dimensional distributions of electron density ($n_e$) and power density as well as the spatially averaged $n_e$ and electron temperature ($T_e$) are shown in Fig. 5.2. Here, all power is delivered to the plasma ($\Gamma = 0$). The peak electron density is $1.4 \times 10^{11}$ cm$^{-3}$. The peak power density of 0.17 W/cm$^3$ is close to the wall adjacent to the coils as the skin depth is only a few cm. Capacitive power coupling is not included in this work. That is, power is not electrostatically coupled to the plasma from the voltage drop on coils. The spatially averaged electron density and electron temperature are plotted over one pulse period (200 $\mu$s). $T_e$ spikes at the beginning of the pulse when $n_e$ is low ($< 4 \times 10^{10}$ cm$^{-3}$) in order to avalanche the electron density from its low prepulse value. This spike of $T_e$ diminishes after 10 $\mu$s as $n_e$ increases. Note that even though $T_e$ is stabilized through almost the entire power-on period, $n_e$ continues to increase, indicating that the plasma is not in a quasi-steady state. The plasma impedance changes with $n_e$ and produces an electrically dynamic load, which then produces an impedance mismatch if no impedance matching system has been implemented.

The IMN implemented between the coils and power supply is shown in Fig. 5.3. From left to right are the power supply, impedance matching network, and the load impedances from the coils, plasma, and the reactor. The output impedance of power supply, $R_G$, is a standard 50 $\Omega$ impedance with no reactive component. $R_{loss}$ represents the stray resistance in the IMN.
However, in this work, $R_{\text{loss}}$ is set to 0 to provide a lossless IMN. The inductance $L_P$ in the IMN is a constant 0.7 $\mu$H, while the capacitances $C_S$ and $C_P$ are analytically solved to produce a perfect impedance match condition. A detailed solution of $C_S$ and $C_P$ is provided in the Appendix. Briefly, $C_S$ and $C_P$ are solved by matching the combined impedance of all the non-power supply components to $R_G$. The loads following the IMN are the coils and plasma, whose impedances are automatically calculated in the HPEM. The impedance of the coil is geometry dependent, and the plasma impedance is a function of plasma geometry, density and impact collision frequency ($v_m$). $Z_P$ is approximated as that of the window. The last two components, $L_T$ and $C_T$, are the termination components representing the impedance between the antenna and ground. In this work, $L_T = 0$, and $C_T = 350$ pF.

Values of $C_P$ and $C_S$ in this IMN are solved through the power-on part of the pulse for a perfect match. The results are shown in Fig. 5.4, where $\text{Im}(Z_L)$ and $\text{Re}(Z_L)$ are the real and imaginary parts of the load impedance $Z_L$. Significant oscillations of $Z_L$ occur during power transitions as both $n_e$ and the collision frequency ($v_m$) experience rapid changes. As shown in Eq. (5.4), a change of $n_e$ and $v_m$ directly affects the electrical properties of the plasma. Because the plasma impedance is one of the major components of $Z_L$, the ignition and decay of the plasma then produce changes in the power reflection coefficient. $Z_L$ stabilizes as plasma approaches the quasi-steady state, with $\text{Re}(Z_L)$ remaining constant at 25 $\Omega$, and $\text{Im}(Z_L)$ slightly decreasing from 46 $\Omega$ (20 $\mu$s) to 41 $\Omega$ (100 $\mu$s). This variation of $\text{Im}(Z_L)$ suggests that the increase in $n_e$ during power-on mainly affects the reactance of the plasma. To have a perfect match, the value of $C_P$ remains nearly constant, with only minor increases from 52 pF at 10 $\mu$s to 63 pF at 100 $\mu$s. $C_S$ is increases by a factor of 1.4, from 182 pF to 253 pF, which indicates that an impedance mismatch will occur if the IMN has fixed values of $C_S$ and $C_P$. 
The power deposition and reflection with the fixed IMN are shown in Fig. 5.5. The method of using a fixed IMN for impedance matching is referred to as set-point matching. With set-point matching, $C_P$ and $C_S$ are obtained from the result shown in Fig. 5.4 to perfectly match at a specific time during the pulse. Set-point values of $C_P$ and $C_S$ are chosen at $\tau_M = 10$ and 90 $\mu$s, and are designated as match points. When $\tau_M = 10$ $\mu$s, the plasma ignites rapidly and reaches the near quasi-steady state within 20 $\mu$s. Because the IMN is selected to match the impedances at $\tau_M = 10$ $\mu$s, the reflected power ($P_{ref}$) drops to 0 at that time, after the initial spike when the plasma first ignites. The impedance of the plasma becomes relatively stable 50 $\mu$s after the leading edge of the pulse (Fig. 5.4). Matching early in the pulse produces a non-zero power reflection coefficient $\Gamma$ through the entire power-on period, starting from $\tau = 10$ $\mu$s. In this case, with $\tau_M = 10$ $\mu$s, 2.6 W out of 50 W input power is reflected back to the power supply at $\tau = 90$ $\mu$s, which translates to a power reflection coefficient of $\Gamma = 5\%$. To minimize this power reflection, a match point is chosen late in the pulse, at $\tau_M = 90$ $\mu$s. As shown in Fig. 5.5b, this approach successfully brings power reflection down to almost zero when $\tau > 40$ $\mu$s. However, the mismatch early in the pulse challenges plasma ignition. Compared to $\tau_M = 10$ $\mu$s, the initial power reflection spike lasts longer when matching at $\tau_M = 90$ $\mu$s. Even though the integral of the reflected power ($P_{ref}$) in the entire power-on period is not large ($\approx 10\%$), the slower plasma ignition might be problematic.

To better optimize power delivery, a near real-time impedance matching technique is needed, along with set-point matching. To accomplish this, we implemented frequency tuning. Typically, the power reflection coefficient is sensitive to the change of frequency, as shown in Fig. 5.6a. Power reflection can be significantly reduced by a small adjustment in operating frequency. In practice, frequency tuning can be done much faster than adjusting the components
in the IMN (μs versus s). In the HPEM, frequency tuning is performed using a search algorithm. A diagram of this process is shown in Fig. 5.6b. Frequency tuning is performed when the fractional variation of the load impedance exceeds the threshold $\varepsilon$, which is 0.01 here.

Results with frequency tuning along with set-point matching are shown in Fig. 5.7. The range for the frequency tuning is $f_{\text{range}} = 4 \, \text{MHz}$, meaning that the frequency can be varied from 11.56 to 15.56 MHz. As the model indicates, with frequency tuning, almost perfect power matching is attained regardless of the choice of match points. Power reflection of less than 30 W occurs in the first 4 μs for both cases ($\tau_M = 10$ and 90 μs). The finite power reflection during start up is a consequence of the frequency have reached its lower limit of 11.56 MHz. However, because of its small magnitude and short duration, this power reflection does not have a significant effect on the plasma. The choice of match points affects the precise frequency during frequency tuning. When frequency tuning is employed, 13.56 MHz is the frequency near the match points because the components in the IMN are chosen when the input power is at 13.56 MHz. By matching at different times, the peak-to-peak frequency oscillation decreases from 3.5 MHz for $\tau_M = 10$ μs to 2 MHz for $\tau_M = 90$ μs. In practice, frequency tuning with a tuning requires at least 10 μs. Therefore, choosing the match point that requires the smallest peak-to-peak frequency oscillation will reduce power reflection by reducing the number of frequency changes. For example, when $\tau_M = 10$ μs, if the frequency is tuned to match early pulse to operate at 13 MHz and remains at this frequency until mid-pulse at $\approx 60$ μs, the offset of 2 MHz from the ideal frequency during power-on will produce a significant impedance mismatch. Conversely, if $\tau_M = 90$ μs and the frequency is tuned to 13 MHz in the early pulse, it only creates $\approx 0.6$ MHz frequency offset in the mid-pulse. This considerably reduces the impedance mismatch.
In the following sections, power delivery to the plasma is computationally investigated by considering power magnitude, power transition time, and duty cycle while using set-point only impedance matching, and a combination of set-point matching and frequency tuning. The IMNs used are the same as it from the base case (50 W, DC = 50%, \(\tau_t = 4 \mu s\) when matching in the late pulse at \(\tau_M = 90 \mu s\).

### 5.3.1 Power Magnitude

The power magnitude of the pulse was varied from 30 to 80 W while the duty cycle (50%) and transition time (4 \(\mu s\)) remained the same as the base case. To quantify the power deposition, power efficiency \(\eta\) is defined as,

\[
\eta = \frac{\int_0^{\tau_P} P_{dep} dt}{\int_0^{\tau_P} P_{forward} dt},
\]

where \(\tau_P\) is the pulsing period, \(P_{dep}\) is the power deposition in the plasma, and \(P_{forward}\) is the power output from the power supply. As a function of \(P_{forward}\), \(\eta\) is plotted in Fig. 5.8. Even in the absence of frequency tuning, the power efficiency remains at a relatively high value of > 90% when \(P_{forward} > 50\) W. This is because the electrical properties of the plasma do not change significantly at high plasma density and so \(Z_L\) is relatively stable. For example, as power increases from 50 to 80 W, \(\text{Re}(Z_L)\) stays at 25 \(\Omega\) while \(\text{Im}(Z_L)\) moderately increases from 35 to 41 \(\Omega\), which induces a minor impedance mismatch and leads to a slight decrease of \(\eta\). Even though the IMN is chosen to match the late pulse when \(P_{forward} = 50\) W, the highest power efficiency with a set-point match occurs when \(P_{forward} = 60\) W. Although the impedance is perfectly matched at the end of the pulse when \(P_{forward}\) is 50 W, \(\eta\) is lower at \(P_{forward} = 50\) W than 60 W. The power reflection produced by the impedance mismatch during other parts of the pulse is larger when \(P_{forward}\) is 60 W. Instead of obtaining perfect match conditions at a specific
match point, when choosing IMN values, the goal should be to minimize the reflection coefficient through the entire period.

Without frequency tuning, the power deposition efficiency drops to almost zero as the pulse power decreases from 50 to 30 W. The electron density and power reflection coefficient with and without frequency tuning are shown in Fig. 5.9, when the pulse power is 30, 40, and 50 W. Note that when power is 40 W, even without frequency tuning, the plasma nearly reaches a quasi-steady state density at the end of the pulse. At $\tau = 90 \mu s$, $Z_L = (24 + j44) \Omega$ when the power is 40 W, compared to $Z_L = (25 + j41) \Omega$ when the power is 50 W. These values of closed $Z_L$ suggest that when $P_{\text{forward}} = 40$ W, using the same IMN setup as in the base case can also optimize power delivery late in the pulse. As shown in Fig. 5.9b, the power reflection coefficient when $P_{\text{forward}}$ is 40 W ($\Gamma_{40W}$) is only 5% at $\tau = 100 \mu s$. The low power deposition efficiency with a decreasing power is caused by the impedance mismatch early in the pulse. At $\tau = 10 \mu s$, $Z_L(40 \text{ W}) = (21 + j47) \Omega$, while $Z_L(50 \text{ W}) = (24 + j51) \Omega$. The difference in $Z_L$, especially in relation to the resistive components, produces a severe impedance mismatch, which results in a high reflection coefficient and a low power deposition efficiency. A low power deposition efficiency early in the pulse delays plasma formation and increases in $n_e$. Therefore, at 40 W, it takes a longer time for the plasma to reach a quasi-steady state.

The impact of the impedance mismatch early in the pulse is maximized when $P_{\text{forward}} = 30$ W. In this case, without frequency tuning, plasma fails to ignite as the power reflection coefficient remains high (Fig. 5.9b). However, with frequency tuning, the power reflection coefficient at 30 W ($\Gamma_{30W}$) is reduced to 80% at the leading edge of the pulse, which shortly increases to 95% and then abruptly decreases to less than 10% in 10 $\mu$s. The final decrease of $\Gamma_{30W}$ is enabled by the power deposition early in the pulse. Even though $\Gamma_{30W}$ is still higher than
80% in the first 5 μs, the small amount of power deposited in the plasma enables plasma ignition
and the increase of \( n_e \), which facilitates the impedance matching and further enables the increase
of plasma density.

### 5.3.2 Power Transition Time

Another parameter that is often varied in a pulsing profile is the power transition time (\( \tau_t \)).
The power transition time was varied from 4 to 80 μs as the power turns on, and remains
constant at 4 μs when the power is turned off. For all cases, full power is 50 W, and the duty
cycle is 50%. Therefore, average power decreases with an increase of \( \tau_t \).

The power deposition efficiency \( \eta \) as a function of \( \tau_t \) is shown in Fig. 5.10a. Without
frequency tuning, \( \eta \) decreases from 93% to 14% as \( \tau_t \) increases from 4 to 80 μs. This is caused by
the long period of time with low input power. The power reflection coefficients when \( \tau_t \) is 4, 40
and 80 μs are shown in Fig. 5.10b. Without frequency tuning, the power reflection coefficient
remains at a high value throughout the power transition. This is because the low power density
produces a low plasma density, which leads to an impedance mismatch that enhances power
reflection and results in even less power deposition to the plasma, again preventing an increase in
\( n_e \). When \( \tau_t = 80 \) μs and there is no frequency tuning, power cannot transfer to the plasma until
the last 20 μs of the pulse when \( P_{\text{forward}} \) reaches 50 W. Even then, the minimum power reflection
coefficient is 60%, which translates to a power deposition of 20 W. The end result is a 20 μs
spike of \( n_e \approx 1.6 \times 10^{10} \text{ cm}^{-3} \) at the end of each pulse with 86% of the total power reflected back
to the power supply.

Applying frequency tuning proves helpful in reducing the power reflection coefficient. A
low frequency is needed for impedance matching when \( n_e \) is low; however, the lower boundary
of the RF is 11.56 MHz, which means there is a minimum \( n_e \) requirement for a functional
frequency tuning. In this work, that electron density is $\approx 10^{10}$ cm$^{-3}$, however $n_e$ takes a longer time to reach this density with a longer $\tau_t$. When $\tau_t = 80$ $\mu$s, frequency tuning starts to reduce $\Gamma_R$ at 30 $\mu$s when $P_{\text{forward}} = 18$ W and nearly all of the power before 30 $\mu$s is reflected. The longer the power transition time is, more power is reflected. As $\tau_t$ increases from 4 to 80 $\mu$s, $\eta$ decreases from 99% to 87% when frequency tuning is implemented. These results demonstrate that frequency tuning or real-time impedance matching is likely to be most impactful when the power profile has a large fraction in the low-power regime, such as a sawtooth waveform.

5.3.3 Duty Cycle

In this section, the duty cycle of the pulse ranges from 40% to 60%. The peak power is 50 W, and the power transition time is 4 $\mu$s, the same as in the base case. Therefore, the average power increases with an increase in the duty cycle. The power deposition efficiency $\eta$ as a function of the duty cycle is shown in Fig. 5.11a.

Changing the duty cycle mainly affects the time the plasma stays in the quasi-steady state. The longer the duty cycle, the longer the time the plasma is in the quasi-steady state. The components of the IMN were chosen to match the load impedance $Z_L$ when the plasma is stabilized at the end of the pulse. The impact of frequency tuning becomes insignificant when the duty cycle is long. The plasma can reach the quasi-steady state with a DC = 40% (Fig. 5.11). As a result, the power deposition efficiency $\eta > 90\%$ without frequency tuning. In these cases, frequency tuning can still optimize power delivery to the plasma during the first 40 $\mu$s, when some level of impedance mismatch occur.

As the duty cycle decreases, the impact of frequency tuning becomes more significant when a longer fraction of the pulse is mismatched. Note that increasing the duty cycle also decreases the inter-pulse period, meaning the plasma has a shorter time to dissipate, and the
initial plasma density will be higher at the leading edge of the pulse. Without frequency tuning, as the duty cycle increases from 40% to 60%, the initial electron density increases from 1.5 to $1.9 \times 10^{10}$ cm$^{-3}$. However, since the plasma takes only $\approx 20$ μs to reach the high-density state, the different $n_e$ at the beginning of the pulse has little impact on power delivery.

5.4 Concluding Remarks

A computational investigation of power deposition in an Ar ICP sustained in the reactor ICAROS with 50 W power pulsed at 5 kHz was performed using the HPEM simulation platform. Two impedance matching techniques were employed: set-point matching using a fixed components in the impedance matching network (IMN), and a combination of set-point matching with a close to real-time frequency tuning. The circuit components in the IMN are first analytically solved for the perfect match and then fixed to match the impedance at a certain time during the pulse. Real-time frequency tuning is then employed with the set-point match to correct impedance mismatches.

We found that using set-point matching alone produces impedance mismatch and results in power reflection at times other than the match point. When frequency tuning is applied, the choice of match point affects the tuning range in such a way that a late match point in a quasi-steady state results in the need for smaller frequency adjustments. The impact of frequency tuning on power deposition with varied power magnitude, power transition time, and duty cycle were discussed. With the IMN set to match the impedance of the quasi-steady state, frequency tuning is found to be most impactful during transients when the input power is low. Therefore, frequency tuning is recommended if the pulse power is low, the power transition time is long, or the duty cycle is short. Impedance match early in the pulse is desirable because a severe
mismatch will extend the time that the plasma reaches the steady state. Therefore, frequency tuning, especially in the early pulse, is recommended.

To summarize, impedance matching not only maximizes the power delivered to the plasma reactor but also minimizes the power reflected back to the supply. Minimizing the reflected power becomes ever more important as power levels increase in plasmas processing – now exceeding 10-20 kW. In addition to minimizing reflected power to protect the power supply, optimum impedance matching enables consistent power pulsing profiles to the plasma. For example, optimum matching helps to avoid issues such as *dropping a pulse*, in which due to impedance mismatch at the onset of applied power, the plasma does not ignite during the pulse. In this chapter, the effects of set-point matching and frequency tuning for impedance matching in plasma processing are discussed. However, these results may also apply to other pulsed power plasma applications. For example, pulsed power thrusters are used in electric propulsion (EP) for accelerating and station keeping of satellites and spacecraft. EP uses plasma exhaust to accelerate the spacecraft. In these systems, minimizing mass is exceedingly important. Minimizing mass is typically achieved by maximizing the efficiency of all on-board systems, which includes the power transfer that generates the plasma.
Fig. 5.1 Geometry of the inductively coupled plasma (ICP) reactor used in this work.
Fig. 5.2 Distributions of electron density and power density, and spatially averaged electron density and electron temperature. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%.
Fig. 5.3 Diagram of power transmission line with power supply, impedance matching network, and load impedance consisting of the coil, plasma, and termination circuit components.
Fig. 5.4 Real and imaginary parts of the load impedance \((Z_L)\) and the capacitances in the matching network \((C_P\) and \(C_S\)) required for the impedance match. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%.
Fig. 5.5 Power deposition ($P_{dep}$) and reflection ($P_{ref}$) and load impedance when the impedance matching network is chosen to match a) in the early pulse at $\tau = 10 \, \mu$s and b) in the late pulse at $\tau = 90 \, \mu$s. Ar, 15 mTorr, 50 W, PRF = 5 kHz, DC = 50%.
Fig. 5.6 a) A typical response of power reflection coefficient (Γ) with radiofrequency, and b) a schematic diagram of frequency tuning in the HPEM.
Fig. 5.7 Power deposition ($P_{dep}$) and reflection ($P_{ref}$) with (FT) and without (no FT) frequency tuning when a) b) IMN is chosen to match early in the pulse at $\tau = 10 \mu s$ and when c) d) IMN is chosen to match late in the pulse at $\tau = 90 \mu s$. 
Fig. 5.8 Power deposition efficiency with and without frequency tuning with different powers. Ar, 15 mTorr, PRF = 5 kHz, DC = 50%.
Fig. 5.9 a) Spatially averaged electron density b) power reflection coefficient without frequency tuning and c) power reflection coefficient in the first 20 μs with and without frequency tuning. Ar, 15 mTorr, PRF = 5 kHz, DC = 50%.
Fig. 5.10 a) Power deposition efficiency as a function of power transition time ($\tau_t$) and b) power reflection coefficient when $\tau_t = 4, 40,$ and $80 \, \mu$s. Ar, 50 W, 15 mTorr, PRF = 5 kHz, DC = 50%.
Fig. 5.11 a) Power deposition efficiency as a function of duty cycle and b) power deposition, power reflection, and frequency with and without frequency tuning when DC = 40%. Ar, 50 W, 15 mTorr, PRF = 5 kHz.
5.6 References

Chapter 6: Customizing Capacitively Coupled Plasma Properties with a Triple-Frequency Power Source

6.1 Introduction

The use of capacitively coupled plasmas (CCPs) to enable reactive-ion etching (RIE) has been widely studied [1-4]. A typical CCP reactor consists of a pair of parallel plate electrodes separated by a few cm, an annular gas outlet surrounding the bottom electrode (substrate), and a showerhead for the gas inlet that overlaps with the top electrode. In conventional RIE, the bottom electrode is powered with up to several kW of radiofrequency (RF) power, and the top electrode is grounded. A negative DC bias voltage is usually self-generated on a blocking capacitor in series with the bottom electrode to balance current to the powered and grounded electrodes [2,5]. This bias voltage partly contributes to the ion acceleration and can accelerate the ion energy incident on the substrate from 100s to thousands eV.

