CONTROLLING ACTIVATION ENERGY TO WAFERS AND WALLS IN PLASMA PROCESSING REACTORS FOR MICROELECTRONICS FABRICATION

BY

ANKUR AGARWAL

B.Tech., Indian Institute of Technology, Bombay, 2003
M.S., University of Illinois at Urbana-Champaign, 2005

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Doctoral Committee:

Professor Richard C. Alkire, Chair
Professor Mark J. Kushner, Iowa State University
Associate Professor Daniel W. Pack
Professor Edmund G. Seebauer
The trend to shrink modern microelectronic devices is pushing processing technologies to unprecedented limits. In particular, plasma processing should meet the stringent requirements of developing features at future technological nodes. Microprocessors now available have oxide layers in gate stacks which are only a few mono-layers (1-2 nm) thick. Therefore, at future technology nodes even a monolayer deviation can have significant implications on performance. In this work, relevance of low pressure, high plasma density discharges for advanced semiconductor processing in the fabrication of fine features in microelectronics are discussed.

To meet the stringent requirements, plasma processing requires unprecedented control of the properties of reactive species onto the wafer (small scale) and walls of reactors (large scale). Ultimately, extreme control over the uniformity, composition, and energy of reactants is required as these are the enablers to processing delivering the requisite activation energy to various processing steps such as etching, deposition, etc. Different methods of controlling activation energy are investigated to achieve the fine balance between the uniformity, composition and energy of the reactants.

Pulsed plasma ion implantation, a technique to form ultra-shallow junctions, is an important technology to enable advances in microelectronics industry. The characteristics of the ion energy and angular distributions (IEADs) incident onto the wafer are critical to determination of the junction properties. In particular, angular asymmetry in the IEADs was observed as a
result of the curvature in the sheath edge. By changing the source design, the sheath symmetry was restored thereby making the IEADs angularly symmetric. Characterizing the IEADs enables improvement in the uniformity, repeatability and reliability of the implantation process.

Extreme control in etching process technologies is critical to etch node feature geometries with high aspect ratios. Typical reactive ions based etching techniques is prone to issues such as microloading and mask charging thus limiting the precise control that can be achieved. Plasma atomic layer etching is therefore suggested to allow for precise atomic scale controllability. Precise control over IEADs incident onto the wafer enables extreme control in etching characteristics of the process. However, to keep integration costs low, it is important to utilize conventional plasma equipment while enabling such control. Recipes utilizing PALE processes have been investigated in conventional plasma sources for different gas mixtures to etch feature geometries of interest at future technological nodes. We found that, while feasible, PALE processes are slow compared to conventional etching. Recipes based on non-sinusoidal bias waveforms were investigated which though increases the throughput are still slow.

Wafer-to-wafer reproducibility during plasma etching presents another challenge. The use of low-pressure, high-density discharges results in increasing buildup of etch products in the plasma reactor resulting in increased interactions of etch products with wafer and non-wafer surfaces, alike. Consequences of such interactions have been investigated for Ar/Cl₂ inductively-coupled plasma etching of poly-Si. The interactions of etch products with the wafer ultimately results in decrease in etch rates while the chamber seasons due to interactions with the non-wafer surfaces. A proportional controller using bias voltage as an actuator and etch rate as the sensor was implemented to achieve real-time, closed-loop control of etch rate to counter the effects of seasoning.
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1. INTRODUCTION

1.1 Plasmas: An Introduction

A gaseous plasma is obtained by ionizing atoms or molecules in the gas, thereby creating a fluid containing ions, electrons and neutral particles. Although some degree of ionization will occur in any gas under most circumstances, the term “plasma” technically refers to the state where charge density in the gas is large enough for 1) the gas to remain almost electrically neutral and 2) electric field generated by the ionized gas to shield out the influence of external electric fields. Plasma is considered to be a distinct state of matter, in contrast to gases because of its unique properties. Parameters such as the degree of ionization (ratio of electrons to neutral particles density, $\frac{n_e}{N}$), density of electrons, $n_e$, and the electron temperature, $T_e$ can be used to characterize a plasma in a broad sense. Different plasma systems are shown in Fig. 1.1 for typical densities and temperatures. Plasmas are radically multi-scale in that they exist over a huge range of densities and temperatures. For example, the interstellar plasmas are at one end of the spectrum, with very low densities and temperatures. At the other end of the spectrum, the high-pressure arcs have large densities ($n_e > 10^{15} \text{ cm}^{-3}$) and degree of ionization and fusion devices which have high electron temperatures in the order of hundreds to thousands of eV (1 eV $\approx 11,600 \text{ K}$).

A certain class of plasmas, those that are partially ionized ($n_{\text{charged}} << n_{\text{neutral}}$), non-equilibrium ($T_e >> T_g, T_i$) and chemically reactive, have been found to be very useful for various processing steps such as etching, deposition and implantation in the semiconductor industry. These plasmas and their related applications form the main focus of the work in this dissertation. These are “cold” plasmas having electron temperatures of 0.1 to 10 eV, and electron densities on
the order of $10^{10}$ to $10^{12}$ cm$^{-3}$. Applications of such plasmas are shown in Table 1.1. In general, these plasmas serve as a power transfer media, where power is deposited via dc, inductive (ICP), or capacitive coupling (CCP). The fields so generated accelerate the electrons that strike the neutral gas in the chamber, thereby ionizing and exciting the constituents. This leads to formation of reactive species like ions and radicals, which are then used for plasma processing technology of choice. For example, for etching of semiconductors, the ions are the primary activators of the etching process.[1,2] In lamps, the light is generated from excited state species.[3,4] For atmospheric gas remediation, neutral radicals are the primary reactive species.[5,6]

Due to the large difference in the masses of electrons and ions, the electrons typically oscillate about the ions which are relatively at rest. This gives rise to fundamental oscillations leading to fundamental length and time scales. The time scale is defined by the plasma frequency:

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

and the length scale, Debye length, is defined as:

$$\lambda_d = \sqrt{\frac{kT_e}{4\pi n_e e^2}}$$  \hspace{1cm} (1.2)

where $n_e$, $m_e$, and $T_e$ are the density, mass and temperature of the electron, and $e$ is the fundamental charge. As such, plasmas are electrically neutral at length scales larger than the
Debye length, and time scales larger than the period of the plasma oscillation. In general, the charge-neutrality of plasmas is valid over the bulk of the plasma. However, this is not so near the electrodes, and dielectric surfaces for the following reason. Because the electron temperature is much higher than the ion temperature, and because the electron mass is much smaller than ion masses, according to the Einstein’s equation for diffusivity, the diffusion coefficient of electrons is much larger than that of ions. The diffusion loss rate for electrons is therefore much larger than that for ions, leading to the formation of a sheath region where there is a net positive space charge and so the charge-neutrality is no longer valid. According to the Poisson’s equation, in order to maintain quasi-neutrality, a sheath potential drop is formed that compensates for the difference in the diffusion loss rates of electrons and ions. The build up of net positive space charge causes a restoring force to develop which accelerates the positively charged ions into the walls, and the negatively charged species away from it until the diffusion loses are balanced. The whole process is depicted in Fig. 1.2. The restoring force that accounts for this is the ambipolar force and the diffusion under such force is termed ambipolar diffusion. The ambipolar diffusion coefficient $D_a$ can be expressed as:

$$D_a = D \left(1 + \frac{T_e}{T_i}\right)$$

(1.3)

where $D$ is the coefficient of diffusion in the absence of ambipolar forces, and $T_e$, $T_i$ are electron and ion temperatures, respectively. Typically, the electron temperatures are a few eV, and the ion temperature is taken as the gas temperature $T_g$. Thus, the ambipolar diffusion can be nearly 50 – 100 times larger than the neutral diffusion. The assumption that $T_g$ equals $T_i$ is valid at
pressures greater than 1 Torr where the ion-neutral collision frequency is large, leading to energies on the order of thermal speeds.

For applications such as semiconductor chip manufacturing, the silicon wafer is modified by a combination of ions and neutral species (in the plasma). The characteristics of which are influenced by the characteristics of the sheath. Therefore, as such, the study of the dynamics and properties of the sheath is very important. For example, in an etching tool, the bias voltage (on the order of tens or hundreds of volts) can control the sheath potential drop above the wafer. The large sheath voltage drop supplies ions with large bombarding energies. And more importantly, once the sheath electric field is oriented normal to the surface, the motions of ions also become perpendicular to the surface. So the ion bombardment of the surface is anisotropic as well as energetic, and this gives plasma etching the great merit of being an anisotropic process.

For a “floating” or an ungrounded surface such as a dielectric material, the build-up of negative charge on the surface causes a “floating” potential to develop. The sheath potential accelerates the positive ions towards the walls. When the energetic ions strike the metal surfaces, they can release the bound electrons in the surface and these free “secondary electrons” are accelerated by the electric field in the sheath and join the bulk plasma. The secondary electrons are important as they can gain enough energy to produce ionization in the gas. The source of the secondary electrons \( S \) is dependent on the ion flux and the surface:

\[
S_j = \sum_i \Phi_i \gamma_{ij}
\]  

where \( S_j \) is the source of secondary electrons from the \( j \)th surface, \( \Phi_i \) is the flux of the \( i \)th ion, and \( \gamma_{ij} \) is the secondary electron coefficient.
A complete description of the various physical processes occurring in plasmas is beyond the scope of this work.

1.2 Controlling Activation Energy

Plasma processing continues to remain an important technology for an increasing number of industries, including semiconductor manufacturing, medical products, and environmental pollution control. In this work, relevance of low pressure, high plasma density discharges for advanced semiconductor processing in the fabrication of fine features in microelectronics are discussed.

Moore’s law has characterized the microelectronics industry since 1970, when Gordon Moore predicted that the number of transistors in microprocessors doubles every 18 months. The doubling cycle was later extended to 24 months, to compensate for expected increases in the complexity of semiconductors. Moore’s law is illustrated in Fig. 1.3.[7] Moore’s law has served as a goal for the microelectronics industry, obeying it for over 20 generations and plasma processing has been a key enabler to that end.

The trend to shrink modern microelectronic devices is pushing processing technologies to unprecedented limits. Microprocessors now available have oxide layers in gate stacks which are only a few mono-layers (1-2 nm) thick. Therefore, at future technology nodes if the feature sizes have even a monolayer deviation there are significant implications on performance. Modern processing techniques should therefore meet both the demands of large scale (reactors) and small scale (features). To meet the stringent requirements, plasma processing requires unprecedented control of the properties of reactive species onto the wafer (small scale) and walls of reactors (large scale). Ultimately, extreme control over the uniformity, composition, and energy of
reactants is required as these are the enablers to processing delivering the requisite activation energy to various processing steps such as etching, deposition, etc.

Activation energy is ultimately determined by the form of sheath and mobility of ions crossing the sheath. For example, precise control over energy of incident ions enables distinction between individual materials in a feature stack giving unprecedented control during etching. In this work, distinct methods of controlling activation energy are described. Specifically, three methods of control are discussed. Activation energy can be controlled via changes in source design which affects the symmetry of the sheath and consequently affect the IEADs. Pulsed plasma ion implantation, a technique to form ultra-shallow junctions has been used as a case study for the investigations. Activation energy control achieved through varying the bias voltage waveform has been investigated earlier.[8] The implications of such a control and its impact on advanced etching process technology, namely, plasma atomic layer etching was investigated. The effect of delivery activation energy to walls of the plasma processing reactors can have negative impact on the process uniformity. Seasoning of plasma etching reactors and controller schemes to mitigate the same were investigated in an ICP chamber as the model tool.

1.3 Pulsed Plasma Ion Implantation

Plasma processing techniques for microelectronics fabrication must now maintain critical dimensions approaching a few nm with high uniformity of less than a few percent over wafer diameters of 300 mm.[9,10] As the characteristic lengths of features in microelectronic devices decrease, so do their depths. For example, the sources and drains in complementary metal oxide semiconductor field effect transistors (CMOSFET), a standard component of microelectronics, become shallower as the channel length decreases.[11] Ultra-shallow junctions (USJ) having
depths of less than 35 nm are required for transistors having channel lengths of <100 nm. These junctions are formed by ion implantation into the silicon substrate.[12] Since the depth of the junction is determined by the energy of the incident ions, formation of USJ require low energy ions, hundreds of eV to a few keV.

The most straightforward fabrication method for forming USJ is to extend the beam-line, accelerator based ion implantation technology used for deep junctions (many tens to hundreds of keV) to lower ion energies as shown in Fig. 1.4.[13] Due to space charge induced divergence, low energy ion beams usually operate at lower currents and current densities than used for conventional deep implantations. These lower currents may result in undesirable low throughput.[14]

Several techniques have been proposed to overcome the space charge limitations of low energy ion beams.[15] One method extracts ions from the source and transport them through the beam-line at high energies before electrostatically decelerating the ions above the wafer to their final implant energy.[16-18] This approach has the advantage of maintaining high beam current but may produce a bimodal ion energy distribution on the wafer.[15] Space charge control can be achieved by increasing the gas pressures within the beam transport path but charge exchange can result in a significant loss of current from the beam.[19]

Several plasma based techniques have been proposed for fabricating USJ, including pulsed plasma implantation (PPI).[20] PPI is capable of delivering high ion doses ($10^{15}$ cm$^{-2}$) at low ion energies (hundreds eV to many keV). In one variation of PPI, a pulsed negative voltage is applied to the wafer to both create a plasma containing the desired dopant species and to accelerate the positive dopant ions from the plasma across the cathode sheath into the wafer. A schematic representation of PPI is shown in Fig. 1.5.[21] The plasma is ignited with each pulse
Typical pulse lengths are many to tens of microseconds. For sufficiently low pressures, the ions can collisionlessly traverse the sheath and are implanted into the wafer with energies largely determined by the pulse voltage and the ion charge. By pulsing the bias and allowing the plasma to extinguish, the heat load to the wafer, undesirable etching and contamination that occur only when the plasma is on are reduced. An alternate configuration for PPI uses an auxiliary plasma source, such as an inductively coupled plasma (ICP). This configuration provides a readily available source of ions and reduces concerns associated with restarting the plasma with each pulse. The disadvantage of having the plasma be continually on is possible unwanted production of etching species.

PPI has a few limitations in comparison to beam-line implantation. Unlike beam-line implantation there is no systematic ion-mass separation that takes place in PPI. All the positive ions in the plasma can be implanted to some degree. Furthermore, the ions are not strictly monoenergetic as the distribution of ion energies to the substrate depends on gas pressure, pulse shape and plasma density. The production of secondary electrons under ion impact for the wide range of implant energies may also be problematic as these electrons can dissipate a significant fraction of the pulse power.

The characteristics of the ion energy and angular distributions (IEADs) incident onto the wafer are critical to determination of the junction properties. The IEADs are sensitive functions of the bias voltage waveform and the plasma parameters that determine the sheath properties (e.g. pressure, power, and reactor configuration). Characterizing the consequences that these parameters have on IEADs is important to improve the uniformity, repeatability and reliability of the implantation process.
1.4 Seasoning of Plasma Reactors

Wafer-to-wafer reproducibility during plasma etching of semiconductor devices continues to remain a challenge.[29,30] To insure that the critical dimensions of devices are consistently reproduced on a wafer-to-wafer basis, a uniform plasma with the same ion density, electron temperature and fluxes to the wafer must be maintained wafer after wafer. Many etch processes employ low pressure (10s mTorr) plasmas, where the mean free paths of radicals and ions may be comparable to the reactor dimensions thereby increasing the importance of plasma-surface interactions on non-wafer surfaces.[31] The use of high plasma density discharges having high processing rates can additionally result in the buildup of etch products in the volume of the process chamber. These etch products can interact with and deposit on the wafer and non-wafer surfaces. When operating at constant pressure, the etch products, if of sufficiently high density, can displace the desired reactant species thereby reducing their fluxes to the wafer.[32,33]

Etch products can alter the gas phase composition of both ions and neutrals, and the electron temperature, not only by their being gas phase collision partners but also by way of wall surface reactions which may change reactive sticking coefficients.[34,35] For example, Zhou et al.[35] investigated the effect of wall conditions (temperature and cleanliness) on gas phase chemistry and Si and SiO\textsubscript{2} etching rates using a CF\textsubscript{4} plasma. They found that if the initial wall is not clean, CF\textsubscript{2} and CF\textsubscript{3} densities increase with wall temperature, varying by as much as \textasciitilde80\% when compared to densities in reactor with clean walls. The etch rate of SiO\textsubscript{2} was found to be fairly independent of the wall temperature or cleanliness while the etch rate of Si decreased with wall temperature and as the walls were deposited on. Ullal et al.[36] observed a gradual increase in gas phase SiCl\textsubscript{x} and Cl densities and an increase in the total ion flux to the substrate in a Cl\textsubscript{2}...
inductively coupled plasma in the absence of a Si wafer. These trends were attributed to the coating of the chamber walls with a glassy silicon oxychloride film resulting from sputtering of the quartz window (the only source of Si and O). Cleaning the walls with an SF₆ plasma restored the plasma to its original properties.

The deposition of etch products (or feedstock gas fragments) on the interior surfaces of the plasma chamber can result in the drift of process variables, such as etch rates, etch profiles, selectivity and uniformity. The gradual change in reactor wall conditions in this manner is referred to as seasoning of the chamber. A reactor undergoing seasoning with changing wall conditions may experience a drift in process conditions whereas a well seasoned reactor has walls that are fully passivated and so will have achieved a steady state set of conditions. For example, Kim et al.[37] demonstrated the consequences of reactor seasoning on etch rate and uniformity of etching p-Si in an inductively coupled Cl₂ plasma. They observed the maximum etch rate to shift from the center of the wafer in an unseasoned reactor to the edge of the wafer when the walls were fully passivated, in this case, with a silicon oxychloride film. Although the sensitivity of process parameters to the wall conditions is well known, at present there is no generally accepted way of controlling reactor wall conditions.

To eliminate process drift, plasma chambers are often seasoned using a sacrificial wafer prior to processing a production wafer to coat the walls with a film that would otherwise be deposited during the course of etching the production wafer. When a reactor is properly seasoned, the inner surfaces are passivated to an unchanging state before starting to process the production wafer. Although the ideal situation is to season the reactor with the same process as used for the production wafer, other chemistries may be used to speed the seasoning step with the choice of the wall passivation depending on the material being etched, and the gas mixture
being used to perform the etch. Several researchers have proposed cleaning procedures but a common consensus is yet to be reached.[38-41]

One such technique is the use of self-cleaning chemistries in which a feedstock gas has the specific role of minimizing (by way of etching) the net deposition rate of etch products on the reactor walls.[38] For example, the deposition of silicon oxychloride film has been shown to decrease with the addition of CF$_4$ in feedstock gas.[39] This approach is promising but does not entirely prevent formation of coatings on the reactor walls. For example, the deposition of SiO$_2$ based species may be reduced but the deposition of carbon-based materials increases. The deposition of these organic polymer layers can be mitigated with the addition of O$_2$. Another strategy is to remove the passivation by plasma cleaning after each production wafer to reset the chamber to known conditions, though wafer throughput is slowed due to the additional cleaning step. For silicon etching processes, the reactor dry-cleans can be achieved using fluorine-based chemistries, typically SF$_6$/O$_2$.[40] However, the use of fluorine-based plasmas with, for example, Al$_2$O$_3$ reactor walls results in formation of and accumulation of nonvolatile AlF$_x$ on reactor walls, eventually results in process drifts.[41]

To eliminate the costs associated with cleaning of reactors after each wafer to combat wafer-to-wafer seasoning and drift, feedback control with in situ diagnostics can be used to monitor plasma properties and take corrective actions to restore a desired performance level.[42-44] Specifically, feedback control schemes have been applied to control p-Si etch rates in a Cl$_2$ plasmas.[45-48] The choice of actuators and sensors are governed by experimentally measurable quantities. For example, Donnelly[49] showed that optical emission actinometry can be used to determine absolute Cl$_2$ densities when p-Si is etched in Cl$_2$ helicon resonator plasma. Garvin et al.[50] developed a microwave cavity resonance sensor to measure plasma density. Direct
measurement of etch rate has also been enabled by using surface characterizing optical techniques such as spectroscopic ellipsometry (SE). However, p-Si is a difficult film to measure using SE because of presence of ~10-20 nm level surface roughness. As such, Sarfaty et al. developed two-color laser interferometry to determine etch rate and etch selectivity of unpatterned p-Si and SiO₂ films in Cl₂ plasma.

The popular choices for actuators include rf power to the wafer and/or to the antenna, gas flow rate and gas pressure. Choe et al. showed that the silicon etch rate is controlled by the ion current to the wafer in a Cl₂ plasma. Patrick et al. showed that the rf peak voltage and sheath voltage have similar correlations. Lin et al. implemented a proportional-integral (PI) controller choosing rf power to the wafer and antenna as actuators to maintain a constant ion current and rms rf voltage (control variables). Sarfaty et al. implemented a proportional integral derivative (PID) controller to maintain etch rate by means of rf power to the wafer in a magnetically confined inductively coupled plasma (ICP) tool.

Although many experiments have investigated wafer-plasma interactions in the context of chamber seasoning, few models have addressed the long term drift of plasma and etch properties resulting from wall contamination and seasoning.

1.5 Plasma Atomic Layer Etching

The thinning of the dielectric in the metal (and non-metal) gate stacks, advanced 3-dimensional structures (e.g., double and tri-gate MOSFETs), extreme selectivity, and atomic layer resolution present extreme challenges for plasma etching in meeting future technology nodes. The most challenging of these requirements may be atomic layer control. Plasma-assisted etching typically relies on energetic ion bombardment to define anisotropic
Although high energy ion bombardment provides high rates of etching it makes obtaining selectivity between materials difficult and so makes precise control of either rate or selectivity on a monolayer basis difficult. Chemically enhanced selective processes which rely upon passivation layers, such as fluorocarbon plasma etching of dielectrics, are additionally challenged to obtain monolayer control or the desired feature size. To obtain the necessary selectivity, plasma atomic layer etching (PALE) may be necessary.

PALE is a technique analogous to plasma atomic layer deposition (PALD) in which processing proceeds in a cyclic, self-limiting manner. The basis of PALE is reliance on a chemically enhanced process whereby passivation of the top layer of the substrate reduces activation energy by ion bombardment required to remove that layer. For example, passivation of the top layer of Si with Cl atoms producing SiClₓ complexes reduces the ion energy required to remove the Si as a gaseous SiClₓ etch product compared to directly sputtering the Si atom. If a single layer of SiClₓ can be formed followed by ion bombardment having an energy below the threshold for directly sputtering Si, atomic layer etching may be achieved. As such, a single cycle of the PALE in which a monolayer of material is removed is schematically shown in Fig. 1. The cycle consists of first exposing the substrate to a minimally etching plasma to passivate the top atomic layer with only that amount of precursor required to remove a single underlying layer. The second step is exposure to an etching plasma to remove the top layer in a self-limiting manner by keeping the incident ion energies below the threshold for sputtering of the substrate but above that for chemically sputtering the passivated layer. In principle, completion of one cycle results in etching of a single monolayer and the cycle can be repeated to etch as many monolayers as required. The self-limiting aspect of PALE is obtained by controlling ion energies in such a way that once the top monolayer of passivated material is
removed no further etching of the underlying material can occur. If this control is not achieved, etching beyond the top monolayer may occur and atomic level resolution is lost.