Energetic ions play an essential role in the microchip etching process as they are the agent for both physical sputtering and surface activation. To optimize the RIE process, one needs precise control over the ion energy and angular distributions (IEADs) incident on the wafer. For example, with the shrinking device dimension (under 10 nm) and increasing aspect ratio (AR, the depth over the width) of the target features, a narrow ion angular distribution (IAD) is required to minimize scattering from the sidewalls [6-8]. If an ion enter a feature with a large incident angle (> 50°), it will strike and be reflected from the sidewalls. Successive collisions result in a loss of energy and broadening of the angular distribution. This results in
bowing at the top of the feature and a lack of energetic ions at the etch front at the bottom, causing a widened opening and slow etch rate. The ion energy distribution (IED) has limitations both high- and low-energies. Too high of an ion energy leads to perhaps unwanted physical sputtering. Too low of an ion energy results in etch-stop [9,10].

IEADs can be modified by changing the plasma operating conditions. However, in a conventional single-frequency (SF) CCP, this usually leads to modification of the magnitude and composition of the ion flux. To decouple the IEADs from the magnitude of the ion flux, and to gain independent control of both, multi-frequency CCPs can be used. The goal is to have more control parameters so that a combination of the parameters can provide a wide range of IEADs and ion flux. In a CCP, electrons are mainly heated through stochastic heating such that hot electrons are created through the fast oscillation of the sheath. A sheath is a high electric field (E-field) region adjacent to a surface exposed to the plasma. Above the surface of a powered electrode, high frequency voltage, usually radiofrequency (RF), leads to a high sheath expansion velocity and a resulting high heating efficiency as well as a high plasma density. Unlike electrons, ions only respond to the low-frequency (LF) due to their larger mass. In a multi-frequency CCP, high-frequency (HF) power is used to control the plasma density while a range of LF powers are applied to the substrate to modify the IEADs. Applying harmonics of a fundamental frequency produces the electrical asymmetry effect (EAE) due to non-linear responses of the sheath to the non-sinusoidal voltage waveforms. The EAE provides an approach to control the DC bias, thereby offering additional control over IEADs [11-15].

The most basic multi-frequency CCP is a dual-frequency (DF) CCP where the power is applied to the plasma through two distinguishable frequencies [16-19]. Boyle et al. studied a DF-CCP using a particle-in-cell model with Monte Carlo collisions (PIC-MCC) [17]. It was
shown that the decoupling nature of the ion energy and flux is related to the low-to-high frequency ratio such that a greater separation of the two frequencies provides a more thorough decoupling between the IED and ion flux. In addition to the frequency ratio, the phase between frequencies (\(\theta\)) can also be used as a method to control a DF-CCP [11, 20]. With investigations using an analytical model, Czarnetzki et al. reported that when applying the fundamental frequency (13.56 MHz) and its second harmonic (27.12 MHz) on the same electrode in a CCP, the ion energy has an almost linear dependence to \(\theta\), but the ion flux remains constant [11]. They suggested that varying \(\theta\) induces significant deviations to the dynamics of power dissipation, and yet, time-averaged power deposition to the plasma is barely changed. Consequently, the acceleration of ions in the sheath, through which they obtain energy, is impacted by \(\theta\), but the ion flux remains constant.

Applying DF power can also have fundamental impacts on the plasma. Sahu et al. reported that while keeping the power input constant, if an ultrahigh-frequency (320 MHz) is added to a SF-CCP sustained by 200 W (13.56 MHz) power, the electron energy distribution function (EEDF) can be changed from a Druyvesteyn to a bi-Maxwellian structure [21]. They concluded that HF enhances stochastic heating and populates warm-electrons (11-15 eV). Despite the advantages of DF-CCP in an RIE process, O’Connell et al. warned that some level of HF-LF coupling can still occur, especially when both frequencies are applied to the same electrode [16]. Such an issue can be solved by distributing the powers to different electrodes and using multi-frequency (> 2) power for even more sophisticated control over the plasma.

Diomede et al. investigated a multi-frequency CCP in a geometrically symmetric reactor powered by a tailored voltage consisting of up to three harmonics of the fundamental frequency (15 MHz) [22]. They found that both the absolute value of the DC bias and the electron density
increase with an increasing number of harmonics. But the ion energy on the grounded electrode
changes monotonically with the number of harmonics. The average ion energy increases with an
increasing number of applied harmonics when the phase of the harmonics $\theta = \pi$, but decreases
when $\theta = 0$. These results suggest using phase as a parameter for modifying plasma properties in
a multi-frequency CCP. Lee et al. investigated the IED from a low-pressure triple-frequency
(TF) CCP sustained in Ar with driving frequencies of 1, 30, and 120 MHz applied to the same
electrode [23]. They concluded that the current density (for the current-driven source) or voltage
(for a voltage-driven source) along with the frequency ratios, determine the average ion energy
and the width of the IED, instead of the absolute values of frequencies.

Focused more on the function of each frequency in a multi-frequency CCP, Kawamura et
al. investigated Ar discharges with the highest frequency, being up to 162 MHz. They also
concluded that LF power predominantly determines sheath development while the HF power
controls plasma production. They reported that the standing wave created by HF power
optimizes the plasma distribution. The high plasma density in the center of the reactor, caused
by the standing wave, counteracts the electrostatic effect at the edge of the wafer and improves
plasma uniformity.

In this chapter, we investigate a TF-CCP sustained in an Ar/CF$_4$/O$_2$ gas mixture and
driven by powers at 5, 10, and 80 MHz. A brief model description is provided in Sec. 6.2.
Results from the simulation while varying power, pressure, high frequency, and geometry are
discussed in Sec. 6.3. Concluding remarks are in Sec. 6.4.

6.2 Model Description

The model used in this chapter is a two-dimensional (2D) kinetic-fluid hydrodynamics
simulation, the Hybrid Plasma Equipment Model (HPEM). A detailed description of HPEM is
provided in Chapter 2 and Ref [25]. Only a brief description is provided here.

The HPEM contains modules addressing different aspects of plasma physics. The modules used in this work are Fluid Kinetics Poisson Module (FKPM), Electron Monte Carlo Simulation (eMCS), Surface Kinetic Model (SKM), and Plasma Chemistry Monte Carlo Module (PCMCM). In the FKPM, the momentum, energy, and continuity equations of all the heavy particles (neutrals and ions) are solved, which provides the densities of these heavy particles along with their source terms. Poisson’s equation is also addressed in the FKPM to provide the electrostatic potential. The SKM interacts with FKPM in a way that the FKPM provides the fluxes to a surface, and SKM uses that information to update the surface reaction probabilities that are used in the FKPM.

The transport of both bulk and secondary electrons are tracked in the eMCS, as discussed in Section 2.1.2 and Ref [26]. In the eMCS, trajectories of pseudoparticles that represent electrons are advanced in the electric field from the FKPM while undergoing statistically chosen collisions. In this work, 60,000 pseudoparticles are launched to provide statistically accurate spatially-dependent electron energy distribution functions (EEDFs), which are then used to produce electron transport and rate coefficients.

Both the ion flux and the IEADs can be obtained using PCMCM. In the PCMCM, similar to the eMCS, pseudoparticles representing ions are launched, moved, and tracked using a Monte Carlo approach. The number of pseudoparticles launched for each species is weighted by its corresponding source term. The electrostatic field solved for in the FKPM provides the acceleration. The IEADs of Ar⁺, CF₃⁺, CF₂⁺, CF⁺, F⁺, O⁺, O₂⁺, and F₂⁺ are recorded when striking the wafer. The IEADs discussed in this chapter averaged over the wafer and cross 0 degree.
In the HPEM, the power sources are independently controlled. For most cases discussed in this chapter, powers at each frequency are specified, and those corresponding voltages are adjusted to deliver the desired power. A 5 nF blocking capacitor is connected to the substrate to produce the DC bias. A Ar/CF$_4$/O$_2$ gas mixture is used as the feedstock gas, and the chemistry is discussed in detail in Ref [26]. The species are Ar, Ar(1s$_5$, 1s$_3$), Ar(1s$_2$,1s$_4$), Ar(4p, 5d), Ar$^+$, CF$_4$, CF$_3$, CF$_2$, CF, C, F, F$^+$, F$_2$, SiF$_4$, SiF$_3$, SiF$_2$, CF$_3^+$, CF$_2^+$, CF$^+$, C$^+$, F$^+$, F$_2^+$, CF$_3^-$, F$, O_2$, O$_2$(1$^\Delta$), O$_2^+$, O, O(1$^D$), O$^+$, O$^-$, CO, CO$^+$, COF, COF$_2$, CO$_2$, FO, and e.

6.3 Plasma Characteristic of TF-CCP

The reactor geometry used in this work is shown in Fig. 6.1. The reactor is cylindrical and is symmetrical across the central axis. The radius of the reactor is 29 cm, and the height is 7.4 cm. The wafer and the top electrode have a radius of 15.0 cm and are separated by 2.8 cm. HF power, 80 MHz and 500 W, is applied to the top electrode, and DF power with 5 and 10 MHz components is applied to the substrate, each delivering 400 W. The voltage at each frequency, time averaged plasma potential, and DC bias are in Table I. A quartz focus ring (relative dielectric constant $\varepsilon_r = 4$) surrounds the wafer. A sacrificial material with the same conductivity as the wafer (0.05 $\Omega^{-1}cm^{-1}$) is placed between the wafer and focus ring to smooth the sheath and help make the plasma uniform to the edge of the wafer. The wall of the reactor is grounded with a thin layer of dielectric coating ($\varepsilon_r = 50$). A fairly large $\varepsilon_r$ is used here to compensate for the thickening of the dielectric layer by the finite mesh size, such that the capacitance of the dielectric coating remains large. In this geometry, the showerhead overlaps with the top electrode and feeds a gas mixture of Ar/CF$_4$/O$_2$ (75/15/10) evenly to the reactor at 500 sccm. The outlet pump is the annulus at the bottom of the reactor, surrounding the substrate. The pressure is measured by a sensor embedded in the chamber wall 0.8 cm above the pump,
which is used to adjust the pumping speed to sustain a constant pressure of 25 mTorr in the reactor.

The spatially averaged cation and neutral densities at the steady state are shown in Fig. 6.2. In the base case, the dominant ions are 
\( \text{Ar}^+ \) \( (2.4 \times 10^{10} \text{ cm}^{-3}) \) and \( \text{CF}_3^+ \) \( (2.0 \times 10^{10} \text{ cm}^{-3}) \). A high \( \text{Ar}^+ \) density results from the higher mole fraction of Ar in the feedstock gas. \( \text{CF}_4 \) has lower mole fraction, but \( \text{CF}_3^+ \) still has a fairly high density because ionization of \( \text{CF}_4 \) is dissociative and produces \( \text{CF}_3^+ \), and carbon fluorides have high charge exchange reaction rates with other ions such as \( \text{Ar}^+ \) and \( \text{O}^+ \). The low \( \text{O}_2 \) input limits the densities of oxygen species. Note that \( \text{O}_2^+ \) has a steady-state density of \( 4.0 \times 10^9 \text{ cm}^{-3} \), an order of magnitude lower than \( \text{Ar}^+ \). The dominant neutrals are \( \text{O} \), \( \text{F} \), and \( \text{F}_2 \), as shown in Fig. 6.2b. \( \text{O} \) is mostly produced through the dissociative attachment reaction of \( \text{O}_2 \), and \( \text{F} \) is from the electron-impact dissociation reaction of \( \text{CF}_4 \).

In the base case, the peak plasma density reaches \( 1.1 \times 10^{11} \text{ cm}^{-3} \) at \( r = 13.0 \text{ cm} \), as shown in Fig. 6.3a. The electron density \( (n_e) \) peaks at the periphery instead of the center of the reactor, partly due to the electrostatic electric field (E-field) enhancement at the corners of the top electrode and the wafer. At 0.5 cm beneath the edge of the top electrode, the current density in both radial \( (J_r) \) and axial \( (J_z) \) are \( 10^{-3} \text{ A/cm}^2 \), while at the same axial position but \( r = 7.5 \text{ cm} \), both \( J_r \) and \( J_z \) are an order of magnitude lower, at \( 10^{-4} \text{ A/cm}^2 \), suggesting a possibly higher power deposition at the edge than the mid-radius of the electrodes. At 0.5 cm beneath the top electrode, the power density is \( P = 0.06 \text{ W/cm}^3 \) at \( r = 13 \text{ cm} \), but only \( 0.03 \text{ W/cm}^3 \) at \( r = 7.5 \text{ cm} \).

In an RIE process, energetic ions are essential for the chemical sputtering and surface activation. A -370 V DC bias is generated on the substrate, producing a time averaged 490 V potential drop across the sheath above the wafer as opposed to a smaller 125 V potential drop by
the top electrode. At 25 mTorr, the mean free path ($\lambda$) of Ar is about 0.2 cm, which is commensurate with the sheath width (0.6 cm). This means some ions can travel across the sheath with very few or no collisions. Such ions preserve most of their kinetic energy (100s eV) before impacting on the wafer.

Electron temperature ($T_e$) is uniform in the plasma bulk, as shown in Fig. 6.3b. The stochastic heating causes high $T_e$ at the edge of sheaths with a value up to 3-4 eV. This high $T_e$ drops rapidly towards the plasma bulk as hot electrons dissipate their energy through inelastic collisions with heavy particles (e.g., ionization and excitation). At the periphery of the plasma bulk ($r > 18$ cm), $T_e$ is slightly higher due to the low $n_e$. However, because this high-temperature region is in the downstream of the gas flow, it does not significantly affect the bulk plasma and therefore is not discussed in detail.

In a CCP, hot electrons with energy high enough to ionize a ground or excited state species can be either bulk, or beam electrons. Bulk electrons are those in the plasma bulk that gain energy mainly through stochastic or ohmic heating. Beam electrons are emitted from a surface as the product of energetic particle bombardments on that surface. Beam electrons accelerated by the sheath can have energy up to the maximum sheath potential, making them effective at ionizing the neutral particles. The secondary electron emission coefficient ($\gamma$) by ions is 0.15 on the wafer, the showerhead, and the sacrificial material, 0.05 on the quartz, and 0.005 for the dielectric coating on the wall [27]. The ionization sources produced by the bulk and beam electrons are shown in Fig. 6.3c and d. The ionization is dominated by bulk ionization. Because bulk electrons are heated through sheath oscillation, the ionization source produced by bulk electrons ($S_e$) is dependent on the plasma distribution and peaks at $1.1 \times 10^{16}$ cm$^{-3}$s$^{-1}$ at $r = 14$ cm where the plasma density is high. In comparison, the ionization source for
beam electrons ($S_{eb}$) is uniform in both radial and axial directions. The high energy of beam electrons allows them to travel across the reactor and initiate ionizations in the mid-gap.

The increase of ion flux in the radial direction (47% from the center to the boundary) is caused by the rise of plasma density but is not high enough to compensate for the decrease of the secondary electron emission coefficient from 0.15 (electrodes and wafer) to 0.05 (quartz), a reduction to 1/3. The rate of secondary electron emission is determined by the ion flux and the secondary electron emission coefficients. $S_{eb}$ decreases abruptly at the boundaries of the top electrode and wafer due to the reduction in rate of emission and the reduction in sheath voltage on the focus ring. Note that the ionization sources have small values outside the plasma bulk, suggesting the power is well confined between the electrodes.

The 2-dimensional (2D) Ar$^+$ distribution is shown in Fig. 6.3e. Similar to $n_e$, a peak Ar$^+$ density of $1.1 \times 10^{11}$ cm$^{-3}$ occurs below the edge of the top electrode where the bulk ionization is at its maximum. The E-field in the sheaths accelerates cations toward the surfaces, causing a low Ar$^+$ density near surfaces. Because the E-field in the sheaths points from the plasma to the wall, it repels anions instead of attracting them. Due to the low anion temperature ($< 0.2$ eV), it is nearly impossible for negative ions to climb the 100s V potential barrier of the sheath. Therefore, the anions are well confined in a thin layer between the electrodes. For example, as shown in Fig. 6.3f, F$^-$ is trapped in a 1.5 cm thick slot in the mid-gap with a peak density of $9.0 \times 10^{10}$ cm$^{-3}$ at $r = 14$ cm where $n_e$ is high. Unlike electrons, F$^-$ is uniformly distributed across the reactor in the radial direction. In the base case, the F$^-$ density is high enough to be commensurate with $n_e$, and the ratio $n(F^-)/n_e > 1$ in the center of the reactor, suggesting an ion-ion plasma composition. Unlike ions and electrons, the distribution of the neutral species is not directly affected by the E-field. For example, O is evenly distributed between the electrodes even within
the sheath (Fig. 6.3g). However, because any O\(^+\) bombarding on a surface is likely returned to the plasma as O, and because the O\(^+\) flux is higher on the wafer than on the top electrode, O density is higher in the bottom half of the gap than in the top half.

Due to their high densities, Ar\(^+\) and CF\(_3^+\) have the highest fluxes \((\Gamma)\) among cations. At mid-radius of the wafer \((r = 7.5 \text{ cm})\), \(\Gamma_{\text{Ar}^+} = 4 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}\) and \(\Gamma_{\text{CF}_3^+} = 1.9 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}\). The IEADs of these two species are shown in Fig. 6.4a and b, plotted in a logarithmic scale with two orders of magnitude. The normalized IEDs are shown in Fig. 6.4c. Both Ar\(^+\) and CF\(_3^+\) have a narrow angular distribution of less than 5 degrees. Most ions hitting the wafer have energy between 300 to 750 eV. Ions with low energy \((< 400 \text{ eV})\) either have had collisions as they cross the sheath, or are produced near or within the sheath through charge exchange reactions. On the other hand, energetic ions residing on the high-energy end of IEDs \((> 600 \text{ eV})\) have encountered no or only a few collisions as they travel across the sheath. Both the IEADs of Ar\(^+\) and CF\(_3^+\) have a maximum at \(\varepsilon = 400 \text{ eV}\), agreeing well with the DC bias \(V_{\text{dc}} \approx -400 \text{ V}\). At 25 mTorr, the transit time of ions across the sheath \(\tau_{\text{ion}} \approx 0.3 \mu\text{s}\), close to the RF cycle of 5 MHz power, \(\tau_{5\text{MHz}} = 0.2 \mu\text{s}\). Therefore, if ions enter the sheath when the 5 MHz voltage is negative, they can be accelerated by both the DC bias and this negative voltage and reach energy higher than 400 eV, which produces the maximum extent of the CF\(_3^+\) IED at 650 eV.

The electron energy distribution function (EEDF) is one of the most fundamental plasma properties. The EEDFs from positions depicted in Fig. 6.5b are shown in Fig. 6.5a. The radial position \(r = 13.5 \text{ cm}\) was chosen because the peak \(n_e\) is at that radius. The EEDFs have noticeable high-energy tails \((> 20 \text{ eV})\) near the sheaths \((z = 3.6 \text{ and } 6.0 \text{ cm})\) due to stochastic heating. This high-energy tail is suppressed in the center of the bulk plasma \((z = 4.8 \text{ cm})\), where electrons are inefficiently heated by a small E-field \((\approx 0.5 \text{ V/cm})\) from ohmic heating. In
addition to this low heating efficiency, in the plasma bulk, electrons can quickly lose their energy through inelastic collisions, preventing them from gaining enough energy to populate the high-energy tail of the EEDF. One counter-intuitive result is that even though the total power from the substrate is higher than the power from the top electrode, the fraction of high-energy electrons is higher near the top electrode. The upper position is 0.1 cm from the top electrode and the lower position is 0.3 cm above the substrate to accommodate the thinner sheath thickness by the top electrode. However, either moving the upper point 0.2 cm away from the top electrode or moving lower point 0.2 cm towards the substrate, does not appreciably change the EEDFs. This difference in EEDFs occurs because the radio frequencies 10s MHz are much smaller than the electron plasma frequency $\omega_{pe}$ (about 20 GHz). Therefore, electrons are capable of responding to the dynamics of the sheath and being heated each time the sheath expands. To that end, a high frequency translates to a higher sheath speed and therefore a higher stochastic heating efficiency. That is why EEDF has a higher high-energy tail near the top electrode, where the power has the higher frequency (80 MHz).

The EEDFs from different radial positions are shown in Fig. 6.6. Note that the height $z = 4.8$ cm is chosen because the peak plasma density occurs there. The difference of the EEDFs from the center and the left point is small and appears Maxwellian. However, at $r = 18$ cm in the periphery of the bulk plasma, the EEDF appears to have a concave structure (Druyvesteyn distribution). Note that to have a Maxwellian distribution, elastic collisions such as electron-electron (e-e) collision should be the dominant collision [5]. Comparing with the center point ($n_e = 1.1 \times 10^{11}$ cm$^{-3}$), both left ($n_e = 7.5 \times 10^{10}$ cm$^{-3}$) and right ($n_e = 7.0 \times 10^{10}$ cm$^{-3}$) points have lower $n_e$, meaning that e-e collisions are not as dominant. However, the stochastic heating and secondary electron emission from the powered electrode and substrate provide high-energy
electrons at $r = 5$ cm (left point). Therefore, the high rate of heating raises the tail of the EEDF.

6.3.1 Power

Input power is one of the most commonly used variables for controlling the plasma. The 80 MHz power ($P_{HF}$) was varied from 50 to 1000 W, while the power from the substrate is held constant at 800 W with 400 W at each frequency. The voltage at each frequency, averaged plasma potential, and DC bias with varying $P_{HF}$ are shown in Table I. The corresponding electron distribution and the ionization source by bulk electrons ($S_e$) are shown in Fig. 6.7. Both $n_e$ and $S_e$ increase with $P_{HF}$. As $P_{HF}$ increases, $S_e$ has a 5-fold increase in the center of the reactor, leading to a high $n_e$ that balances the local maxima at the edge of the electrode. When $P_{HF} = 50$ W, $n_e$ in the center of the reactor ($r = 1$ cm) is only 13% of the peak $n_e$. This ratio increases to 72% as $P_{HF}$ increases to 1000 W, suggesting a much more uniform plasma distribution with high $P_{HF}$. Note that the location having the peak $n_e$ moves inwards, with an increase of $P_{HF}$, implying the effect of electrostatic E-field enhancement at the edge of electrodes is weakened with an increasing $P_{HF}$. Because of the sheath thickness $s \propto n_e^{-1/2}$, a non-uniform plasma distribution when $P_{HF}$ is low leads to a bending of the sheath edge. This may consequently cause tilting of IADs when the boundary of the sheath is not parallel to the surface of the wafer.

The EEDFs were recorded at upper and center points shown in Fig. 6.5b with varying $P_{HF}$. The EEDFs from the center point are almost identical when $P_{HF}$ increases from 500 W to 1000 W. However, as $P_{HF}$ decreases from 500 to 50 W, the EEDF perceptibly evolves from a Maxwellian distribution to a Druyvesteyn distribution with a concave structure. This is partly because when $P_{HF} = 50$ W, the recording point ($r = 13.5$ cm, $z = 4.8$ cm) is no longer within the high-density plasma center. When $P_{HF}$ decreases from 500 to 50 W, $n_e$ at the center point is
reduced by 66% from $1.1 \times 10^{11}$ cm$^{-3}$ to $3.7 \times 10^{10}$ cm$^{-3}$. The lower $n_e$ translates to low e-e elastic collision frequency, which produces a deviation of the EEDF from a Maxwellian distribution. At the upper point, near the sheath of the top electrode, the high-energy tail ($E > 20$ eV) of EEDFs falls with lower $P_{HF}$ due to its decreasing power density. The high-energy tail decreases when moving further away from the top electrode. As $P_{HF}$ decreases from 1000 to 50 W, the power density decreases from 1.2 to 0.3 W/cm$^3$ at the upper point. The low power density causes less electron heating and thus smaller high-energy tails of EEDFs.

The 2D IEADs and the normalized IEDs of the dominant ions Ar$^+$ and CF$_3^+$ are shown in Fig. 6.9. For both species, the ion energy tends to decrease as the $P_{HF}$ increases. As $P_{HF}$ increases from 50 to 1000 W, the DC bias drops from -660 to -121 V, and the plasma potential increases from 138 to 167 V, providing a net decrease of 510 V potential drop across the sheath. The decreased sheath potential with an increasing $P_{HF}$ results in lower ion bombardment energy. When $P_{HF}$ is 1000 W, the peak Ar$^+$ energy is about 600 eV lower than that when $P_{HF}$ is 50 W. The low plasma density also thickens the sheath. At the mid-radius ($r = 7.5$ cm) of the wafer, the sheath thickness $s = 0.9$ cm when $P_{HF} = 50$ W, but only 0.2 cm when $P_{HF} = 1000$ W. With the same pressure, the thicker the sheath, the more collisional the sheath becomes. A collisional sheath deviates ion trajectories and broadens the IAD. Therefore, the IAD is much broader when $P_{HF} = 50$ W. The breadth of the IAD decreases from $10^\circ$ to $5^\circ$ as the $P_{HF}$ increases from 50 to 1000 W. If $P_{HF}$ is between 500 and 1000 W, the IAD barely changes because the sheath thickness only moderately decreases with the increase of power.

6.3.2 Pressure

Chamber pressure affects collision frequency and the mean free path of both ions ($\lambda_{ion}$) and electrons ($\lambda_e$) and is another parameter that determines the plasma distribution and density. The pressure was varied between 15 and 50 mTorr. The corresponding electron distribution, and
the ionization source by bulk electrons ($S_e$), are shown in Fig. 6.10. The voltage at each frequency, averaged plasma potential, and DC bias with varying pressure are shown in Table I. Increasing the pressure from 15 to 50 mTorr, the peak $n_e$ is decreased by 14%. As pressure increases from 15 to 50 mTorr, $\lambda_e$ decreases from 1.7 cm to 0.7 cm at the edge of the sheath, meaning at 50 mTorr, the number of hot electrons reaching the mid-gap ($z = 4.8$ cm) is sharply decreased. This reduces the ionization and hence produces a low $n_e$. Note that when the pressure is 50 mTorr, $S_e$ is confined to a thin layer near the top electrode, and its magnitude is halved compared with the $S_e$ at the same position when the pressure is 15 mTorr. The decrease of $S_e$ in the bulk plasma increases the relative importance of ionization by beam electrons ($S_{eb}$). When the pressure is 50 mTorr, at mid-gap ($r = 7.5$ cm and $z = 4.8$ cm), $S_{eb} = 1.7 \times 10^{15}$ cm$^{-3}$s$^{-1}$, surpassing $S_e = 1.3 \times 10^{15}$ cm$^{-3}$s$^{-1}$. $S_{eb}$ becomes more important in high pressure because beam electrons with an energy of 100s eV having longer mean free path, allowing them to travel into and ionize the plasma bulk.

The EEDFs at the center point ($r = 13.5$ cm, $z = 4.8$ cm) with varying pressure are shown in Fig. 6.11a. As the pressure increases from 15 to 50 mTorr, the high-energy tail is suppressed as the result of the shortening of $\lambda_e$. A steeper slope of EEDF with increasing pressure translates to the lower $T_e$. As shown in Fig. 6.11b, the reactor averaged $T_e$ drops from 3.1 to 2.7 eV as the pressure increases from 15 to 50 mTorr, while $n_e$ decreases from 4.3 to $2.6 \times 10^{14}$ cm$^{-3}$. Note that the gas mixture used in this work contains attaching gases such as F$_2$ and O$_2$, thereby increasing the pressure significantly enhances the attachment reactions, causing the decrease of $n_e$.

The IEADs and normalized IEDs of Ar$^+$ and CF$_3$ at pressures of 15, 30, and 50 mTorr are shown in Fig. 6.12. Increasing the pressure broadens the IADs because the sheath becomes
thicker and more collisional. As the pressure increases from 15 to 50 mTorr, the IAD is extended from 8° to 16°. The maximum ion energy increases with the increase in pressure. For example, as the pressure increases from 30 to 50 mTorr, the peak Ar⁺ energy is increased from 780 to 850 eV. This increase of ion energy with pressure is caused by the increase of both plasma potential and the magnitude of DC bias on the substrate. As the pressure increases from 15 to 50 mTorr, the DC bias increases from -382 V to -450 V, and the plasma potential from 108 to 150 V. This high plasma potential and more negative DC bias creates high maximum ion energy when the pressure is 50 mTorr. However, at high pressure, the sheath is more collisional. Therefore, even though the maximum ion energy is almost 900 eV, the majority of ions still come with energy ≈ 400 eV. At 50 mTorr, the fraction of ions with energy less than 300 eV is more than that when the pressure is 15 mTorr, as shown in Fig. 6.12c, and d. Therefore, the average ion bombardment energy can be similar for cases with different pressures even though the maximum ion energy is significantly different.

### 6.3.3 Frequency

The driving frequency of the power source is considered to be one of the most important parameters in an rf-power driven CCP. The frequency from the top electrode was varied from 20 to 120 MHz, while the power from the substrate remains the same as in the base case (5 MHz 400 W and 10 MHz 400 W). The voltages at each frequency, averaged plasma potential and DC bias with varying HF are shown in Table I. The electron distribution and the ionization source by bulk electrons ($S_e$) are shown in Fig. 6.13. With the same input power, the peak value of the $S_e$ and $n_e$ barely changes with the HF. However, as the HF increases from 20 to 120 MHz, the spatial distribution of both $n_e$ and $S_e$ becomes more uniform. As discussed before, electrons can respond to the change of rf, and higher frequency has higher stochastic heating efficiency.
Therefore, as the HF increases, more hot electrons are created at the sheath edge, leading to a high ionization rate and high $n_e$ in plasma bulk. Note that even though the power is fixed, the power dissipated to ions and electrons can vary under different operating conditions. In this work, the power delivered to electrons increases from 125, 328 to 355 W, as the HF increases from 20, 60, and 120 MHz, showing that increasing the driving frequency amplifies electron heating efficiency. However, the effect of the changing HF is not as significant when it rises from 60 to 120 MHz comparing to when it increases from 20 to 60 MHz, suggesting a saturation frequency above which $n_e$ will not have significant change with the increase of frequency.

The EEDFs at the center point ($r = 13.5$ cm, $z = 4.8$ cm) are recorded as the HF increases from 20 to 120 MHz, as shown in Fig. 6.14. Similar to the effect of HF on $n_e$, increasing HF from 60 to 120 MHz only has a minor impact on EEDF. The low sensitivity of EEDF to a changing HF is because when the HF is higher than 60 MHz, the plasma properties are governed by the magnitude of power input instead of the heating efficiency. Even though the heating efficiency still increases, the impact is simply not significant enough to cause any substantial change to the plasma. Therefore, the similar $n_e$ and the e-e elastic collision frequencies occur, resulting in nearly identical EEDF. On the other hand, if the HF decreases from 60 MHz, both $n_e$ and the EEDF are affected by the decreasing stochastic heating efficiency, which causes a decrease of the hot electron density, hence low $S_e$ and $n_e$. The power transferred to electrons when the HF is 20 MHz is only approximately 1/3 compared with that when the HF is 120 MHz. A low $n_e$ translates to a low e-e collision frequency. Therefore, when the HF is 20 MHz, the EEDF in the bulk plasma has a concave structure, characterized by suppression on both the high and low energy ends.

The IEADs of Ar$^+$ and CF$_3^+$ on the wafer when the HF is 20, 60, and 120 MHz are shown
in Fig. 6.15. Ions gain their highest energy when the HF is 60 MHz. As the HF decreases from 60 to 20 MHz, the DC bias becomes less negative, from -320 V to -145 V. Meanwhile, the plasma potential increases from 151 to 316 V. With both DC bias and plasma potential considered, the sheath potential by the wafer is 10 V higher when the HF is 60 MHz, which provides slightly higher ion energy. However, the ion energy is not monotonically increased with the increase of the HF. As the HF increases from 60 to 120 MHz, the plasma potential decreases from 151 to 117 V, and the DC bias from -320 to -305 V. The net decrease of 49 V of sheath potential as HF increases from 60 to 120 MHz results in a decline of the maximum ion energy. Increasing HF still produces an increase of stochastic heating efficiency, thus high $n_e$, especially in the center of the reactor ($r < 5$ cm). With similar DC bias and higher power deposition into electrons, the plasma potential then decreases to reduce the power dissipated to ions, and maintain the constant power delivery to the plasma.

### 6.3.4 Gap Length

The effect of gap length between the top electrode and the substrate on the plasma was also investigated. The voltage at each frequency, averaged plasma potential, and DC bias when the gap length is varied are shown in Table I. The distributions of $n_e$ and the ionization source by bulk electrons ($S_e$) when the gap length $d = 2.3, 3.3, \text{and } 4.3$ cm are shown in Fig. 6.16. The peak $n_e$ barely changes with $d$ because the power input is constant (1300 W). The plasma is more uniformly distributed with an increasing $d$, due to the weakened electrostatic effect at the edge of the electrodes and the decreased loss of charged particles with decreasing surface to volume ratio. When $d = 2.3$ cm, from 0.3 cm above the wafer, power density increases from 1.1 W/cm$^3$ at $r = 1$ cm to 2.3 W/cm$^3$ at $r = 14$ cm. This uneven power deposition leads to a non-uniform plasma distribution. When $d = 4.3$ cm, a wider gap minimizes the coupling between the top electrode and the substrate and weakens that electrostatic effect. When $d = 4.3$ cm, at 0.3 cm
above the wafer, power density is 1.9 W/cm³ at \( r = 1 \text{ cm} \), and 2.0 W/cm³ at \( r = 14 \text{ cm} \), with only a minor increase of 0.1 W/cm³. A uniform power deposition leads to uniform \( S_e \) and \( n_e \) distributions. When \( d = 4.3 \text{ cm} \), \( n_e \) from mid-gap is almost constant across the reactor, which is desired for most applications. Increasing \( d \) also reduces the surface to the volume ratio of the reactor. In a low temperature plasma, the diffusion loss to the wall is one of the major sinks for the charged species. Reducing the surface to volume ratio effectively reduces the wall loss; therefore, despite the decreasing magnitude of \( S_e \) with the increasing \( d \), \( n_e \) still increases.

The EEDFs with varying \( d \) was recorded at \( r = 13.5 \text{ cm} \) at mid-gap for each case, shown in Fig. 6.17. The high-energy component is suppressed as \( d \) increases. Because the data is gathered at the mid-gap, increasing \( d \) increase the distance between the recording point and the sheath. Therefore, hot electrons created at the sheath edge are more likely to be cooled by collisions before reaching the position where EEDF is recorded. Also, power is more evenly distributed in the reactor when \( d \) is large. Therefore, the power density at \( r = 13.5 \text{ cm} \) is lower with larger \( d \) as more power is delivered to the plasma in the center of the reactor \((r < 5 \text{ cm})\). Consequently, fewer hot electrons are produced near the edge of electrodes, which also contributes to the suppression of the high-energy tail of EEDF at mid-gap when \( d \) increases.

The IEADs of the \( \text{Ar}^+ \) and the \( \text{CF}_3^+ \) as \( d \) increases from 2.3 to 4.3 cm are shown in Fig. 6.18. The ion energy increases with an increasing \( d \) as a result of a more negative DC bias. As \( d \) increases from 2.3, 3.3 to 4.3 cm, the DC bias changes from -300 V, -395 to -411 V, while the plasma potential increases from 126, 132, to 138 V. Note that the DC bias is a function of multiple parameters including areas of the grounded and powered surfaces, \( n_e \) at the edge of sheaths adjoining these surfaces and the RF voltage from the power source. Usually, in an SF-CCP, a well-confined plasma between the electrodes translates to a weak geometrical asymmetry.
since the boundary of the bulk plasma is evenly distributed on the powered (bottom electrode) and grounded (top) surfaces, which usually have a similar surface area. However, in this TF-CCP setup, both the top electrode and the substrate are powered, meaning the main reactor itself, where the plasma is generated, is highly electrically asymmetric. Therefore, simply having the plasma confined between the electrodes does not guarantee a zero DC bias. In this particular setup, as $d$ increases, the plasma is more confined between the electrodes, and the DC bias significantly increases. This is partly because as $d$ increases from 2.3 to 3.3 cm, $n_e$ by the grounded surface (above the pump) decreases to notably lower than that in the center of the bulk plasma, which leads to a more negative DC bias. Because the plasma potential has only a mild increase with $d$, the average ion energy is predominantly determined by the magnitude of DC bias. The IED shifts about 100 eV to higher energy as $d$ increases from 2.3 to 3.3 cm. The IAD becomes slightly narrower with increasing $d$ as the high DC bias generates higher acceleration perpendicular to the wafer surface. However, this decrease of the IAD with a varying $d$ is insignificant since the sheath thickness barely changes.

### 6.4 Concluding Remarks

In this chapter, a low temperature TF-CCP sustained in Ar/CF$_4$/O$_2$ is computationally investigated under different operating conditions. The electrostatic electric field enhancement at the edge of the electrodes was found to raise the local plasma density. Changing operating conditions, such as increasing the HF or increasing HF power, can enhance the electron heating at the center of the reactor (< 5 cm), thereby weakening the electrostatic effect and leading to a more uniform plasma distribution. The electron energy distribution function (EEDF) was found to have a Maxwellian structure in the regions with high electron density ($n_e$) due to the high electron-electron (e-e) collision frequency. However, the EEDF has a concave structure.
(Druyvesteyn) where $n_e$ and the stochastic heating efficiency are low.

Ideally, in a multi-frequency CCP, the HF power governs the plasma density while the LF power determines the ion energy and angular distributions (IEADs) onto the wafer. However, varying HF power was found to have some effects on the IEADs. Increasing HF power directly increases the power density in the plasma, while increasing HF itself promotes the stochastic heating. Both of these result in an increase of $n_e$ in the center of the reactor and a more uniform plasma distribution. A re-distributed plasma changes the symmetry of the reactor that in turn determines the DC bias. Therefore, varying the HF power (magnitude, frequency) often modifies the DC bias. Also, both the plasma potential and sheath thickness ($s$) are sensitive to the change of $n_e$, meaning they are also functions of the HF power. The plasma potential and DC bias together determine the potential drop across the sheath, which establishes the ion energy distribution (IED). The sheath thickness $s$ affects the collisionality of the sheath and the energy width of the IED. For the same pressure, thicker $s$ translates to a more collisional sheath, and a broader ion angular distribution (IAD). Evidently, the IEAD has a non-linear dependence on HF power. In general, low $n_e$ results in high sheath potential and thick sheath, therefore a broad IAD and high ion energy. The dependence of IEADs on HF power was investigated varied from 50 to 1000 W. In practice, when using HF power to adjust plasma behavior, the range of the varying power is often not as big. Therefore, the effect of HF power on the IEADs will be less recognizable.

The effects of pressure and gap length (d) between the electrodes on the plasma were also investigated in this work. Increasing the pressure shortens the mean free path of electrons, thus reducing the ionization in the bulk plasma. Meanwhile, high pressure translates to a highly collisional sheath, which broadens the IAD. Increasing the gap length makes the plasma more
uniform and makes a more negative DC bias. The effect of gap length on IEADs saturates once $d > 3.3$ cm.