Atomic layer etching technology has been previously investigated for GaAs and Si devices. Atomic layer etching was first demonstrated for GaAs devices using an electron beam excited plasma.[64] The sequence consisted of a Cl₂ gas pulse to passivate the GaAs surface, a purge cycle to remove excess Cl₂, bombardment with 100-eV electrons followed by purge of the by-products. The etch rate was 0.1 nm per cycle and was independent of the Cl₂ exposure time. Meguro et al.[65] used a beam of 25 eV Ar⁺ ions using a similar method to increase the etch rate to 0.2 nm per etch cycle. However, increasing the Cl₂ dose required longer Ar⁺ irradiation to remove the excess adsorbed Cl₂ before etching occurred. Other investigations in PALE of GaAs involved energetic electron bombardment[66], KrF excimer laser irradiation[67] and chemical beam etching.[68]

PALE of Si has also been investigated using halogen gases for passivation and Ar⁺ ion bombardment for removal of the passivation layer. Horiike et al.[69] demonstrated atomic layer etching of Si using cryogenic adsorption of F atoms followed by Ar⁺ ion bombardment. Cooling of the substrate to 113 K decreased spontaneous etching of the Si by F₂. The etch rate was a function of F atom mole-fraction in the flow and of the exposure time of Si to F atoms. As a result, self-limiting etching was not achieved. Matsuura et al.[70,71] demonstrated PALE of Si at room temperature using Cl₂ gas and Ar⁺ ions generated in an electron cyclotron resonance plasma. However, the Ar⁺ ion bombardment energy or fluence were not sufficient to remove a complete atomic layer of silicon per cycle. Athavale and Economou[72] demonstrated complete removal of an atomic layer of silicon per cycle using Cl₂ as a passivant and a helicon plasma as a source of Ar⁺ ions. By adjusting the dc bias on the substrate, the Ar⁺ ion bombardment energy
could be controlled to etch one atomic layer of silicon per cycle. The etch was self-limiting with respect to both chlorine dose and the ion dose.

S.D. Park et al.[73] used an inductively coupled plasma (ICP) ion gun as the source for Ar⁺ ions and investigated PALE of Si by chlorine. The etch rate was dependent on chlorine flow-rate (necessary for complete passivation of the substrate surface) and the fluence of Ar⁺ ions (necessary for complete removal of an atomic layer). However, self-limiting etch rates could be achieved for most conditions. Previous efforts at achieving PALE of Si employed ions, albeit at low energy, which although eliminating physical damage may not eliminate electrical damage. To address the damage issue, PALE of Si was investigated by Park et al. using Cl₂ passivation followed by irradiation with an Ar neutral beam.[74,75] Although, the etch rates dependent on the Cl₂ pressure and Ar neutral beam fluence, one atomic layer etching per cycle of Si for (100) and (111) orientations was obtained.

The PALE strategies demonstrated thus far typically employed a specialized plasma equipment. When coupled with the need to rapidly etch overlying layers prior to reaching the interface, implementing theses strategies will likely require at least two processing chambers; the first to rapidly etch to the interface (the main etch) and the second more specialized apparatus to obtain monolayer resolution at the interface. This represents additional costs to integrate the specialized equipment with conventional plasma equipment and to provide space in the clean room, as well as additional processing times and wafer handling steps. To address these additional costs, it is desirable to perform PALE in conventional plasma equipment in which both the main etch and monolayer capable processes are performed, and which can be more economically integrated with current technologies. Even if this goal is achieved, if different gas mixtures are used for the passivation and etching steps, PALE could be slowed by having to
purge the different gas mixtures between steps. As such, the speed of PALE could be increased, if the purge steps can be eliminated and the entire cycle performed using a single gas mixture. To eliminate the purge step, precise control of the ion energy and angular distribution (IEAD) is necessary to discriminate between the threshold energies of the passivated and unpassivated surfaces.[76]

One method to control the ion energies incident on the wafer is using a non-sinusoidal bias waveform to narrow the spread in energy.[77-80] It has been demonstrated in both reactive ion beam etching[81] and plasma etching[77,78] that selectivity can be significantly improved using a narrow (in energy) IEAD where the average ion energy is tuned to a value between the threshold energies of the two materials. Rauf computationally demonstrated that the sheath voltage can be manipulated by the shape of the applied waveform.[79] One strategy for PALE would be to employ non-sinusoidal biases to discriminate between the threshold energies during the passivation and etch steps, and thereby possibly eliminate the need to use different gas mixtures (and so eliminate the purge step). Since this strategy requires only a change in the bias waveform, which in principle requires no change in the plasma etching chamber, the same chamber and gas mixture could be used for both the main etch and the PALE steps.

1.6 Modeling of Plasma Processes

Plasma processes are physically and chemically complex phenomena, and are often difficult to thoroughly characterize experimentally. Further, the high cost of equipment design and experiments for plasma processes in the semiconductor industry, plasma modeling and simulation are desirable to assist in predicting trends. Another benefit of modeling is that by making comparisons between experiments and simulations the understanding of plasma
processes can be improved. Considerable attention has therefore been paid to computational modeling of plasmas processes in the last 15 years. Some aspects of plasma processes can now be reliably analyzed using commercially available software, while other areas remain topics of intense research. With growing complexity of plasma processing applications, introduction of new materials at an unprecedented pace, and structure dimensions approaching nanometer scale, it is imperative that modeling will play a strong role in design of future plasma processing tools and processes. A brief review of plasma models is included in this section. More details can be obtained in the cited references. Attention here will focus only on computational models. The importance of analytical models (e.g., Refs. 82 and 83) cannot however be de-emphasized as they remain invaluable tools for plasma tool design and engineering analysis.

Computational plasma process models can generally be sub-divided into three categories: equipment models, feature scale models and atomistic models. These models are often inter-coupled to analyze complicated problems but large disparity in time and spatial scales makes simultaneous simulation of all pertinent physical and chemical phenomena very challenging. Equipment models typically address gas flow in the plasma reactor, plasma generation, chemistry within the plasma, reactor electrodynamics, plasma interactions with driving circuits and sheath dynamics. These models address phenomena on relatively large spatial scales (cm) and moderate time scales (ns-ms). Feature scale models simulate etching and related surface phenomena within small structures. Analysis often relies on macro-variables (sticking coefficients, sputtering yields etc.) to represent surface processes. Feature scale models address issues on small spatial scales (μm) and relatively long time scales (seconds). A new class of models utilizes molecular dynamics or ab-initio techniques to investigate etching relevant
surface processes from first principles. These models address issues on very small spatial (nm) and temporal (fs-ps) scales.

Kinetic, fluid and hybrid techniques have all been explored since the early days of multi-dimensional plasma reactor modeling. Kinetic models include models that attempt to directly solve the Boltzmann equation[84] and particle-in-cell models[85] which self-consistently track macro-particles and their interactions. As such, these techniques are computationally expensive and it becomes progressively difficult to represent the complexity of actual plasma processes, these techniques are primarily used now for research or specialty applications. Fluid[86] and hybrid[87] techniques, however, have been explored in considerable detail and several commercial software[88,89] based on these techniques are available. In fluid and hybrid plasma models, Maxwell equations are solved in conjunction with equations governing species mass, momentum and energy balance to determine important plasma properties. Electrons generally drive etching relevant plasmas and have a broad energy distribution that strongly impacts their transport properties and plasma chemistry. Fluid and hybrid models either assume a Maxwellian electron energy distribution, solve Boltzmann equation to determine electron energy distribution or use Monte Carlo techniques. Fluid models solved either through finite element or finite difference methods tend to be far faster than Monte Carlo methods, but for very low pressures (<100s mTorr) the mean free path becomes comparable to the system dimensions. At this point, the plasma fluid can no longer be considered to be at thermodynamic equilibrium. By using Monte Carlo methods to examine the electron kinetics and/or the heavy body transport, the nonequilibrium effects can be accounted for when coupled with the fluid models. Fluid plasma models have been coupled to models of external matching circuits[90], kinetic models to compute quantities not well captured by fluid model (for example, ion and neutral energy and
angular distributions at surfaces)\cite{91}, and surface physics models.\cite{92} It is fair to state that plasma equipment modeling is a mature area and plasma reactor dynamics can be simulated with reasonable fidelity. Uncertainty of plasma chemistry\cite{93} (atomic and molecular processes, heavy particle reactions) is often the biggest hurdle that hinders the use of plasma equipment models for an even broader set of applications. Plasma equipment models have been successfully applied to the modeling of capacitively coupled plasma etchers (single frequency, dual frequency,\cite{94} magnetized\cite{95}), inductively coupled plasma sources,\cite{87} ECR\cite{96} and helicon\cite{97} plasmas. Fair to adequate mechanisms exist for many of the commonly used plasma etching gases.

Feature scale models have immensely grown in maturity in the last few years. Several techniques have been explored for feature scale modeling and they all remain equally important for problem solving. Broadly speaking, feature scale modeling has been done using Monte Carlo methods,\cite{98} string-based methods\cite{99} and level-set methods.\cite{100} In models based on Monte Carlo techniques, surface and material underneath is represented using macro-particles. Plasma species, whose characteristics are either assumed or determined (using plasma equipment models), are then bombarded on the material stack. A surface reaction mechanism is used to determine how the surface (representing a feature) evolves in time. Monte Carlo models allow representation of detailed surface processes and can easily account for sub-surface processes. In 1988, Cotler et al.\cite{101} developed a Monte Carlo topography model to examine argon ion sputtering of silicon and later extended the model to include chemical processes to compare physical, chemical, and physically enhanced chemical processes.\cite{102} May et al.\cite{103} developed a sputter etch topography model for argon impinging on silicon showing the effects of ion angular distribution on trench undercutting. However, there are negative aspects to these
methods. To overcome the statistical noise in the simulations, large number of particles often have to be used slowing down simulations considerably.

In string-based methods, the surface of the structure is represented using a set of interconnected strings in 2-dimensional models (or patches in 3-dimensional simulations). Fluxes on material surface are used in conjunction with a surface mechanism to determine how the strings or patches evolve in time. One model of this type is SPEEDIE, developed by Ulacia and McVittie[104] as well as Singh et al.[105], which has been used to examine etching and deposition related to metallization processes in VLSI fabrication. SPEEDIE originally utilized Monte Carlo methods to determine fluxes at the surface and calculate nodal motion and has been used to examine the relative importance of surface reemission in SiO₂ chemical vapor deposition. In 1991, Islamraja et al.[106] included the capability of producing analytic expressions for surface fluxes based on radiative heat transfer equations. Etching of overhang test structures investigated using SPEEDIE[107] showed very good agreement to experimental results. Another model of this type, EVOLVE, developed by Cale et al.[108] has also shown the capability to simulate deposition in VLSI fabrication. String-based techniques are computationally fast and it is relatively straightforward to implement most surface processes. Representation of sub-surface material and simultaneous etching and deposition is nonetheless a non-trivial task in string-based models. Level-set methods have been used for both etching and deposition modeling. The material is represented by a function, one of whose equipotential planes coincides with the structure surface. Simulation methodology is similar to string based models although the surface is evolved by solving a differential equation governing the function. Level-set methods are slower than string-based technique but are numerically more stable. Representation of sub-surface materials and simultaneous etching and deposition are however
challenges that level-set methods share with string-based models. Feature scale models have been applied to the modeling of a wide variety of plasma etching processes including polysilicon[109] and photoresist[110] etching, and SiO$_2$[111] and low-$\kappa$[112] dielectric etching.

Molecular dynamics (MD) models have in recent years started playing a major role in unearthing the fundamentals of interaction of plasma with features on a wafer. In the MD models, quantum mechanical interactions between atoms (both material and plasma based) are represented using pseudo-potentials that are either determined experimentally or using ab initio quantum mechanics models. These pseudo-potentials are used in classical mechanics models to simulate the dynamics on the material surface in contact with the plasma. MD models have been used to understand the formation of reactive layers on a variety of films, and the role that different ions and radicals play in plasma etching or surface passivation. These models have been used to examine, for example, Cl$_2$[113] and fluorocarbon etching of Si[114], fluorine etch of SiO$_2$[115] and fluorocarbon etching of SiO$_2$[116]

1.7 Conclusions

The relevance of plasma discharges in semiconductor processing is clear. However, to continue the trend of shrinking critical dimensions at advanced technological nodes, advanced methods of plasma operation need to be investigated. Further, physics issues mediated at low pressures in well-established and advanced processing techniques need to be resolved. In this work, two advanced processing techniques have been investigated. First, pulsed plasma ion implantation technique is investigated to achieve doping of silicon based substrates to obtain ultra-shallow junctions. Second, atomic layer etching using in situ plasmas has been investigated for feasibility of integration with conventional plasma processes thereby minimizing the cost of
ownership related to integration of specialty plasma equipment to achieve the same. The low pressure operation regime being employed today in plasma etching has raised concerns related to the interactions of plasma with non-wafer surfaces. There is clear evidence of process drifts arising out of such interactions due to interactions of etch by-products with the wafer. A more clear understanding of the underlying physical phenomena is mandated to address such issues.

The algorithms developed in this work were incorporated into the 2-dimensional (2d) Hybrid Plasma Equipment Model (HPEM) which is discussed in detail in Chapter 2. As an introduction, the HPEM consists of three modules: the Electromagnetics Module (EMM), Electron Energy Transport Module (EETM), and Fluid Kinetics Module (FKM). The modules are executed iteratively until convergence. The rates and the source functions of electron impact reactions are calculated in the EETM module using Monte Carlo techniques. Investigation of the surface profile evolution for the etch profiles have been done using the 2-dimensional (2d) Monte Carlo Feature Profile Model (MCFPM) which is discussed in detail in Chapter 3.

These models were then used to computationally investigate plasmas sustained in Ar/NF3 gas mixtures in an ICP reactor to study pulsed plasma ion implantation and the results are presented in Chapter 4. Design optimization to obtain a uniform plasma leading to uniform ion energy distributions incident on the wafer has been explored. Plasma atomic layer etching has been investigated for geometries of interest to future technological nodes, using ICP and CCP reactors as model tools. Etching strategies utilizing PALE processes in conventional plasma equipment are discussed in Chapter 5.

To enable the investigation of plasma-surface interactions, the Surface Chemistry Module (SCM) was linked to the HPEM. Surface reactions in the HPEM are addressed using a flux in – flux out boundary conditions. In addition to providing the surface boundary conditions for the
HPEM, the SCM computes rates of material addition and removal on all surfaces in contact with the plasma. The SCM is discussed in detail in Chapter 6. The algorithm was modified to include real-time ion energy distribution to obtain surface reaction rates. Results from a computational investigation of the effect of interactions of etch by-products with wafer are presented in Chapter 7 using Si etching in Ar/Cl₂ plasma sustained in an ICP reactor as the case study. Feedback control to minimize process drifts was achieved using a proportional controller algorithm.
1.8 Tables

**Processing:**
- Surface Processing
- Nonequilibrium (low pressure)
- Thermal (high pressure)

**Flat-Panel Displays:**
- Field-emitter arrays
- Plasma displays

**Volume Processing:**
- Flue gas treatment
- Metal recovery
- Waste treatment

**Radiation Processing:**
- Water purification
- Plant growth

**Chemical Synthesis:**
- Plasma spraying
- Diamond film deposition
- Ceramic powders

**Switches:**
- Electric power
- Pulsed power

**Energy Converters:**
- MHD converters
- Thermionic energy converters

**Light Sources:**
- High intensity discharge lamps
- Low pressure lamps
- Specialty sources

**Medicine:**
- Surface treatment
- Instrument sterilization

**Surface Treatment:**
- Ion implantation
- Hardening
- Welding
- Cutting
- Drilling

**Isotope Separation**

**Propulsion**

**Beam Sources**

**Lasers**

**Material Analysis**

*Table 1.1.* Some applications of technological plasmas
Fig. 1.1: Classification of plasmas based on density and temperature of electrons.
Fig. 1.2: The formation of the sheath potential drop near a surface. (a) The electron diffusion flux is much larger than the ion diffusion flux to the surface due to different diffusivities. (b) A positively charged region is formed near the surface. (c) The net charge produces a plasma potential drop and a sheath field.
Fig. 1.3: Current trend for transistor scaling as per Moore’s Law.[7]
Fig. 1.4: Schematic of an beam-line ion implanter. The electron confinement beam guide maintains high currents at energies less than 10 keV.[11]
Fig. 1.5: Schematic of pulsed plasma implantation. The pulsed dc negative bias is set at the desired implant voltage. Ions are extracted from the plasma, accelerated across the sheath and implanted into the wafer.[19]
Fig. 1.6: Schematic of the Plasma Atomic Layer Etching (PALE) process. At the end of one cycle, a monolayer is etched. If ion energies exceed the threshold energy of the underlying material, more monolayers may also be etched.
1.10 References


excimer laser: Approach to Atomic-Order-Controlled Etching by Photo Induced


Miyazaki, and M. Hirose, “Digital chemical vapor deposition and etching technologies

70. T. Matsuura, J. Murota, Y. Sawada, and T. Ohmi, “Self-limited layer-by-layer etching of
Si by alternated chlorine adsorption and Ar\(^+\) irradiation,” *Appl. Phys. Lett.* **63**, 2803
(1993).

dependence of self-limited atomic-layer etching of Si with chlorine adsorption and low-

72. S.D. Athavale and D.J. Economou, “Realization of atomic layer etching of silicon,” *J.

(2005).

74. S.-D. Park, D.-H. Lee, and G.-Y. Yeom, “Atomic Layer Etching of Si(100) and Si(111)


89. http://www.cfdrc.com


2. HYBRID PLASMA EQUIPMENT MODEL

2.1. Introduction

In this chapter, the models and the techniques used for these investigations are described. All the algorithms developed in this work have been integrated into the Hybrid Plasma Equipment Model (HPEM). An overview of the HPEM is given here so that the thesis work can be understood in the context of the entire hierarchy.

2.2 Hybrid Plasma Equipment Model (HPEM)

The HPEM is a plasma equipment model developed by the Computational Optical and Discharge Physics Group to numerically investigate low-pressure and low temperature plasma processing reactors in two and three dimensions.[1-8] The HPEM can model a variety of reactor geometries, and it can analyze different gas chemistries and generate the corresponding plasma parameters. A flow diagram of the HPEM is shown in Fig. 2.1. The HPEM addresses the plasma physics and plasma chemistry in a modular fashion. The main modules are the Electromagnetics Module (EMM), Electron Energy Transport Module (EETM), and Fluid Kinetics Module (FKM). The HPEM iterates on these different coupled modules to generate the plasma parameters.

The inductively coupled electromagnetic fields and magnetostatic fields are computed in the EMM, which is discussed in Section 2.2.1. These fields are used in the EETM to produce electron transport coefficients. Electron Temperature and electron impact rate coefficients, as a function of position, are obtained by either using an Electron Monte Carlo simulation (EMCS) or by solution of the fluid electron energy equation coupled with a solution of the Boltzmann
equation. The EMCS is also used for electron beam transport. This module is discussed in Section 2.2.3. Results of the EETM are transferred to the FKM to determine plasma source and sink terms. The FKM solves the fluid continuity equations for species densities and plasma conductivity and solves Poisson’s equation for the electrostatic fields. The densities, conductivity, and electric fields obtained from the FKM are then transferred to the EMM and EETM. These three modules are solved successively in a time slicing manner or until a converged solution.

Several in-line modules of the HPEM have been developed for other specific purposes. The Plasma Chemistry Monte Carlo Module (PCMCM) computes energy and angular dependencies of fluxes at specified surface locations by using outputs of the FKM.[9] This module is discussed in Section 2.2.4. Surface reactions in the HPEM are addressed by the Surface Chemistry Module (SCM) which not only provides the boundary conditions for the HPEM but also computes rates of material addition and removal on all surfaces in the reactor which, for the wafer, yields an etch rate.[10] The structure of the SCM will be discussed in Chapter 6. Feedback control strategies and algorithms on plasma processing equipment are addressed by the Virtual Plasma Equipment Model (VPEM) which uses the HPEM for simulating the plasma equipment.[11] The structure of the VPEM is discussed in Section 2.3.

2.2.1 The Electromagnetics Module

The solution for the electromagnetic fields requires knowledge of the plasma conductivity, which is obtained from the other modules. The EMM provides time-harmonic azimuthal electromagnetic fields, and it provides the static magnetic fields generated by the
permanent magnets or by equivalent dc loops, that is, currents that change on time scales which are long compared to the time in which the plasma reaches quasi-equilibrium.

The EMM module calculates the spatially dependent azimuthal electric fields by solving Maxwell’s equation under time harmonic conditions. Assuming azimuthal symmetry, Maxwell’s equation for electric fields is reduced to

$$-\nabla \cdot \left( \frac{1}{\mu} \nabla E_\phi \right) = \omega^2 e E_\phi - i \omega J_\phi$$  \hspace{1cm} (2.1)

where $\mu$ is the permeability, $E_\phi$ is the azimuthal electric field, $\omega$ is the frequency of the source current, $\varepsilon$ is the permittivity, and $J_\phi$ is the total current consisting of driving and conduction currents. The conduction current $J_c$ is calculated from $J_c = \sigma E_\phi$, where $\sigma$ is the conductivity or by explicitly calculating electron currents in the EMCS[12]. At pressures where the electrons are sufficiently collisional, the conductivity of the plasma is

$$\sigma = \frac{q_e^2 n_e}{m_e} \frac{1}{\nu_{me} + i\omega}$$  \hspace{1cm} (2.2)

where $q_e$ is the unit electron charge, $n_e$ represents electron density, $m_e$ denotes electron mass, $\nu_{me}$ is the momentum transfer collision frequency of electrons, and $\omega$ is the driving frequency.

Maxwell’s equations are solved using the method of successive over relaxation (SOR). The weighting coefficients and the convergence criterion for the SOR are adjustable simulation parameters.
The static magnetic fields are solved in the radial and axial directions assuming azimuthal symmetry. Under these conditions, the magnetic field can be represented as a vector potential which has only a single component in the $\phi$ direction. The current loops, which provide source terms when solving for vector potential $A$, by differentiation, yields the static magnetic fields

$$\nabla \times A = B; \nabla \times \frac{1}{\mu} \nabla \times A = j$$  \hspace{1cm} (2.3)

where $\mu$ is the permeability, and $j$ is the current density of the source current loops. The vector potential is solved as a boundary value problem using SOR, with the same convergence criteria as the electric field.

A circuit module (CM) is included in the EMM which models a matchbox circuit as well as the coils. The impedance of the matchbox is matched to the coil impedance, allowing the deposited power to be maximized. The source voltage is also adjusted from iteration to iteration allowing the power specified by the input file to be matched and maintained.

2.2.2 The Fluid Kinetics Module

In the FKM, the continuum transport equations for the gas species are solved simultaneously with the electrostatic potential to determine the spatial distribution of species densities as well as the momentum flux fields within the reactor. To solve for these plasma properties, the electron transport properties and the chemical reaction rates are obtained from the EETM. Ion and neutral transport coefficients are obtained from a database or by using Lenard-Jones parameters. To self consistently consider the electrostatic fields, either Poisson’s equation
can be included, or quasi-neutrality allowing ambipolar fields can be assumed. The continuity
equation for all species is

$$\frac{\partial N_i}{\partial t} = -\nabla \cdot \Gamma_i + S_i \quad (2.4)$$

which can be used to solve for the species densities where $N_i$, $\Gamma_i$, and $S_i$ are the respective
density, flux, and sources for species $i$.

The electron flux $\Gamma_i$ is determined by the drift diffusion equation

$$\Gamma_i = \mu_i q_i N_i \overline{E_x} - D_i \nabla N_i \quad (2.5)$$

where $\mu_i$ is the mobility of species $i$, $D_i$ is the diffusion coefficient, $q_i$ is the species charge in
units of elementary charge, and $E_x$ is the electrostatic field. In this work, we instead used the
Scharfetter-Gummel discretization for fluxes.[13] In this method the flux $\tilde{\phi}_{i+1/2}^i$ between density
mesh points $(i, i+1)$ separated by $\Delta x$ is given by

$$\tilde{\phi}_{i+1/2}^i = \frac{\alpha \bar{D}(n_{i+1} - n_i \exp(\alpha \Delta x))}{1 - \exp(\alpha \Delta x)} \quad (2.6)$$

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

(2.7)

and \( \bar{D} \) and \( \bar{\mu} \) are the average diffusion coefficient and mobility in the interval. The ion and neutral flux calculation can be performed using the drift diffusion equation or by including the effects of momentum by the replacement of the diffusional term with terms for pressure, advection, and collisionality:

\[
\frac{\partial \Gamma_i}{\partial t} = \frac{1}{m_i} \nabla (N_i k T_i) - \nabla \cdot (N_i \bar{v}_i \bar{v}_i) + \frac{q_i}{m_i} N_i \bar{E} - \sum_j \frac{m_j}{m_i + m_j} N_i N_j (\bar{v}_i - \bar{v}_j) \nu_{ij} 
\]

(2.8)

where \( T_i \) is the species temperature, \( \bar{v}_i \) is the species velocity given by \( \frac{\Gamma_i}{N_i} \), and \( \nu_{ij} \) is the collision frequency between specie \( i \) and specie \( j \). The viscosity is included for neutrals only. The gas and ion temperatures are determined from the energy equation for each species:

\[
\frac{\partial N_i c_v T_i}{\partial t} = \nabla \cdot \kappa_i \nabla T_i - P_i \nabla \bar{v}_i - \nabla \cdot (\bar{\phi}_i \varepsilon_i) + \frac{Nq_i^2}{m_i \bar{v}_i} E_z^2 + \frac{Nq_i^2 \bar{v}_i}{m_i (v_i + \omega^2)} E^2
\]

\[
+ \sum_j 3 \frac{m_j}{m_i + m_j} N_i N_j R_{ij} k (T_j - T_i) 
\]

(2.9)

where \( N_i \) is the density of specie \( i \), \( c_v \) is specific heat, \( T_i \) is the species temperature, \( \kappa_i \) is the thermal conductivity of specie \( i \), \( P_i \) is the partial pressure of specie \( i \), \( \bar{v}_i \) is the specie velocity, \( \bar{\phi}_i \) is the flux of specie \( i \), \( \varepsilon_i \) is the internal energy of specie \( i \), \( E_z \) is the electrostatic field, \( E \) is the RF field, \( m_i \) is the mass of specie \( i \), \( m_{ij} \) is the reduced mass, \( v_i \) is the momentum transfer collision
frequency for specie \(i\), and \(R_{ij}\) is the collision frequency for the collision process between specie \(i\) and specie \(j\).