In conclusion, in a TF-CCP, the plasma properties can be adjusted by using different HF power, pressure, and reactor geometry. It has been confirmed that some coupling of HF power to the IEADs occurs, and fully independent control of plasma density and IEADs onto the wafer is hard to achieve. However, with only moderate adjustments of the operating conditions, the consequences of HF on IEADs can be minimized. Using a high power with high frequency, low pressure, and long gap length between the electrodes is recommended strategy to achieve uniform plasma distributions. A uniform plasma distribution across the reactor makes the DC bias less sensitive to changes in the HF power, which helps decouple the control of IEADs and the plasma density.
Table I. Voltage of Each Frequency, Plasma Potential and DC bias with Varying Conditions

The following table contains voltage at each frequency, time averaged plasma potential and DC bias with varying conditions. For each case, only one parameter differs from the base case, and that parameter is used to label the corresponding case. In the base case, \( HF = 80 \) MHz, \( P_{HF} = 500 \) W, pressure is 25 mTorr, gap length between top and bottom electrodes is 2.8 cm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Voltage ((V_{5MHz}/V_{10MHz}/V_{HF})/V)</th>
<th>Potential /V</th>
<th>DC bias /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case</td>
<td>448/357/117</td>
<td>128</td>
<td>-370</td>
</tr>
<tr>
<td>Power</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 W</td>
<td>768/488/44</td>
<td>138</td>
<td>-660</td>
</tr>
<tr>
<td>200 W</td>
<td>619/437/77</td>
<td>124</td>
<td>-556</td>
</tr>
<tr>
<td>700 W</td>
<td>362/310/141</td>
<td>142</td>
<td>-252</td>
</tr>
<tr>
<td>1000 W</td>
<td>276/266/176</td>
<td>167</td>
<td>-121</td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 mTorr</td>
<td>438/336/108</td>
<td>108</td>
<td>-382</td>
</tr>
<tr>
<td>20 mTorr</td>
<td>436/344/113</td>
<td>120</td>
<td>-372</td>
</tr>
<tr>
<td>30 mTorr</td>
<td>468/375/120</td>
<td>136</td>
<td>-384</td>
</tr>
<tr>
<td>40 mTorr</td>
<td>507/401/126</td>
<td>147</td>
<td>-414</td>
</tr>
<tr>
<td>50 mTorr</td>
<td>541/418/129</td>
<td>150</td>
<td>-450</td>
</tr>
<tr>
<td>Frequency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 MHz</td>
<td>440/367/342</td>
<td>316</td>
<td>-145</td>
</tr>
<tr>
<td>40 MHz</td>
<td>491/390/192</td>
<td>203</td>
<td>-301</td>
</tr>
<tr>
<td>60 MHz</td>
<td>444/347/144</td>
<td>151</td>
<td>-320</td>
</tr>
<tr>
<td>100 MHz</td>
<td>431/347/103</td>
<td>119</td>
<td>-352</td>
</tr>
<tr>
<td>120 MHz</td>
<td>396/330/96</td>
<td>117</td>
<td>-305</td>
</tr>
<tr>
<td>Gap Length</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 cm</td>
<td>396/330/116</td>
<td>126</td>
<td>-300</td>
</tr>
<tr>
<td>3.3 cm</td>
<td>472/375/119</td>
<td>132</td>
<td>-395</td>
</tr>
<tr>
<td>3.8 cm</td>
<td>476/378/121</td>
<td>136</td>
<td>-403</td>
</tr>
<tr>
<td>4.3 cm</td>
<td>485/383/124</td>
<td>138</td>
<td>-411</td>
</tr>
</tbody>
</table>
6.5 Figures

Fig. 6.1 Geometry of the reactor. 80 MHz power (500 W) is applied to the top electrode, 5 and 10 MHz power (400 W each frequency) are applied to the substrate. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr.
Fig. 6.2 Spatially averaged a) ion and b) neutral species’ densities. An acceleration technique was used to help the plasma reach the quasi-steady state faster, causing rapid density changes in the first 250 μs. Ar/CF₄/O₂ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.3 2D profile of a) electron density, b) electron temperature, c) ionization source by bulk electrons, d) ionization source by beam electrons, e) Ar$^+$ density, f) F$^-$ density and g) O density in base case. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.4 The a) IEADs averaged over 0° and b) normalized IEDs of CF$_3^+$ and Ar$^+$ at mid-radius of the wafer ($r = 7.5$ cm). Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.5 a) EEDFs from different axial locations and b) the locations from where the EEDFs are recorded. Ar/CF₄/O₂ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.6 a) EEDFs from different radial locations and b) the locations from where the EEDFs are recorded at $z = 4.8$ cm. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.7 2D profiles of the electron density and ionization source by bulk electrons when the power from 80 MHz power source is 50, 500 and 1000 W. Ar/CF₄/O₂ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.8 The EEDFs from a) center ($r = 13.5$ cm, $z = 4.8$ cm) and b) upper ($r = 13.5$ cm, $z = 6.0$ cm) point when the power from 80 MHz power source is 50, 500 and 1000 W. Inset of a) is the zoom-in on the low energy component of EEDFs at center point and the inset of b) is the spatially averaged electron density and electron temperature with increasing HF power. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.9 IEADs of a) Ar$^+$ and b) CF$_3^+$ and the normalized IEDs of c) Ar$^+$ and d) CF$_3^+$ when the power from 80 MHz power source is 50, 500 and 1000 W. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: varied power (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.10 2D profiles of the electron density and ionization source by bulk electrons when the pressure is 15, 30 and 50 mTorr. Ar/CF₄/O₂ (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.11 a) EEDFs from the center point ($r = 13.5$ cm, $z = 4.8$ cm) when the pressure is 15, 30 and 50 mTorr. And the b) spatially averaged electron density and electron temperature. Ar/CF₄/O₂ (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.12 The IEADs of a) Ar$^+$ and b) CF$_3^+$ and the normalized IEDs of c) Ar$^+$ and d) CF$_3^+$ when the pressure is 15, 30 and 50 mTorr. Ar/CF$_4$/O$_2$ (75/15/10), varied pressure, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.13 2D profiles of the electron density and ionization source by bulk electrons when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.14 EEDFs at the center point ($r = 13.5$ cm, $z = 4.8$ cm) when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.15 IEADs of a) Ar$^+$ and b) CF$_3^+$ and the normalized IEDs of c) Ar$^+$ and d) CF$_3^+$ when the frequency from the HF power source is 20, 60 and 120 MHz. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (varied frequency), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.16 2D profiles of the electron density and ionization source by bulk electrons when the gap length is 2.3, 3.3 and 4.3 cm. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.17 EEDFs from the center point \((r = 13.5\) cm, \(z = 4.8\) cm) when the gap length is 2.3, 3.3 and 4.3 cm. The inset is the spatially averaged electron density and electron temperature with increasing gap length. \(\text{Ar/CF}_4/\text{O}_2\) (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
Fig. 6.18 IEADs of a) Ar$^+$ and b) CF$_3^+$ and the normalized IEDs of c) Ar$^+$ and d) CF$_3^+$ when the gap length is 2.3, 3.3 and 4.3 cm. Ar/CF$_4$/O$_2$ (75/15/10), 25 mTorr, top electrode: 500 W (80 MHz), substrate: 400 W (5 MHz), 400 W (10 MHz).
6.6 References
Chapter 7: Computational Investigation of Plasma Enhanced Atomic Layer Deposition of SiO$_2$ Film Using Capacitively Coupled Ar/O$_2$ Plasmas

7.1 Introduction

Atomic layer deposition (ALD) is a material deposition technology that enables minutely delicate control over film quality at the angstrom-scale. An ideal ALD process is self-limiting, meaning that the kinetics of the film growth saturates, resulting in a maximum of only one monolayer of deposition per cycle. The deposited films often yield high conformality and uniformity, which is necessary for applications ranging from conventional semiconductor manufacturing and solar panel fabrication, to novel applications such as energy storage fuel cell manufacturing [1-5]. For semiconductor manufacturing, deposition of silicon-based dielectrics is still one of the most targets for refinement of ALD technologies [6-12].

Thin SiO$_2$ film is widely used as an isolation liner and sidewall spacer in microelectronics devices [13-15]. Even though some relatively sophisticated film deposition approaches are available, the current technology nodes at the less than 10 nm scale, having more challenging demands for high-conformality film deposition. More severe operating conditions require highly uniform thin dielectric films, to deliver consistent performance. For example, one of the most pressing issues challenging the dependability of SiO$_2$ films is electrical breakdown [16-17]. This is more likely to happen if the SiO$_2$ film contains defects in the film. Stathis reported that in films thinner than 2 nm, a single defect is enough to cause a breakdown and inconsistent performance [17].
Thermal ALD is one of the more well established SiO₂ film deposition techniques. Typically, in a thermal ALD process, the target surface is sequentially treated with inorganic silicon precursor (e.g., SiCl₄, SiCl₃H) and oxidant (e.g., H₂O, O₃). Each cycle produces a fraction of a monolayer of film. Repeating the 2-steps builds the film layer by layer. To activate these processes the substrate is usually heated to > 300 °C. Using a SiCl₄ and H₂O binary reaction sequence, Sneh et al. achieved controlled SiO₂ film deposition at temperatures of 330-410 °C at a growth rate of 1.1 Å/cycle in 1995 [18]. In a later work, Lee et al. proposed a SiO₂ ALD mechanism having cycles of alternating Si₂Cl₆ and O₃ with a substrate temperature of 403-453 °C [19]. A temperature of 471 °C or higher was needed for a deposition rate higher than 0.32 nm/cycle. Even though this temperature is already lower than that used in many other SiO₂ deposition techniques, such as low-pressure chemical vapor deposition, it is still high enough to tax the allowed thermal budget of the manufacturing process. This higher temperature also limits the use of temperature-sensitive materials such as those used for flexible electronics.

One way to decrease the temperature of ALD of SiO₂ deposition is to use plasma-enhanced ALD (PE-ALD). In a typical SiO₂ PE-ALD process, the target surface is first treated with the silicon precursor and then oxidized in an oxygen plasma. The process is repeated itself, and the SiO₂ is thus grown layer-by-layer. Unlike thermal ALD, in a PE-ALD, oxidation reactions are enabled by reactive species in the plasma. Fang et al. reported that O₂(¹Δ), O₃ and O(¹D) are the primary reactants that oxidize a precursor-dosed surface during plasma exposures in SiO₂ PE-ALD, and this enables the low-temperature deposition [20]. Choi et al. also reported the deposition of SiO₂ films of 10s nm using PE-ALD with a temperature of less than 200 °C [21]. Jeon et al. used plasma-activated triisopropylsilane [TIPS, ((iPr)₃SiH)] as a silicon precursor during dosing in a PE-ALD process [11]. They found that the deposition temperature
can be decreased to as low as 50 °C, and these SiO₂ films have no detectable impurities.

In side-by-side comparison of SiO₂ films deposited using PE-ALD and plasma-enhanced chemical vapor deposition (PECVD), Jung et al. found that the PE-ALD prepared film had higher purity, more proper stoichiometry, and lower leakage current [12]. When tested as the gate insulator in a thin film transistor, PE-ALD SiO₂ film appeared to be less susceptible to the negative threshold voltage shift than PECVD SiO₂ film due to a smoother insulator/channel contact interface. Civale et al. studied 200 nm-thick SiO₂ liners for a high aspect ratio (25:1) through silicon via (TSV) as used in 3D interconnections, prepared using PE-ALD [13]. They reported near-ideal film conformality and electrical properties, suggesting a role of PE-ALD grown SiO₂ films in high aspect ratio applications. However, the quality of SiO₂ films grown using PE-ALD is sensitive to the scale of the feature. For example, growing a SiO₂ film in a high aspect ratio feature having a critical dimension of less than 20 nm can be more challenging than depositing this film in a feature with a critical dimension of 10s to 100s nm and the same aspect ratio.

Similar to other thin film deposition techniques, many parameters can affect the quality of a PE-ALD process. Shin et al. found that for SiO₂ PE-ALD, the deposition rate measured as growth-per-cycle (GPC) depends on the plasma exposure time [8]. The GPC decreased from 2.0 to 1.6 Å/cycle as O₂ plasma exposure time increased from 0.5 to 5.0 s, which was thought to be the result of surface heating and film densification. Kobayashi et al. found that the deposition temperature can also affect PE-ALD [6]. A higher GPC was achieved with lower deposition temperature. Using BDEAS (Bis(diethylamino)silane, SiH₂[N(CH₂CH₃)₂]₂) as the silicon precursor, they found that the saturated GPC increases from 0.10 to 0.15 nm/cycle as the deposition temperature decreases from 300 to 50 °C. They concluded that as the substrate
temperature increases, desorption reactions decrease the GPC.

Other than the external operating conditions, the chemical properties of silicon precursors have a significant impact on the PE-ALD process [22-23]. In work comparing SiO₂ PE-ALD by silicon precursors: BTBAS (bis(tertiary-butylamino)silane, SiH₂[NH(C₄H₉)]₂), BDEAS, and DSBAS (di-sec-butylaminosilane, SiH₃[N(C₄H₉)₂]), Mallikarjunan et al. concluded that because DSBAS is a monoaminosilane precursor, it has fewer organic substitutions than BTBAS and BDEAS [23]. Therefore, the surface packing density of silicon-containing components after the precursor dosing is higher when using DSBAS, and so is the growth rate. From this work, it is clear that the structure of the precursor can affect PE-ALD through steric hindrance.

Steric hindrance occurs when the ligand group from the silicon precursor remains on the target surface and blocks the otherwise exposed neighboring surfaces. The blockage reduces the surface coverage of the desired species and hinders the growth of the film. Using density functional theory (DFT) to study the steric effect in an ALD process, Murray et al. concluded that a sizeable steric bulk of alkyl ligand groups is less likely to form bound reactant structures with the surface, resulting in reduced adsorption probability [7]. Once deposited, these large ligand groups can cause significant steric hindrance and impede further deposition.

In this chapter, we discuss results from computational investigations of PE-ALD of SiO₂ films for blanket deposition, and in trench and via structures. We performed a parametric study on the input power of the oxidizing plasma from 400 to 1000 W, and the pressure from 0.5 to 2 Torr. We have found that changing power has a small effect on film quality, but decreasing pressure promotes ion bombardment, and produces a more porous film. The deposition probability of ligand groups with precursors was varied from 0.001 to 0.5. Both film growth rate, and film density, decrease with an increase of the ligand group co-deposition probability.
The model used in this investigation is briefly discussed in Sec. 7.2. Plasma and film properties as a function of power, pressure, and ligand group co-deposition probability are discussed in Sec. 7.3. Concluding remarks are in Sec. 7.4.

7.2 Description of the Model

The computational investigation platforms used in this work are the Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM). The details of the models are discussed in Chapter 2, Ref [24] and Ref [25]. Only a brief description of these is provided here.

The modules from the HPEM that are used in this work are the Fluid Kinetics Poisson Module (FKPM), the Electron Energy Transport Module (EETM), and the Plasma Chemistry Monte Carlo Module (PCMCM). In the FKPM, the continuity, momentum, and energy equations of the heavy particles are solved coincidently with Poisson’s equation to provide heavy particle densities and electrostatic potential. The Boltzmann equation is solved in the EETM for the electron energy distribution function (EEDF), from which electron transport and rate coefficients are obtained. The PCMCM is used when the plasma reaches the quasi-steady state to calculate energy and angular distributions (EADs) of ions and reactive neutrals onto the wafer.

In the MCFPM, gas-phase pseudoparticles with EADs providing by the HPEM are launched on at the top of the target feature and tracked using Monte Carlo technique. Elastic collision of gas-phase particles is included with isotropic scattering. The steric hindrance of large ligand groups in the Si precursor is addressed by “co-depositing” a ligand-representing cell in the neighbor cells of the primarily deposited silicon cell.

The following process is used to co-deposit the ligands. The Si precursor is specified to have N ligand groups. Upon deposition of the Si precursor, a random number \( r=(0,1) \) is selected.
If \( r \leq p_R \), then a co-deposition of the first ligand is attempted. A search is made of the sites surrounding the deposition site for an empty voxel to co-deposit the ligand. The search order is randomized. For a 2D simulation, there are 8 possible sites. For a 3D simulation, there are 26 possible sites. When an empty site is found, a ligand is placed in that voxel. The process is then repeated for the \( N \) ligand groups.

The species included in the reactor scale simulation are \( \text{Ar, Ar}(1s_3), \text{Ar}(1s_4), \text{Ar}(1s_3), \text{Ar}(1s_2), \text{Ar}(4p), \text{Ar}(4d), \text{Ar}_2^*, \text{Ar}^+, \text{Ar}_2^+, \text{O}_2, \text{O}_2(v), \text{O}_2(\text{a}^1\Delta_g), \text{O}_2(b^1\Sigma_g^+), \text{O}_2^+, \text{O}_2^-, \text{O}(1D), \text{O}(3s^5\text{S}^0), \text{O}(3s^3\text{S}^0), \text{O}(3p^5\text{P}), \text{O}(1\text{S}), \text{O}^+, \text{O}^-, \text{O}_3, \text{O}_3^- \) and electrons.

### 7.3 Surface Reaction Mechanism for SiO\(_2\) PE-ALD Using Ar/O\(_2\) Plasma

The gas-phase species, surface sites, and surface reaction mechanism of SiO\(_2\) PE-ALD using a silicon precursor with two ligand groups (such as BTBAS) and Ar/O\(_2\) plasma as oxidation agent are shown in Table II.

The gas-phase species included the feature scale simulation can be classified as follows.

- **a)** Ions bring high energy to the feature due to acceleration in the sheath.
- **b)** Hot neutrals have similar energy as ions. They are produced when ions hit a surface, lose their charge, and are reflected from the wall.
- **c)** Thermal neutrals have energy less than 0.1 eV. Many thermal neutrals, such as O and O\(_3\), are the primary species for surface oxidation.
- **d)** Reaction products are gas phase particles removed from the surface by ions and hot neutrals or chemical reactions. Many reaction products can be re-deposited on the surface.

Surface sites are classified by the layer they belong to. A silicon layer contains sites that are produced from precursor dosing, and an oxygen layer contains sites that are produced during plasma exposure. Each voxel in the MCFPM represents a site in the oxygen layer containing
two physical bonds due to Si/O = 1:2 in SiO₂ film. For example, x-Si-y(s) denotes x and y sites connected to a shared silicon atom, although this silicon atom is not included in that voxel.

The PE-ALD process starts with precursor dosing on a surface covered with hydroxyl sites. The ligand group R from the precursor SiH₂R₂ combines with the hydrogen from hydroxyl sites and forms a volatile species HR. The remaining precursor SiH₂ is then bonded to the oxygen, and deposited on the surface as SiH₂(s). In a process that completely eliminates the ligands:

\[
\text{OH-Si-OH}(s) + \text{SiH₂R₂} \rightarrow \text{O}_2(s) + \text{SiH₂(s)} + 2\text{HR} \quad (7.1a)
\]

However, there are cases where deposition of SiH₂(s) can occur on some surface sites with insufficient hydroxyls.

\[
\begin{align*}
\text{OH-Si-H}(s) + \text{SiH₂R₂} & \rightarrow \text{O}(s) + \text{SiH₂(s)} + 2\text{HR} \quad (7.1b) \\
\text{OH-Si(s)} + \text{SiH₂R₂} & \rightarrow \text{O}(s) + \text{SiH₂(s)} + p_R\text{R}(s) + (1-p_R)\text{HR} + \text{HR} \quad (7.1c) \\
\text{O-Si-H}(s) + \text{SiH₂R₂} & \rightarrow \text{O}(s) + \text{SiH₂(s)} + p_R\text{R}(s) + (1-p_R)\text{HR} + \text{HR} \quad (7.1d) \\
\text{OH-Si-O}(s) + \text{SiH₂R₂} & \rightarrow \text{O}(s) + \text{SiH₂(s)} + p_R\text{R}(s) + (1-p_R)\text{HR} + \text{HR} \quad (7.1e)
\end{align*}
\]

In reactions 7.1b, 7.1c, and 7.1d, O(s) instead of O₂(s) is deposited. If this happens too often, the O/Si ratio will decrease, leading to an disordered film structure. Note that ligand groups R(s) are not co-deposited with SiH₂(s) even when the direct surface reactant has insufficient hydroxyl sites, such as in reaction 7.1c, 7.1d, and 7.1e. This is because, if any of the nearest neighbors of the direct surface reactant can provide hydrogen atoms, the ligand from the silicon precursor can combine with them and form volatile HR. That said, it would be very computationally expensive to check the nearby neighbors of a direct surface reactant wherever a deposition occurs. Therefore, we rely on the co-deposition probability \(p_R\) for the deposition of ligand remnants R(s). For example, if a SiH₂(s) is deposited on a surface with SiH₂R₂ as a reactant, an R(s) site is co-deposited with the probability \(p_R\).
During plasma exposure, the surface is oxidized by ROS (reactive oxygen species) from the plasma. The oxidation can be a multi-step process.

\[
\text{SiH}_2(s) + O \rightarrow \text{Si}(s) + \text{OH-Si-H}(s) \quad (7.2a)
\]
\[
\text{OH-Si-H}(s) + O \rightarrow \text{OH-Si-OH}(s) \quad (7.2b)
\]

Both the excited state oxygen radical (such as O\(^{(1D)}\)) and O\(^+\) can have the same reactions with higher probability. The oxidation can also become a one-step process by excited state oxygen molecules.

\[
\text{SiH}_2(s) + O_2(^{1}\Delta) \rightarrow \text{Si}(s) + \text{OH-Si-OH}(s) \quad (7.2c)
\]

The goal of plasma exposure is to deposit the oxygen layer on the film and populate the surface with hydroxyl sites.

Despite a high pressure of up to a few Torr, some ions reach the surface with energy exceeding 30 eV can produce damage by sputtering.

\[
\text{OH-Si-OH}(s) + \text{I}^+ \rightarrow \text{OH-Si}(s) + \text{OH} + \text{I}(h) \quad (7.3a)
\]
\[
\text{SiH}_2(s) + \text{I}^+ \rightarrow \text{SiH}_2 + \text{I}(h) \quad (7.3b)
\]
\[
\text{R}(s) + \text{I}^+ \rightarrow \text{R} + \text{I}(h) \quad (7.3c)
\]

The sputtering thresholds for oxygen and hydroxyl are 30 eV, and for silicon, SiH\(_2\)(s), and SiH(s) are 35 eV. The sputtered particles can be re-deposited on the surface when they have collided with sites having dangling bonds. Gas-phase OH and R particles can combine with hydrogen and create a dangling bond on the surface.

\[
\text{SiH}_2(s) + \text{OH} \rightarrow \text{SiH}(s) + \text{H}_2\text{O} \quad (7.4a)
\]
\[
\text{OH-Si-OH}(s) + \text{OH} \rightarrow \text{OH-Si-O}(s) + \text{H}_2\text{O} \quad (7.4b)
\]
\[
\text{SiH}_2(s) + \text{R} \rightarrow \text{SiH}(s) + \text{HR} \quad (7.4c)
\]
\[
\text{OH-Si-OH}(s) + \text{R} \rightarrow \text{OH-Si-O}(s) + \text{HR} \quad (7.4d)
\]

Hydrogen is typically bonded to Si or O. No hydrogen-only sputtering is included due to the low kinetic energy transfer efficiency between a light hydrogen atom and a heavy incident particle.
Besides sputtering, the recombination reactions of oxygen radicals and O$_3$ can also reduce the oxygen contents of SiO$_2$ film.

\[
\begin{align*}
O(s) + O & \rightarrow O_2 \quad (7.5a) \\
O_2(s) + O & \rightarrow O(s) + O_2 \quad (7.5b) \\
O_2(s) + O_3 & \rightarrow O_2 + O_2 \quad (7.5c)
\end{align*}
\]

Despite low reaction rates ($p_0 = 6 \times 10^{-5}$), the high O density in the plasma makes these reactions common.