Time-dependent electrostatic fields are obtained either by solution of Poisson’s equation or based on quasi-neutrality allowing an ambipolar approximation. Poisson’s equation is given by

\[
- \nabla \cdot \varepsilon \nabla \Phi^{t+\Delta t} = \rho^{t+\Delta t}
\]  

(2.10)

where \(\varepsilon\) is the permittivity, \(\Phi^{t+\Delta t}\) is the electric potential at time \(t+\Delta t\), and \(\rho^{t+\Delta t}\) is the net charge density at time \(t+\Delta t\). Poisson’s equation is calculated semi-implicitly by approximating the charge density linearly as

\[
\rho^{t+\Delta t} = \rho' + \Delta t \left. \frac{\partial \rho}{\partial t} \right|_{t+\Delta t}
\]

(2.11)

where \(\rho^{t+\Delta t}\) is the charge density at time \(t+\Delta t\), and \(\rho'\) is the charge density at time \(t\). The evolution rate of the charge density \(\frac{\partial \rho}{\partial t}\) is determined by the divergence of the total current density \(\mathbf{j}\):

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{j} + S
\]

(2.12)
where $S$ is the source function of charges. When using drift-diffusion, in the plasma region, 
\[ j = q_i (-D_i \nabla n_i + q_i \mu_i (-\nabla \phi)) \] for electrons and \[ j = q \Gamma \] for ions. When using Scharfetter-Gummel fluxes, \[ j = f(\Phi, N) \], and so:

\[
\frac{\partial \rho}{\partial t} = \nabla \cdot \left( j + \frac{\partial j}{\partial \Phi} \Delta \Phi + \frac{\partial j}{\partial N} \Delta N \right) + S \tag{2.13}
\]

In materials, \[ j = \sigma (-\nabla \phi) \] where $\sigma$ is the material conductivity. By making the potential fully implicit in this scheme while using explicit terms for the assumedly more slowly varying species properties such as density and temperature, the time step used in the SOR solution can be lengthened beyond the dielectric relaxation time and greatly accelerate solution over the fully explicit formulation.

The second option is to compute electrostatic fields using a quasi-neutrality approximation over the entire plasma region. Under such an assumption the electron density can be set equal to the total ion density at all locations. To maintain this charge neutrality requires that

\[
- \nabla \cdot \Gamma_e + S_e = \sum_i q_i (-\nabla \cdot \Gamma_i + S_i) \tag{2.14}
\]

or

\[
\nabla \cdot (\mu_e n_e \nabla \phi + D_e n_e) + S_e = \sum_i q_i (\nabla \cdot (-\mu_i n_i \nabla \phi + D_i \nabla n_i) + S_i) \tag{2.15}
\]
where $S_e$ and $S_i$ represent electron and ion source functions, respectively, due to both internal and external sources such as electron beams. The flux terms are replaced by their drift diffusion approximations and the terms are rearranged to get

$$\sum q_i \nabla \cdot \left( q_i n_i \mu_i \nabla \phi - D_i \nabla n_i \right) = \sum q_i S_i$$

(2.19)

where the summations are taken over all charged species including both electrons and ions. By reducing the system to a steady-state solution, the dielectric relaxation time is removed as a limit allowing much larger time steps to be taken, which are limited only by the Courant limit.

A semi-analytic sheath model (SM) has also been integrated with the FKM to represent the fields and fluxes at gas-solid boundaries under conditions where the actual sheath thickness is less than the mesh spacing. A multi-species form of Riley’s unified sheath model[14] is used to relate the sheath charge $Q$ and boundary conditions to the potential drop. This potential drop across the sheath produced by the semi-analytic sheath model is then applied as a jump condition at plasma wall boundaries in solving Poisson’s equation for the entire reactor.

### 2.2.3 The Electron Energy Transport Module

In the Electron Energy Transport Module, the power deposition into the electrons, as well as the electron impact sources, are modeled and the electron transport properties are computed. These can be solved in two different ways. The first method is to solve the 2d electron energy equation. Electron transport properties as a function of temperature are obtained by solving the 0d Boltzmann equation. The second method is to utilize a Monte Carlo simulation, in which
electron pseudo-particles are moved in the computed fields and have collisions with the other plasma species. The trajectories are integrated over a period of time and the statistics are collected to generate the electron energy distribution functions (EEDs), which are then used to calculate the rate coefficients.

### 2.2.3.1 The Electron Energy Equation Method

When solving the electron energy equation the 0d Boltzmann equation is solved for a range of values of electric field divided by total gas density (E/N) in order to create a lookup table correlating average energy with a transport coefficient. The Boltzmann equation is expressed as

$$\frac{\partial f_e}{\partial t} + \mathbf{v} \cdot \nabla r f_e - \frac{e(E + \mathbf{v} \times \mathbf{B})}{m_e} \cdot \nabla v f_e = \left( \frac{\partial f_e}{\partial t} \right)_{\text{collision}}$$  \hspace{1cm} (2.17)

where $f_e = f_e(t, r, v)$ is the electron distribution function, $\nabla r$ is the spatial gradient, $\nabla v$ is the velocity gradient, $m_e$ is the electron mass, and $\left( \frac{\partial f_e}{\partial t} \right)_{\text{collision}}$ represents the effect of collisions. The resulting values are then used as a lookup table, which yields electron mobility, thermal conductivity, and energy-loss rate due to collisions and electron impact rate coefficients as a function of electron temperature. $T_e$ is defined as $\frac{2}{3} < \varepsilon >$, where $< \varepsilon >$ is the average energy computed from the EEDs.

With the EEDs known as a function of temperature, the steady state electron energy equation is solved as follows
\[ \nabla \kappa \nabla T_e + \nabla \cdot (\Gamma_e T_e) = P_h - P_l \]  

(2.18)

where \( \kappa \) is the thermal conductivity, \( T_e \) is the electron temperature, \( \Gamma_e \) is the electron flux, \( P_h \) is the electron heating due to deposition, and \( P_l \) is the power loss due to inelastic collisions. The electron flux \( \Gamma \) is computed in the FKM, and the power deposition rate is computed from the time-averaged value of \( j \cdot E \), where \( j = q \phi_e \). The electric field includes both the inductive field computed in the EMM and the electrostatic field computed in the FKM. The above equation is discretized and solved by SOR, with the transport coefficients updated based on the local electron temperature.

Alternatively, the electron energy equation can be implicitly integrated in time in the FKM to provide electron temperature, and impact and transport coefficients.

### 2.2.3.2 The Electron Monte Carlo Method

The Monte Carlo method is a fully kinetic treatment, which resolves the transport of electrons in electric and magnetic fields using a semi-implicit technique. Noncollisional heating can be kinetically resolved by producing electron currents, which are used to correct the assumption of collisional power deposition in the EMM.

The Electron Monte Carlo Simulation (EMCS) tracks the trajectory of electron pseudo-particles by moving them in the computed electric and magnetic fields as a function of time. A group of electrons is initialized from a Maxwellian distribution and randomly distributed within the rf period (when using harmonic fields), with starting locations randomly determined within the reactor volume weighted by the electron density computed in the FKM. The electron energy
range is divided into discretized energy bins for collision determination and this binning also helps in collecting statistics. The collision frequency, \( \nu_i \), within any energy bin is computed by summing all possible collision within the energy range

\[
\nu_i = \left(\frac{2 \varepsilon_i}{m_e}\right)^{\frac{1}{2}} \sum_{j,k} \sigma_{jk} N_j
\]

(2.19)

where \( \varepsilon_i \) is the average energy within the bin, \( \sigma_{jk} \) is the cross section at energy \( i \), for species \( j \) and collision process \( k \), and \( N_j \) is the number density of species \( j \). The time between the collisions is randomly determined using the maximum collision frequency for all energy bins. \( \Delta t = -\frac{1}{\nu} \ln(r) \), \( r \in (0,1) \). At the time of a collision, the reaction that occurs is chosen randomly from all the possible reactions for that energy bin. A null collision cross section makes up the difference between the actual collision frequency and the maximum collision frequency at any given spatial location. In this work electron-electron collisions are not considered. The velocity of the electrons is adjusted based on the type of collision it undergoes. If the collision is null then the electron’s trajectory is unaltered. Particle trajectories are integrated using the Lorentz equation.

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

(2.20)

and
where \( \vec{v}, \vec{E}, \) and \( \vec{B} \) are the electron velocity, local electric field, and magnetic field respectively.

Eq. (2.20) and (2.21) are updated using a second-order predictor corrector scheme. Electric fields are both the inductive fields computed in the EMM and the time-dependent electrostatic fields computed in the FKM. Time steps are chosen to be less than both 1% of the rf period and 1% of the cyclotron frequency, and small enough that the particles do not cross more than one-half computational cell in one time step. Several hundred to a few thousand particles are integrated in time for many rf cycles, typically greater than 100 rf cycles.

The statistics for computing the electron energy distributions (EEDs) are updated every time an electron is moved in the mesh, that is, at every time step using finite particle techniques. These statistics are collected into an array for energy \( i \) and location \( l \).

\[
F_{il} = \sum_j w_j \delta((\varepsilon_i \pm \frac{1}{2} \Delta \varepsilon_j) - \varepsilon_j) \delta((\vec{r}_i \pm \Delta \vec{r}) - \vec{r}_j) \tag{2.22}
\]

where the summation is over particles, \( w_j \) is the weighting of the particle, \( \varepsilon_i \) is the energy and \( \vec{r}_k \) is the bin location. The weighting \( w_j \) is a product of three factors; the relative number of electrons each pseudo-particle represents, the time step used to advance the trajectory, and a spatial weighting obtained using the method of finite-sized particles (FSP). At the end of the EMCS, the electron temperature, collision frequency and electron-impact rate coefficients are computed as a function of position from the EEDs. The EEDs, \( f_{ik} \), are obtained from the raw statistics, \( F_{ik} \), by requiring normalization of each spatial location.
\[ \sum_i F_{ik} \Delta \varepsilon_i = \sum_i f_{ik} \varepsilon_i^2 \Delta \varepsilon_i = 1 \] (2.23)

The electron temperature is defined by convention to be \( \frac{2}{3} < \varepsilon > \). The electron impact rate coefficient \( k_{ml} \) for electron impact process \( m \) and location \( l \) is computed as

\[ k_{ml} = \int_0^{\infty} \left( \frac{2\varepsilon}{m_e} \right)^{1/2} \sigma_m(\varepsilon) f_i(\varepsilon) \varepsilon_i^{1/2} d\varepsilon = \sum_i \left( \frac{2\varepsilon}{m_e} \right)^{1/2} \sigma_{ml} f_{il}(\varepsilon) \varepsilon_i^{1/2} \Delta \varepsilon \] (2.24)

### 2.2.4 The Plasma Chemistry Monte Carlo Module

To obtain the energy and angular distributions of reactive species to the surfaces in contact with the plasma, the PCMCM was developed for the HPEM. The PCMCM calculates the trajectories of plasma species in the gas phase and their collisions with surfaces. This module was originally a postprocessor to the HPEM. It used volumetric sources of plasma species, time-dependent electric fields, and sheath properties exported from the HPEM to obtain the angular and energy distributions of the fluxes using Monte Carlo techniques.[10] The PCMCM functions in a similar manner but also accounts for nonthermal, or in-flight fluxes, resulting from sputter sources in addition to the volumetric sources. Sputtered atoms and neutralized ions which are reflected from the target have kinetic energies of several eV. These species are not initially in thermal equilibrium with the buffer gas which has a temperature of \( \leq 0.3 \) eV. Under certain process conditions, these energetic particles may not thermalize prior to reaching the wafer. The trajectories and energies of these nonequilibrium particles are already
tracked by the sputter algorithms in the FKM. Statistics are collected on the energy and angle of pseudo-particles as they strike surfaces to produce angle-averaged energy distributions during the time evolution of the process and at the end of the process, the time-averaged ion energy and angular distributions (IEADs).

Based on these quantities, a rate of generation of species \( i \) as a function of position, \( G_i(\vec{r}) \) (cm\(^{-3}\)s\(^{-1}\)), is computed. This generation term accounts for all sources of species \( i \) on the right-hand side of reactions in the mechanism. The rate \( G_i(\vec{r}) \) also includes source functions on surfaces due to, for example, sputtering. In a similar fashion, a consumption rate \( C_i(\vec{r}) \) (cm\(^{-3}\)s\(^{-1}\)) is computed based on all reactions containing species \( i \) on the left-hand side of reactions in the mechanism. A local elastic collision frequency with each species is also computed. These elastic frequencies are added to the local consumption frequency \( C_i(\vec{r})\Delta V(\vec{r}) \) (\( \Delta V(\vec{r}) \) is the volume of the computational cell at location \( \vec{r} \)) to yield a total interaction frequency \( \nu_{\text{T}}(\vec{r}) \).

Null collision techniques are used at each spatial location to provide a reactor wide collision frequency \( \nu_{\text{i}} \) for each species \( i \).

Pseudo-particles of species \( i \) are launched from each computational cell at a time randomly chosen in the rf cycle with a weighting (or total number) proportional to \( G_i(\vec{r})\Delta V(\vec{r}) \). The velocity is randomly chosen from a Maxwell-Boltzmann distribution having a local temperature \( T_i(\vec{r}) \) for volumetric sources where the spatially dependent temperature for each species is computed by HPEM. The trajectories of the pseudo-particles are integrated for the time

\[
\Delta t = -\frac{1}{\nu_i} \ln(\tau)
\]  

(2.25)
where $\Delta t$ is the time step for movement of the pseudo-particle and $r$ is a random number distributed on (0,1). For ions, acceleration by the local electric field is accounted for. The time step used to increment the trajectory is limited by the time required to cross a specified fraction of the cell (typically 0.2). For ions, additional constraints are applied including a specified fraction of the rf cycle (typically 0.05), or the time to cross a specified fraction of the sheath width (typically 0.01).

At the end of the time step, Monte Carlo techniques are used to determine if the collision is real or null. If real, another random number is used to determine if the collision is elastic or consuming. If consuming, the particle is removed from the simulation. If elastic, the collision partner is identified using another random number and the velocity of the pseudo-particle is changed appropriately using standard elastic collision techniques. The one exception is for charge exchange collisions which are separately accounted for in the sum of collision frequencies. If an ion undergoes a charge exchange collision, its identity is changed to the neutral counterpart and the trajectory is retained. The trajectories are advanced until the pseudo-particles reach the vicinity of a surface. If the surface is chosen as one for which statistics on incident species are desired, ions are then integrated through the sheath, a computationally expensive process. For surfaces not selected, the particles are removed from the simulation. A similar process is followed for the neutrals, except for integration through the sheath.

### 2.3 Virtual Plasma Equipment Model (VPEM)

Feedback control with *in situ* diagnostics is typically used to monitor plasma properties and take corrective actions to restore a desired performance level. To make the HPEM suitable
for studying issues related to feedback control, the sensor, actuator, and programmable controller modules were developed.\[11\] The VPEM uses the HPEM for simulating the plasma equipment. A flow chart of the controller modules integrated HPEM is shown in Fig. 2.2.

The sensor module emulates quantities that are ideally measured by experimental sensors. The actuator module changes process parameters that can be externally controlled in experiments such as inductively coupled power, applied voltage on electrodes, gas pressure, flow rate, and mole fractions of gases in the feed. The sensors (and their experimental analog) include the following for any species or combination of species:

\(\begin{align*}
(\text{a}) & \text{ Density at a given point (rf probes and optical diagnostics);} \\
(\text{b}) & \text{ Spatially averaged density in the reactor (optical and microwave diagnostics);} \\
(\text{c}) & \text{ Spatially averaged density within a cone (optical diagnostics);} \\
(\text{d}) & \text{ Flux at a given point in a given direction (mass spectrometer);} \\
(\text{e}) & \text{ Total reactant flux impinging on the wafer (etch rate);} \\
(\text{f}) & \text{ Total flux at the pump port (residual gas analyzer);} \\
(\text{g}) & \text{ Energy flux at a given point on the wafer (etch rate).}
\end{align*}\)

The sensor and actuator modules are linked together through a programmable controller.

In a typical VPEM simulation, the user sets up a HPEM simulation and, in addition, specifies the sensors and actuators. The HPEM then computes the quasisteady-state plasma conditions. This information is used by the sensor module to emulate sensor data, which is checked against a user specified termination condition. If that condition is not satisfied, sensor data is passed to the controller module. The controller module computes how much the actuators need to be adjusted, and passes this information to the actuator module. The actuator module
adjusts the actuators and reruns the HPEM simulation. This procedure is repeated until the
termination condition is satisfied.

The sampling time of the controller is assumed to be much longer than the equilibration
time of the plasma following perturbations to its operating conditions. Therefore, in between
actuator adjustments, the plasma reaches quasisteady-state conditions. While this condition is
strictly valid for a run-to-run control scenario, for real-time control it imposes a fundamental
limitation on the maximum controller frequency that could be used.

Since a variety of approaches can be used to design feedback controllers, the structure of
the controller module is general enough to implement any type of controller scheme
(proportional, proportional-integral, and proportional-integral-derivative). The controller design
is typically based on a response surface based technique. A response surface of sensor is
constructed based on actuator parameters range. For controller design, the relevant information
that is extracted from these response surfaces is the least mean square polynomial approximation
linking the sensors and actuators. We found that a quadratic polynomial is adequate for
designing stable controllers. If the actuator parameter range of interest is broader or the system
is strongly nonlinear, this procedure can be extended to handle polynomials of higher order. For
a $n$-actuator $n$-sensor system, these polynomials have the form

$$y_j = c_j + \sum_{k=1}^{n} a_{jk} (x_k - x_{k0}) + \sum_{k=1}^{n} \sum_{l=1}^{n} b_{jkl} (x_k - x_{k0})(x_l - x_{l0})$$

(2.26)

where $j = 1, 2, \cdots, n$. $y_j$ are the outputs (sensors), $x_k$ are the inputs (actuators), $x_{k0}$ is the center
point within the range of $x_j$, and $c_j$, $a_{jk}$, and $b_{jkl}$ are constants obtained from response surfaces.
The basic goal is to adjust the actuators $X = [x_1, x_2, \ldots, x_n]^T$ so that the sensor signal $Y = [y_1, y_2, \ldots, y_n]^T$ can be made to approach a desired target $T = [t_1, t_2, \ldots, t_n]^T$. To determine how much the actuators need to be adjusted in a given situation, we consider a small change $\delta x_k$ in actuators in Eq. 2.26. This will modify the sensor outputs to $y_j + \delta y_j$. Assuming that $\delta x_k << x_k$, we can differentiate in Eq. 2.26, linearize the resulting equation and write it in matrix form as

$$\delta X = A^{-1} \cdot \delta Y$$

(2.27)

where $\delta Y = [\delta y_1, \delta y_2, \ldots, \delta y_n]^T$, $\delta X = [\delta x_1, \delta x_2, \ldots, \delta x_n]^T$ and $A$ is an $n \times n$ matrix with elements

$$A_{jk} = a_{jk} + \sum (b_{jk} + b_{jk})(x_i - x_{i0})$$

(2.28)

Setting $\delta Y = T - Y_m$ and $\delta X = X_{m+1} - X_m$, where the subscript $m$ denotes the current settings and $m+1$ denotes the new values, we can write Eq. 2.27 as

$$X_{m+1} = X_m + B \cdot A^{-1} \cdot (T - Y_m)$$

(2.29)

We multiply $A^{-1}$ by a $n \times n$ diagonal matrix $B$ so that the actuator gains can be individually changed to improve stability. Eq. 2.29 is used for implementing the controllers in the VPEM.
2.4 Figures

Fig. 2.1: Schematic of the modular HPEM.
Fig. 2.2: (a) Schematic of the Virtual Plasma Equipment Model (VPEM). (b) A block diagram of the plasma chamber along with the controller. $d$ is an external disturbance that modifies the plasma system. $1/z$ designates a delay of one controller time step.
2.5 References


3. MONTE CARLO FEATURE PROFILE MODEL

3.1 Introduction

The Monte Carlo Feature Profile Model (MCFPM) has been developed to allow self-consistent determination of topographical feature profile evolution for semiconductor processing in plasma reactors.[1-3] Till date, the model has focused on etching, stripping and ionized metal physical vapor deposition (IMPVD), but has the generality and capability to include other processes such as plasma enhanced physical vapor deposition (PECVD) and physical vapor deposition (PVD). In this chapter, a brief overview of the MCFPM is given.

3.2 Monte Carlo Feature Profile Module (MCFPM)

The MCFPM is a Monte Carlo model, which simulates the use of statistically weighted pseudo-particles representative of the fluxes of active species to the feature surface. Through ballistic transport and interaction with the mesh delineated surface, time integrated surface evolution is obtained. The MCFPM is integrated with the Hybrid Plasma Equipment Model (HPEM) through the use of energy and angular distributions (EADs) as obtained from the Plasma Chemistry Monte Carlo Module (PCMCM) in the HPEM for arbitrary radial locations on the substrate. The HPEM and PCMCM have been described earlier in Chapter 2.

The computational mesh and particle motion algorithms are discussed in Section 3.2.1. The physics of the interaction of energetic particles with the surface is described in Section 3.2.2. The surface diffusion algorithm used for deposition processes is described in Section 3.2.3. The surface reaction mechanisms used in this work are discussed in Section 3.3. In particular,
surface reaction mechanisms for fluorocarbon etching of SiO$_2$/Si substrates and for Ar/Cl$_2$ plasma etching of Si/SiO$_2$ substrates are discussed.

3.2.1 Computational Mesh and Particle Motion

The MCFPM resolves the features on wafer (masks, photoresists, semiconductors) using a two-dimensional rectilinear mesh. Each cell in the mesh has a material identity (for example, poly-Si, SiO$_2$, plasma), which may change during the simulation. Solid species, including adsorbates or passivation, are represented by computational pseudo-particles. In order to resolve single layers for investigation of atomic layer processing, the numerical mesh must resolve single atoms. As such, modeling feature sizes relevant to the current technology nodes (e.g., 50-100 nm in width with more than a 10:1 aspect ratio) would be computationally prohibitive. Since the majority of feature-dependent trends depend on aspect ratio (AR), we have chosen to maintain relevant AR while shrinking the absolute extent of the feature to a computationally manageable size. The mesh used to resolve the features consisted of square cells having dimensions of 0.3 nm or approximately $\approx$1 monolayer (atomic spacing).

Pseudo-particles representing the incident plasma species are randomly selected from the distributions obtained from the PCMCM and launched toward the surface. The EADs produced from the PCMCM are flux-weighted probability distribution functions, $F$, which are converted and normalized as cumulative distribution functions, $f$.

$$f(\varepsilon, \theta, r) = \frac{F(\varepsilon, \theta, r)}{\int \int F(\varepsilon, \theta) d\varepsilon d\theta} \quad (3.1)$$
The pseudo-particles are launched with a frequency computed from the total flux of radicals or ions incident onto the substrate so that each pseudo-particle represents a fraction of the number of atoms in a mesh cell based on the gas-to-material weighting ratio.

\[ W_g = \frac{1}{\gamma} W_s \]  

(3.2)

where \( W_g \) is the gas particle weighting, \( W_s \) is the mesh or surface cell weighting, and \( \gamma \) is the gas-to-surface ratio, which was set to 1.0 for this work. The pseudo-particle trajectories are advanced in time where the calculation of position and velocity are separated, allowing solution of two linear equations:

\[ v_i = v_{i-1} + \frac{qE}{m} \Delta t \]  \[ x_i = x_{i-1} + v_i \Delta t \]  

(3.3)

where \( v \) and \( x \) represent the velocity and position of the particle. The subscripts indicate the former and current velocity and position; \( q \) and \( m \) indicate the charge and mass of the particle, respectively; and \( \Delta t \) indicates the time-step. This method is used because under the majority of cases the effects of charging can be ignored and the electric field, \( E \), is set to zero, allowing solution of the second linear equation only. At any instant of the particle’s motion, the time-step for its current move is determined by the time required to move the minimum distance to a surface or a fraction of the mesh cell in the case of an ion. In the scenario when \( \gamma > 1 \), if the particle is within one mesh cell of a surface, the particle is moved back to its previous position, the previous time-step is halved, and the particle is moved again. This process is iterated until
the particle moves within a fraction of the material containing cell, generally 0.05 × (Cell Width).

The effects of surface charging on the profile evolution can also be addressed. Electron trajectories can be simulated as low-temperature isotropic fluxes, which impinge upon the feature during the low-potential swing of the sheath. This macroscopically balances the current due to the ions. To resolve the electric fields due to the charged surfaces of the feature, an iterative explicit solution of Poisson’s equation is determined using successive over-relaxation (SOR) method.[4]

\[ \nabla \cdot \varepsilon \nabla \varphi^{i+\Delta t} = -\rho^i \]

SOR is used to accelerate solution by multiplying the calculated \( \Delta \varphi \) by an over-relaxation factor greater than one. Neumann boundary conditions are used at the top and bottom of the feature by assuming that the electric field above the feature matches the sheath field from the Fluid Kinetics Module (discussed in Chapter 2) and that the electric field below the feature is approximately zero. The left and right boundaries are assumed to follow a periodic Dirichlet condition.

### 3.2.2 Energetic Particle Interaction

The specifics of the interaction of energetic particles with surface species are determined by the EADs from PCMCM in HPEM. The source of energetic particles is ions accelerated through the sheath, with energies of up to 100s eV and angular spreads \( \approx 5-10^\circ \) from the vertical. In the model, ions are assumed to neutralize upon interaction with the surface and the energetic neutrals thus formed have the same effect as the energetic ions. Energetic particles can either
specularly or diffusively reflect from surfaces, with an energy loss which is larger for diffusive scattering than for specular scattering.

A generalized surface reaction mechanism controls the interaction between the gas-phase pseudo-particles and the computational mesh cells which represent the surface. Energy dependence of the reaction can be specified in the reaction mechanism which also allows for any reactant-product recombination. The classes of reactions in the model include adsorption, passivation, ion activated etching, thermal etching, sputtering, ion or neutral reflection, and re-emission. When a pseudo-particle strikes a given material cell, a reaction is chosen based on probabilities from a surface reaction mechanism using Monte Carlo techniques. Based on the selected reaction, the identities of the mesh cells are changed thereby representing deposition or a chemical reaction, or the cell is removed and turned into a gas phase particle constituting an etch product. Gas-phase species evolving from these reactions are tracked as new gas-phase pseudo-particles.

The reaction probability for a particle of energy $E$ incident onto a surface at an angle $\theta$ from the local vertical of the surface is \[5,6\]

\[
p(\theta) = p_o \frac{E^n - E_{th}^n}{E_r^n - E_{th}^n} f(\theta)
\]  

(3.5)

where $E_{th}$ is the threshold energy of the process, $E_r$ is a reference energy, $p_o$ is the probability for normal incidence at $E_r$ and $f(\theta)$ is the relative probability at angle of incidence $\theta$. $f(\theta)$ is an empirical function typical of chemically enhanced sputtering with a maximum value near $\theta = 60^\circ$.\[6\]
The reflection of particles from surfaces was given both specular and diffusive character. To account for surface roughness on spatial scales not resolved by the model, we specified a fraction, $f_d = 0.25$, was diffusively scattered. The energy of specularly reflected particle was scaled such that forward scattered particles retain majority of their energy. The specularly reflected particle energy for incident energy $E_i$ is

$$E_s(\theta) = E_i \left( \frac{E_i - E_c}{E_{ts} - E_c} \right) \left( \frac{\theta - \theta_c}{90^\circ - \theta_c} \right)$$

(3.6)

for $\theta > \theta_c$, $E_c < E_i < E_{ts}$. Particles having $\theta < \theta_c$ or $E_i < E_c$ are said to diffusively scatter. Particles having $E_i > E_{ts}$ are said to retain all of their energy subject to the angular correction. We used $E_{ts} = 100$ eV, $E_c = 0$ eV and $\theta_c = 60^\circ$. The final reflected energy of the particle is a weighted sum of the specularly reflected energy and diffusively reflected energy.

The construction of the probability arrays for interaction of gas phase with surface cells is problematic due to the energy dependence of the reaction probability and the requirement that probabilities add to unity. This process is facilitated by use of a null process for all combinations of incident gas phase species and surface species. The null process is reflection without reaction. As the probability of energy dependent process change, the null portion of the probability array is rescaled to ensure that the sum of probabilities is unity. Should an etch yield exceed unity, the null reaction is eliminated and array rescaled.

### 3.2.3 Surface Diffusion

The MCFPM is also capable of addressing surface diffusion during deposition of materials.[3] This option is used in the case when metal atoms diffuse on metal underlayers. All
depositing metal atoms are first physisorbed, which are treated differently from the underlying material even if they have the same composition. The physisorbed atoms diffuse on the surface before they are chemisorbed onto the underlying material. An adsorbed cell can diffuse into any unoccupied adjacent cell in the mesh. The probability that an adsorbed cell, \( i \), moves to another cell, \( j \), is dependent on their potential energy values which are based on effective Morse potentials.

\[
\Phi_{ij} = \Phi_o \left\{ \exp \left( -2 \frac{r_{ij} - r_o}{a_o} \right) - 2 \exp \left( - \frac{r_{ij} - r_o}{a_o} \right) \right\} 
\]

(3.7)

where \( r_{ij} \) is the distance between the center of the cells. Typical value of \( \Phi_o \) is chosen to be 0.3 eV, based on the predictions by Lu and Kushner.\(^3\) Typical values for \( r_o \) and \( a_o \) are 1.6 nm and 5 nm based on mesh scale lengths as opposed to atomic lengths. The probability of diffusion to all possible locations is summed and normalized. The final diffusion path is then chosen randomly. Based on the chosen value of the activation energy, \( E_{ij} \), for diffusion from \( i \) to \( j \), the adsorbed cell either chemisorbs or diffuses. The frequency of such trials is governed by the jump frequency \( \nu \),

\[
\nu = -\nu_{ij} \ln(r)
\]

(3.8)

where
\[ v_{ij} = v_o \exp \left( -\frac{E_{ij}}{k_b T_s} \right) \] (3.9)

and

\[ v_o = \frac{2 k_b T_s}{h} \] (3.10)

where \( h \) is the Planck’s constant, \( k_b \) is the Boltzmann’s constant and \( T_s \) is the substrate temperature. At 393 K, \( v_o = 1.6 \times 10^{12} \text{ s}^{-1} \). Based on the specified threshold jump frequency, \( v_r \), the cell chemisorbs if \( v < v_r \). Typical value of \( v_r \) is \( 10^8 \text{ s}^{-1} \) based on earlier studies.[3]

3.3 Surface Reaction Mechanism

Surface reaction mechanisms, in general, are an intrinsic property of the gas phase reactant species (incident on the surface) and the surface species. As such reaction mechanisms should be independent of the process conditions, such as the plasma source or the gas chemistry. The process conditions may determine the energies and magnitudes of the incident reactant fluxes, however the reaction mechanism should not itself.

To enable the investigation of plasma atomic layer etching, the reaction mechanism for etching of Si in Ar/Cl\(_2\) plasmas, as developed by Hoekstra et al.[1] has been used and is listed in Appendix A. Silicon etching in chlorine plasmas takes place by first successively chlorinating the surface, forming SiCl\(_n\) (SiCl followed by SiCl\(_2\) and SiCl\(_3\)).[1,5] This chlorination is predominantly accomplished by neutral Cl atoms and does not entail growth of a layer (i.e., multiple layers of SiCl growing on top of SiCl). Etching of the SiCl\(_n\) etch product then occurs
through ion activation. Silicon etching in chlorine plasma can be spontaneous since successive chlorination of the Si surface can ultimately form SiCl₄ which is a volatile product.

Plasma atomic layer etching has also been investigated for etching of SiO₂ in fluorocarbon plasmas. The fluorocarbon plasma etch reaction mechanism, developed by Sankaran and Kushner[7], is listed in Appendix B. Fluorocarbon etching of SiO₂ proceeds through the deposition of an overlying fluorocarbon polymer layer.[8] Polymer is necessary for chemical sputtering of SiO₂ as the carbon in the polymer aids in removal of oxygen in the SiO₂. CₓFᵧ radicals form the precursors to the polymer layer which regulates the delivery of activation energy and the transport of neutral and ion fluxes to the underlying materials.[9] Polymer formation is promoted by low-energy ion bombardment, whereas the etch process and polymer removal are initiated by high-energy ion bombardment. The thickness of the polymer layer controls the etch process. While a thick polymer layer impedes the delivery of activation energy to the polymer-SiO₂ interface, thereby slowing or stopping the etch, a thin polymer layer can reduce the etch, a thin polymer layer removes the reaction precursor, thereby reducing the etch rates even at high ion energies.

3.4 References


4. CHARACTERISTICS OF PULSED PLASMA DOPING SOURCES FOR ULTRA-SHALLOW JUNCTION FORMATION

4.1. Introduction

The characteristics of the ion energy and angular distributions (IEADs) incident onto the wafer are critical to determining the junction properties. The IEADs are sensitive functions of the bias voltage waveform and the plasma parameters that determine the sheath properties (e.g. pressure, power, and reactor configuration). Characterizing the consequences of these parameters have on IEADs is important to improve the uniformity, repeatability and reliability of the implantation process. In this chapter, results of a computational investigation of PPI performed using an auxiliary ICP ion source and a pulsed dc bias on the substrate, are presented. The effect of bias waveform, ICP power, pressure, and reactor configuration on pulsed plasma characteristics and IEADs to the wafer will be discussed for an Ar/NF3 gas mixture, used as a surrogate for Ar/BF3.

The IEADs are dominantly populated by ions with energies near the bias voltage. A low energy tail of the IEAD can be produced by slowly rising voltage pulses or conditions having thick sheaths where ionization occurs in the sheath. The angular symmetry of the IEAD is, to some degree, controlled by the curvature of the sheath edge. During the pulse, the sheath edge may sample regions of the reactor where the ion density is non-uniform, thereby producing a gradient (or curvature) in the sheath thickness across the wafer. This may result in angular skew to the IEAD.

4.2. Reaction Mechanism

The Ar/NF3 reaction mechanism and species used in this study are listed in Appendix
NF$_3$ was used as a surrogate for BF$_3$ as would be used in actual plasma doping. This choice was made based on the more reliable database for electron impact and heavy particle reactions available for NF$_3$ compared to BF$_3$. Both gases are highly attaching at low electron energies and have similar inelastic thresholds. As such, for the scaling studies performed here, similar trends are expected for systems using BF$_3$. Rate coefficients for gas phase chemistry were taken from independent studies in the literature\cite{2} or estimated from measurements for related species.\cite{3} All pertinent electron impact events which affect electron transport, such as elastic collisions, and vibrational and electronic excitations, are included in the EETM. Only those excited states which were judged to be significant to the plasma chemistry reaction mechanism were tracked in the FKM and appear in the reaction mechanism.

To lessen the complexity of the reaction mechanism, lumped effective excited states were used. Excited states of Ar were lumped into Ar$^*$, which is effectively Ar(4s). Excitation to the electronic states of N$_2$ were lumped into N$_2^*$ which is effectively N($A^3\Sigma_u^+$). Similarly, the higher excited states of N [N($^2D$) and N($^4P$)] are lumped together and denoted as N$^*$. Many of the rate coefficients involving fragments of NF$_3$ (i.e., NF$_2$, NF) for electron impact and neutral heavy particle reactions were estimated. Associative reactions of NF$_x$, F + NF$_x + M \rightarrow$ NF$_{x+1} + M$ have been included. However, these reactions are not very important at the pressures used in this study (10s mTorr).

Ion-neutral reactions listed were classified as exothermic reactions, which occur independent of ion energy. Ion molecule reactions with NF$_3$ feedstock gas and its fragments are mostly dissociative. For example, Ar$^+$ has an ionization potential of 15.8 eV sufficient to produce dissociative ionization of NF$_3$ having a threshold of about 13.0 eV. The probability of
dissociative ionization between Ar$^+$ and NF is likely to be small as NF has a dissociative ionization potential of about 14 eV and is so not included in the mechanism.

The ion-ion reactions listed are mostly ion-ion neutralization reactions. Neither products of recombination nor reaction rates are typically known. Theres reactions are fast as typical rate constants are $10^{-7}$ cm$^3$s$^{-1}$. Dissociative electron-ion recombination reactions included typically have rate coefficient in the range of $10^{-7} T_e^{-0.5}$, where $T_e$ is in eV.

Although an exhaustive sensitivity analysis has not been performed, the systematic trends discussed here are not sensitive functions of the values of these coefficients.

4.3. Effect of Pulsed-dc Bias on Ieads and Plasma Characteristics

The cylindrically symmetric reactor used in this study is schematically shown in Fig. 4.1. Inductive power is supplied through a 3-turn coil, 42 cm in diameter. The coils are behind a 1 cm thick ring of dielectric having, in the model, the electrical properties of alumina. Process gases, Ar/NF$_3$ in this case (a surrogate for Ar/BF$_3$ that would normally be used for ion implantation processes), enter the chamber from the nozzle at the top and center of the reactor, and are exhausted from an annular pump port. The top reactor surface is metal as it intercepts significant secondary electron current from the sheath accelerated electrons. The 30 cm diameter wafer is on a substrate which is biased by a pulsed dc power supply. The wafer is about 14 cm below the nozzle. A 10 mTorr, Ar/NF$_3$=80/20 gas mixture at a flow rate of 100 sccm was used for the base case. The coil delivered 500 W at 10 MHz excitation frequency.

The pulsed-dc bias voltage waveform used for the base case is shown in Fig. 4.2. The excitation waveform was applied at 8.7 kHz and consisted of sequences of 45 $\mu$s long negative voltage pulses followed by a pulse-off time ($\Delta t_i$) of 70 $\mu$s. The pulse has a linear rise of voltage
to a constant bias and a linear fall to zero. The rise-time and fall times, $\Delta t$, for the base case are 5 $\mu$s. As explained below, the rate of voltage rise and voltage pulse length are critical in determining plasma characteristics and are important to the shape of the IEADs.

A typical computational strategy is as follows. Initial conditions (e.g. plasma density, dissociation fraction) are estimated and the model executed with only ICP power for 60 $\mu$s to achieve a quasi-steady state in plasma characteristics. The effective integration time is actually 10-100 times longer than 60 $\mu$s as acceleration techniques are used to speed the convergence of plasma properties. Four voltage pulses (and their inter-pulse periods) are then applied using direct time integration in the model without applying acceleration techniques. The plasma properties we discuss below are those for the fourth pulse at different times during the pulse. We confirmed that the plasma properties do not significantly change with application of additional pulses as the inter-pulse period is usually long enough to lose memory of the prior pulse. The PCMCM is executed approximately every 1 $\mu$s to obtain the time history of the IEADs, which is then time integrated to obtain a pulse averaged IEAD.

The inductively coupled power deposition, total positive ion density and $F^-$ density are shown in Fig. 4.1 for the base case, when the bias voltage is midway through the fourth pulse and has an amplitude of $\pm 1000$ V. Similarly the densities of $Ar^+$, $NF_3^+$, and $NF_2^+$ are shown in Fig. 4.3. The high electron thermal conductivity produces a fairly uniform electron temperature (4-5 eV) in spite of the localized power deposition in the vicinity of the coils. The ion density is maximum at $2.7 \times 10^{11}$ cm$^{-3}$ near the peak in power deposition, with $Ar^+$ being the major ion and $NF_3^+$ and other dissociation fragments being an order of magnitude lower in densities. The off axis maximum in ion density is a consequence of the low aspect ratio of the reactor[4] and highly attaching nature of the gas mixture which rapidly consumes electrons. Although the total ion
density peaks off-axis, the density of NF$_3^+$ peaks below the nozzle where its neutral density is largest. As discussed below, the large bias voltage creates a sheath that can be many cm thick and depletes both electrons and ions near the substrate. The islands of ions in the periphery of the reactor will be discussed later.

Time-averaged radical and ion fluxes to the wafer are shown in Fig. 4.4 for the base case conditions. The radicals having the largest fluxes to the substrate are, on axis, F ($5.9 \times 10^{17}$ cm$^{-2}$s$^{-1}$), NF$_2$ ($2.6 \times 10^{17}$ cm$^{-2}$s$^{-1}$) and NF ($0.9 \times 10^{17}$ cm$^{-2}$s$^{-1}$). Dissociation of the NF$_3$ down to N atoms produces a flux that is an order of magnitude smaller. The largest flux of ions is due to Ar$^+$ ($2.9 \times 10^{15}$ cm$^{-2}$s$^{-1}$) due to its low rates of charge exchange to NF$_3$ and its dissociation fragments. Fluxes of NF$_3^+$ and NF$_2^+$ are an order of magnitude lower. The ion fluxes are maximum on the outer radius near the coils where the total ion density and the power deposition also peak. This non-uniformity is not a characteristic of PPI but merely a consequence of this particular chamber design.

The electron and NF$_2^+$ densities for a bias voltage of –1000 V are shown in Fig. 4.5 at the end of the constant voltage portion of the bias for pressures of 5, 10 and 20 mTorr. The ICP power is held constant. The electron density, $n_e$, decreases from $7.5 \times 10^{10}$ cm$^{-3}$ at 5 mTorr to $2.4 \times 10^{10}$ cm$^{-3}$ at 20 mTorr. This decrease results from the higher rate of electron attachment and the higher rate of power dissipation per electron at higher pressure. When holding the power constant, the electron density required to deliver the power decreases with increasing pressure. The NF$_2^+$ density increases from $7.8 \times 10^9$ cm$^{-3}$ to $1.5 \times 10^{10}$ cm$^{-3}$ with increasing pressure due to higher rates of charge exchange from Ar$^+$. The longer mean free path for energy loss by electrons heated near the coils produce more uniform ionization sources at the lower pressure, and so a more uniform plasma is produced. To first order, the sheath thickness scales as
\[ \lambda_s \sim \frac{V_s}{n_e}, \]
where \( V_s \) is the sheath voltage and \( n_e \) is the electron density at the sheath edge. Since \( n_e \) decreases with increasing pressure, \( \lambda_s \) increases. \( \lambda_s \) is nearly uniform as a function of radius at 5 mTorr which reflects the uniformity in \( n_e \). As \( n_e \) is less uniform at higher pressure (larger at large radii) and so \( \lambda_s \) is also less uniform, being smaller at large radii.

IEADs for all ions averaged over the voltage pulse and the inter-pulse periods are shown in Fig. 4.6(a) for base case conditions with bias voltages of \(-1,000\) V to \(-10,000\) V. The ions that arrive at the sheath edge during the pulse-off period form the low energy, wide angular portion of the IEAD. The high energy and angularly narrow portion of the IEAD is produced during the voltage pulse. The peak value of the IEAD is located in energy a few tens of volts above the magnitude of the applied bias voltage. This is a consequence of the additional acceleration provided by the ambipolar potential.

The speed of the sheath into the plasma is as large as \(10^6\) cm-s\(^{-1}\) which is commensurate to or exceeds the thermal speed of the ions. The sheath is dominantly formed by expelling the more mobile electrons, exposing the less mobile ions and creating, at least initially, an ion-matrix sheath.[5] The flux of the ions into the sheath during the voltage ramp-up period consists of ions which drift or diffuse into the sheath edge, and those ions which are enveloped by the growth of the sheath. During the constant voltage period of the pulse, the sheath grows only at the rate required to replenish ions that are extracted out of the sheath into the substrate.

The low energy tail of the IEAD results, in part, from ions that enter or are enveloped by the sheath during the ramp-up and ramp-down voltage pulses. These ions do not experience the full sheath voltage and so arrive at the substrate with lower energies. The tail of the IEAD is more prominent at higher bias voltages in large part because the sheath is thicker and there is
significant ionization in the sheath resulting from secondary electrons emitted from the substrate. The ions produced in the sheath obtain in energy at most the difference between the plasma potential where they were produced and the bias voltage. The thicker sheath also produces a larger fraction of the ion flux which results from ions being captured by the sheath when electrons are expelled by expansion of the sheath (the ion matrix component). The maximum energy of these ions is the sheath potential at the time at which the sheath captures them.

Ions experience only a nominal number of collisions (the mean free path for charge exchange is \( \approx 1 \text{ cm} \)) during their transit through the sheath. As such, collisions contribute only in a minor way to the tail of the IEAD at low biases. At higher biases (>5 kV) where the sheath thickness approaches the mean-free-path, collisions begin to populate the tail of the IEAD.

The IEADs of individual ions display both mass and positional characteristics. The IEAD of the lightest ion, \( \text{N}^+ \), is the most mono-energetic in spite of the fact that it will respond most quickly to changes in sheath potential which should broaden the energy spread of the IEAD. (This would be the case for a continuously applied, radio frequency sinusoidal bias of a few MHz.) On the other hand, the heavier ions \( \text{Ar}^+ \) and \( \text{NF}_3^+ \), have the broadest energy spread, which is counter intuitive since these ions should be the slowest to respond. These apparent discrepancies in the IEADs result from where the ions are formed. \( \text{Ar}^+ \) and \( \text{NF}_3^+ \), being parent ions of the feedstock gases, can be formed by single electron impact events in the sheaths by secondary electrons. As a result, the tails of the IEADs for \( \text{Ar}^+ \) and \( \text{NF}_3^+ \) are populated by ions formed in the sheath and which do not experience the full sheath potential. \( \text{N}^+ \) is formed dominantly by electron impact ionization of dissociation products, which occurs most often in the bulk plasma since many electron impact collisions are required. As such, the \( \text{N}^+ \) drifts or diffuses into the sheath from the bulk plasma and so attains the full sheath potential.
The tail of the IEAD can also be influenced by the duration of the ramp-up and ramp-down times ($\Delta t_r$) of the voltage pulses. For example, the time-averaged IEADs for all ions are shown in Fig. 4.7(a) for a bias voltage of -1000 V with $\Delta t_r$ of 1 $\mu$s to 15 $\mu$s. With increasing $\Delta t_r$, sheath expansion and retraction occupy a larger fraction of the duty cycle of the voltage pulse. As a result, a larger fraction of the ion flux entering the sheath does so while the sheath voltage is less than the maximum. The lower energy tail of the IEAD becomes particularly prominent for $\Delta t_r >$ 10 $\mu$s. Nearly mono-energetic IEADs for all ions are obtained for $\Delta t_r < 2$ $\mu$s, as shown in Fig. 4.7(b).

The importance of the tail of the distribution at large bias voltages is demonstrated by the total ion energy distribution (IEDs), integrated over angle, shown in Fig. 4.8(a) for base case conditions with bias voltages of –1,000 V to –10,000 V. The absolute maxima in the IEDs occur at low energies, corresponding to times when the bias voltage is off (indicated by a horizontal line in the figure). Secondary maximum occur at high energies corresponding to when the applied bias voltage is at its largest absolute value. The tail of IED represents only a small fraction of the total IED at low bias energies. The low energy tail increases in importance, as the bias increases, as indicated by the decrease in the height of the high energy peak. More detail of the tail of the IEADs are shown by the time-averaged distributions for Ar$^+$, NF$_3^+$, NF$_2^+$, and N$^+$ ions in Fig. 4.8(b) for base case conditions and a bias voltage of -10,000 V. To emphasize the tail, the IEADs are plotted as a 3 decade log scale.