Removal of the R(s) ligands can occur through 2 processes. The first is a removal process is sputtering by ions and hot neutrals. R(s) This can also be removed through replacement reactions with reactive oxygen species (ROS) where O inserts into the Si-R(s) bond and displaces the R.

\[
\begin{align*}
R(s) + O & \rightarrow O(s) + R \quad (7.6a) \\
R(s) + O^* & \rightarrow O(s) + R \quad (7.6b) \\
R(s) + O_3 & \rightarrow O(s) + R + O_2 \quad (7.6c)
\end{align*}
\]

At low substrate temperatures, these reactions have low reaction probabilities. In experiments by Lu et al., the oxygen plasma exposure time to remove the ligands was up to several minutes, which is much longer than the exposure time for of any given cycle (1 s) addressed here [26].

### 7.4 Plasma Characteristics and Film Deposition Profile

The reactor used in this work is shown in Fig. 7.1. It is a cylindrically symmetric capacitively coupled plasma (CCP) reactor maintained at a pressure of 2 Torr. The reactor is designed to process a wafer with a 30 cm diameter that is on a grounded substrate with a 4 cm quartz (relative permittivity $\varepsilon_r = 4.0$) focus ring. 500 W (10 MHz) radiofrequency (RF) power is applied to the top electrode 1.5 cm above the substrate. Two gas inlets are used in this reactor. The primary showerhead overlaps with the top electrode and injects an Ar/O$_2$ (80/20) mixture at
5 standard liters per minute (slm). The secondary inlet is located at the top of the reactor at \( r > 20 \) cm, from which pure \( \text{O}_2 \) is flowed at 6 slm. The purpose of the secondary inlet is to entrain flow from the primary showerhead towards the pump, which is located at the bottom of the reactor surrounding the substrate. The secondary electron emission coefficient for ions is 0.05 for all the surfaces exposed to the plasma.

The base case conditions produce a time averaged plasma potential of 137 V. A DC bias of -30 V is generated on the blocking capacitor connected to the top electrode. The dominant cations and anions are \( \text{O}_2^+ \) and \( \text{O}^- \). The \( \text{O}_2 \) flow, electron density \( (n_e) \), \( \text{O}_2^+ \) density, and \( \text{O}^- \) density are shown in Fig. 7.2. The flow of \( \text{O}_2 \) demonstrates that the gas from the secondary inlet has little impact on the plasma between the electrode and substrate. The plasma properties are predominantly determined by the gas mixture from the primary showerhead. The electron density \( n_e \) peaks at \( r = 19 \) cm at \( 2.3 \times 10^{10} \text{ cm}^{-3} \) due to electric field (E-field) enhancement at the edge of the top electrode, and is otherwise uniform in the radial direction across the wafer. The wafer has a fairly high conductivity (\( \sigma \)) of 0.05 \( \Omega^{-1}\text{cm}^{-1} \), while the quartz focus ring is an ideal dielectric. When solving Poisson’s equation using the substrate as a ground, the E-field is negligible in the wafer but relatively high in the focus ring (150 V/cm). The end result is a higher potential on the surface of the focus ring (50 V) than on the wafer (4 V), which perturbs the sheath on the wafer-quartz interface and causes a non-uniform plasma distribution above the focus ring. However, both the hot spot of \( n_e \) and this perturbation of the plasma distribution occur downstream of the gas flow. Therefore, their impact on the bulk plasma is insignificant.

In a high pressure CCP, ionization can be sustained by bulk electrons, which are mostly resistively heated, and beam electrons that are from secondary electron emission. At 2 Torr, the electron mean free path is much smaller than the gap length. Therefore, it is difficult for bulk
electrons heated at the edge of the sheath to transport to mid-gap with enough energy to enable further ionization. However, when accelerated by the sheath, beam electrons can have energy up to 10s to more than 100 eV, enabling them to travel further into the bulk plasma.

The ionization source for bulk electrons ($S_e$) near the sheath is comparable with that for beam electrons ($S_{eb}$), with $S_e = 6.7 \times 10^{15}$ cm$^{-3}$s$^{-1}$ and $S_{eb} = 4.4 \times 10^{15}$ cm$^{-3}$s$^{-1}$. However, at 0.3 cm below the top electrode, $S_e$ drops to zero, and the ionization is maintained only by beam electrons ($S_{eb} = 2.7 \times 10^{15}$ cm$^{-3}$s$^{-1}$). Because the plasma is mainly sustained by beam electrons, the plasma is thereby operated in the $\gamma$-mode.

The dominant cation $O_2^+$ shares the same uniform radial distribution with electrons, and peaks at $6.2 \times 10^{10}$ cm$^{-3}$ at the corner of the top electrode. In the axial direction, $O_2^+$ density decreases from $2.4 \times 10^{10}$ cm$^{-3}$ near the sheath adjacent to the top electrode to $1.9 \times 10^{10}$ cm$^{-3}$ at the mid-gap. $O_2$ undergoes dissociative attachment producing $O^-$ which has a relatively high density. The $O^-$ density is nearly 70% of $n_e$ in the bulk plasma. However, because of its low temperature, $O^-$ is confined in the bulk plasma and has a negligible flux to the wafer.

The energy and angular distributions (EADs) of Ar$^+$, $O_2^+$, and O are shown in Fig. 7.3a. These data are averaged over the wafer and averaged in angle across the normal. Both Ar$^+$ and $O_2^+$ have relatively narrow angular distributions with an incident angle of less than 20°. The sheath by the wafer accelerates ions up to 45 eV. However, the plasma potential is 137 V, almost three times the peak ion energy, indicating that the sheath is highly collisional such that ions dissipate their energy through multiple collisions as they travel across the sheath. Because the majority of ions have energy less than 20 eV, smaller than the sputtering threshold of SiO$_2$ (30 eV), only minor ion bombardment damage to the film is expected. Unlike ions, neutral species have close to thermal energy and wide angular distribution. The peak O energy reaches
0.3 eV, which is likely caused by charge exchange reactions near the wafer. When hot O\(^+\) atoms collide with O, they exchange the charge but preserve their initial kinetic energy and form a hot O and a cold O\(^+\). The hot neutral will no longer gain energy from E-field but will lose its energy through collisions with other particles as it moves toward the wafer. Consequently, when it hits the surface, its energy is much lower than the energy of most ions but is still higher than the thermal energy of many neutral species. This slightly higher energy of 0.2 eV is unlikely to cause any significant difference regarding the surface reaction rates.

The fluxes of some major species as a function of radius are shown in Fig. 7.3b. Most species have a fairly uniform flux across the wafer. For example, the O flux remains at \(1.6 \times 10^{18} \text{ cm}^{-2}\text{s}^{-1}\) at \(r < 12 \text{ cm}\) with only minor fluctuation (\(\pm 1.0 \times 10^{16} \text{ cm}^{-2}\text{s}^{-1}\)). However, it increases to \(1.7 \times 10^{18} \text{ cm}^{-2}\text{s}^{-1}\) at \(r = 15 \text{ cm}\) due to a slight increase of O density near the edge of the top electrode. Note that the high pressure produces a reasonably high \(\text{O}_3\) density (\(3.6 \times 10^{11} \text{ cm}^{-3}\) at mid-gap), which produces a \(\text{O}_3\) flux of \(\approx 3 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}\). Even though it is three orders of magnitudes smaller than the O flux, \(\text{O}_3\) is an important oxidant that is commonly used in the deposition of oxides due to its highly reactive nature. The dominant cations \(\text{Ar}^+\) and \(\text{O}_2^+\) also have fluxes of \(\approx 10^{15} \text{ cm}^{-2}\text{s}^{-1}\). Even though the resulting ion bombardment sputtering is not expected to be severe with the default setup, changing the operating conditions such as decreasing the pressure can increase ion energy and produce damage.

A deposition schematic of PE-ALD of SiO\(_2\) film is shown in Fig. 7.4. The wafer is repeatedly exposed to the silicon precursor and Ar/O\(_2\) plasma. Gas purge is not included in the simulation and we assume that no gas remains from the previous steps. The cubic voxels used in the MCFPM are \(0.5^3 \text{ nm}^3\). Each cycle deposits 2 layers of voxels representing a monolayer of silicon dioxide. Si voxels are displayed in two colors to help distinguish deposition from other
steps. In the base case, the precursor dosing time is 0.8 s, and the plasma exposure time is 1.0 s. During precursor dosing, precursor flux of $1 \times 10^{20} \text{ cm}^{-2}\text{s}^{-1}$ is launched from the top of the feature; while during plasma exposure, the fluxes are obtained from the HPEM results. Unless otherwise specified, the ligand group co-deposition probability $p_R = 0.005$. As shown in Fig. 7.4b, the impact of a buried ligand group increases as the film grows thicker. The initial disruption of the layered structure caused by the embedded ligand group escalates to misalign in the upper layers and produces an increasingly coarse surface. Some unoccupied gas voxels appear in the film as vacancies. A vacancy occurs when the fast-growing neighbors of a gas voxel bridge over an unoccupied site. A vacancy is defined as a gas phase voxel with less than two consecutive gas voxel neighbors in any direction. The vacancy density reduces the quality of a film. Generally, a high vacancy density translates to a high wet etch rate (WER).

Blanket film deposition was first performed on a 65 nm (L) × 10 nm (W) area and meshed with 130 × 20 computational voxels. A reflective boundary condition was used on all the boundaries. A gas phase particle crossing the boundary is specularly reflected back. For these results, R(s) ligands are only removed by sputtering. The SiO$_2$ film deposited in 10 cycles is shown in Fig. 7.5. Note that every two colored layers represent one monolayer of SiO$_2$. The film is fairly dense and uniform in the first 5 cycles but becomes less ordered later in the process. Early in the deposition, misalignments that are partly caused by the ligand remnants affect only their direct neighbors. For a single ligand site, the immediate next layer will have only local imperfections, and with a low co-deposition probability ($p_R = 0.005$), the impact of these imperfections is reasonably small. By the end of the 5th cycle, irregularities are only sparsely distributed on the surface such that the film can still be considered smooth. However, imperfections that occur in the early stages affect a larger area as the film grows.
The exposure of the side of a site enables non-epitaxial deposition. For example, if the side of an OH-Si-OH(s) site is left open after the plasma exposure, in the following precursor dosing, a SiH_2(s) site can deposit next to it instead of above it, causing a silicon atom to be embedded in an oxygen layer. The OH-Si-OH(s) site this SiH_2(s) is attached to (its neighbor) will be redefined as O_2(s) and be exposed to the plasma. An O_2(s) cannot be easily deposited on by a silicon precursor because it cannot provide a hydrogen atom to combine with the ligand group from the precursor SiH_2R_2. In this case an exposed O_2(s) often produces a halt to the local deposition. As a result, a single missing OH-Si-OH(s) induces two potential defects: a SiH_2(s) embedded in an oxygen layer, and an exposed O_2(s). Both lead to staggered depositions in the layers above, and the following deposition on these misaligned sites occur in different steps as their neighbors.

For example, when the SiH_2(s) is deposited with O(s) during plasma exposure, most of its neighboring OH-Si-OH(s) are deposited upon in precursor dosing. This staggered deposition may expose more sites with open sides and consequently enlarge the misaligned areas and eventually lead to non-ordered layers. Because sparsely distributed defects and imperfections in the early stage can make the film highly disordered and rough later in the deposition, it is vital to perform quality control from the beginning of PE-ALD.

O_2(s) cannot be directly deposited on with a silicon precursor. Therefore, the O_2(s) surface coverage ratio increases through the deposition process, as shown in Fig. 7.6a. The surface coverage ratio of O_2(s) is the fraction of surface sites that are occupied by O_2(s). The sampled area occupies the center of the feature in a 10 nm × 10 nm square. In this work, the surface coverage ratio of O_2(s) does not reach saturation in 10 cycles. However, it eventually saturates ≈ 50% as the exposure of O_2(s) is balanced through recombination reactions with other
gas phase species such as O and O₃.

The accumulation of O₂(s) on the surface is part of the reason for the decreasing film growth rate. The concentration of O (ηₒ), Si (ηₛ𝑖), vacancy (ηᵥ𝑎𝑐), and ligand groups (ηᵣ) in the entire film is shown in Fig. 7.6b. Note that hydrogen is not counted, so that ηₛ𝑖 + ηₒ + ηᵥ𝑎𝑐 + ηᵣ = 1. In the first 10 cycle (18 s), both ηₛ𝑖 and ηₒ are relatively stable, with ηₒ/ηₛ𝑖 ≈ 2.0. Excessive O(s) deposition occurs when an already saturated Si(s) (silicon with four bonds occupied) is exposed to the plasma. This is not a physical process. To reduce its impact, the oxygen deposition probability on Si(s) was decreased to a smaller value (1 × 10⁻⁴), which is not expected to artificially decrease the O content. With minor sputtering in a PE-ALD, the exposed Si(s) are often saturated with all of its bonds occupied and are exposed because of the slow growth of its neighbors. It is unlikely for O to deposit on these silicon sites. Ideally, the end surface after the precursor dosing is SiH₂(s), which will be oxidized to OH-Si-OH(s). Therefore, the film growth does not rely on the oxidation of Si(s) using this mechanism.

The ligand group co-deposition probability, pᵣ = 0.005, is constant through the ALD process, thereby ηᵣ is constant ≈ 0.2%. The film becomes coarser and more disordered as it thickens. The vacancy density increases and peaks at 1% by the end of the 10th cycle. The complicated surface concentration causes uneven growth on different parts of the surface and this ultimately results in more bridging and therefore more vacancies.

The average (ζavg) and instantaneous (ζins) growth rate are shown in Fig. 7.6c. A 1-layer/cycle refers to ideal PE-ALD of a monolayer SiO₂ deposition in each cycle, which is represented by 2 computational layers. ζavg is calculated by dividing the spatially averaged film thickness with the number of cycles, while ζins is the increase of the film thickness from the last cycle. The film thickness is also averaged in the center of the blanket deposition in a 10 nm x 10
nm square. Both \( \xi_{\text{avg}} \) and \( \xi_{\text{ins}} \) decrease with time, partly because of the growing complexity of the surface contents as the film becomes more disordered later in the process. Compared to \( \xi_{\text{avg}} \), \( \xi_{\text{ins}} \) decreases much faster, from 1 to 0.7 layer/cycle in 10 cycles. In practice, \( \xi_{\text{ins}} \) is often < 1 layer/cycle.

The deposition of SiO\(_2\) film was also investigated in a trench structure, shown in Fig. 7.7. The process flow and reaction mechanisms are identical to the blanket deposition. The precursor dosing is 0.8 s and the plasma exposure is 1.0 s. The width of the trench is 30 nm and the height is 120 nm, the depth of the simulation domain is 10 nm with reflective boundary conditions. The voxels are 0.5\(^3\) nm\(^3\) cubes. The size of the computational geometry, including the walls is 70 (W) \( \times \) 243 (H) \( \times \) 20 (D) voxels. The film deposited in a trench, similar to the blanket deposition, has a relatively uniform structure early in the process that becomes coarse and disordered as it grows thicker.

Deposition into a trench is also subject to conduction limits, which does not apply to a blanket deposition. A conduction limit is basically a limitation of the distance a neutral particle can travel into a 3-dimensional feature. For thermal neutrals hitting the surface without a surface reaction, they are diffusively reflected back to the plasma. There is a 50% probability that these neutral particles come off a surface with a velocity component pointing upwards toward the opening of the feature. This leads them to transporting out of the feature instead of deeper inside. Due to the conduction limit, the neutral fluxes in the bottom of the feature are often smaller than those in the top. For example, an O flux logged at the bottom center is \( 9.7 \times 10^{17} \) cm\(^{-2}\)s\(^{-1}\) during plasma exposure in the first cycle. That is reduced by almost 40% compared to the O flux at the top (\( 1.6 \times 10^{18} \) cm\(^{-2}\)s\(^{-1}\)). As the film thickens, the aspect ratio increases and conduction limits increase. The oxidant fluxes are high enough that even at the bottom of the
feature, an epitaxial deposition with a clear, layered structure is obtained in the first several cycles. However, the conduction limit still affects the film deposition, especially for the oxidation process by reducing the excited state $\text{O}_2^*$ flux deep into the trench.

Concentrations of the solid materials and vacancy, $\eta_{\text{O}}/\eta_{\text{Si}}$ and average and instantaneous growth rate of the film at the bottom of the trench are shown in Fig. 7.8. Similar to blanket deposition, when depositing a SiO$_2$ film in the trench, concentrations of Si and O are relatively stable in the first 10 cycles, providing $\eta_{\text{O}}/\eta_{\text{Si}} \approx 1.9$. A $\eta_{\text{O}}/\eta_{\text{Si}} < 2$ suggests insufficient oxidation. This is partly caused by lack of oxidant in the lower trench due to conduction limits. This could be addressed by longer plasma exposure. At the end of the 10$^{\text{th}}$ cycle, $\eta_{\text{O}}/\eta_{\text{Si}}$ is 1.95 in the top half of the trench and 1.88 in the bottom half, indicating a significant non-stoichiometric growth at the bottom. In an oxygen plasma, O and $\text{O}_2^*$ are the main oxidants. Their fluxes decrease by factors of 1.6 and 9.6, respectively at the bottom of the trench. The $\text{O}_2^*$ flux has a much faster fractional decrease than O flux because, when hitting a surface, $\text{O}_2^*$ loses its energy and becomes a ground state inactive $\text{O}_2$ molecule, while O retains its highly reactive nature. Therefore, the $\text{O}_2^*$ reaching the bottom of the trench have zero contact with any surface.

As the film grows thicker, the aspect ratio of the feature increases, from 4 to 4.8 in 10 cycles, which further exacerbates the conduction limit, and significantly affects the $\text{O}_2^*$ flux. Compared to the flux at the bottom of the feature in the first cycle, by the end of the 10$^{\text{th}}$ cycle, $\text{O}_2^*$ flux has further decreased by a factor of 4, but the O flux remains almost the same. These results demonstrate that unlike blanket deposition, when depositing in a 3-dimensional structure such as a trench, the main oxidant is O rather than a combination of O and $\text{O}_2^*$. This is especially true at the bottom of a high aspect ratio feature. Because the oxidation by O is a multi-step process, insufficient oxidation is all the more common in a film deposited in a trench.
than blanket deposition, which explains the lower $\eta_O/\eta_{Si}$. With the decrease of $O_2^*$ flux during plasma exposure as the film grows, the film growth rate decreases faster in a trench. The deposition drops from 1 layer/cycle to 0.5 layer/cycle in 10 cycles as opposed to from 1 layer/cycle to 0.7 layer/cycle for a blanket deposition.

### 7.4.1 Power

The CCP power was varied from 400 W to 1 kW. Its impact on the SiO$_2$ PE-ALD process is discussed.

The EADs of Ar$^+$ and O when the power is 400 W, and 1 kW are shown in Fig. 7.9a. Neither the ion energy and angular distribution (IEAD) nor the neutral energy and angular distribution (NEAD) experience significant changes based on power. For this reactor, the blocking capacitor is connected to the top electrode. This means that the DC bias is not on the substrate, and ion energy distribution (IED) is only affected by the oscillation of the plasma potential. From 400 W to 1 kW, the bulk plasma density increases from $4.3 \times 10^9$ cm$^{-3}$ to $1.2 \times 10^{11}$ cm$^{-3}$, while the plasma potential increases from 127 to 137 V. As shown in Fig. 7.9a, with the increase of power the peak Ar$^+$ energy is increased by $\approx 5$ eV from 40 to 45 eV, but the majority of the ions have lower energy, less than 5 eV, due to the highly collisional sheath. The almost identical IEADs and ion fluxes (Fig. 7.9b) suggest minimal changes in the sputtering with varying power. The NEAD also stays nearly the same when changing power.

The fluxes of some main oxidants have notable variations with power that can potentially affect SiO$_2$ film deposition. As the power increases from 400 W to 1 kW, $O_3$ flux decreases by a factor of 10, from $6.5 \times 10^{15}$ cm$^{-2}$s$^{-1}$ to $7.5 \times 10^{14}$ cm$^{-2}$s$^{-1}$ owing to the decreased $O_3$ density caused by additional dissociative reactions. At the same time, the excited state $O_2^*$ density increases with the power from $1.9 \times 10^{18}$ cm$^{-2}$s$^{-1}$ at 400 W, to $5.6 \times 10^{18}$ cm$^{-2}$s$^{-1}$ at 1 kW, which
may lead to a higher growth rate especially when in blanket deposition. However, with a plasma exposure time of 1 s, the deposition is already self-limiting during plasma exposure when the input power is 500 W. Therefore, any increase of the film growth rate with power is not large.

The SiO₂ film was deposited on a blanket feature while varying power. The film concentrations and growth rate are shown in Fig. 7.10. The data are gathered at the end of the 5th cycle. As expected, with a long enough plasma exposure time, changing the power has a limited effect on the film quality. Both oxygen and silicon have almost the same constant concentrations in the film. Because the minimum sputtering threshold on SiO₂ film is 30 eV, which is much higher than the energy of most ions (1-5 eV), the ion bombardment damage to the film is negligible. In this example, ordered growth of oxygen and silicon layers occurs in the first 5 cycles, as shown in the 2D film profile at the top of Fig. 7.10. However, the increased O₂⁺ flux indeed promotes the oxidation process. Therefore, the \( \eta_O/\eta_{Si} \) has a slight increase as power increases from 400 W to 1 kW. Both the average and instantaneous growth rates are close to 1 layer/cycle with varying power. The lower than average instantaneous growth rate suggests some presence of surface coarseness and the occurrence of slowly growing sites. Even though input power has little effect on film deposition in this setup, it is expected to have a more significant impact on film deposition when the plasma exposure time is shorter. By increasing power from 400 W to 1 kW, the O₂⁺ flux is tripled, which will significantly increase the oxidation rate to the level of self-limiting during plasma exposure.