Time-averaged IEADs for all ions are shown in Fig. 4.9(a) for a bias voltage of –1000 V and for ICP powers of 250 W to 1000 W. Time-averaged IEADs for Ar$^+$, NF$_3^+$, NF$_2^+$ and N$^+$ are shown in Fig. 4.9(b) for base case conditions and an ICP power of 750 W. The increase in ICP power produces an increase in ion density at the edge of the sheath and thinning of the sheath, as
shown in Fig. 4.10. The total ion flux increases at higher ICP powers, as shown in Fig. 4.11, with there being a larger proportion of lighter ions (more dissociation at higher powers). As a result, as the ICP power increases the sheath becomes less collisional, the ion transit time decreases (in particular, for the lighter ions) and the amount of ionization by secondary electrons in the sheath decreases. These factors combine to reduce the population of ions in the low energy tail of the IEAD as the ICP power increases.

The electron density for a bias voltage of –10,000 V is shown in Fig. 4.12 for different times during the pulse between prior to the application of bias (frame 1) through the end of the voltage pulse (frame 10). The maximum electron density is $6.3 \times 10^{10}$ cm$^{-3}$. Note the thickening of the sheath as the applied voltage becomes more negative; and the collapse and thinning of the sheath as the voltage is removed. The sheath initially has a nearly uniform thickness across the substrate as the electron and ion densities near the wafer are fairly uniform. As the sheath thickens, the edge of the sheath penetrates into the middle of the reactor near the ionization source where the electron and ion density are significantly larger at large radii. At this time, the sheath expansion stalls at larger radii while continuing to penetrate into the lower plasma density in the center of the reactor. The end result is that the sheath is thinner at the large radii.

The rapid switching on of the negative voltage pulse causes the electrons to move rapidly out of the sheath. At the same time positive ions are slowly accelerated in the opposite direction towards the substrate. This rapid charge separation leads to the launching of electrostatic waves which may disrupt the plasma. The electrostatic wave is first evident in the third frame of Fig. 4.12 and is most prominent (and shown propagating into the plasma) in the fourth frame. The electrostatic waves traverse through the entire reactor, reflecting off the boundaries (as in the fifth frame) before collisionally damping by the end of the voltage pulse (frame 7). The
launching of electrostatic waves is more significant as the bias becomes more negative and the rate of voltage rise increases.

As the voltage pulse terminates, electrons quickly repopulate the sheath so as to recover charge neutrality as the sheath collapses. The sheath properties during this collapse can often be asymmetric. For example, the asymmetry of the sheath above the substrate is shown in Fig. 4.13 for different times during the ramp down of the voltage pulse. This period corresponds to the end of the flat-top in the voltage (frame 3) and the ramp-down in voltage to zero (frame 8). The electron density is shown for 8 cm above the substrate. Upon application of the bias, sheath formation proceeds as electrons are expelled from the near substrate volume to form the positive space charge. During the ramp-up period of the pulse, the sheath front propagates into the plasma to unveil more positive space charge to drop the additional voltage. At the end of the flat-top part of the pulse, the sheath has reached a thickness of approximately 7.4 cm with smaller thickness at large radii. As the voltage is ramped down, the mobile electrons rapidly fill in behind the collapsing sheath, thereby reducing its thickness. The thermal speed of the electrons is large compared to the time rate of the change in sheath thickness, and so the electrons are in quasi-equilibrium with the receding sheath. As the sheath collapses, its thickness becomes even less uniform, being thinner near the outer radius where the electron density is larger.

The sheath expands deeper into the plasma at higher biases. It also increases its extent into the plasma as the total pulse length increases for a given bias. For example, the electron density is shown in Fig. 4.14 in the 8 cm above the substrate for pulse lengths of 10 μs to 75 μs for a bias voltage of –10,000 V. The densities are shown at the end of the flat-top part of the voltage pulse. For short pulses (10 μs) the sheath appears similar to an ion-matrix sheath where
there is not a large change in the ion density due to transport. As a result, the sheath is able to generate enough space charge to drop –10,000 V over only 4.7 cm. As the pulse length increases, there is depletion of the ion density in the sheath, thereby resulting in an extension of the sheath into the plasma, expelling electrons from a larger volume to produce more positive charge. A steady state is achieved only when the flux of ions into the sheath equals the ion flux into the substrate. This steady state is achieved for pulse lengths >50 μs. For the IEADs to be as uniform as possible throughout the voltage pulse, the majority of the ion flux through the sheath should be collected under quasi-steady state conditions. Using this criterion, for a bias of –10,000 V the pulse length should be >50 μs.

The ionization produced by secondary electrons emitted from the substrate for a bias voltage of –10,000 V is shown in Fig. 4.15, at different times during the pulse between prior to application of bias (frame 1) until after the end of the voltage pulse (frame 10). The transit of electrons through the sheath borders on being collisionless, resulting in significant secondary electron current being collected by the top surface of the reactor, though clearly collisions occur to produce these ionization sources. The peak energy of the electrons as they transit the sheath is nearly equal to the instantaneous sheath potential. The maximum in the ionization cross section for Ar is approximately 100 eV and for NF₃ is 90 eV. When the sheath potential is low prior to the bias pulse (25-30 eV prior to frame 2) the ionization by secondary electrons is low and their range through the plasma is roughly half the height of the reactor due largely to non-ionizing collisions. As the bias is gradually increased to its flat-top value (frame 2 to frame 4), the secondary electron energy leaving the sheath increases up to 10,000 eV, an energy above the maximum for ionization. The maximum ionization source occurs in the sheath when the beam electrons pass through the maximum in the ionization cross section. As electron energies
increase above 90-100 eV, their mean free path lengthens, thereby producing a low source of ionization that extends across the reactor. In fact, the majority of the electron flux penetrates through the reactor and impacts on the top metal plate. As the bias voltage ramps down (corresponding to frames 7 to 10), the energy of the secondary electron beam energy also decreases, passing through the maximum in the ionization cross section and producing a momentary maximum in ionization.

The yield of secondary electrons per ion varies greatly with the ion energy and the surface the ion strikes.[6] For these conditions, the yield per ion increases at energies above 3000 eV. At higher biases, the increase in secondary electron yield and secondary electron current as the sheath voltage increases somewhat compensates for the decrease in ionization cross-sections at higher electron energy.

We have observed in many instances a pulsation effect in which islands of plasma are ejected through the gap between the upper dielectric structure and the focus ring. This sequence of the plasma ejection is shown by the NF$_2^+$ and F$^-$ densities appearing in Figs. 16 and 17 for a bias voltage of $-10,000$ V. Densities are shown at different times beginning early in the bias pulse (frame 1), through the inter-pulse period and ending with just prior to the following voltage pulse (frame 10). The peak NF$_2^+$ density, $1.8 \times 10^{10}$ cm$^{-3}$, occurs near the source of production adjacent to the coils. The peak F$^-$ density, $3.1 \times 10^{10}$ cm$^{-3}$, occurs in the same location, which is also where the plasma potential is maximum. (The dominant positive ion is Ar$^+$.) In the absence of pulsing the bias, the plasma is essentially continuous through the gap between the upper dielectric structure and the focus ring. As the bias is applied, the sheath expands bringing with it a large negative plasma potential. Negative ions (and electrons) are accelerated out of this region which pinches off an island of plasma in the periphery of the reactor. (On the outer radius of the
substrate, the majority of the applied voltage is dropped across the focus ring and so the sheath thickness is smaller.) The electron temperature is low in the periphery and so electron attachment rapidly occurs, resulting in the plasma being dominated by negative ions. This plasma island is somewhat stabilized by the negative ions being trapped in a local maximum in plasma potential that occurs in the periphery of the reactor. Ambipolar electric fields provide a net outward force on the plasma island while negative ion-positive ion recombination depletes the density in the plasma island.

When the bias pulse is terminated, the sheath shrinks and plasma extends towards the gap. Plasma then flows into the periphery of the reactor. If the sheath is thin and inter-pulse period short, the plasma flow may connect with a nearby island. If the sheath is thick and inter-pulse period long, the prior plasma island has drifted far and the reinitiated plasma flow may seed a new island. The repetitive pulsing of the bias then gives the appearance of successive islands of plasma being ejected through the gap.

The formation of the islands is facilitated by the rapid negative ion formation afforded by the thermal attachment cross-section of NF₃. The electron temperature drops from 4.8 eV in the bulk plasma to 4.1 eV in the periphery of the reactor. This decrease in electron temperature takes the plasma from having net positive ionization in the bulk to being attachment dominated in the periphery.

4.4. The Effect of Reactor Design on Symmetry of IEADs

For this particular reactor configuration, ions are dominantly produced at larger radii near the coils and diffuse towards the wafer. These ions approach the sheath with velocities
preferentially oriented towards the axis. At low bias voltages, the sheath is thin and fairly uniform, and the majority of the reactor is occupied by plasma, as shown in Fig. 4.3(c). As a result, the ions have sufficient time while they transport from their source to the sheath edge to reorient their velocities to be nearly perpendicular to the substrate. Since the sheath thickness is uniform and parallel to the substrate, after acceleration through the sheath, the angular distribution of the ions incident onto the wafer is symmetric, as shown by the IEADs in Fig. 4.6(a) for a bias voltage of $V_o = -1.0$ kV.

As the bias voltage increases and the sheath extends far into the plasma, it impinges onto that portion of the reactor where there is a significant variation in plasma density, lower on the axis and higher at large radius. The sheath thickness, which scales inversely with plasma density, therefore becomes larger at small radius and smaller at larger radius. This produces a gradient to the sheath thickness across the reactor. At the same time, a smaller fraction of the volume of the reactor is plasma (as opposed to the sheath), providing less opportunity for ions that are preferentially produced off-axis and have a large radial component to their velocity to reorient their velocities to a more axial direction. The ions entering the sheath with an off-axis velocity are initially accelerated perpendicular to the sheath edge which is not parallel to the substrate. Although the electric field in the sheath eventually does become perpendicular to the substrate, the perpendicular electric field is not large enough to offset the inwardly axial velocity of the ions produced in the first portion of the sheath. The end result is that these ions arrive at the wafer with an asymmetric angular distribution which is skewed to one side, as shown in Fig. 4.6(a) for a bias voltage of $V_o = -10$ kV.

For the ions to arrive at the substrate with a symmetric angular distribution, the ions should ideally enter the sheath with axially oriented velocities and the sheath should be parallel
to the substrate (that is, the electric field in the sheath is perpendicular to the substrate) or the voltage drop in the portion of the sheath which is not parallel to the substrate should be a small fraction of the total. The parallel nature of the sheath is determined, in part, by the uniformity of the plasma into which the sheath is propagating. The uniformity of the plasma is determined by the location of the ionization sources and transport of the charged species after ionization. Due to the need for the top of the reactor to be metal to collect the secondary electron flux that penetrates across the reactor with large biases, there is limited freedom in choosing the location of the coils that determine the location of ionization sources. The shape of the reactor can, however, be used to change the uniformity of the plasma and so the angular symmetry of the IEADs.

For example, the height of the reactor was increased from 22 cm to 35 cm while keeping the radius constant. The total ion density is shown in Fig. 4.18 in the vicinity of the substrate for base case conditions with a bias voltage of $-10,000 \text{ V}$. IEADs incident on axis, mid-radius and on the outer-radius of the wafer for these conditions are shown in Fig. 4.19. As the height of the reactor is increased, the plasma density transitions from being largest in the periphery of the reactor to assuming a more diffusion dominated shape emphasizing the center of the reactor. As such, as the height of the reactor increases, the sheath thickness transitions from being thinnest on the outer periphery, as shown in Fig. 4.18(a), to being thinnest on the axis, as shown in Fig. 4.18(c). The angular symmetry of the IEADs reflects the change in the direction of the gradient of the sheaths as the height of the reactor increases. For the short reactor with a thin sheath at large radius [Fig. 4.18(a)], the skew in the IEAD is to positive angle [Fig. 4.19(a)] and is most severe at large radius. For the tall reactor with the sheath thinner at smaller radius [Fig. 4.18(c)], the skew in the IEAD is towards negative angle [Fig. 4.19(c)]. The intermediate height reactor
having the most uniform sheath thickness has the most angularly symmetric IEADs.

Small modifications to the original reactor can also affect the uniformity of the sheath thickness and so the angular symmetry of the IEADs. For example, the height of the focus ring outside the wafer was increased by about 1 cm. The resulting total ion density and IEADs are shown in Fig. 4.20 for base case conditions with a bias voltage of -10,000 V. The higher focus ring produces a fairly uniform sheath that is slightly thicker at large radius which compensates for the inward trajectories of ions as they approach the sheath. The end result is that the IEADs are more angular symmetric with the elevated focus ring that with a flat focus ring.

4.5. Conclusions

The characteristics of inductively coupled reactors for pulsed plasma doping of semiconductors was computationally investigated. We found that the IEADs of ions incident on the wafer are sensitive functions of the ICP power deposition and bias pulse shape. The ideal IEAD is angularly symmetric and mono-energetic. Plasma conditions that produce thick sheaths for an extended period during the bias (e.g., low ICP power producing low ion density or large bias voltage) produce low energy tails to the IEADs resulting from ionization that occurs in the sheath by secondary electrons. Since the sheath can extend many cm into the plasma, the uniformity of the plasma far from the substrate is important. Gradients in the thickness of the sheath may produce angularly asymmetric IEADs. The angular symmetry can be controlled through the shape of the reactor or modifications such as the height of the focus ring that decrease the gradient in the sheath thickness across the wafer.
Fig. 4.1: Plasma properties for the base case (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -1000 V substrate bias. (a) Power (b) Total ion density and (c) F$^-$ density.
Fig. 4.2: Schematic of the pulsed voltage waveform. The voltage pulse is 45 μs long with a pulse-off time of 70 μs between the pulses. Four such voltage pulses are applied to reach a steady state.
Fig. 4.3: Plasma properties for the base case (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -1000 V substrate bias. (a) Ar$^+$ (b) NF$_3^+$ and (c) NF$_2^+$ density.
Fig. 4.4: Fluxes to the wafer as a function of radius for the base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm). (a) Ion fluxes and (b) neutral fluxes.
Fig. 4.5: Electron and NF$_2^+$ densities at base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 100 sccm) and -1000 V substrate bias as a function of pressure. (a) 5 mTorr (b) 10 mTorr and (c) 20 mTorr.
Fig. 4.6: IEADs averaged over the wafer for base case conditions ($\text{Ar/NF}_3=80/20$, 500 W ICP power, 10 mTorr, 100 sccm) (a) IEADs for bias voltages of 1, 2.5, 5, 10 kV.
(b) IEADs for $\text{Ar}^+$, $\text{NF}_3^+$, $\text{NF}_2^+$ and $\text{N}^+$ ions for a bias of -2,500 V.
Fig. 4.7: IEADs averaged over the wafer for base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) (a) Total ion energy and angular distributions for different lengths of the bias ramp-up period, $\Delta t_r$. (b) IEADs for Ar$^+$, NF$_3^+$, NF$_2^+$ and N$^+$ ions at base case conditions (-1,000 V substrate bias) and $\Delta t_r = 2 \mu$s.
Fig. 4.8: IEADs typically have more prominent tails at higher biases. (a) Ion energy distributions for all ions integrated over angle striking the wafer for different dc bias voltages. (b) IEADs, averaged over the wafer, for Ar$^+$, NF$_3^+$, NF$_2^+$ and N$^+$ ions at base case conditions and -10,000 V substrate bias.
Fig. 4.9: Plasma properties as a function of ICP power for otherwise the base case conditions (Ar/NF$_3$=80/20, -1,000 V substrate bias, 10 mTorr, 100 sccm). (a) IEADs for all ions, averaged over the wafer, for base case conditions with different ICP powers. (b) IEADs for Ar$^+$, NF$_3^+$, NF$_2^+$ and N$^+$ ions at base case conditions and 750 W ICP power.
Fig. 4.10: Total ion density at the edge of the sheath and sheath thickness as a function of ICP power for otherwise the base case conditions (Ar/NF₃=80/20, 10 mTorr, 100 sccm) for a substrate bias of -1,000 V. The ion densities are measured 0.05 cm above the sheath at the center of the reactor.
Fig. 4.11: Total ion flux as a function of radius for otherwise the base conditions (Ar/NF$_3$ =80/20, 10 mTorr, 100 sccm, -1000 V bias) for different ICP powers.
Fig. 4.12: Electron density for the base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias for different times during the pulse (as indicated in the lower figure).
Fig. 4.13: Electron density above the substrate (region indicated in the top frame) as the pulse voltage is ramped down for the base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias. The frames are for times indicated in the lower figure.
**Fig. 4.14:** Electron density above the substrate (region indicated in the top frame) at the end of the constant portion of the substrate voltage pulse for different pulse lengths. The results are otherwise for base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias.
Fig. 4.15: Ionization produced by the secondary electrons emitted from the substrate and accelerated by the sheath at different times during the pulse (as indicated in the figure). The conditions are the base case (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -1,000 V substrate bias.
Fig. 4.16: $\text{NF}_2^+$ density for the base case conditions (Ar/NF$_3$ = 80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias during the pulse and inter-pulse period (as indicated in the lower figure).
Fig. 4.17: $F^-$ density for the base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias during the pulse and inter-pulse period (as indicated in the lower figure).
Fig. 4.18: Total ion density for the base case conditions (Ar/NF$_3$=80/20, 500 W ICP power, 10 mTorr, 100 sccm) and -10,000 V substrate bias at the end of the constant portion of the substrate voltage pulse for increasing height of the reactor. (a) 22 cm (b) 30 cm and (c) 35 cm.
Fig. 4.19: Total ion energy and angular distributions at different radial positions along the wafer for increasing height of the reactor. (a) 22 cm (b) 30 cm and (c) 35 cm.
Fig. 4.20: Plasma characteristics for a reactor with a raised focus ring. (a) Total ion density when the bias is -10,000 V. (b) IEADs for inner, middle, and outer regions of the wafer.
4.7 References


5. PLASMA ATOMIC LAYER ETCHING: ACHIEVING MONOLAYER RESOLUTION USING CONVENTIONAL PLASMA EQUIPMENT

5.1 Introduction

The decrease in equivalent gate oxide thickness at future technological nodes in microelectronics fabrication will require plasma etching processes with atomic scale resolution. Conventional plasma etching processes typically do not provide sufficient control to achieve this resolution and so avoid damage to underlying layers. As such, it is desirable to use a self-limiting process which is less dependent on the process time. The basis of plasma atomic layer etching (PALE) is the formation of a monolayer of passivation followed by the removal of the layer which also removes a single layer of the underlying material. If these goals are met, the process is self-terminating. A complete cycle of the PALE is schematically shown in Fig. 5.1. A challenge of PALE is the high cost of specialized equipment and slow processing speed. In this chapter, results from a computational investigation of PALE will be discussed with the goal of demonstrating the potential of using conventional plasma etching equipment with reasonable processing speeds. Results will be discussed for PALE of Si in Ar/Cl₂ plasma in an inductively coupled plasma (ICP) reactor and for PALE of SiO₂ in fluorocarbon plasma in a capacitively coupled plasma (CCP) reactor. We found that repeatable and self-limiting etching can be obtained. The selectivity of PALE and integrity of the etch (e.g., degree of roughening) depends on the ion energy of the etch step. However, depending on the reaction mechanism the emphasis may shift from control of ion energies to control of length of a cycle. Etching recipes combining a main etch with PALE were also investigated.
5.2 PALE of Si in Ar/Cl₂ Inductively-coupled Plasmas

PALE of Si was investigated using the ICP reactor shown schematically in Fig. 5.2 as a model tool for conventional plasma equipment. Inductive power at 13.56 MHz is supplied through a 3-turn coil, 16 cm in diameter in contact with 0.8 cm thick quartz window, which is 23 cm in diameter. The wafer is on a substrate which can be independently biased 9 cm below the quartz window. The PALE process for Si etching by a chlorine plasma consists of passivation of a single layer of the Si surface with Cl atoms followed by ion bombardment of the surface to ideally remove this one layer of Si. For the first step, a 20 mTorr Ar/Cl₂=80/20 gas mixture was used. (The reaction mechanism for Ar/Cl₂ is discussed in Ref. 1). The flow rate was 100 sccm, the coil delivered a purely inductive power of 500 W. In this step, Cl atoms produced in the plasma passivate Si surface sites to produce SiₓC𝐥ᵧ complexes.[2] The substrate was not biased in order to minimize etching while passivating the surface. For the second step, the plasma was sustained in pure Ar at 16 mTorr with a flow rate of 100 sccm. The substrate was independently biased with a 100 V sinusoidal waveform at 2 MHz to produce sufficient ion energies to remove the passivated layer.

The total positive ion density for the passivation step and the Ar⁺ density for the etching step are shown in Fig. 5.2. The peak ion density is $9.1 \times 10^{11}$ cm$^{-3}$ during the passivation step and $8.8 \times 10^{11}$ cm$^{-3}$ during the etching step. Corresponding ion fluxes to the wafer surface are shown in Fig. 5.3(a). Cl⁺ has the largest flux, $3.6 \times 10^{16}$ cm$^{-2}$s$^{-1}$, in the first step due to dissociation of the Cl₂ feedstock and charge exchange from Ar⁺, which has a flux of $1.3 \times 10^{16}$ cm$^{-2}$s$^{-1}$. The lack of any competing ionization or dissociation processes results in a larger Ar⁺ flux in the second step of $8 \times 10^{16}$ cm$^{-2}$s$^{-1}$. The passivating Cl radical flux is two orders of magnitude higher at $1 \times 10^{18}$ cm$^{-2}$s$^{-1}$ and is uniform across the wafer. The uniformity of the flux
is important to ensure that each layer is uniformly passivated to maintain atomic etching basis during each cycle.

Time-averaged IEADs for sum of for all ions are shown in Fig. 5.3(b) for one PALE cycle. During the passivation step, low ion energies are necessary to minimize etching and enable passivation of the top Si layer as SiCl$_x$. Note that in our model, we do not allow passivation of greater than a monolayer when in reality there is likely some mixing of the top layers and diffusion into the mixed zone that allows more than a single monolayer to be passivated. In the etching step moderately high ion energies are necessary to activate etching of the SiCl$_x$ layer (based on purely chemical sputter mechanism) while being low enough to minimize purely physical sputtering.

The feature first investigated is Si-FinFET having a 10:1 AR as shown in Fig. 5.4. The desired process is to thin the FinFET uniformly in both axial and lateral directions. The computational mesh has a spacing of one monolayer (ML) in both directions, so the removal of one mesh cell corresponds to etching a monolayer. Predicted etch profiles are shown in Fig. 5.4. After one cycle, approximately 1 ML is removed in both axial and lateral directions. The top surface is, however, rough due, in part, to a small amount of etching that takes place during the passivation step by the low energy, but anisotropic, ion flux. In extending the PALE process to 3 cycles, one layer per cycle was removed in the lateral direction. In the axial direction, however, 4 ML were removed, the cumulative effect of there being fractionally more than 1 ML removed per cycle. The extra etching primarily occurs during the passivation step, emphasizing the need to control the length of exposure (process cycle time) and the ion energies.

For example, the evolution of the feature at the bottom of the Si-FinFET is shown in Fig. 5.5 for 3 cycles of PALE. The original feature surface height is indicated by the arrow. The
location labeled $A$ is etched during the initial passivation step and creating a locally rough surface. From that point onward, each cycle removes an additional monolayer, thereby preserving the initial roughness and propagating this defect through additional PALE cycles. The ion-activated etching during the passivation step tends to be more stochastic than during the etch step due to the activation resulting from ion in the tail of the IEAD which is sparsely populated. For example, there is no etching during the second passivation cycle but there is etching, adding to the surface roughness, taking place during the third passivation cycle (shown as $B$ in frame 5). In addition to the ion-activated process, etching during passivation may be thermally activated. Too long of exposure during the passivation step that over-chlorinates the surface could contribute to etching by either thermal means or by reducing the activation energy for the ion activated process. Therefore, controlling the ion energies and/or the passivation cycle time step (depending on the etch mechanism) is very important to achieving atomic etch resolution with minimal roughness.

The consequences of ion energies on surface roughness during the passivation step of a PALE cycle are shown in Fig. 5.6. The final profiles for the upper left edge of the Si-FinFET after the passivation step are shown in Fig. 5.6(a). The IEADs for this parameterization are those for Step 1 as shown in Fig. 5.3(b) while adding (or subtracting) a fixed energy. The cited energy is the average, which is approximately that of the peak (17.4 eV for Fig. 5.3b). The surface roughness increases with increasing ion energies. The probability for an ion of energy $\epsilon$ activating an etch scales as $(\epsilon-\epsilon_0)^{1/2}$, where $\epsilon_0$ is a threshold energy.[3] In this work, $\epsilon_0 = 16.0$ eV.[4] For average energies less than this threshold energy the surface roughness is a result of the ions in the tail of the distribution or thermal etching. As ion energies increase beyond the threshold energy, additional ion-enhanced etching occurs. Since the passivation occurs rapidly,
an etched site can be re-passivated and etched a second time, thereby producing roughness with an average greater than 1 ML. These effects are enhanced at the corner which, on average, see higher fluxes than flat surfaces.

The consequences of the time length of the passivation step on profile roughness are shown in Fig. 5.7. The upper left edges of the Si-FinFET after one cycle are shown in Fig. 5.7(a) for varying length of the passivation period, \( \tau \). A value of \( \tau=1 \) corresponds to the passivation step being performed for one second with the ion energy distributions as shown in Fig. 5.3(b). The surface roughness increases with length of exposure to the passivating plasma due to two effects. The first is the increasing likeliness of thermal etching. The second is the stochastic etching, repassivation and etching of isolated sites. For an average ion energy of 17.4 eV the ions arriving with energies above the etching threshold are sparse, and etching during passivation is somewhat stochastic. Should that stochastic etch occur early during the passivation step, the likelihood that the site will be repassivated (and perhaps etched again) increases. Keeping the average ion energy significantly below threshold reduces the stochastic etching during passivation.

The extreme selectivity that PALE potentially provides can be especially useful in providing soft-landing (that is, a process that slowly approaches the underlying interface) during the over-etch portion of a conventional etch recipe. For example, such a process might use a rapid but not particularly selective etch using a sinusoidal bias for a soft landing. For example, etch profiles for a 5:1 aspect ratio Si-over-SiO\(_2\) feature are shown in Fig. 5.8. The main etch was performed using a 20 mTorr Ar/Cl\(_2\)=80/20 mixture in the ICP reactor described earlier (100 sccm, 500 W ICP, sinusoidal substrate bias of 100 V). The profile at the end of the main etch is shown in frame 2. The main etch is tapered, thereby requiring that it be stopped many
monolayers before the Si-SiO$_2$ interface is reached to insure that a soft-landing is achieved. Following the main etch, 25 cycles of PALE are used to clear the trench to the bottom, the large number of cycles being necessitated by the initial heavy taper. Due to the taper, the interface is reached during PALE after 14 cycles (frame 7). The potential extreme selectivity provided by PALE enables the feature to cleared using an additional 11 cycles with there being minimal damage to the underlying SiO$_2$ limited to the first monolayer. There will be a tradeoff between the process variation which motivates one to stop the etch significantly above the interface to minimize potential damage and the larger number of PALE cycles that extends the time of the process.

5.3 PALE of SiO$_2$ in Ar/$c$-C$_4$F$_8$ Capacitively-coupled Plasmas

PALE of SiO$_2$ was investigated using the MERIE (Magnetically Enhanced Reactive Ion Etching) reactor, shown schematically in Fig. 5.9. The metal substrate is powered at 10 MHz through a blocking capacitor. The wafer, 20 cm in diameter, sits in electrical contact with the powered substrate and is surrounded by dielectric focus rings. All other surfaces in the reactor are grounded metal including the showerhead, which extends to a radius of 12 cm, and the annular pump port. The gas mixture is Ar/$c$-C$_4$F$_8$ during the passivation step and pure Ar during the etching step. (The Ar/$c$-C$_4$F$_8$ reaction mechanism is discussed in Ref. 5.) Discrimination between passivation and etching will be obtained by controlling ion energies by applying a magnetic field parallel to the substrate.

For the passivation step, a 40 mTorr Ar/$c$-C$_4$F$_8$=75/25 gas mixture with a flow rate of 300 sccm was used with a bias power of 500 W at 10 MHz obtained with a sinusoidal voltage amplitude of approximately 200 V. The goal is to rapidly deposit a single layer of fluorocarbon
passivation sufficient to remove a ML of SiO$_2$. Since low energy ion bombardment enhances the rate of polymer formation, a parallel magnetic field of 250 G was used to lower ion energies to being dominantly below the etching threshold.[6] For the etch step, the plasma was sustained in pure Ar at 40 mTorr with a flow rate of 300 sccm. The bias on the substrate was varied to deliver a power deposition of 100 W (obtained with approximately a 130 V sinusoidal amplitude). Since the etch is facilitated by high-energy ion bombardment, the magnetic field was not used.

The CF$_2$ radical density during the passivation step and Ar$^+$ ion density during the etching step are shown in Fig. 5.9. The peak CF$_2$ density is $3.4 \times 10^{12}$ cm$^{-3}$ during the passivation step and the peak ion density is $1.6 \times 10^{10}$ cm$^{-3}$ during the etching step. Radical and ion fluxes to the wafer during the passivation step are shown in Fig. 5.10. The CF$_2$ radical density is uniform over the radius of the wafer which is critical to achieving a uniform polymer coverage during the passivation step. The ion density is radially uniform over the inner two thirds of the wafer to better than 10%, with there being a maximum near the edge of the wafer, characteristic of narrow gap, capacitively coupled discharges. The large electron density ($\approx 10^{11}$ cm$^{-3}$) highly dissociates the c-C$_4$F$_8$ feedstock. As a result, the major radical fluxes are CF$_3$, C$_3$F$_5$, and F; and the major ion fluxes consist of Ar$^+$, C$_2$F$_4^+$, and CF$_x^+$ (x=1-3). The Ar$^+$ flux ($2.3 \times 10^{15}$ cm$^{-2}$s$^{-1}$) during the second etching step is nearly uniform across the wafer although the etch rate may not be uniform owing to there being non-uniform passivation layers.

Time-averaged IEADs for all ions are shown in Fig. 5.11 for the Ar/c-C$_4$F$_8$ passivation and Ar etching steps. Low ion energies are important for rapidly depositing the passivating polymer layer which is the precursor to etching of SiO$_2$ in the second step. With the parallel magnetic field, the reduction in the cross-field mobilities of electrons thickens the sheath,
increases the voltage drop across the bulk plasma and, in some cases, causes a reversal of the
electric field in the sheath.[6] The result is that the voltage drop across the sheath is lower and,
in some cases, decelerates ions, both of which produce an IEAD which is lower in energy and
broader in angle. Although there is a high energy component in the IEAD for the passivation
step, the average ion energy is only 24 eV with the ions above 45 eV constituting <10% of the
total flux. The broad angular distribution will produce additional side-wall impacts as the
bottom of the trench is approached which further contributes to polymer formation.

The IEAD for the etching step is fairly narrow with an average energy of 71 eV which is
marginally higher than the etch threshold energy (69 eV) for the polymer and SiO$_2$C$_x$F$_y$
complexes at the interface of the SiO$_2$. Maintaining the average energies near threshold reduces
the likelihood of physical sputtering by ions in the higher energy tail of the IEAD.

The feature investigated is the 10:1 aspect ratio SiO$_2$-over-Si trench shown in Fig. 5.12.
The proof of principle demonstration for PALE is shown at the bottom of the trench when
selectivity and CD requirements are most stringent in Figs. 5.12 and 5.13. The desired process is
to remove all of the SiO$_2$ at the bottom of the feature without damaging the underlying Si while
maintaining an anisotropic profile. In these demonstrations, there are 20 monolayers of SiO$_2$
above the Si underlayer. Removal of the first three layers is shown in Fig. 5.12. The feature
after the first passivation step is shown in frame 2, and following the first three etch steps in
frames 3-5. A single ML is removed during each step in the vertical direction with some small
amount of non-uniformity. Although most sites are passivated with a single layer of polymer,
statistically some sites are not passivated and others have multiple layers of passivation. During
the following etch step, the SiO$_2$ at neither of these sites are removed, the former because its
threshold energy is greater than the energy of the majority of the ions and the latter because the
etch step is not long enough to both sputter the overlying polymer and etch the passivated site. Subsequent etching step that removes additional monolayers tend to preserve this initial roughness. The locally rough surfaces are mediated by having a uniform coverage of the passivating polymer. The fluxes of polymerizing radicals and low-energy ions over the time of exposure must be long enough to passivate all sites but not so long that multiple passivating layers are deposited.

The clearing of the bottom of the feature during 20 cycles of PALE is shown in Fig. 5.13 for various cycles of PALE. In each case, the SiO₂ surface advances a monolayer indicating ML etch resolution. Although a layer-by-layer etch is achieved in the vertical direction, requiring only 20 cycles to remove the 20 layers, there is etching of and deposition on the sidewalls. This results from redeposition of etch products and the low energy, broad angular distribution during the passivation step that efficiently produces polymer. The side-wall polymer, which is not fully removed during the etch step, produces some narrowing of the feature. The thick passivation layers on the side-walls might require use of a cleaning step following the etch step (e.g., an oxygen plasma), thereby making PALE a 3-step process.

Control of the IEAD is critical to achieving ML resolution with minimal roughness. For example, the consequences of increasing ion energies on surface roughness during the etching step of an Ar/c-C₄F₈ PALE cycle of SiO₂ are shown in Fig. 5.14. The bottom surfaces of the SiO₂-over-Si trench after an intermediate etching step and MLs of roughness are shown for different ion energies. The IEADs are those for Step 2 shown in Fig. 5.11 while adding (or subtracting) a fixed energy. The cited energy is the average, which is approximately that of the peak (71 eV for Fig. 5.11). Increasing ion energies have the advantage of enabling an etch even if the passivation layer is thicker than a single ML and sputtering passivation layers on the side-
walls. There is also the disadvantage of increasing the surface roughness as shown in Fig. 5.14(b). The surface roughness is compared for two cycle times: 13 s and 26 s. For a total cycle time of 13 s, the passivation step time is 1 s which is not sufficient to provide a uniform coverage. For a total cycle time of 26 s, the passivation step time was increased to 2 s which although ensures the complete coverage of the first monolayer, multiple passivation layers also result. The etching step time consequently increased to 24 s to ensure complete removal of all passivation layers.

The general trend if that surface roughness increases with increasing ion energy and decreasing cycle time. The larger roughness at the lower cycle time results from there being incomplete passivation. As a result, passivated sites are chemically etched with lower ion energies whereas adjacent sites are not or require higher ion energies to etch. The more complete passivation afforded by the longer cycle time enables more sites to be chemically etched by lower ion energies. The increasing roughness with increasing ion energy indicates two etching regimes. For ion energies \(<110\ eV\), the etch mechanism is dominated by chemically enhanced processes benefiting from passivation. The transition to physical etching occurs at higher ion energies, resulting in a steep increase in surface roughness.

Many steps in IC fabrication can be “self-aligned” to previous steps if a part of the deposited insulating layer is resistant to the process that is used to etch the silicon dioxide. For example, a self-aligned etch process allows a contact etch to land on both the source/drain and gate regions simultaneously or source/drain and isolation regions simultaneously. While such a process improves packing density and relaxes the lithography requirements, they impose tough selectivity requirements on the etch process as multiple materials are landed upon in one process. Typical self-aligned contact (SAC) etch processes are high aspect ratio oxide etch processes that
are generally selective to an etch profile guiding layer above a gate or a spacer serving as an etch stop layer. Several different stop layers have been suggested, for example, polysilicon[7], silicon-rich nitrides[8] and oxynitrides.[9]

An important requirement for etching of self-aligned contacts (SAC) is high etch selectivity of the overlying silicon-dioxide with respect to the stop layer and so the high selectivity of PALE processes may be appropriate for etching of SACs. For example, the Ar/c-C$_4$F$_8$ PALE process was used to etch a Si-SiO$_2$ self-aligned contact as shown in Fig. 5.15. The feature has a 10:1 aspect ratio with 20 monolayers of Si aligned with 20 monolayers of SiO$_2$. The protruding feature and the underlying material is Si. The IEADs used to clear the feature are those shown in Fig. 5.11. The high selectivity of the PALE process enables the exposed Si feature to maintain its critical dimension while the adjacent SiO$_2$ is etched away during 20 cycles of PALE. The damage to the top surface of Si is 1-2 monolayers with the corner of the feature most eroded. The side-wall of the trench is less prone to damage as redeposition etch products provide sufficient passivation to slow etching.

### 5.4 PALE using Non-sinusoidal Bias Waveforms

In the previous sections we discussed the feasibility of achieving ML etch resolution using conventional plasma etching tools. The high selectivity of PALE is enabled by using two gas mixtures which allow the passivation component to be independent of the etching component by controlling ion energies. The speed of a PALE cycle using this strategy is limited by having to purge the gas mixture of the previous step prior to performing the next step. If the purge step can be eliminated by using the same gas mixture for both steps, the speed of PALE processes can be improved. This goal can only be achieved by having a highly precise control over the IEADs
to discriminate between etch thresholds. This can be achieved by using a non-sinusoidal waveform in which narrow IEADs can be obtained.

The non-sinusoidal bias waveform used in this work consists of a quasi-dc negative bias with a narrow positive voltage spike to accelerate both the ions and electrons during one rf cycle.[10] The quasi-dc bias produces a nearly constant sheath potential as a function of time during the rf cycle which, if unperturbed by the positive voltage spike, would produce a narrow IEAD.[11] As long as the positive excursion is of short enough duration the sheath potential, as seen by the heavy ions, is largely undisturbed and the perturbation to the narrow IEAD is minimal.

PALE of SiO$_2$ was investigated for an Ar/$c$-C$_4$F$_8$=75/25 (100 sccm flow-rate), 15 mTorr plasma in our ICP reactor utilizing a tailored bias waveform that produces a narrow IEAD.[10] The inductive power is 500 W at 5 MHz, and the non-sinusoidal bias is applied at 2 MHz. Since during the first step, a C$_x$F$_y$ polymer passivates the top layer of SiO$_2$ without etching, this step is performed with a bias producing low energies. The second step, etching of the SiO$_2$C$_x$F$_y$ polymer complex, is performed with a bias producing above threshold ion energies. The recipe uses a conventional etch for the majority of the feature followed by PALE to clear the bottom of the trench. The main etch is performed using a 200 V (peak-to-peak) sinusoidal bias waveform.

Time-averaged IEADs for all ions are shown in Fig. 5.16 for the main etch and PALE using non-sinusoidal waveforms. For PALE, a 50 V (peak to peak) bias was used for passivation and a 100 V (peak to peak) bias for etching. The sinusoidal bias waveform produces the familiar broad IEAD which results from ions of different masses entering the sheath at random times during the rf cycle. The lighter ions arrive at the substrate with nearly the instantaneous sheath potential while the heavier ions arrive with an average sheath potential. The end result is a fairly
broad IEAD, in this case extending for 85 eV. The tailored waveforms generally produce a narrower IEAD than the sinusoidal case in large part because the sheath voltage remains constant between the positive going spikes of the bias. The transit time across the sheath for the lighter ions is short compared to the pulse period, so the energy of each ion depends on the instantaneous potential drop when it enters the sheath.

Corresponding radical and ion fluxes to the wafer are shown in Fig. 5.17. The major radical fluxes are CF, C_2F_3, and F; and the major ion fluxes consist of Ar^+, CF_3^+, and CF^+. Lower F atom and ion fluxes may result in a thicker passivation layer near the edge of the wafer. In contrast, decreasing polymerizing fluxes may result in thinner polymer layer near the edges. The net result of the two opposing effects is that the etch rates near the edge of the wafer are slightly lower than at the center.

The feature is a 10:1 aspect ratio SiO_2-over-Si trench and profiles during the main etch are shown in Fig. 5.18. The main etch is stopped just after the SiO_2-Si interface is breached. Microtrenching at the sides of the trench expose the underlying Si and an aggressive over-etch to remove the central peak of SiO_2 is necessary to avoid further damage. The subsequent over-etch was performed using a tailored bias voltage waveform and a PALE recipe as shown in Fig. 5.19. The over-etch was completed in 5 PALE cycles. A PALE process should, in principle, have etch rates of 1 ML/cycle. However we found that with this PALE recipe using the tailored bias waveform an effective etch rate of ~4-5 ML/cycle was achieved. The high etch rates are enabled because of there being polymerizing radicals and low energy ions during the etching step which remove the self-limiting nature of an atomic layer (deposition or etching) process. The polymer layer is, however, thick enough and the ion energies low enough that the underlying Si is not etched.
The speed of the process must ultimately be a tradeoff between ML control and the onset of roughness. The number of tailored bias PALE cycles required to perform the over-etch of the feature shown in Fig. 5.19 and the roughness are shown in Fig. 5.20 as a function of ion energy of the etch step. The IEADs are for Step 2 as shown in Fig. 5.16 while adding (or subtracting) a fixed energy. The cited energy is the average, which is approximately that of the peak (70 eV for Fig. 5.16). Higher ion energies enable higher etching rates thus decreasing the number of cycles required for the same over-etch. (Note that the non-uniformity of the initial feature profile requires at least two cycles even at high ion energies.) However, the roughness increases with increasing ion energy. This is, in large part, due to the etching of exposed underlying Si after the main etch.

If the main etch were stopped well before the SiO\textsubscript{2}-Si interface is reached, the tailored bias PALE steps should be able to clear the feature without any damage to the underlying Si. For example, for the etch sequence shown in Fig. 5.21, the main etch was stopped prior to reaching the SiO\textsubscript{2}-Si interface. This was followed by tailored bias PALE cycles to clear the feature. The IEADs for this etch sequence are as shown in Fig. 5.16. The damage to the underlying Si is less than a ML. Etching of the Si underlying the SiO\textsubscript{2} by PALE also contributes to the roughness at high ion energies.

5.5 Conclusions

The potential of utilizing conventional plasma etching tools for plasma atomic layer etching (PALE) has been discussed based on results from a computational investigation using a reactor scale model coupled to a feature scale model. PALE of Si (using Ar/Cl\textsubscript{2} plasma) in an ICP reactor and PALE of SiO\textsubscript{2} (using Ar/C\textsubscript{4}F\textsubscript{8} plasma) in a CCP reactor as model tools were
investigated. In both cases, atomic level (one monolayer) control was achieved. Highly precise control of the ion energies is, however, critical to achieving monolayer resolution with minimal roughness. The use of two different gas mixtures separates the passivation and etching components enabling very high selectivity important at material interfaces. However, the speed of PALE is slowed by having to purge the different gas mixtures between steps. The feasibility of eliminating the purge step by utilizing tailored bias waveforms was investigated. Tailored bias waveforms enable narrow IEADs which allows for precise control over the IEADs to discriminate between threshold energies of different materials while using a single gas mixture. PALE of SiO₂ (using Ar/c-\textsubscript{4}F₈ plasma) was achieved in an ICP reactor by using a tailored bias waveform by changing amplitudes to alternate between the passivation and etching regimes. PALE recipe using the tailored bias waveforms yield effective etch rates >1 ML/cycle as the self-limiting nature is removed as a consequence of there being polymerizing radicals and low energy ions during the etching step. The high selectivity at high speeds make PALE using a tailored bias waveform a useful complement to conventional etching for soft-landing processes.
Fig. 5.1: Schematic of the Plasma Atomic Layer Etching (PALE) process. At the end of one cycle, a monolayer is etched. If ion energies exceed the threshold energy of the underlying material, more monolayers may also be etched.
Fig. 5.2: Total positive ion densities during the Si PALE process using ICP as a model tool. (a) Passivation step of the cycle is performed in Ar/Cl₂=80/20, 500 W ICP power, 16 mTorr, 100 sccm. (b) Etching step of the cycle is performed in pure Ar, 500 W ICP power, 16 mTorr, 100 sccm and 100 V sinusoidal rf bias at 2 MHz. Contour levels shown are on a scale of 10¹¹.
Fig. 5.3: (a) Ion fluxes to the wafer as a function of radius for the Si PALE process. Cl$^+$ is the major ion in the passivation step due to dissociation of the Cl$_2$ feedstock.
(b) Total IEADs averaged over the wafer for the Si PALE process. The low ion energies are necessary to minimize etching during the passivation step. The higher ion energies in the second step enable etching of the SiCl$_x$ passivation layer. Log scale plotted over 2 decades.
Fig. 5.4: Final predicted etch profiles of 10:1 aspect ratio Si-FinFET using Ar/Cl₂ followed by Ar PALE process. In the first half of the cycle, SiClₓ passivation covers each monolayer. In the second half of the cycle, the passivation is etched. After one cycle, approximately a monolayer is removed from both axial and lateral directions. In extending PALE to 3 cycles, one layer per cycle was removed in the axial direction but 4 layers in the axial direction indicating some physical etching. The mesh resolution is 3 Å.
Fig. 5.5: Final predicted etch profiles for the bottom of the Si-FinFET using Ar/Cl$_2$ followed by Ar PALE process. Location $A$ is etched during the initial passivation step creating a locally rough surface. Any initial roughness is preserved and the defect propagates through additional PALE cycles. Etching during the third passivation cycle (shown as $B$ in frame 5), adding to the surface roughness, indicates the stochastic nature of ion-activated etching during passivation step.
Fig. 5.6: Consequences of ion energies on surface roughness during the passivation step using Ar/Cl₂ plasma for Si PALE. (a) Final profiles for upper left edge of the Si-FinFET after passivation steps with ion energies of 15, 25, and 40 eV. (b) Surface roughness (in monolayers) increases with increase in ion energies. For average ion energies above the threshold energy, surface roughness is a result of thermal etching. As ion energies increase beyond threshold energy, additional ion-enhanced etching occurs.
Fig. 5.7: Consequences of time length of the passivation step on profile roughness. The parameter $\tau$ defines the time for which the passivation step was performed relative to the time for PALE in Fig. 4. (a) Upper-left edges of Si-FinFET after one cycle for varying length of the passivation period, $\tau$. (b) Surface roughness increases with length of exposure to the passivating plasma due to two effects: thermal etching and stochastic etching.
Fig. 5.8: Etch profiles for a 5:1 aspect ratio Si-over-SiO$_2$ feature based on an etching recipe which combines a conventional sinusoidal bias main etch with PALE (for soft landing). The profile at the end of the main etch is shown in frame 2. The tapered feature after the main etch is etched in 25 cycles of PALE with extreme selectivity with little damage to the underlying SiO$_2$. The slow, extreme selectivity of PALE is a useful complement to the speeds of main etch.
Fig. 5.9: PALE of SiO$_2$ in Ar/c- C$_4$F$_8$ capacitively-coupled plasmas. (a) Schematic of the MERIE reactor used in this study. The magnetic field, when applied, is purely radial. (b) Passivation step of the cycle is performed in Ar/c-C$_4$F$_8$=75/25, 500 W power, 40 mTorr, 300 sccm and 250 G magnetic field. The high magnetic field shifts the peak energy of the ions to low energies. (c) Etching step of the cycle is performed in pure Ar, 100 W power, 40 mTorr, and 300 sccm. Magnetic field is not applied to enable higher ion energies. Log scale plotted over 2 decades.
Fig. 5.10: Fluxes to the wafer as a function of radius for the base case conditions for Ar/c-\( \text{C}_4\text{F}_8 \) plasma. (a) Neutral and (b) ion fluxes. \( \text{CF}_3 \), \( \text{C}_3\text{F}_5 \), and \( \text{F} \) are the dominant neutral radicals. \( \text{Ar}^+, \text{C}_2\text{F}_4^+, \) and \( \text{CF}_x^+ (x=1-3) \) are the dominant ions.
Fig. 5.11: Total IEADs averaged over the wafer for the SiO$_2$ PALE process. The high radial magnetic field enables low ion energies which promotes polymer formation. The high ion energies during the etching step enables sputtering of the polymer. Controlling ion energies during the second step avoids physical etching and enables the self-limiting nature.
Fig. 5.12: Predicted etch profiles of 10:1 aspect ratio SiO$_2$-over-Si trench using Ar/$c$-C$_4$F$_8$ followed by Ar PALE process. Etch profiles over the first 3 cycles of PALE are shown. In the first half of the cycle (frame 2), SiO$_2$C$_x$F$_y$ polymer covers each monolayer. In the second half of the cycle (frames 3-5), the polymer is etched. During each cycle, a monolayer is removed.
Fig. 5.13: Final predicted etch profiles of 10:1 aspect ratio SiO$_2$-over-Si trench using Ar/c-C$_4$F$_8$ followed by Ar PALE process. There are 20 monolayers of SiO$_2$ which are etched in 20 cycles of PALE. The thick passivation on the sidewalls is a consequence of redeposition of etch products. The selectivity of PALE is very high as a result of great control over IEADs.
Fig. 5.14: Consequences of increasing ion energies on surface roughness during the etching of an Ar/c-C₄F₈ PALE cycle of SiO₂. (a) Bottom surfaces of the SiO₂-over-Si trench after intermediate etching steps with ion energies of 75, 100, and 120 eV. (b) Surface roughness increases with increasing ion energy and decreasing cycle times. The larger roughness at the lower cycle time results from there being incomplete passivation.
Fig. 5.15: Etch profiles for Ar/c-C₄F₈-Ar PALE etching of Si-SiO₂ self-aligned contact. There are 20 monolayers of Si aligned with 20 monolayers of SiO₂. A highly selective etch of the contact is achieved in 20 cycles of SiO₂. A sidewall of the Si in the contact is prone to less damage as a result of passivation by redeposited etch products.
Fig. 5.16: Total IEADs averaged over the wafer for the tailored bias PALE recipe. First, a main etch is performed with a 200 V (peak-to-peak) sinusoidal bias followed by PALE cycles utilizing a non-sinusoidal bias with biases of 50 V (peak-to-peak) for passivation and 100 V (peak-to-peak) for etching. The narrow distribution of IEAD for non-sinusoidal biases enables using a single gas mixture for the entire cycle of PALE.
Fig. 5.17: Fluxes to the wafer as a function of radius for the non-sinusoidal bias PALE process. (a) Neutral and (b) ion fluxes. CF₂, CF, and CF₃ are the dominant fluorine containing neutral radical fluxes. Ar⁺, CF₃⁺, CF₂⁺, and CF⁺ are the dominant ion fluxes.
Fig. 5.18: Etch profiles for a 10:1 aspect ratio SiO$_2$-over-Si trench during the main etch process. The main etch is stopped just after the SiO$_2$-Si interface is breached. Microtrenching at the sides of the trench expose the underlying Si and an aggressive over-etch to remove the central peak of SiO$_2$ is necessary to avoid further damage.
Fig. 5.19: Predicted etch profiles for the over-etch of the SiO$_2$-Si trench utilizing an Ar/$c$-C$_4$F$_8$-Ar non-sinusoidal PALE recipe. The narrow IEADs enabled by the non-sinusoidal bias waveform demonstrate extreme selectivity. The central peak of SiO$_2$ is etched without significant damage to the underlying Si and already exposed Si over 5 cycles of PALE.
**Fig. 5.20:** Surface roughness and number of PALE cycles as a function of ion energies during the etching step. Surface roughness in general increases with increase in ion energies. The primary contributor to surface roughness being the already exposed Si. The non-uniform initial feature profile limits the number of cycles to two even at very high ion energies.
Fig. 5.21: Predicted etch profiles for the SiO$_2$-Si trench when the main etch is stopped well before the SiO$_2$-Si interface. The high selectivity of the non-sinusoidal bias PALE recipe is highlighted as the damage to the underlying Si is less than a ML. The feature is cleared in about 15 tailored bias PALE cycles with an average etch rate of ~ 5 ML/cycle.
5.7 References