Deposition in the trench with varying power was also studied. Varying power had a more significant impact when depositing a film in a trench than blanket deposition. As the power increases from 400 to 700 W, the \( \eta_O/\eta_{Si} \) ratio decreases from 1.94 to 1.85, and then rises up to 1.90 as the power keeps increasing to 1 kW. This non-monotonic of \( \eta_O/\eta_{Si} \) is mainly caused by
the change of $\eta_0$ owing to the variation of O flux with power. Film oxidation in a trench heavily relies on O instead of O$_2^*$. Therefore, even though the flux of O$_2^*$ is tripled as the input power increases from 400 W to 1 kW, it has little effect on film deposition deep in a trench. Even with 1 kW, by the end of the 5$^{th}$ cycle, the O$_2^*$ flux is $2.8 \times 10^{17}$ cm$^{-2}$s$^{-1}$ at the bottom of the trench, as opposed to $6.9 \times 10^{17}$ cm$^{-2}$s$^{-1}$ for O flux, which is more than twice of the O$_2^*$ flux. As a result, when depositing in the trench, the film quality is directly affected by the magnitude of O flux, such that a lower O flux leads to less oxidation, hence more imperfections and misalignments in the film, more vacancies and a slower film growth rate.

### 7.4.2 Pressure

The IEAD is affected by sheath collisionality and thus the plasma pressure. Increasing pressure makes a sheath more collisional, which broadens the ion angular distribution (IAD) and reduces the overall ion energy. At the same time, with decreasing pressure, ions travel across a sheath with fewer or no collisions, resulting in a higher ion energy up to the maximum of sheath potential. The pressure was varied from 0.5 to 2 Torr, and its effect on SiO$_2$ film deposition was studied. Power is 500 W, the same as the base case.

The EADs of Ar$^+$ and O when pressure is 0.5, and 2 Torr are shown in Fig. 7.12a. The maximum ion energy reaches 50 eV at 0.5 Torr, and 40 eV at 2 Torr. Even though the maximum ion energy only differs by 10 eV, there is a much higher fraction of ions with energy higher than 30 eV when the pressure is 0.5 Torr than 2 Torr. The higher ion energy at low pressure is collectively caused by the higher plasma potential and low collision frequency. At 0.5 Torr, the plasma potential is 170 V, which decreases to 138 V at 2 Torr. As pressure increases from 0.5 to 2 Torr, the mean free path of Ar$^+$ shortens from 0.1 mm to 0.02 mm, suggesting more collisions as ions are accelerated towards the wafer, which helps dissipate the ion energy.

Again, the EAD of neutral species is not significantly affected by changes of pressure. O
has almost identical thermal EADs when the pressure is both 0.5 and 2 Torr. The fluxes of some major species are shown in Fig. 7.12c. For most of these species, increasing pressure causes an increase in their fluxes as high pressure leads to higher ionization and excitation reaction rates. However, at high pressure, even though the ion fluxes are high, most of these ions have low energy. Therefore, their effect on the SiO$_2$ film deposition process is minor. The O$_3$ flux decreases with an increasing pressure O$_3$ due to increased rates of electron collision quenching.

Film concentrations and growth rates with varying pressure for blanket deposition are shown in Fig. 7.13. The film properties show only minor changes when the pressure is higher than 1 Torr. However, at 0.5 Torr, because of increased ion bombardment damage to the film, there are higher vacancy concentration and lower $\eta_{O}/\eta_{Si}$ ratio. As pressure increases from 0.5 to 1 Torr, vacancy concentrations decrease by a factor of 3 from 1.5% to 0.5%. In spite of a higher rate of sputtering at 0.5 Torr the ion flux is orders of magnitude smaller than that of the neutral species. Therefore, any vacant sites caused by sputtering during plasma exposure are likely to be “repaired” by the reactive oxidants. If a thicker film is being deposited, this slight increase of $\eta_{Vac}$ in the early stage can cause much coarser and disordered structure in the top layers of the film.

Similar to film concentration, the growth rate is lower when pressure is 0.5 Torr. This is, again, caused by ion bombardment sputtering. Sputtering of the film compromises the continuous structure of the layers, which complicates surface structure and causes a low deposition rate. For example, if a SiH$_2$(s) site is sputtered from the surface at the beginning of a plasma exposure step, the exposed O$_2$(s) below it cannot be deposited upon with more oxygen until it is covered with another SiH$_2$(s) in the following precursor dosing. The end result is that it takes two instead of one cycle to deposit a monolayer of SiO$_2$ at that position. The spatially
averaged layer thickness is then thinner, and the film growth rate will be slower.

The results of film deposition with varying pressure in a trench are given in Fig. 7.14. Generally, increasing pressure has the same effect on film deposited in a trench as for blanket deposition. Increasing the pressure results in less ion bombardment damage, thereby a higher $\eta_O/\eta_{Si}$ ratio, lower vacancy concentrations, and higher film growth rates. When deposited in a trench, by the end of the 5th cycle, as pressure increases from 0.5 to 2 Torr, the vacancy concentration halves from 2.1% to 1.1%. However, for blanket deposition, it decreases by a factor of 5, from 1.5% to 0.3%. The vacancy concentration is less sensitive to pressure in a trench because ion bombardment damage to the film is not as significant in a trench for blanket deposition. Note that sputtering is angularly dependent, and the sputtering yield is close to 0 when the incident angle of the particle is grazing near 90°. Therefore, in a trench, ions lose some energy by grazing the vertical walls but cause little sputtering. Once contacted with a surface, ions lose their charge and become hot neutrals. By continually colliding on the walls, hot neutrals loss more energy and become thermal neutrals. Neutrals are also subject to the conduction limit such that their fluxes decrease from the top to bottom of a trench. When the pressure is 0.5 Torr, in the 5th cycle, the total flux of ions and hot neutrals in the bottom of the trench is $2.8 \times 10^{14}$ cm$^{-2}$s$^{-1}$, which is smaller by a factor of 7 comparing to the summation of ion fluxes from the top ($2.0 \times 10^{15}$ cm$^{-2}$s$^{-1}$). Therefore, the ion bombardment damage is weak at the bottom; even though it is in that position that the incident angle of ions and hot neutrals is small enough to most likely cause sputtering.

Changing the pressure has the same impact for films in a trench as for blanket deposition. However, the film in a trench is less sensitive to the pressure changes due to conduction limits.

7.4.3 Co-deposition Probability

Steric hindrance occurs when ligands from the precursor fail to react with hydrogen
atoms from the surface and thus remain bonded with the silicon that is deposited on the surface. Ligands may block nearby sites from reacting with the gas phase particles and hinder the deposition process. In the current mechanism, steric hindrance is addressed by co-depositing a ligand group \( R(s) \) along with the precursor at probability \( p_R \) with a default value of 0.005. In this section, \( p_R \) is varied from 0.001 to 0.5, and its impact on the SiO\(_2\) film quality is studied.

The resulting film concentrations and growth rates with varying \( p_R \) for blanket deposition are shown in Fig. 7.15. The effect of \( p_R \) becomes noticeable only when \( p_R \geq 0.01 \). As \( p_R \) increases, both oxygen and silicon concentrations decrease. Also, the \( R(s) \) deposition directly affects the \( \eta_{Si} \) since co-deposition occurs during precursor dosing, such that when an \( R(s) \) is co-deposited next to a \( SiH_2(s) \), it occupies a space that otherwise should be taken by another \( SiH_2(s) \) site. Therefore, with a high \( p_R \), it is unlikely to attain 100% \( SiH_2(s) \) surface coverage at the end of precursor dosing, which then leads to a lower \( \eta_{Si} \). However, it is also possible for \( R(s) \) to be co-deposited above the primarily deposited \( SiH_2(s) \) and occupy voxels in the oxygen layer. With the same \( SiH_2R_2 \) flux and the deposition probability of \( SiH_2(s) \), higher \( p_R \) results in more \( R(s) \) in the oxygen layer, thus less OH-Si-OH(s) formation during the plasma exposure.

When \( p_R > 0.01 \), \( \eta_O \) starts to decrease faster than \( \eta_{Si} \), leading to an abrupt drop of the \( \eta_O/\eta_{Si} \) ratio from 1.98 at \( p_R = 0.01 \) to 1.78 at \( p_R = 0.5 \). The increase of \( R(s) \) concentration also complicates the affected surface components as the film growth becomes highly uneven, which encourages bridging and prompts the formation of vacancies. As \( p_R \) increases from 0.05 to 0.5, vacancies increase from 1% to 3%. Note that in many applications, after deposition, the ligand remnants are removed through annealing, such that the final vacancy concentration in the film is \( \eta_{Vac} + \eta_R \). In that scenario, the vacancy concentration reaches 2.5% even when \( p_R = 0.05 \). As described earlier, the growth rate of a film decreases as the surface becomes rougher. Decreases
in both average and instantaneous growth rates occur when \( p_R \) increases from 0.001. When \( p_R = 0.001 \), the deposition process is almost ideal, with a growth rate of 1 monolayer per cycle. At \( p_R = 0.5 \), the instantaneous growth rate decreases to almost 0.4 layer/cycle.

The results of film deposition with a varying \( p_R \) in the trench are shown in Fig. 7.16. The result is similar to that for blanket deposition. With an increasing \( p_R \) from 0.001 to 0.5, by the end of the 5\(^{th} \) cycle, \( \eta_{O}/\eta_{Si} \) decreases from 1.88 to 1.68, and \( \eta_{\text{vac}} \) increases from 1% to 3%. Film quality is notably affected by conduction limits in the trench. When \( p_R \) is small, insufficient oxidation caused by a low oxidant flux already produces a \( \eta_{\text{vac}} = 1\% \). This high vacancy concentration overshadows the impact of the increasing \( p_R \) until it is \( \geq 0.05 \). The same occurs to the instantaneous film growth rate. Owing to conduction limits, the film growth rate is only 0.8 layer/cycle at the bottom of the trench even with small \( p_R \). A clear decrease of \( \xi_{\text{ins}} \) occurs only when \( p_R \geq 0.01 \). Before that, the impact of \( p_R \) on growth rate is outweighed by the effects of conduction limits.

Varying \( p_R \) affects precursor dosing, which is a thermal process that is not significantly affected by the target feature. Therefore, other than the high vacancy concentration and low instantaneous deposition rate when \( p_R < 0.05 \), changes of the film properties with a varying \( p_R \) when depositing in a trench are quantitatively similar to that for blanket deposition.

Reaction probabilities are not known for these reactions of ROS with co-deposited R(s). Based on analogies to gas phase processes and reaction probabilities for removal of R(s) by O, O\(^{1}\) and O\(_3\) (reactions 7.6a, b and c) were estimated as \( 1 \times 10^{-4}, 1 \times 10^{-3}, \) and \( 1 \times 10^{-5} \). Film concentrations of R(s), vacancies and \( \eta_{O}/\eta_{Si} \) with and without oxygen replacement reactions as a function of \( p_R \) are shown in Fig. 7.17. These properties do not significantly change with oxygen replacement reactions until \( p_R > 0.1 \). The oxygen replacement reactions enable more complete
oxidation during plasma exposure, thereby resulting in higher oxygen concentration and higher $\eta_O/\eta_Si$. With $p_R = 0.5$, reactions of R(s) with ROS decrease $\eta_R$ by 2% from 15% to 13%, and $\eta_O/\eta_Si$ increases from 1.79 to 1.86. With $p_R < 0.1$, there are not enough R(s) deposition on the film to make oxygen replacement reactions important when the plasma exposure time is only 1 s. The average and instantaneous film growth rates with and without the oxygen replacement reactions with varying $p_R$ are shown in Fig. 7.17b. Almost identical film growth rates are obtained.

For small $p_R$ and short plasma exposure time, oxygen replacement reactions with R(s) do not significantly affect the SiO$_2$ PE-ALD discussed in this chapter. However, these conclusions could certainly change if the reaction probabilities for ROS at low substrate temperature are significantly higher than estimated here.

### 7.4.4 Aspect Ratio

Conduction limits predominantly affects film deposition in high aspect ratio features. Because conduction limits are significantly affected by the aspect ratio (AR) of the feature, in this section, the AR of a 3D feature is varied, and its impact on film deposition is discussed.

SiO$_2$ film deposition was first performed in a trench. The width of the trench is 30 nm, the same as that used for the previous investigations. The AR was varied by changing the height of the trench. AR was varied from 2 to 8, meaning the height of the trench was varied from 60 to 240 nm. The concentrations of solid materials in the entire film, as well as the $\eta_O/\eta_Si$ ratio are shown in Fig. 7.18a. The instantaneous and average film growth rates logged in the bottom of the trench are shown in Fig. 7.18b. Increasing AR increases conduction limits as particles encounter more collisions with walls before reaching the bottom of the feature. This has the most impact on the unstable or excited state reactive species. For example, as recorded in the bottom of a trench, when the aspect ratio increases from 2 to 8, O$_2^*$ flux decreases by a factor of
4.4, from $5.7-1.3 \times 10^{17}$ cm$^{-2}$s$^{-1}$ in the first plasma exposure. This reduction of oxidant results in insufficient film oxidation, which then causes a slow film growth rate. In the 5th cycle, the instantaneous growth rate in the bottom of the trench when AR = 8, is 0.69 layers/cycle, only 83% of that when AR = 2 (0.83 layers/cycle). Note that conduction limits only affect film quality in the bottom of the trench. For example, there is a slight decrease instead of an increase of $\eta_{Vac}$ as AR increases when sampling the entire film, owing to the film deposition in the top of the trench outweighing the effect of film deposition in the bottom. If sampled using the film deposited at the bottom 30 nm of the trench, $\eta_{Vac}$ increases from 1.3% to 1.5% as the AR increases from 2 to 8.

To further study the impact of aspect ratio on film deposition, a SiO$_2$ film was deposited in a via. A via is a cylindrical connection between two devices located in different layers of an integrated structure. A thin layer of dielectric material is often deposited on the wall of a via as an electrical insulator. The diameter of the via is 30 nm and the height was between 60 to 240 nm, providing an AR between 2 to 8. Because a via is a symmetrical structure, only a quarter of a via was used for the simulation (Fig. 7.19a) in deference to being computationally efficient. A reflective boundary condition was applied to all vertical boundaries. The process flow is the same as depositing in a trench: 0.8 s precursor dosing and 1 s plasma exposure.

The film deposited in a via is reasonably conformal, the structure of a via can still be seen after 5 cycles of deposition. Similar to the deposition in a trench or blanket deposition, in a via, layers deposited in the first several cycles are more uniform, having only sparsely distributed imperfections and misalignments that would affect the deposition of upper layers.

The concentrations of materials and the elementary ratio $\eta_O/\eta_{Si}$ at the end of the 5th cycle are shown in Fig. 7.19b. Note that compared to the film deposited in a trench, the film deposited
in a via has a lower $\eta_O/\eta_{Si}$ ratio and higher vacancy concentration, indicating an even more insufficient oxidation process and more porous film structure. This occurs because a via has a higher surface to volume ratio than a trench when their AR is the same. With unbounded front and back sides, a trench of 30 nm (W) $\times$ 120 nm (H) $\times$ 10 nm (D) has a surface to volume ratio of 0.075, while a via with a 30 nm diameter and 120 nm height has a surface to volume ratio of 0.142. Doubling the surface to volume ratio produces more severe conduction limits that restrain the fluxes to the bottom of the feature. For example, with AR = 8, in the first plasma exposure, the O flux at the bottom center of the trench is $9.0 \times 10^{17}$ cm$^{-2}$s$^{-1}$, as opposed to $2.0 \times 10^{17}$ cm$^{-2}$s$^{-1}$ in the via. The decrease of flux in the via is even more significant for unstable species such as O$_2^*$, which is $2.0 \times 10^{15}$ cm$^{-2}$s$^{-1}$ in the bottom of a via, but $1.1 \times 10^{17}$ cm$^{-2}$s$^{-1}$ in the bottom of a trench. Remember that low oxidant fluxes result in insufficient oxidation. At the end of the 5th cycle, at the bottom 30 nm of the feature, a SiO$_2$ film deposited in a trench has a $\eta_O/\eta_{Si}$ ratio of 1.79, but the film deposited in a via only has a $\eta_O/\eta_{Si}$ ratio of 1.61. The vacancy concentration almost doubles when depositing in a via compared to a trench.

### 7.5 Concluding Remarks

Plasma enhanced atomic layer deposition (PE-ALD) of SiO$_2$ film on a nm-scale blanket target was investigated using 3-dimensional voxel-based simulation, the MCFPM. The computational investigation was performed at the reactor scale for an Ar/O$_2$ (80/20) capacitively coupled plasma (CCP) using the 2-dimensional hybrid plasma simulator, the HPEM. Fluxes on the wafer, and energy and angular distributions (EADs) of major species obtained from the HPEM were transferred to the MCFPM for feature-scale investigation.

In the base case, 500 W power was applied to the top electrode of the CCP reactor to sustain an Ar/O$_2$ plasma at 2 Torr. The dominant neutrals were O$_2$(a$^1\Delta_g$), O, and O$_2$(b$^1\Sigma_g^+$), all
with close to thermal EADs. The dominant ions, $\text{Ar}^+$ and $\text{O}_2^+$, had incident angle less than 20° and peak energy up to 40 eV. Due to the high pressure and highly collisional sheath, most ions had energy less than 20 eV, which is smaller than the sputtering threshold of SiO$_2$ (30 eV). These, as well as low ion fluxes suggest insignificant impact of ion bombardment damage to the film.

A deposition mechanism of SiO$_2$ using silicon precursors with two ligand groups and Ar/O$_2$ plasma was developed. The PE-ALD process consisted of repeated precursor dosing (0.8 s) and plasma exposure (1.0 s). Steric hindrance was addressed by co-depositing a ligand site along with the silicon during precursor dosing at a co-deposition probability $p_R$. The impact of the insertion of ligand remnants at the early stage of deposition were shown to increase as the film grows thicker. The end result is a disordered film structure and large areas of roughness on the surface above the initial ligand remnant. The roughness on the surface exposes both silicon and oxygen layers to the plasma. Because the silicon precursor cannot directly be deposited on the oxygen sites O$_2$(s), and because of the low sputtering rate, the surface coverage ratio of O$_2$(s) increases with time and causes the decrease of the instantaneous film growth rate. Film deposition in a trench follows many of the same trends as blanket deposition. Vacancy concentrations increase while the film growth rate decreases. Due to conduction limits, the film growth rate at the bottom of a trench decreases faster than that for blanket deposition.

The impact of power, pressure and the co-deposition probability of the ligand remnant $p_R$ on the SiO$_2$ film blanket deposition and a trench were investigated. Varying the power from 400 W to 1 kW, showed no obvious changes of IEADs and NEADs due to the highly collisional sheath at 2 Torr. With a plasma exposure time of 1.0 s, the film growth is found to be almost self-limiting. Therefore, neither the film concentration nor the growth rate was significantly
sensitive to variations of input power for blanket deposition. However, conduction limits do restrain the O$_2^*$ flux in a trench, making the growth rate and elementary ratio $\eta_O/\eta_{Si}$ sensitive to the change of O flux.

Varying pressure was found to significantly affect film quality for blanket deposition. Decreasing pressure resulted in a less collisional sheath and a longer ion mean free path. As a result, when the pressure is 0.5 Torr, the peak ion energy reaches 50 eV and sputtering rates increase. Consequently, using lower pressure during plasma exposure promotes the production of vacancies and slows film growth. However, when depositing in a trench, conduction limits buffer the impact of a varying of pressure. Both the material concentration and growth rate experience smaller variation with pressure compared to blanket deposition.

Varying the co-deposition probability of a ligand group has similar effect to blanket deposition as in a trench, due to the fact that it affects the film deposition through precursor dosing, which is a thermal process. The co-deposition of ligand group probability $p_R$ was increased from 0.001 to 0.5. At low $p_R < 0.05$ the film is uniform and conformal. A high $p_R \geq 0.05$ produces disordered and rough films. If annealing is used to remove ligand remnants after film deposition, the sum of vacancy and ligand concentrations translate to the vacancy concentration in the final product. When $p_R = 0.05$, at the end of the 5$^{th}$ cycle, this value reaches 2.5% for blanket deposition and 3.2% when depositing in a trench.

Finally, the effect of aspect ratio (AR) on film deposition when depositing in a trench and a via was discussed. For both cases, increasing AR leads to a decrease of oxidant fluxes in the bottom of the feature, which lowers film growth rate and causes porous film structure. However, for the same AR, a via has a bigger surface to volume ratio when the diameter of a via equals the width of a trench. Therefore, conduction limits are more significant in a via, which suggests a
longer period for self-limited deposition in a via.

To conclude, due to conduction limits, deposition in different structures depend on different species. The O radical is the dominant oxidant in a 3-dimensional feature such as a trench or a via, while both O and O$_2^*$ are important for blanket deposition. The effect of power on PE-ALD is insignificant with a sufficiently long plasma exposure time. Sputtering can still be a major concern when the pressure is lower than 2.0 Torr. Ligand remnants in the film can greatly affect the film quality. With a co-deposition probability >5%, the vacancy concentration of the final product can reach more than 2% for blanket deposition and more than 3% in a trench. In summary, high pressure (> 1.0 Torr) and low $p_R$ (< 0.05) are desired for the PE-ALD of SiO$_2$ films.

The results discussed in this chapter should help guide the design of SiO$_2$ PE-ALD processes. These results suggest that it is important to reduce ligand remnants on the surface after precursor dosing, especially in the early stage of the deposition. The roughness that remnant ligand groups produce starting in the first several layers enlarges as the film grows. To deposit a uniform and dense film, surface reactions during each step (precursor dosing and plasma exposure) should reach the stage of being self-limiting, which is achieved by employing long cycles and high reactants fluxes. Longer cycles are not necessarily desirable in high volume manufacturing.

In practice, the quality of films is gauged by the wet etch rate (WER). A high WER infers a less dense film, a high vacancy concentration and thus a poor film quality. Based on the simulation results, the WER is expected to increase with decreasing pressure (from 2 Torr), increasing ligand remnant density, and increasing aspect ratio.
Table II. Surface Reaction Mechanism for PE-ALD of SiO₂ Using Ar/O₂ Plasma as Oxidation Agent and BTBAS as Si Precursor

<table>
<thead>
<tr>
<th>Gas Phase Species</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ions or excited states, hot neutrals, and neutral partners</td>
<td>a)</td>
</tr>
<tr>
<td>Ar⁺, Ar₂⁺, Ar(h), Ar⁺, O₂⁺, O₂(h), O₂⁺, O(h), O₂⁺, O₂, O⁺, O</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precursor</th>
<th>SiH₂R₂</th>
</tr>
</thead>
</table>

| Sputtered materials and deposition by-products | SiH₂, SiH, Si, OH, R, HR, H₂O |

<table>
<thead>
<tr>
<th>Surface Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon layer</td>
</tr>
<tr>
<td>Oxygen layer</td>
</tr>
</tbody>
</table>

a) O₂⁺ denotes O₂(a¹Δg) and O₂(b¹Σ⁺g). O⁺ denotes O(1D) and O(1S).
b) R represents ligand group from silicon precursor, in the case of BTBAS, R denotes [NH(C₄H₉)]⁻ group.
c) SiO₂ is represented by a Si(s) voxel connected to two O₂(s) voxels. Ideally, SiO₂ film consists of staggered layers of Si(s) (silicon layer) and O₂(s) (oxygen layer). x-Si-y(s) represents two sites connected to Si(s) with this Si(s) not included in this voxel.

<table>
<thead>
<tr>
<th>Reactionsᵃ⁾</th>
<th>p₀ᵇ⁾</th>
<th>E₀(h)⁵)</th>
<th>E_r(⁵)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial deposition of SiH₂R₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W(s) + SiH₂R₂ → W(s) + SiH₂(s) + 2HR</td>
<td>0.01</td>
<td></td>
<td></td>
<td>c)</td>
</tr>
<tr>
<td><strong>SiH₂R₂ deposition on hydroxyl-rich surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH-Si-OH(s) + SiH₂R₂ → O₂(s) + SiH₂(s) + 2HR</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH-Si-H(s) + SiH₂R₂ → O(s) + SiH₂(s) + 2HR</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH-Si(s) + SiH₂R₂ → O(s) + SiH₂(s) + HR</td>
<td>0.005</td>
<td></td>
<td></td>
<td>d)</td>
</tr>
<tr>
<td>O-Si-H(s) + SiH₂R₂ → O(s) + SiH₂(s) + HR</td>
<td>0.005</td>
<td></td>
<td></td>
<td>d)</td>
</tr>
<tr>
<td>OH-Si-O(s) + SiH₂R₂ → O₂(s) + SiH₂(s) + HR</td>
<td>0.005</td>
<td></td>
<td></td>
<td>d)</td>
</tr>
<tr>
<td><strong>Oxidation of surface sites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + O → Si(s) + OH-Si-H(s)</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + O⁺ → Si(s) + OH-Si-H(s)</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + O₃ → Si(s) + OH-Si-H(s) + O₂</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + O⁺ → Si(s) + OH-Si-H(s)</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + O₂⁺ → Si(s) + OH-Si-OH(s)</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

²⁾ R represents ligand group from silicon precursor, in the case of BTBAS, R denotes [NH(C₄H₉)]⁻ group.
₃⁾ SiO₂ is represented by a Si(s) voxel connected to two O₂(s) voxels. Ideally, SiO₂ film consists of staggered layers of Si(s) (silicon layer) and O₂(s) (oxygen layer). x-Si-y(s) represents two sites connected to Si(s) with this Si(s) not included in this voxel.
\[
\begin{array}{ll}
\text{SiH}_2(\text{s}) + O_2^- \rightarrow \text{Si}(\text{s}) + \text{OH-Si-OH}(\text{s}) & 0.015 \\
\text{SiH}(\text{s}) + O \rightarrow \text{Si}(\text{s}) + \text{O-Si-H}(\text{s}) & 0.015 \\
\text{SiH}(\text{s}) + O \rightarrow \text{Si}(\text{s}) + \text{OH-Si}(\text{s}) & 0.01 \\
\text{SiH}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{O-Si-H}(\text{s}) & 0.02 \\
\text{SiH}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{OH-Si}(\text{s}) & 0.015 \\
\text{SiH}(\text{s}) + O_3 \rightarrow \text{Si}(\text{s}) + \text{O-Si-H}(\text{s}) + O_2 & 0.002 \\
\text{SiH}(\text{s}) + O_3 \rightarrow \text{Si}(\text{s}) + \text{OH-Si}(\text{s}) + O_2 & 0.015 \\
\text{SiH}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{O-Si-H}(\text{s}) & 0.02 \\
\text{SiH}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{OH-Si}(\text{s}) & 0.015 \\
\text{SiH}(\text{s}) + O_2^+ \rightarrow \text{Si}(\text{s}) + \text{OH-Si-O}(\text{s}) & 0.02 \\
\text{SiH}(\text{s}) + \text{OH} \rightarrow \text{Si}(\text{s}) + \text{OH-Si-H}(\text{s}) & 0.02 \\
\text{OH-Si-H}(\text{s}) + O \rightarrow \text{OH-Si-OH}(\text{s}) & 0.01 \\
\text{OH-Si-H}(\text{s}) + O^+ \rightarrow \text{OH-Si-OH}(\text{s}) & 0.015 \\
\text{OH-Si-H}(\text{s}) + O_3 \rightarrow \text{OH-Si-OH}(\text{s}) + O_2 & 0.015 \\
\text{OH-Si-H}(\text{s}) + O^+ \rightarrow \text{OH-Si-OH}(\text{s}) & 0.02 \\
\text{Si}(\text{s}) + O \rightarrow \text{Si}(\text{s}) + \text{O}(\text{s}) & 10^{-4} \\
\text{Si}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{O}(\text{s}) & 2 \times 10^{-4} \\
\text{Si}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{O}(\text{s}) + O_2 & 2 \times 10^{-4} \\
\text{Si}(\text{s}) + O^+ \rightarrow \text{Si}(\text{s}) + \text{O}(\text{s}) & 2 \times 10^{-4} \\
\text{Si}(\text{s}) + O_2^+ \rightarrow \text{Si}(\text{s}) + \text{O}_2(\text{s}) & 2 \times 10^{-4} \\
\text{Si}(\text{s}) + O_2^+ \rightarrow \text{Si}(\text{s}) + \text{O}_2(\text{s}) & 2 \times 10^{-4} \\
\text{Si}(\text{s}) + \text{OH} \rightarrow \text{Si}(\text{s}) + \text{OH-Si}(\text{s}) & 0.001 \\
\text{O}(\text{s}) + O \rightarrow \text{O}_2(\text{s}) & 0.01 \\
\text{O}(\text{s}) + O^+ \rightarrow \text{O}_2(\text{s}) & 0.015 \\
\text{O}(\text{s}) + O_3 \rightarrow \text{O}_2(\text{s}) + \text{O}_2 & 0.015 \\
\text{O}(\text{s}) + O^+ \rightarrow \text{O}_2(\text{s}) & 0.015 \\
\text{O}(\text{s}) + O_2^+ \rightarrow \text{O}_2(\text{s}) + \text{O} & 0.001 \\
\text{O}(\text{s}) + O_2^+ \rightarrow \text{O}_2(\text{s}) + \text{O(h)} & 0.005 \\
\text{O}(\text{s}) + \text{OH} \rightarrow \text{OH-Si-O}(\text{s}) & 0.03 \\
\text{OH-Si}(\text{s}) + O \rightarrow \text{OH-Si-O}(\text{s}) & 0.015 \\
\text{OH-Si}(\text{s}) + O^+ \rightarrow \text{OH-Si-O}(\text{s}) & 0.02 \\
\text{OH-Si}(\text{s}) + O_3 \rightarrow \text{OH-Si-O}(\text{s}) + \text{O}_2 & 0.02 \\
\text{OH-Si}(\text{s}) + O^+ \rightarrow \text{OH-Si-O}(\text{s}) & 0.02 \\
\text{OH-Si}(\text{s}) + O_2^+ \rightarrow \text{OH-Si-O}(\text{s}) + \text{O} & 0.001 \\
\text{OH-Si}(\text{s}) + O_2^+ \rightarrow \text{OH-Si-O}(\text{s}) + \text{O(h)} & 0.005 \\
\text{OH-Si}(\text{s}) + \text{OH} \rightarrow \text{OH-Si-OH}(\text{s}) & 0.03 \\
\text{O-Si-H}(\text{s}) + O \rightarrow \text{O-Si-O}(\text{s}) & 0.01 \\
\text{O-Si-H}(\text{s}) + O^+ \rightarrow \text{O-Si-O}(\text{s}) & 0.015 \\
\text{O-Si-H}(\text{s}) + O_3 \rightarrow \text{O-Si-O}(\text{s}) + \text{O}_2 & 0.015 \\
\text{O-Si-H}(\text{s}) + O^+ \rightarrow \text{O-Si-O}(\text{s}) & 0.015 \\
\text{O-Si-H}(\text{s}) + O^+ \rightarrow \text{O-Si-O}(\text{s}) & 0.015 \\
\text{Sputtering by ion and hot neutrals}
\end{array}
\]
\[
\begin{array}{cccc}
\text{SiH}_2(s) + I^+ \rightarrow \text{SiH}_2 + I(h) & 0.9 & 35 & 140 \\ 
\text{SiH}(s) + I^+ \rightarrow \text{SiH} + I(h) & 0.9 & 35 & 140 \\ 
\text{Si}(s) + I^+ \rightarrow \text{Si} + I(h) & 0.9 & 35 & 140 \\ 
\text{OH-Si-OH}(s) + I^+ \rightarrow \text{OH-Si}(s) + \text{OH} + I(h) & 0.9 & 30 & 120 \\ 
\text{OH-Si-H}(s) + I^+ \rightarrow \text{OH} + \text{H} + I(h) & 0.9 & 30 & 120 \\ 
\text{O-Si-H}(s) + I^+ \rightarrow \text{O} + \text{H} + I(h) & 0.9 & 30 & 120 \\ 
\text{O-Si-O}(s) + I^+ \rightarrow \text{O}(s) + \text{OH} + I(h) & 0.45 & 30 & 120 \\ 
\text{O}(s) + I^+ \rightarrow \text{O} + I(h) & 0.9 & 30 & 120 \\ 
\text{O}_2(s) + I^+ \rightarrow \text{O}(s) + \text{O} + I(h) & 0.9 & 30 & 120 \\
\end{array}
\]

\textit{R(s) removal by reactive oxygen species}

\[
\begin{array}{c}
\text{R}(s) + \text{O} \rightarrow \text{O}(s) + \text{R} \\
\text{R}(s) + \text{O}^* \rightarrow \text{O}(s) + \text{R} \\
\text{R}(s) + \text{O}_2 \rightarrow \text{O}(s) + \text{R} + \text{O}_2 \\
\end{array}
\]

\textit{Redeposition of sputtered species}

\[
\begin{array}{c}
\text{SiH}(s) + \text{SiH}_2 \rightarrow \text{SiH}(s) + \text{SiH}_2 \\
\text{SiH}(s) + \text{SiH} \rightarrow \text{SiH}(s) + \text{SiH}(s) \\
\text{SiH}(s) + \text{Si} \rightarrow \text{SiH}(s) + \text{Si}(s) \\
\text{SiH}(s) + \text{R} \rightarrow \text{SiH}(s) + \text{R}(s) \\
\text{Si}(s) + \text{SiH}_2 \rightarrow \text{Si}(s) + \text{SiH}_2(s) \\
\text{Si}(s) + \text{SiH} \rightarrow \text{Si}(s) + \text{SiH}(s) \\
\text{Si}(s) + \text{Si} \rightarrow \text{Si}(s) + \text{Si}(s) \\
\text{Si}(s) + \text{R} \rightarrow \text{Si}(s) + \text{R}(s) \\
\text{O}(s) + \text{SiH}_2 \rightarrow \text{O}(s) + \text{SiH}_2(s) \\
\text{O}(s) + \text{SiH} \rightarrow \text{O}(s) + \text{SiH}(s) \\
\text{O}(s) + \text{Si} \rightarrow \text{O}(s) + \text{Si}(s) \\
\text{O}(s) + \text{R} \rightarrow \text{O}(s) + \text{R}(s) \\
\text{O}_2(s) + \text{SiH}_2 \rightarrow \text{O}_2(s) + \text{SiH}_2(s) \\
\text{O}_2(s) + \text{SiH} \rightarrow \text{O}_2(s) + \text{SiH}(s) \\
\text{O}_2(s) + \text{Si} \rightarrow \text{O}_2(s) + \text{Si}(s) \\
\text{O}_2(s) + \text{R} \rightarrow \text{O}_2(s) + \text{R}(s) \\
\text{OH-Si}(s) + \text{SiH}_2 \rightarrow \text{OH-Si}(s) + \text{SiH}_2(s) \\
\text{OH-Si}(s) + \text{SiH} \rightarrow \text{OH-Si}(s) + \text{SiH}(s) \\
\text{OH-Si}(s) + \text{Si} \rightarrow \text{OH-Si}(s) + \text{Si}(s) \\
\text{O-Si-H}(s) + \text{SiH}_2 \rightarrow \text{O-Si-H}(s) + \text{SiH}_2(s) \\
\text{O-Si-H}(s) + \text{SiH} \rightarrow \text{O-Si-H}(s) + \text{SiH}(s) \\
\text{O-Si-H}(s) + \text{Si} \rightarrow \text{O-Si-H}(s) + \text{Si}(s) \\
\text{OH-Si-O}(s) + \text{SiH}_2 \rightarrow \text{OH-Si-O}(s) + \text{SiH}_2(s) \\
\text{OH-Si-O}(s) + \text{SiH} \rightarrow \text{OH-Si-O}(s) + \text{SiH}(s) \\
\text{OH-Si-O}(s) + \text{Si} \rightarrow \text{OH-Si-O}(s) + \text{Si}(s) \\
\end{array}
\]

245
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-Si-O(s) + R → OH-Si-O(s) + R(s)</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Oxidation by hydroxyl radical</strong></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + OH → SiH(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>SiH(s) + OH → Si(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-OH(s) + OH → OH-Si-O(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-H(s) + OH → O-Si-H(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-H(s) + OH → OH-Si(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>O-Si-H(s) + OH → O(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-O(s) + OH → O₂(s) + H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Recombination by sputtered ligand group</strong></td>
<td></td>
</tr>
<tr>
<td>SiH₂(s) + R → SiH(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td>SiH(s) + R → Si(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-OH(s) + R → OH-Si-O(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-H(s) + R → O-Si-H(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td>OH-Si-H(s) + R → OH-Si(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td>O-Si-H(s) + R → O(s) + HR</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Oxygen Recombination</strong></td>
<td></td>
</tr>
<tr>
<td>O(s) + O → O₂</td>
<td>6 × 10⁻⁵</td>
</tr>
<tr>
<td>O(s) + O⁺ → O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O(s) + O₃ → O₂ + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O(s) + O⁺ → O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O₂(s) + O → O(s) + O₂</td>
<td>6 × 10⁻⁵</td>
</tr>
<tr>
<td>O₂(s) + O⁺ → O(s) + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O₂(s) + O₃ → O(s) + O₂ + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O₂(s) + O⁺ → O(s) + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O-Si-H(s) + O → O₂ + H</td>
<td>6 × 10⁻⁵</td>
</tr>
<tr>
<td>O-Si-H(s) + O⁺ → O₂ + H</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O-Si-H(s) + O₃ → O₂ + O₂ + H</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>O-Si-H(s) + O⁺ → O₂ + H</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>OH-Si-O(s) + O → OH-Si(s) + O₂</td>
<td>6 × 10⁻⁵</td>
</tr>
<tr>
<td>OH-Si-O(s) + O⁺ → OH-Si(s) + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>OH-Si-O(s) + O₃ → OH-Si(s) + O₂ + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>OH-Si-O(s) + O⁺ → OH-Si(s) + O₂</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td><strong>Dissociation of O₂</strong></td>
<td></td>
</tr>
<tr>
<td>Surface(s) + O₃ → Surface(s) + O + O₂</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a) All ions neutralize on surfaces, returning to gas phase as their hot neutral partner. Ions and their hot neutral partners have the same surface reactions with the same probability. Only surface reactions for ions are shown in the table. All such reactions (with the exception of neutralization) should be duplicated for the ion’s hot neutral partner. Ar₂⁺ is reflected from the surface as two Ar hot neutrals.

b) If \(E_{th}\) and \(E_r\) are blank, the reaction has no energy dependence and the probability of the reaction is a constant, \(p_0\). If \(E_{th}\) and \(E_r\) have non-zero values, the reaction has an energy dependence.
dependent probability. When the probability of reaction is less than unity, the remaining probability is allocated to no energy-dependent reactions.

c) W(s) is the ideal surface upon which the SiO₂ PE-ALD is performed, it provides sufficient hydroxyl sites for the first-step silicon precursor dosing.

d) The ligand group remnants R(s) during precursor dosing is addressed using co-deposition probability. Extra $n_R$ voxel is deposited with the silicon, at a deposition probability $p_R$.

e) Oxidation probability of Si(s) is reduced to avoid the excessive oxidation when more than one surfaces of the Si(s) voxel is exposed to the plasma. The adjustment is only made for Si(s) as it is the final product upon which a high-density reactant (O) can be deposited.

f) The hydrogen site is removed along with the oxygen or hydroxyl sites in an sputtering and oxygen recombination process due to the lack of information of the neighbors of the direct surface reactant. This has minor effect in the current work due to the low concentrations of OH-Si-H(s) and O-Si-H(s) ($< 1\%$), and low etching probability. One method to improve the accuracy of the regarding surface reactions is to check the immediate neighbors of the surface reactant and transfer hydrogen remnant to the nearby Si(s) or SiH(s) to form SiH(s) or SiH₂(s) accordingly.

g) Reaction with physical sputtering angular dependence.