6. SURFACE CHEMISTRY MODEL

6.1 Introduction

During plasma processes such as etching and deposition, the reactive species in the plasma interact with substrates and reactor walls. This is especially true in the current low-pressure operating conditions being employed for processing where the mean free path for transport of species is large.[1] In the case of etching tools, the consequences of the plasma-surface interactions on the etch as well as the bulk plasma has been studied.[2-6] Schaepkens et al. have shown that the wall temperature of an etch chamber affects the sticking coefficient of the fluorocarbon radicals on the walls.[4] This change has an effect not only on the etch rate, but as well as on the bulk gas phase densities. Although models exist that address the plasma equipment and the bulk and surface processes separately[7-11], very few models consistently address both simultaneously, to account for the feedback of surface interactions to bulk processes.

To this end, the capability to address surface reactions in the HPEM was added. Surface reactions in the HPEM are addressed by the Surface Chemistry Model (SCM) using a flux in – flux out boundary condition. Most of the physics of this model has been developed earlier, and is reviewed again here.[12]

6.2 Surface Chemistry Model (SCM)

The SCM implements a modified surface-site balance algorithm along the plasma-surface boundary, and outputs the surface coverages, thickness and composition of overlaying films, sticking coefficients, and modified fluxes of species returning to the plasma. Aside from the
gaseous species being directly available as surface reactants, there is also possibility (for example, in fluorocarbon plasmas), of overlaying films, through which the gaseous species diffuse to the available surface sites. In addition, the constituents of the film may also react with the gaseous species and the underlying substrate. The SCM is capable of handling all above scenarios. A comparison of a conventional surface site balance model and the SCM is shown in Fig. 6.1.

For each \( i^{th} \) plasma specie interacting with the \( m^{th} \) surface, a reaction probability, \( S_{im} \), is defined. Depending on the surface reaction mechanism, species are “reflected” back into the plasma. The reflecting flux of a species back to the bulk plasma is

\[
\Phi^R_{im} = (1 - S_{im})\Phi^I_{im}
\]  

(6.1)

Where \( \Phi^I_{im} \) is the incident flux of the species \( i \) to the surface \( m \). Each incident species may also produce other species on the surface. Therefore, for the \( i^{th} \) specie incident on the surface \( m \), the flux of the \( j^{th} \) generated specie returning to the plasma is

\[
\Phi^R_{ijm} = f_{ijm} \cdot \Phi^I_{im}
\]  

(6.2)

where \( f_{ijm} \) is the fractional rate of generation. For example, consider a CF\(_2\) ion (species 1) striking a wall passivated by a CF\(_3\)p polymer (material 4), neutralizing to form ground state CF\(_2\) (species 2) with unity probability and sputtering CF\(_3\) (species 3) with probability of 0.01. The coefficients are \( S_{14} = 1, f_{124} = 1, f_{134} = 0.2 \).
The values of $S_{im}$ and $f_{ijm}$ ultimately depend on surface coverages, and on the fluxes and energies of reactants. The SCM identifies specified surface locations on chosen materials, sets the initial surface species coverages, and extracts reactive fluxes to the surface. Based on a specified surface reaction mechanism, differential equations for fractional occupancy of surface sites and thickness and composition of overlaying polymer layers are integrated in time. The integration may or may not be performed in lockstep integration with the plasma model. This process is continued for a user-specified time, and the resulting coefficients $S_{ik}$ and $f_{ijk}$ are fed back to the plasma model for the subsequent iteration. Etching or deposition rates are obtained based on the surface coverages and reactive fluxes at the end of the call to the SCM. The flow chart of the integrated model is shown in Fig. 6.2.

There are three classes of surface processes used in SCM. The first class involves the reactions of non-ionic plasma species with the first exposed layer of the boundary. This may be an exposed substrate site, or a polymer site. In the absence of overlayer formation, this class of reactions would be sufficient to model the surface evolution. The generic form of these reactions is

$$A_g + B_s \xrightarrow{k_i} C_s + D_s + E_g$$

(6.3)

where the subscript $g$ denotes a gas species and the subscript $s$ denotes a surface resident species or a surface site, and $k_i$ is the reaction probability for the $i^{th}$ reaction. The evolution rate of the surface coverage of species $B$ on $m$ contributed by the $i^{th}$ reaction, $\left(\frac{\partial \theta_{Bm}}{\partial t}\right)_i$, is
\[
\left( \frac{\partial \theta_{Bm}}{\partial t} \right) = -\frac{1}{T} R_{im}
\]  

where \( T \) is the total surface site density per unit area, and

\[
R_{im} = k_i \cdot \Phi_i^A \cdot \theta_{Bm}
\]

where \( \theta_{Bm} \) is the fractional surface coverage of surface species or site \( B \) on \( m \). The surface reaction coefficient \( S_{Am} \) for incident plasma species \( A \) on material \( m \), which is used in the bulk plasma model, is obtained by summing the reaction rates of all processes including \( A \) as a reactant:

\[
S_{Am} = \sum_{j=1}^{s} \sum_{i=1}^{n} \frac{R_{ijm}}{\Phi_{Am}} = \sum_{j=1}^{s} \sum_{i=1}^{n} k_{ijm} \theta_{jm}
\]

where \( s \) is the total number of surface species and \( n \) is the number of reactions of \( A \) with surface species \( j \).

The rate coefficients for a surface process involving ions (e.g. sputtering) are typically functions of incident ion energy. The form used here is[13]

\[
p(E) = p_o \frac{E_r^m - E_r^m}{E_r^m - E_i^m}
\]  

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where \( p(E) \) is the reaction probability for an ion with energy \( E \), \( E_t \) is the threshold energy of the process, \( E_r \) is a reference energy, and \( p_o \) is the reaction probability at the reference energy. Typically, \( m = 0.5 \) for sputtering or ion activated etching, and that value was used in this work.

To represent these probabilities on different surfaces of the reactor, the PCMCM is used to compute the ion energy and angular distributions (IEADs) separately striking those surfaces. The flow chart of the HPEM-PCMCM-SCM integrated model is shown in Fig. 6.3. The probability for a given reaction along the surface is then given by,

\[
p(x) = \frac{\int f_i(E, x) p(E) dE}{\int f_i(E, x) dE}
\]  

(6.8)

where \( f(E,x) \) is the ion energy distribution function as a function of position and \( p(E) \) the surface reaction probability at energy \( E \) (which may vary due to the local surface composition) as given by Eq. 6.7.

The second class of reactions is between surface species, or between a surface species and a polymer species. This includes reactions that form, for example, \( \text{SiO}_2-\text{CF}_x \) complexes at the interface between substrate and polymer. The rates of these reactions are (for polymer species \( B \) and surface species \( A \)):

\[
R_{AB} = \nu \frac{[A]}{T} \frac{[B_p]}{T \cdot L'}
\]  

(6.9)
where \( v \) is a user-specified “frequency”, \( T \) is the surface site density (typical value is \( 10^{15} \text{ cm}^{-2} \)), \( L' \) is the thickness of the polymer (in monolayers), \([B_p]\) is the contribution of species \( B \) to the polymer (in monolayers), and \([A_s]\) is the surface density of species \( A \).

The third class of reactions involves transport of species through the overlayers. For example, in fluorocarbon etching plasmas, the thickness of the layers regulates the energy transferred by the ions to the substrate. The SCM first solves for the thickness of the polymer layer. In the case of the resolved composition of the polymer, this is given by

\[
L' = \sum_{i=0}^{i=3} [CF_{ip}]
\]

(6.10)

where \([CF_{ip}]\) is the effective thickness of the \( CF_{ip} \) component of the polymer layer.

The ion inhibition at the substrate due to the traversal through the overlayer is governed by

\[
p(E) \propto \frac{1}{(1 + \alpha L')^2}
\]

(6.11)

where the typical value of parameter, \( \alpha \), is 0.3. Thus, as the polymer becomes thicker, the ion loses most of its energy in the first few monolayers.

6.3 Surface Reaction Mechanisms for Si Etching in Ar/Cl\(_2\) Plasmas

The consequences of seasoning of the reactor on etching of Si using chlorine plasmas were investigated. The p-Si etching surface mechanism and species we used is listed in
Appendix F and is based on the works of Cheng et. al.[14] and Meeks and Shon[15] and is discussed in detail in Ref. 16. The mechanism is schematically shown in Fig. 6.4(a). Etching of the Si wafer takes place by first successively chlorinating the polysilicon surface, forming SiCl\(_n\)(s) [SiCl(s) followed by SiCl\(_2\)(s) and SiCl\(_3\)(s)], where (s) denotes a surface species. Following passivation, etching of the SiCl\(_n\) etch product then occurs through ion activation. To simplify the gas phase reaction mechanism here, etch products were limited to be SiCl\(_2\) and SiCl\(_4\). Etch products in the bulk plasma can redeposit on the wafer forming Si\(_2\)Cl\(_y\)(s) species which are treated as etch blocks. The etch blocks must be removed by ion bombardment to allow etching of the underlying Si to proceed. The reaction mechanism is summarized as

\[
\begin{align*}
\text{Cl} + \text{Si}(s) & \rightarrow \text{SiCl}(s) \quad p = 0.99 \\
\text{Cl} + \text{SiCl}_n(s) & \rightarrow \text{SiCl}_{n+1}(s) \quad p = 0.2 \\
\text{M}^+ + \text{SiCl}_n(s) & \rightarrow \text{SiCl}_n + \text{M} \quad p = 0.6 \\
\text{SiCl}_2 + \text{Si}(s) & \rightarrow \text{Si}_2\text{Cl}_2(s) \quad p = 0.8 \\
\text{SiCl}_2 + \text{SiCl}_n(s) & \rightarrow \text{Si}_2\text{Cl}_{n+2}(s) \quad p = 0.1-0.2 \\
\text{M}^+ + \text{Si}_2\text{Cl}_{n+2}(s) & \rightarrow \text{SiCl}_n(s) + \text{SiCl}_2 \quad p = 0.99
\end{align*}
\]

where M\(^+\) represents any ion and \(p\) is the default probability or the probability at the reference energy of 150 eV. Threshold energies for ion processes are 20 eV unless otherwise specified.

The plasma-surface reaction mechanism on non-wafer surfaces is based on the work of Cunge et al.[17] and is also summarized in Appendix F, and shown schematically in Fig. 6.4(a). To simplify the mechanism, the reaction of etched products with surfaces was limited to SiCl\(_2\),
since SiCl$_4$ is a saturated species. The etch products can stick to the walls which can then be further sputtered or etched by ions and hot neutrals.

\[
\text{SiCl}_2 + \text{W(s)} \rightarrow \text{SiCl}_2(s) \quad p = 0.2 \quad (6.18)
\]

\[
\text{SiCl}_2 + \text{SiCl}_2(s) \rightarrow \text{(no reaction)} \quad (6.19)
\]

\[
\text{M}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{Cl} \quad p = 0.1; E_t = 30 \text{ eV} \quad (6.20)
\]

\[
\text{M}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2 + \text{W(s)} \quad p = 0.8; E_t = 30 \text{ eV} \quad (6.21)
\]

where M$^+$ represents any ion. W is a native wall surface, $p$ is the probability at the reference energy of 150 eV. Cl atoms may adsorb onto bare wall sites and abstract adsorbed Cl but are otherwise unreactive with passivated sites,

\[
\text{Cl} + \text{W(s)} \rightarrow \text{Cl(s)} \quad p = 0.1 \quad (6.22)
\]

\[
\text{Cl} + \text{Cl(s)} \rightarrow \text{Cl}_2 + \text{W(s)} \quad p = 0.1 \quad (6.23)
\]

\[
\text{Cl} + \text{SiCl}_2(s) \rightarrow \text{(no reaction)} \quad (6.24)
\]

ICP reactors typically have dielectric windows above which the antenna sits and through which the electromagnetic field from the antenna enters the plasma. Quartz is a common material for the window. Sputtering of the quartz window by ions is a potential source of oxygen atoms in the plasma[18-20] which may lead to the formation of silicon oxychloride films. We included sputtering of O atoms from the quartz window using the algorithms discussed in Ref. 21. O atoms were sputtered with a threshold energy of 60 eV with a probability of 1.0 at a reference energy of 150 eV. The surface reaction mechanism including oxygen atoms is
schematically shown in Fig. 6.4(b) and is summarized in Appendix G. The oxygen atoms in the bulk plasma may undergo electron impact reactions like ionization as summarized in Appendix H. The species in the mechanism include ground-state neutral, O; electronic state, O(1D) and its ion, O⁺. Oxygen atoms can adsorb on any SiₓClᵧ passivated surface site forming SiOCl which, if on the wafer, is treated as an etch block. The etch block is removed, allowing the etch to proceed, when an oxygen atom is extracted from the oxychloride film by energetic ions,

\[
\begin{align*}
O + Si_xCl_y(s) & \rightarrow SiOCl(s) & p = 1.0 & (6.26) \\
M^+ + SiOCl(s) & \rightarrow SiCl(s) + O + M & p = 1.0; E_i = 60 \text{ eV} & (6.27)
\end{align*}
\]

The surface reaction mechanism described above will be used to investigate effects of seasoning of plasma reactors during etching of p-Si in Ar/Cl₂ plasmas. The results from the investigations are presented in Chapter 7.

### 6.4 Conclusions

The Surface Chemistry Model was discussed in this chapter. A more detailed description of the model can be found in the work by Zhang and Kushner[12]. The SCM uses the incident fluxes as an input from the bulk plasma model, HPEM. A surface reaction mechanism for Si etching in Ar/Cl₂ plasmas was developed to include interactions of etched products with non-wafer surfaces. Interactions of oxygen atoms sputtered from quartz window were also included. In the next chapter, the integrated model of HPEM-PCMCM-SCM will be used to investigate seasoning effects in a plasma etching reactor.
6.5 Figures

Fig. 6.1: Schematic of the (a) conventional site balance model and (b) the Surface Chemistry Model.
Fig. 6.2: Flow chart of the integrated bulk plasma (HPEM) and surface (SCM) model.
Fig. 6.3: Flow chart of the integrated HPEM-PCMCM-SCM model. PCMCM provides ion energy and angular distributions to compute rate coefficients for a surface process involving ions.
Fig. 6.4: Schematic of the surface mechanisms for Si etching in Ar/Cl$_2$ plasma.  
(a) Si,Cl$_x$ etch products form etch blocks, Si,Cl$_y$ on wafer. and  
(b) Sputtering of dielectrics introduces oxygen atoms in the bulk plasma forming etch blocks, SiOCl, on the wafer.


7. ION ENERGY DISTRIBUTIONS TO CHAMBER WALLS, AND REAL-TIME AND WAFER-TO-WAFER CONTROL STRATEGIES TO ADDRESS SEASONING OF PLASMA REACTORS

7.1 Introduction

Wafer-to-wafer process reproducibility during plasma etching often depends on the conditioning of the inside surfaces of the reactor. Passivation of reactor surfaces by plasma generated species can change the reactive sticking coefficients for radicals, thereby changing the composition of the radical and ion fluxes to the wafer. Ion bombardment of the walls may influence these processes through activation of sites or sputtering. As such the spatial variation of ion energies on the walls and their evolution as the chamber seasons are important. These seasoning processes may occur during a single etching sequence or on a wafer-to-wafer basis as wall passivation builds. Schematic representations of reactive processes on the various internal surfaces of the plasma chamber are shown in Fig. 7.1. In this chapter, the seasoning of plasma etching reactors will be discussed using results from a computational investigation of Si etching in chlorine plasmas. The ion energy distributions to all inside surfaces of the reactor were used to calculate the energy dependent surface reaction rates. Sputtered products from passivated side walls, and their transport to the wafer were accounted. The consequences on reactive fluxes to the substrate due to both wall sputtering and changes in reactive sticking coefficients will be discussed. A real-time, closed-loop control of etch rate to counter the effects of seasoning was achieved using the bias voltage as an actuator.

We found that the etch rate decreases as the chamber walls are seasoned due to a decrease in sticking coefficient for etch products which increases their gas phase density and increases their redeposition on the wafer as etch blocks. We also found that fairly subtle changes in the
placement of the coils above the quartz window can have profound effect on the seasoning of the reactor. The height of the coils above the quartz determines the amount of capacitive coupling to the plasma and the ion energies incident onto the quartz. This in turn determines the amount of sputtering of the quartz and the flux of O atoms injected into the plasma. The O atoms are a potential source of etch blocks (e.g., SiOCl) and wall passivation. The feedback control scheme is a proportional controller which uses the etch rate variation to vary the bias voltage to maintain a constant etch rate on both a real-time and run-to-run basis. We found that such a scheme can stabilize the process during a single etch while wafer-to-wafer control is sometimes complicated by disparity between the fresh state of a newly inserted wafer compared to the seasoned walls.

7.2 Seasoning of Reactors during Etching of Si in an Ar/Cl₂ Plasma

The model system is an ICP reactor schematically shown in Fig. 7.2(a). Inductive power is supplied through a 3-turn coil, 16 cm in diameter in contact with 0.8 cm thick quartz window, which is 23 cm in diameter. The wafer is on a substrate, which can be independently biased, 9 cm below the quartz window. The process conditions are a 15 mTorr Ar/Cl₂=90/10 gas mixture with a flow rate of 25 sccm. The coil delivers 500 W at 10 MHz. Both purely inductive and capacitively coupled configurations of the coil will be considered. The amplitude of the 5 MHz rf bias waveform at the electrode will be varied.

A typical computational strategy is as follows. Initial conditions (e.g. plasma density, dissociation fraction) are estimated and the model is executed with only ICP power for 60 μs to achieve a quasi-steady state in plasma characteristics. (The effective integration time is actually 10-100 times longer as acceleration techniques are used to speed the convergence of plasma properties.) Silicon etching is then enabled by applying the bias voltage using direct time
integration technique (that is, no acceleration) in the SCM. The surface reaction rate coefficients for gas phase species are updated by the SCM every 2 s. The etching of a series of wafers was modeled for a total of 180 s for each wafer. When a new wafer is started the surface of the wafer is initialized to have unprocessed conditions while the reactor walls maintain their seasoned surface coverages.

The densities of all positive ions and the SiCl₂ etch product are shown in Fig. 7.2(b) for a bias voltage of 75 V. Cycle-averaged radical and ion fluxes to the wafer are shown in Fig. 7.3. The peak ion density is $2.8 \times 10^{11}$ cm$^{-3}$ and the SiCl₂ has a peak density of $9 \times 10^{11}$ cm$^{-3}$ near its source of production at the wafer. The average density of SiCl₂ in the bulk plasma of $1.5 \times 10^{11}$ cm$^{-3}$, results, in part, due to passivation of the walls of the reactor which reduces the sticking coefficient for SiCl₂. The high density of SiCl₂ results in redeposition on the wafer which is largely responsible for the process drifts. The radicals having the largest flux, on axis, are Cl $(0.9 \times 10^{17}$ cm$^{-2}$s$^{-1}$), SiCl₂ $(6.9 \times 10^{15}$ cm$^{-2}$s$^{-1}$) and SiCl₄ $(2.5 \times 10^{15}$ cm$^{-2}$s$^{-1}$). The largest flux of ions is due to Ar$^+$ $(2.2 \times 10^{16}$ cm$^{-2}$s$^{-1}$) and Cl$^+$ $(2.0 \times 10^{15}$ cm$^{-2}$s$^{-1}$). The fluxes of Cl$^+$ and SiCl₂$^+$ are an order of magnitude lower. The fluxes are center peaked (no attempt was made to optimize the radial uniformity of the fluxes). Since the flux of Cl is essentially uniform across the wafer, spatially dependent etch rates results from the radial dependence of the ion and redeposition fluxes.

The ion energy and angular distributions (IEADs), for all ions, averaged over the wafer, the side wall and the quartz window (see locations in Fig. 7.2a) without capacitive coupling from the coils are shown in Fig. 7.4(a) for an rf amplitude on the substrate of 75 V and a dc bias of -37 V. The IEAD for the wafer extends from 25 to 160 eV and the 2-peak shape characteristic of nearly collisionless ion transport through a thin sheath. The ion energies extend well beyond the
threshold energy for Si etching, with the probability for etching a SiCl$_2$(s) site being 0.63 at the peak ion energy. The ion energies incident onto the metal side wall and the quartz window peak at about 35 eV and are marginally above the threshold energies (30 eV) of surface reactions involving Si containing species. The probability for sputtering a SiCl$_2$(s) site on the side wall is 0.05 at 35 eV.