h) Surface(s) represents any solid-state surface site.
Fig. 7.1 Geometry of the reactor. 500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm.
Fig. 7.2 O₂ flux, 2-dimensional distribution of electron density, O₂⁺ density and O⁻ density. 500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm.
Fig. 7.3 a) Energy and angular distributions (EADs) of dominant cations Ar$^+$ and O$_2^+$, and radical O.  b) Fluxes of major species across half-wafer.  500 W (10 MHz), 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm.
Fig. 7.4 a) Flowchart of SiO$_2$ PE-ALD process and b) impact of ligand remnant on the upper layer of SiO$_2$ film deposition.
Fig. 7.5 a) 2-dimensional film profile of the middle slice at \( y = 5 \) nm and b) 3-dimensional profile of the SiO\(_2\) film at the end of 5\(^{th}\) and 10\(^{th}\) cycle.
Fig. 7.6 a) $O_2(s)$ sites surface coverage ratio, b) concentrations of oxygen, silicon, vacancy and ligand group in entire film and oxygen to silicon ratio and c) time-averaged and instantaneous film growth rate using the default setup. 0.5 nm/cell, 1 nm per SiO$_2$ layer, blanket deposition.
Fig. 7.7 a) 2D film profile at the end of the 10th cycle and b) 3D film profiles at the end of the 5th and 10th cycle when depositing in a trench of 30 nm (W) × 120 nm (H) × 10 nm (D).
Fig. 7.8 a) Concentrations of oxygen, silicon, vacancy and ligand group in entire film and oxygen to silicon ratio and c) time-averaged and instantaneous film growth rate at the bottom of the trench. 0.5 nm/cell, 1 nm per SiO₂ layer, trench deposition.
Fig. 7.9 a) Energy and angular distributions (EADs) of \( \text{Ar}^+ \) and \( \text{O} \) when power is 400 W and 1 kW and b) fluxes of major species at mid-radius of wafer. 10 MHz, 2 Torr, primary gas inlet: \( \text{Ar}/\text{O}_2 \) (4/1), 5 slm; secondary gas inlet: \( \text{O}_2 \), 6 slm.
Fig. 7.10 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying power. Data are from 5th cycle. 10 MHz, 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.11 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying power. Data are from 5th cycle. 10 MHz, 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.12 a) Energy and angular distributions (EADs) of Ar$^+$ and O when pressure is 0.5 and 2 Torr, b) energy distribution function of all cations and c) fluxes of major species at mid-radius of wafer. 500 W, 10 MHz, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm.
Fig. 7.13 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying pressure. Data are from 5th cycle. 10 MHz, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.14 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying pressure. Data are from 5th cycle. 10 MHz, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.15 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate with varying co-deposition probability $p_R$. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O$_2$ (4/1), 5 slm; secondary gas inlet: O$_2$, 6 slm. 0.5 nm/cell, 1 nm per SiO$_2$ layer.
Fig. 7.16 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate at the bottom of a trench with varying co-deposition probability \( p_R \). Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O\(_2\) (4/1), 5 slm; secondary gas inlet: O\(_2\), 6 slm. 0.5 nm/cell, 1 nm per SiO\(_2\) layer.
Fig. 7.17 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate for blanket deposition with and without oxygen replacement reactions. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.18 a) Concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and b) time-averaged and instantaneous film growth rate in the bottom of a trench with varying aspect ratio from 2-8. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O₂ (4/1), 5 slm; secondary gas inlet: O₂, 6 slm. 0.5 nm/cell, 1 nm per SiO₂ layer.
Fig. 7.19 a) Geometry of the via and film profile at the end of the 5th cycle and b) concentrations of oxygen, silicon, vacancy, and ligand groups in the entire film and oxygen to silicon ratio, and c) time-averaged and instantaneous film growth rate in the bottom of this via with varying aspect ratio from 2-8. Data are from 5th cycle. 500 W, 10 MHz, 2 Torr, primary gas inlet: Ar/O\textsubscript{2} (4/1), 5 slm; secondary gas inlet: O\textsubscript{2}, 6 slm. 0.5 nm/cell, 1 nm per SiO\textsubscript{2} layer.
7.7 References

Chapter 8: Conclusions and Future Work

Some of the most critical challenges in semiconductor fabrication processes involving low-temperature plasma are maintaining a high stability and uniformity of the plasma, increasing the power deposition efficiency, as well as accomplishing independent control of the plasma density and ion energy on the wafer. In addition, approaches that help us to understand the physics in an nm-scale feature within a plasma-enhanced atomic layer deposition (PE-ALD) process are highly desirable in order to improve the current technology. In this dissertation, a 2-dimensional reactor-scale hybrid hydrodynamic simulation platform (the HPEM) and a 3-dimensional feature-scale voxel-based model (the MCFPM) were utilized to study these challenges. The insights provided in this dissertation can help further optimize the design of low-temperature plasma (LTP) reactors for industrial applications, and help us to understand the SiO₂ PE-ALD process. Summaries of each chapter are presented in Sec. 8.1. Contributions of this work are described in Sec. 8.2. Future work is discussed in Sec. 8.3.

8.1 Summary

In Chapter 1, the fundamental properties and equations governing low temperature plasma are introduced. Two types of plasma source—inductively coupled plasma (ICP) and capacitively coupled plasma (CCP)—were reviewed. The fabrication process of using a plasma-enhanced atomic layer deposition (PE-ALD) technique in order to grow a thin silicon dioxide
(SiO\textsubscript{2}) film was reviewed. A review and comparison of both reactor- and feature-scale plasma models were then presented.

In Chapter 2, the models used in this thesis were discussed in detail. The 2-dimensional reactor-scale hybrid hydrodynamic model, the HPEM, was updated and equipped with a circuit model to address the impedance matching network (IMN) and frequency tuning. The eMCS module in the HPEM was updated with parallel computation enabled, utilizing an application programming interface, OpenMP, to be more computationally efficient. The 3-dimensional feature scale model, the MCFPM, was updated to address steric hindrance caused by the ligand group remnants on a surface in the PE-ALD process.

In Chapter 3, the uniformity of an inductively coupled plasma (ICP) powered with a high-low pulsed power while being sustained in an Ar/Cl\textsubscript{2} gas mixture was investigated. An upward spike of electron temperature ($T_e$) was observed at the leading edge of the pulse; likewise, a downward spike was observed during power transition from high-to-low. The instabilities of $T_e$, electron density, and ion densities caused by the pulse diminish toward the bottom of the reactor as distance from the power source increases, due to the long transportation time and low power density. This work demonstrates that a pulsed plasma is a highly dynamic system with strong time- and spatial-dependency.

In Chapter 4, power deposition to an Ar/Cl\textsubscript{2} ICP was investigated with both inductive and capacitive power coupling included. The set-point impedance matching technique was then applied. In an ICP, when power is mainly transferred to the plasma through electromagnetic fields (EM-fields) with a solenoidal electric field (E-field), plasma is in H-mode. When the power is predominantly coupled to the electrons and ions near the coils through an electrostatic E-field, the plasma is in E-mode. Choosing the IMN to match the early pulse promotes E-mode,
which assists in plasma ignition, but the tradeoff is a high reflection coefficient through the pulse. In contrast, matching to the late pulse encourages H-mode and reduces the power reflection coefficient for the majority of a pulse, but delays the onset of the H-mode. This elongates the time plasma operates in E-mode. A severe E-mode was found to launch electrostatic waves to the plasma in the leading RF cycles during pulsed-on due to the oscillation of the sheath produced by the electrostatic field from the coil. The implications of duty cycle and geometry on the impedance match were also studied. Short duty cycle promotes the E-mode at the beginning of a pulse owing to the low electron density caused by the sufficient loss during inter-pulse period. A big gap between coil and dielectric window produces low capacitance that constrains capacitive power coupling, which then weakens the E-mode and delays the onset of the H-mode.

In Chapter 5, utilizing a pure Ar ICP sustained in pulsed power, two impedance matching techniques were investigated: the first used only a fixed impedance matching network (IMN), referred to as set-point matching, and the second utilized a combination of set-point matching with a real-time impedance matching approach (frequency tuning). When only the IMN was used to match impedance, it created an impedance mismatch during other times within the pulse, resulting in a high power reflection coefficient and low power transition efficiency. This impedance mismatch can be minimized by frequency tuning. Matching impedance in the early pulse was found to be vital for plasma ignition. An impedance matching procedure that utilizes set-point matching for a coarse match and then refines it using frequency tuning was proposed.

In Chapter 6, reactor-scale modeling was used to investigate the triple-frequency, capacitively coupled plasma (TF-CCP) sustained in Ar/CF$_4$/O$_2$ mixtures. A high frequency (HF) 80 MHz continuous wave (CW) power was applied to the top electrode, while lower frequency
powers (5, and 10 MHz) were applied to the substrate. The high frequency was found to be more
efficient in heating electrons, due to the fact that stochastic heating is proportional to the
frequency. Ion energy on the substrate decreases with the increase of HF power, due to the less
negative DC bias (-660 to -121V as power increases from 50 to 1000 W). Increasing pressure
results in a more collisional sheath above the substrate, which broadens the ion angular
distribution (IAD). Increasing HF promotes stochastic heating, which in turn causes the increase
of plasma density in the center of the reactor. Increasing the gap length between electrodes leads
to a more uniform plasma distribution in the plasma bulk and a more negative DC bias.

In Chapter 7, using integrated reactor- and feature-scale models, we examined plasma-
enhanced atomic layer deposition (PE-ALD) of a thin SiO₂ film deposited on blanket, trench and
via structures using Ar/O₂ plasma as oxidation agents. A SiO₂ deposition mechanism was
developed for the feature scale simulation. The steric hindrance was included by depositing the
ligand group along with the primary silicon sites at a probability p_R. Sparsely distributed
imperfections and misalignments in the layers deposited in the early stages affected film
deposited later in upper layers, resulting in disordered film structure. The growth rate of the film
decreases as it thickens due to the increased complexity of the surface components. Both
oxygen radical O and excited state oxygen molecule O₂* affect film deposition on a blanket, but
O was found to be the dominant oxidant when depositing in a trench or a via due to the
significant impact of the conduction limit on the O₂* flux. Varying power affects the SiO₂ film
deposition differently when the film is on a blanket, compared to in a trench, because O₂* and O
fluxes follow different paths as the power varies. Increasing pressure results in a more
collisional sheath, which reduces the ion energy and consequently reduces the ion bombardment
damages to the film. Changing the co-deposition probability of ligand group has a similar effect
on the film deposition, regardless of the structure of the target feature. Higher $p_R$ leads to lower film growth rate and higher vacancy concentration in the film. Because a via has higher surface to volume ratio than a trench when their aspect ratio is the same, conduction limit has a more significant effect in a via than in a trench.

8.2 Contributions

The work in this dissertation helps us to understand the fundamental physics in low temperature plasmas within industrial applications, and provides information needed to optimize the design of a LTP reactor and operating conditions.

1. IMN circuit components are analytically solved for the perfect matching condition. Frequency tuning is implemented for real-time impedance matching.

A new method of analytically solving the values of circuit components used in the IMN in order to create perfect matching was added to the HPEM in order to provide more accurate results with less time consumption. Frequency tuning was also implemented in the HPEM to enable a real-time impedance matching. Using these updates, plasma behaviors were investigated using different impedance matching approaches. The results can be used to guide the selection of IMN to maximize power deposition efficiency while minimizing plasma instability. Results that utilize frequency tuning can help with choosing frequencies to match the impedance at various transients during processing. Applications using a continuously changing power profile, such as a sawtooth waveform, will especially benefit from real-time impedance matching like frequency tuning.

2. Implementation of parallel computation in electron Monte Carlo Simulation module.

A parallel computing technique using the application programming interface OpenMP was implemented into the HPEM to enable efficient modeling in electron Monte Carlo
Simulation module (eMCS). In order to prevent the cross-talks between variables during parallel computing, variables are made thread-aware at the beginning of the eMCS. That is, parts of each variable are distributed to individual threads with the thread number logged. These threads perform the computation independently through the eMCS and then merge the variables back into their initial form at the end of executing the eMCS. This technique prevents cross-talks between the parts of variables and enables independent calculations on pseudoparticles. The most conspicuous acceleration was achieved when a large amount of pseudoparticles was launched.

3. Integrated investigation of plasma enhance atomic layer deposition system of SiO$_2$ film deposition on blanket, trench and via features.

The reactor-scale plasma properties (e.g., electron density, ion fluxes to the wafer, ion energy and angular distributions, etc.) of an Ar/O$_2$ capacitively-coupled plasma (CCP) were studied using a 2-dimensional hybrid hydrodynamic model (the HPEM). The surface reaction mechanism of plasma-enhanced atomic layer deposition (PE-ALD) of SiO$_2$ film was developed for the feature-scale investigations. Steric hindrance was addressed by depositing the ligand sites along with the primary deposited silicon sites at a co-deposition probability $p_R$. The impact of microscopic parameters on film quality was investigated using the feature-scale model (the MCFPM). These microscopic parameters could be controlled through varying macroscopic parameters, such as the input power to the plasma, pressure in the reactor, and the choice of silicon precursor. Results from this work provide guidance for SiO$_2$ PE-ALD fabrication process optimization and for reactor design. Parametric studies of power, pressure, and the ligand group remnant co-deposition probability were performed on blanket deposition and film deposition in a
trench. Impact of aspect ratio on the SiO$_2$ film quality was explored when depositing the film in a trench and in a via structure.

8.3 Future Work

Reactor- and feature-scale models were updated and executed to simulate low temperature plasmas involved in industrial applications. Future work that will improve the performance of the plasma modeling is proposed as follows:

1. Enable neighbor checks in the MCFPM for specified reactions.

In the current version of the surface reaction mechanism of PE-ALD for an SiO$_2$ film, the deposition probability of gas-phase oxygen radical O on the silicon site Si (s) is reduced to $10^{-4}$, to accommodate the exposure of saturated silicons, with all of their bonds occupied. This reduction of deposition probability of O on Si (s) was empirically derived and is somewhat arbitrary; this can be avoided if the neighbor of the surface reactant is checked to determine if that surface reactant is in a saturated state. Considering that performing this check will be highly time consuming if it is executed every time a surface reaction occurs, some form of tag —such as a special number— should be given to specified reactions so that if a tagged reaction occurs, a neighbor check is conducted.

2. Parallel calculation in module PCMCM.

Like eMCS, PCMCM tracks particles (charged and neutral) using a Monte Carlo approach. Because pseudoparticles are moved and tracked independently, PCMCM is also suitable for parallel computation. Similar to the eMCS, parameters of pseudoparticles should be distributed to a number of threads and become thread-aware at the beginning of the PCMCM; each thread then independently moves and tracks the pseudoparticles assigned to it and returns the information back to the master thread at the end of the PCMCM. Using parallel computing
for the PCMCM should greatly reduce the time spent in the module especially when a large amount of the pseudoparticles are used, for instance, when neutral energy and angular distribution (NEAD) are to be recorded.

3. Implement IMN and frequency tuning for CCP reactor.

   In the current version of the HPEM, the IMN and frequency tuning are only implemented for the calculation in an ICP reactor. These should also be enabled in a CCP reactor so that the simulation can have better agreement with the experimental results.

4. Apply machine learning to determine optimal operating conditions for fabrication processes.

   Machine learning (ML) can be employed to help choose the optimal operating conditions and reduce the number of test wafers to run during process development. Simulation results from models such as the HPEM and MCFPM could be used for preliminary training datasets to reduce the number of wafers that need to be run. Quantifiable physics parameters such as the reaction probabilities for ion and radical fluxes to the wafer should be a desired outcome of the ML so that the results can be transferred to other system. ML algorithm are typically based on describing the flux to the wafer as a function of operating conditions (power, pressure, etc.) when the plasma is sustained in a certain gas mixture and certain reactor. These outcomes do not necessarily transfer to other systems (different gas mixture, different method of excitation). Building the ML algorithm to isolate physical parameters that are not functions of operating conditions should make the outcome of ML more broadly applicable, for example, applying to both ICP and CCP.
Appendix: Analytical Solution of Components in Impedance Matching Networks

The components used in the impedance matching network (IMN) is analytically solved in the HPEM to provide perfect impedance matching. The solutions of theses components are subjected to the choice of IMN schematic. In the HPEM, three types of the IMNs can be used. The schematics of these IMNs and solutions of the components in the IMN that can produce perfect impedance matching are provided in this Appendix.

A.1 IMN Type 1

The schematic of type 1 IMN is

where $R_G$ is the resistance of the power supply, $R_{loss}$ is the resistance in the IMN, $C_P$ and $C_S$ are capacitors that are tuned to produce perfect impedance matching, $L_S$ is an inductor with fixed user-defined inductance, $Z_L$ is the impedance of the load consisting of plasma and reactor, $Z_P$ is the impedance of the plasma, $L_T$ and $C_T$ are the termination components connected to ground.

The total impedance including match box components, plasma and termination components is
\[ Z = R_{\text{loss}} + \frac{1}{j \omega C_p + \frac{1}{j \omega L_s + \text{Re}(Z_L)} + j \text{Im}(Z_L)} \]  

(A.1)

where \( \text{Re}(Z_L) \) denotes the real component of \( Z_L \) and \( \text{Im}(Z_L) \) is the imaginary component of \( Z_L \), \( \omega \) is the radian frequency of the power supply, and \( j \) is the imaginary unit. For a perfect matching, \( Z = Z_G \), utilizing \( \text{Im}(Z) = \text{Im}(Z_G) \) provides:

\[
C_S = \frac{C_S \left\{ \omega L_s + \text{Im}(Z_L) \right\} \omega C_S - 1}{A_1 C_S^2 + B_1 C_S + 1} \]  

(A.2)

where

\[
A_1 = \omega^2 |Z_L|^2 + \omega^4 L_s^2 + 2\omega^3 L_s \text{Im}(Z_L) \]  

(A.3)

\[
B_1 = -2\omega^3 L_s - 2\omega \text{Im}(Z_L) \]  

(A.4)

where \( |Z_L| \) is the modulus of \( Z_L \). Then by requiring \( \text{Re}(Z) = \text{Re}(Z_G) \),

\[
C_S = \frac{-B_1 \pm \sqrt{B_1^2 - 4 \left\{ A_1 - \omega^2 \text{Re}(Z_L) \left[ \text{Re}(Z_G) - R_{\text{loss}} \right] \right\}}}{2 \left\{ A_1 - \omega^2 \text{Re}(Z_L) \left[ \text{Re}(Z_G) - R_{\text{loss}} \right] \right\}} \]  

(A.5)

A.2 IMN Type 2

The schematic of type 2 IMN is
The denotations are the same as type 1 IMN other than instead of utilizing a series inductor $L_S$, a parallel inductor $L_P$ is used in the IMN. In a type 2 IMN, the total impedance of the match box components, plasma and termination components is

$$Z = R_{loss} + \frac{1}{j\omega C_s} + \frac{1}{j\omega L_P + \frac{1}{j\omega C_p} + \frac{1}{\text{Re}(Z_L) + j\text{Im}(Z_L)}}$$ (A.6)

Matching $\text{Re}(Z) = \text{Re}(Z_G)$, we obtain

$$C_p = \frac{-B_2 \pm \sqrt{B_2^2 - 4A_2C_2}}{2A_2}$$ (A.7)

where

$$A_2 = [\text{Re}(Z_G) - R_{loss}] \left\{ |Z_L|^2 \omega^4 L_P^2 + |Z_L|^4 + 2\omega^3 L_P \text{Im}(Z_L) |Z_L|^2 \right\} - \text{Re}(Z_L)\omega^4 L_P^2 |Z_L|^2$$ (A.8)

$$B_2 = 2\omega^2 L_P \text{Re}(Z_L) |Z_L|^2 - 2\omega |Z_L|^2 \left[ \text{Re}(Z_G) - R_{loss} \left( \omega L_P + \text{Im}(Z_L) \right) \right]$$ (A.9)

$$C_2 = \left\{ [\text{Re}(Z_G) - R_{loss}] - \text{Re}(Z_L) \right\} |Z_L|^2$$ (A.10)

Then $C_S$ is solved by matching the imaginary part of the impedance $\text{Im}(Z) = \text{Im}(Z_G)$:

$$C_S = -\frac{\text{Re}^2(Z_L) \left( 1 - \omega^2 L_P C_P \right)^2 + \left[ \omega C_P |Z_L|^2 - \text{Im}(Z_L) \left( 1 - \omega^2 L_P C_P \right) \right]^2}{\omega \left( 1 - \omega^2 L_P C_P \right) |Z_L|^2 \left[ \omega C_P |Z_L|^2 - \text{Im}(Z_L) \left( 1 - \omega^2 L_P C_P \right) \right]}$$ (A.11)

A.3 IMN Type 3

The schematic of type 3 IMN is
The denotations are the same as those used in type 1 and 2 IMNs. However, \( C_P \) and \( C_S \) are in series in the circuit. Constant inductor and capacitor \( L_C \) and \( C_C \) are added in the IMN. In a type 3 IMN, the total impedance of the match box components, plasma and termination components is

\[
Z = R_{loss} + \frac{1}{j\omega C_S} + \frac{1}{j\omega L_C + \frac{1}{j\omega C_C}} + \frac{1}{j\omega L_S + \frac{1}{j\omega C_P} + \text{Re}(Z_L) + j\text{Im}(Z_L)}
\]  

(A.12)

Matching \( \text{Re}(Z) = \text{Re}(Z_G) \), we obtain

\[
C_P = \frac{-B_3 \pm \sqrt{B_3^2 - 4A_3C_3}}{2A_3}
\]

(A.13)

where

\[
A_3 = \alpha^2 \text{Re}(Z_L) - [\text{Re}(Z_G) - R_{loss}]\text{Re}^2(Z_L) - [\text{Re}(Z_G) - R_{loss}]\beta^2
\]

(A.14)

\[
B_3 = \frac{2\beta[\text{Re}(Z_G) - R_{loss}]}{\omega}
\]

(A.15)

\[
C_3 = \frac{\text{Re}(Z_G) - R_{loss}}{\omega^2}
\]

(A.16)

\[
\alpha = \omega L_C - \frac{1}{\omega C_C}
\]

(A.17)

\[
\beta = \alpha + \text{Im}(Z_L) + \omega L_S
\]

(A.18)
Then $C_S$ is solved by matching the imaginary components of the impedances

$$C_S = \frac{\text{Re}^2(Z_L) + (\alpha + \gamma)^2}{\omega \alpha \left\{ \gamma (\alpha + \gamma) + \text{Re}^2(Z_L) \right\}}$$  \hspace{1cm} (A.19)

where

$$\gamma = \text{Im}(Z_L) + \omega L_S - \frac{1}{\omega C_p}$$ \hspace{1cm} (A.20)