The shape of the IEADs differs between metal side wall and the quartz window. The sheath at the electrically grounded metal side wall oscillates with the amplitude of the plasma potential. For example, the IEADs, for all ions, averaged over the quartz window are shown in Fig. 7.4(b) for rf biases of 25 V to 100 V. For a 75 V rf bias and dc bias of -37 V, the plasma potential oscillates with an amplitude of 38 V but spends the majority of the rf period near the floating potential. As such, the IEAD has a peak near the floating potential (37 V) with a tail reflecting the positive excursion of the plasma potential during the anodic part of the rf cycle above the plasma potential. As the bias voltage increases, the plasma potential oscillates with higher amplitude, thereby having a longer tail at higher biases. However, since the floating potential is nearly independent of the rf bias, the low energy peak of the IEAD does not significantly vary.

The IEAD incident on the quartz window has a single peak corresponding to the floating potential which is a weak function of the rf bias. The quartz, being a low capacitance dielectric, acts as an electrically floating body in contact with the plasma and so negatively charges to the floating potential (with respect to the instantaneous plasma potential) in near equilibrium with the oscillation of the plasma potential. As such, ions incident onto the quartz see a quasi-dc floating potential.
The sum of the coverages of SiCl\textsubscript{x} on all internal surfaces after processing a single wafer is shown in Fig. 7.5(a) for rf biases of 25 V to 100 V. The locations of the surfaces are shown in Fig. 7.2(a). (Note that the surface between 10.6 cm and 14.3 cm correspond to the pump port which, in principle, does not have surface coverages.) As the bias voltage increases, the coverage of SiCl\textsubscript{x} increases on all chamber surfaces except for the wafer. On the wafer, increasing the bias voltage increases the probability and rate of etching which reduces the residence time for a SiCl\textsubscript{x} site before it is removed by etching. As such, at high bias voltages, the proportion of SiCl\textsubscript{x} sites that are SiCl(s) increases since the average degree of chlorination of any given site is lower, as discussed below. The SiCl\textsubscript{x} coverage increases on non-wafer surfaces as the bias increases due to an increase in total etch rate, producing larger fluxes of etch products, which deposits on the side walls as SiCl\textsubscript{2}(s) sites.

The coverage of SiCl(s), and fluxes of Cl and sum of all ions on internal surfaces are shown in Fig. 7.5(b) for an rf bias of 100 V. The fluxes of Cl incident upon the non-wafer surfaces are uniform within about 10% resulting in a uniform Cl adsorption on these surfaces. With ion bombardment, the SiCl\textsubscript{2}(s) etch product deposits on sidewalls. Following subsequent sputtering of Cl, a coverage of SiCl(s) is produced. As such, non-wafer surfaces having higher ion fluxes (but low energy) have a higher surface coverage of SiCl(s). The SiCl(s) coverage is low on the wafer due to high energy of the ions that rapidly sputters passivated sites. The non-uniformity in ion fluxes to non-wafer surfaces, in large part, contributes to the non-uniform coverage of SiCl\textsubscript{x}. For the following discussion when radial dependencies are not shown, the surface coverages and etch rates for the wafer are for \textit{l}=0 (center of the wafer) in Fig. 7.5(a) and those for the sidewall are for \textit{l}=19.5 cm (mid-height of the wall).
Etch rates at the end of 180 s process as a function of position on the wafer for an rf bias of 75 V are shown in Fig. 7.6(a) for five wafers sequentially etched in the reactor undergoing wafer-to-wafer seasoning. On a wafer-to-wafer basis, the etch rate decreases. For the first wafer, the etch rate is center peaked as a consequence of the center-peaked ion flux. (The small scale variation in etch rate results from noise in the IEADs which are derived from a Monte Carlo simulation.) The etch rates decrease with subsequent wafers after the first due, in large part, to the increase in flux of SiCl$_2$ to the wafer, as shown in Fig. 7.6(b) which produces Si$_2$Cl$_4$(s) etch blocks. As the walls are passivated by etch products, the sticking probability for SiCl$_2$ decreases, thereby increasing the gas phase density and flux to the wafer. (Note that the subsequent removal of etch blocks does not contribute to the net etch rate.) The amount of the decrease in etch rate decreases for subsequent wafers, eventually saturating by about the fifth wafer when the reactor is fully seasoned. A coincidental synergy is that the radial uniformity of etching improves with wafer number as the larger flux of etch blocking SiCl$_2$ to the center of the wafer compensates the higher ion fluxes.

This trend of decreasing etch rate occurs for all bias voltages. For example, etch rates for sequentially processed wafers for rf biases of 25 V to 100 V are shown in Fig. 7.6(c). The change in etch rate between wafer 1 and wafer 2 increases with increasing bias voltage, a consequence of the higher flux of etch products from and re-depositing on the wafer. The etch rates eventually stabilize as a result of wall coverages reaching a steady state. That is, the reactor becomes fully seasoned.

The coverages of silicon containing species after sequentially processing five wafers are shown in Fig. 7.7 for the wafer and in Fig. 7.8 for the metal chamber walls for rf biases of 25 V to 100 V. As additional wafers are etched, the fluxes of etch products to the wafer increases (as
shown in Fig. 7.6) resulting in higher coverages of etch block species, \( \text{Si}_2\text{Cl}_3(s) \) as shown in Fig. 7.7(c). The etch blocks can only occupy the surface sites occupied by \( \text{SiCl}(s) \) and \( \text{SiCl}_2(s) \) and not by \( \text{SiCl}_3(s) \). For any wafer in the sequence, \( \text{SiCl}_3 \) coverage is largest at low biases as high bias voltages facilitate more rapid removal of higher chlorinated sites on the wafer \([\text{SiCl}_2(s) \text{ and } \text{SiCl}_3(s)]\) resulting in a decrease of their coverage. Consequently, more native Si sites get chlorinated resulting in an increase of the coverage of \( \text{SiCl}(s) \).

With increasing number of wafers having been processed, the sidewalls are exposed to a larger total fluence of etch products, and so the total coverage of \( \text{SiCl} \) and \( \text{SiCl}_2 \) increases, as shown in Fig. 7.8. As the coverage of this passivation increases, the sticking coefficients for both etch products and Cl decrease. Since the higher etching rates at larger bias voltages increase the densities of \( \text{SiCl}_2 \) in the plasma and so produce larger fluxes of \( \text{SiCl}_2 \) to the walls which produces more passivation which blocks the adsorption of Cl. These higher biases also produce larger excursions of the plasma potential which in turn produces higher ion energies to the walls. These higher ion energies enable sputtering of Cl from the \( \text{SiCl}_2(s) \) sites, leaving \( \text{SiCl}(s) \) passivation. The ratio of \( \text{SiCl}(s) \) to \( \text{SiCl}_2(s) \) on the sidewalls depends on the relative probabilities of sputtering Cl, \( \text{SiCl} \), or \( \text{SiCl}_2 \) from a \( \text{SiCl}_2(s) \) site.

The coverages for the quartz window are shown in Fig. 7.9 after sequentially processing five wafers for an rf bias of 100 V. As more wafers are processed, the total flux and the gas phase density of etch products increases, and so the total coverage of \( \text{SiCl}_2 \) increases. The ion energies incident on the quartz window peak at about 35 eV at which the probability of sputtering the \( \text{SiCl}_2(s) \) is only about 0.05. Consequently, the change in the surface coverage of \( \text{SiCl}(s) \) is not significant. As the surface coverage of the \( \text{SiCl}_2 \) increases, the sticking coefficient for Cl decreases, thus contributing to the decreasing surface coverage of Cl. As such, when only
purely inductive coupling is considered the quartz window has only a marginal effect on the gas phase densities since the ions incident onto the quartz see only a quasi-dc floating potential.

Sputtering of the quartz window resulting from capacitive coupling from the coil can be a source of oxygen atoms which can lead to deposition of silicon oxychloride films on the chamber walls.[1-4] To investigate these processes, capacitive coupling of the coils through the quartz window was included. The coil voltages were 300, 400, and 500 V for the inner, middle and outer coils, assuming the coils are powered on the outside turn and terminated on the inner turn. The flux of sputtered O atoms from the quartz window is ultimately determined by the sheath voltage under the coils which in turn depends on the degree of capacitive coupling of the coils through the window. The amount of capacitive coupling can be controlled by the height of the coils above the quartz. Coils in contact with the quartz have the largest amount of coupling and so the largest sheath voltages. Lifting the coils off the window decreases the amount of coupling.

The IEADs incident on the quartz in the 0.8 cm centered directly under the coils are shown in Fig. 7.10 for two different coil configurations: where the coils are in contact with the quartz (the standard) and where the coils are displaced by about 0.4 cm above the quartz. The density and flux vectors of O atoms resulting from sputtering of the quartz for the coils in contact with the window are shown in Fig. 7.11. For the standard coil configuration, the IEADs under the outer coil exceed 140 eV and are well above the threshold for sputtering. The IEADs are only marginally above the threshold under the middle coil. Below the inner coil, the IEADs differ little from those on floating surfaces. With the raised coils, there is less capacitive coupling, lower sheath potential and so the IEADs under the outer and middle coils have lower energies, with threshold for sputtering being exceeded only under the outer coil. As a result,
sputtering of O atoms occurs dominantly under outer coil in both cases, producing a peak density of \(7.2 \times 10^{11}\) cm\(^{-3}\) near their source for the standard configuration.

The fluxes of O and O\(^+\) to the wafer resulting from sputtering are shown in Fig. 7.10(c). The flux of O\(^+\) is two orders of magnitude lower (\(2.2 \times 10^{13}\) cm\(^{-2}\) s\(^{-1}\)) than the fluxes of the majority ions, Ar\(^+\) and Cl\(^+\), and so does not play a significant role. The flux of O (\(3.9 \times 10^{15}\) cm\(^{-2}\) s\(^{-1}\)) is comparable to that of the etch products, and of sufficient magnitude to affect the etch rates. The lower ion energies when coils are displaced sputter fewer O atoms, and so the fluxes of O and O\(^+\) to the wafer, decrease by about 50%.

O atoms to the wafer can adsorb on the chlorinated silicon sites forming silicon oxychloride (SiOCl) which is an etch block. For example, the coverages of silicon containing species on the wafer, after etching one wafer, are shown in Fig. 7.12 for rf biases of 25 V to 100 V. Since the sputtering of the quartz window is the only source of oxygen, the flux of oxygen atoms to the wafer does not significantly change with bias voltage. At low bias voltages, ion energies are not high enough to remove the etch block and so the coverage of SiOCl(s) is high. As the bias increases, the rate of removal of SiOCl(s) increases, thereby removing the etch block and allowing the etch to proceed. The increase in coverage of SiCl(s) with increasing bias voltage results from at least two effects. At high biases, the higher chlorinated sites are etched more rapidly exposing native Si sites which get chlorinated as SiCl(s). Further, the etch block SiOCl(s) is eliminated by removing the adsorbed oxygen, leaving SiCl(s). This latter trend results from our particular surface model in which sputtering of the etch block preferentially removes O as opposed to Cl. Preferential sputtering of Cl would retain the etch block nature, requiring a second sputtering event to enable etching to proceed, and so intensify the etch blocking nature of the sputtered oxygen.
The oxygen sputtered from the quartz window and from the wafer surface, adsorb on the reactor wall maximizing their coverage. The IEADs incident on the metal wall peak at about 35 eV and so are not high enough to remove the SiOCl(s) which, as a result, ultimately saturate the metal wall. Consequently the etch product density in the bulk plasma increases with bias voltage. The high SiCl₂ density contributes to the increase in coverage of Si₂Cl₃(s) etch block on the wafer with increase in bias voltage. Overall, the total coverage of all etch block species, SiOCl(s) and Si₂Cl₃(s) decreases with increase in bias voltage.

Etch rates as a function of radius for a bias of 75 V are shown in Fig. 7.13(a) for sequential etching of five wafers in a seasoning reactor with sputtering of the quartz. Etch rates of the first wafer peak at the center of the wafer. With processing of successive wafers, the etch rate decreases and the uniformity improves. The decrease in etch rates occurs for all biases, as shown in Fig. 7.13(b). The etch rates eventually stabilize as a result of the balance between the flux of etch block forming species [O and SiCl₂] and the flux of etching species (ions).

The uniformity during subsequent processing is due to the increase in flux of etch block forming species, O and SiCl₂, as shown in Fig. 7.13(c) which have a maximum on axis. When new wafers are etched in a progressively seasoned reactor, the etch products are not deposited on the reactor wall that is saturated with SiOCl(s). SiCl₂ therefore redeposits on the wafer as Si₂Cl₃(s), forming the etch block. The higher flux of etch blocks at the center of the wafer decreases the etch rate more rapidly than at outer radii, thereby balancing the center peaked ion flux and providing a more uniform etch.

The importance of tool design and maintaining critical dimensions in construction of the tool are demonstrated by the etch rates (for an rf bias of 100 V) at the center of the wafer as a function of wafer number shown in Fig. 7.14 for different coil configurations. Etch rates are
uniformly higher in the absence of capacitive coupling, as might be obtained with a Faraday shield. With the coils set directly on the quartz window, the capacitive coupling is maximum and sputtering of O atoms is greatest. Offsetting the coils from the quartz window reduces the capacitive coupling while decreasing the sputtering of O atoms. During the first run, despite the etch-block nature of the sputtered O atoms, the etch rate decreases by only 5%. The ion energies at an rf bias of 100 V are significantly higher than the etching threshold of the etch block thus sputtering of the etch blocks is efficient. As more wafers are processed, the metal wall is saturated with SiOCl(s) thus reducing the adsorption of etch product. Consequently, the redeposition flux to the wafer is higher increasing the etch block coverage on the wafer. As a result, the impact on the etch rate is higher as more wafers are processed, the disparity in etch rates when capacitive coupling is considered to ~20%. The effect is less prominent for when the coils are offset, where the behavior mimics that of when purely inductive coupling is considered.

7.3 Real-time and Run-to-run Control Strategies

To mitigate process drifts, cleaning and conditioning steps are often employed between production wafers to insure that the initial conditions of the reactor are the same for each wafer. These drifts can occur while processing a single wafer as well as on a wafer-to-wafer basis. RTC and wafer-to-wafer control are therefore both options to maintain uniform etch rates. The choice of the sensor-actuator pair (or pairs) is largely governed by the ability to measure the desired properties and to correlate an actuator setting with a desired change in reactive fluxes. In this study, we chose etch rate as the sensor output, as might be measured by a multi-color interferometer, and bias voltage as the actuator. In the parameter space of interest, etch rate is a monotonic function of bias voltage and so allows for a simple control scheme. The disadvantage
to varying voltage is the possibility of compromising selectivity. A simple proportional control algorithm was used to adjust the bias voltage to maintain a constant etch rate.

The computational strategy to investigate control schemes is as follows. A desired etch rate is specified as the set point. Changes in the measured etch rate from the set point resulting from seasoning of the reactor are treated as the perturbations of the system. Sensor measurements (referred to as controller time steps) are made at intervals of approximately 20 s. The proportional controller resets the bias to obtain the set point etch rate using a gain of 0.3. This constitutes the RTC aspect of the control. When a new wafer is placed into a seasoned reactor, the bias voltage (actuator) is set to the value used at the end of the prior wafer process. This constitutes the run-to-run aspect of the control.

Etch rates are shown in Fig. 7.15 for biases of 25 V and 100 V for 5 wafers with and without control. In the absence of control, the etch rate decreases as a wafer is processed, due to the effect of feedback (redeposition) of etch products from the metal wall and the wafer. The initial etch rate is lower, when a new wafer is processed, as a result of the adsorbed etch products from the metal wall which increase the SiCl₂ flux to the wafer increasing the etch block coverage. The control scheme is implemented to maintain the etch rate at its set point, in this case the etch rate at T=1 from T=3. For each wafer processed in the same reactor, the etch rate is restored by T=6. In general, the bias voltage is increased to sputter the redeposition products. Resetting of the actuator to a higher bias voltage (actuator output from the previous run) increases the initial etch rate even as more wafers are processed in the seasoned chamber. In response to the higher etch rate, the bias voltage (actuator) is lowered at T=4. However, as the wafer is processed, the redeposition fluxes increase and the low bias voltage lower the etch rate.
Subsequently, the bias voltage is increased to enable the set point etch rate. On a run-to-run basis, the bias voltage is higher than for the prior wafer process.

7.4 Conclusions

Plasma-surface interactions were modeled to investigate the seasoning of reactor walls during plasma etching. The effect of seasoning on etch rates, uniformity and coverage of species on the wafer and chamber walls was discussed for varying bias voltages in a chlorine plasma etch of Si. The etch rates decreased significantly, despite higher biases, as the chamber was seasoned due to the buildup of etch blocks. Capacitive coupling through the coils can lead to sputtering of oxygen atoms from the quartz window. The oxygen atoms adsorption on the chlorinated silicon passivation on the wafer results in the formation of silicon oxychloride film, an etch block which leads to lower etching rates. The capacitive coupling through the coils can be mitigated by changes in the placement of the coils above the quartz window plasma. To mitigate the negative effect on the etch rates of seasoning, a feedback control algorithm was implemented. Real-time and run-to-run control was achieved using a proportional controller was implemented using etch rate as a sensor and bias voltage as an actuator. We found that achieving control at high biases is complicated due to the transition between ion limited to neutral limited processes. As such, the effects were overcome by lowering the rate of change of voltage.
Fig. 7.1: Schematic of the surface mechanisms for Si etching in Ar/Cl₂ plasma.
(a) Si,Cl₂ etch products form etch blocks, Si,Cl₂ on wafer.
(b) Sputtering of dielectrics introduces oxygen atoms in the bulk plasma forming etch blocks, SiOCl, on the wafer.
Fig. 7.2: Schematic of the ICP plasma etching reactor used as model tool for investigation of seasoning of plasma reactors. (a) Location and orientation of the individual primary surfaces inside the plasma reactor on which surface reactions are assumed. (b) Plasma properties for the process conditions Ar/Cl$_2$=90/10, 500 W ICP power, 15 mTorr, 100 sccm and 75 V substrate bias. Total positive ion density is on the left and SiCl$_2$ density on the right. Note the high density of SiCl$_2$ in the bulk plasma in contact with reactor walls.
Fig. 7.3: Fluxes to the wafer as a function of radius for the base case conditions (Ar/Cl$_2$=90/10, 500 W ICP power, 15 mTorr, 100 sccm) and 75 V substrate bias. (a) Ion and (b) Neutral fluxes. Cl is the major neutral radical flux. Ar$^+$ and Cl$^+$ are the dominant ions.
Fig. 7.4: (a) Total IEADs averaged over the wafer, metal wall and quartz window for Ar/Cl\textsubscript{2}=90/10, 500 W ICP power, 15 mTorr, 100 sccm and 75 V substrate bias. (b) Total IEADs averaged over the metal wall for bias voltages of 25 to 100 V. The IEAD has a peak near the floating potential with a tail reflecting the positive excursion of the plasma potential. Log scale plotted over 2 decades.
Fig. 7.5: Typical output from SCM on unified chamber surface of coverages and fluxes. (a) Coverage of sum of all SiCl$_x$ (s) on all chamber surfaces, after one run, for bias voltages of 25 to 100 V. The arrows point in the direction of decreasing voltages. (b) Coverage of SiCl(s), flux of Cl and sum of all ions on internal surfaces for an rf bias of 100 V. The non-uniformity in ion fluxes contribute to the non-uniform coverage of SiCl(s). The results will be discussed for the wafer, at $l=0$ (center of the wafer) and for the metal wall, at $l=19.5$ cm (mid-height of the wall).
Fig. 7.6: Sequential processing of five wafers in the same reactor. (a) Radial profile of etch rate for bias voltage of 75 V. (b) Flux of etch product, SiCl$_2$, to the wafer as a function of radius for a bias voltage of 75 V. As more wafers are processed, the total flux of SiCl$_2$ increases to the wafer. SiCl$_2$ forms an etch block on the wafer which reduces the etch rate. (c) Etch rate at center of the wafer for bias voltages of 25 to 100 V. Etch rate decreases for a new wafer due to the increase in formation of Si$_2$Cl$_2$ etch blocks. Etch rates eventually saturate by about the fifth wafer.
Fig. 7.7: Wafer surface coverages of silicon containing species for processing of five wafers in the same reactor for varying bias voltages. (a) SiCl(s), (b) SiCl\(_x\)(s), and (c) Si\(_2\)Cl\(_y\)(s). High bias voltages facilitate rapid removal of higher chlorinated sites on the wafer. As flux of etch products increases with etching of additional wafers, coverage of etch block species, Si\(_2\)Cl\(_y\)(s) increases.
Fig. 7.8: Side wall surface coverages of silicon containing species for processing of five wafers in the same reactor for varying bias voltages. (a) Cl(s), (b) SiCl$_2$(s), and (c) SiCl(s). High densities of SiCl$_2$ and SiCl$_2^+$ in the plasma at high bias voltages enable high ion energies to sputter Cl from SiCl$_2$(s) sites, leaving SiCl(s) passivation.
Fig. 7.9: Surface coverages on the quartz window after sequential processing of five wafers for an rf bias of 100 V. As additional wafers are etched, the flux and density of etch products increases, increasing the total coverage of SiCl2. The change in the surface coverage of SiCl(s) is not significant due to low incident ion energies on the quartz window.
Fig. 7.10: Effect of including capacitive coupling through the coils on total IEADs averaged over the coil turns and flux of sputtered of oxygen to the wafer. (a) Standard coils. (b) Offset coils by 0.4 cm. (c) Fluxes to the wafer of sputtered oxygen ions and neutrals for the two coils configurations. When coils are in contact with the quartz window, the degree of capacitive coupling is the highest enabling high ion energies. With the raised coils, there is less capacitive coupling which lowers ion energies thus sputtering fewer O atoms.
Fig. 7.11: Density of oxygen atoms sputtered from quartz window via capacitive coupling through coils for 75 V substrate bias voltage. The oxygen radical flux vectors are noted. The peak density is below the first turn where the capacitive coupling is maximum. Log scale plotted over 2 decades.
Fig. 7.12: Surface coverages of silicon containing species and etch blocks on the wafer, after one run, for bias voltages of 25 to 100 V. High bias voltages enable high ion energies to sputter etch-block on the wafer, decreasing their coverage.
Fig. 7.13: Sequential processing of five wafers in the same reactor, when oxygen sputter from quartz window is considered. (a) Radial profile of etch rate for bias voltage of 75 V. (b) Etch rate at center of the wafer for bias voltages of 25 to 100 V. Etch rate decreases for a new wafer due to the increase in formation of SiOCl and Si$_2$Cl$_y$ etch blocks. Etch rates eventually saturate by about the fifth wafer. (c) Flux of etch-block forming species, SiCl$_2$ and O, to the wafer as a function of radius for a bias voltage of 75 V. As more wafers are processed, the total flux of etch-block forming species increases reducing the etch rate.
Fig. 7.14: Etch rates, at the end of the process, for sequential etching of five wafers without sputtering of the quartz, with sputtering and with offset coils. The process conditions are: Ar/Cl₂=90/10, 500 W ICP power, 15 mTorr, 100 sccm, and 100 V substrate bias.
Fig. 7.15: Sensor and actuator time history for run-to-run etch rate control achieved for sequential processing of five wafers in a seasoned chamber at an rf bias of 75 V. A proportional controller is implemented using the etch rate as a sensor and bias voltage as an actuator. The etch rate is restored in 6 control time steps.
7.6 References


8. CONCLUSIONS

8.1 Conclusions

The prevalence of plasma processing equipment in microelectronics fabrication will continue through future technology nodes. As feature sizes continue to shrink below 45 nm and below, equipment and processes need to be optimized to allow for the continuation of Moore’s Law. However, increasing competition and technical challenges have made conventional empirical methods of equipment and process design prohibitively expensive and time-consuming in the semiconductor industry. Computational modeling and simulation tools provide a better understanding of the requirements and help overcome these technological and economic barriers. The characteristics of any plasma-aided microelectronics manufacturing process are governed by the uniformity, composition and energy of the reactants that deliver the activation energy for a process. In this work, effect of activation energy to wafers and walls in a plasma processing reactor was investigated using plasma processing techniques for sub-45 nm nodes as case studies. Activation energy to wafers was controlled by affecting source design and/or the bias voltage waveform on the substrate. Activation energy to walls is undesirable and has a negative effect on the processes’ uniformity. A feedback control loop was implemented to achieve real-time and run-to-run optimization of the process.

Pulsed plasma ion implantation is a plasma-based technique proposed for fabricating ultra-shallow junctions which provides distinct advantages over its beam-line counterpart. The characteristics of the ion energy and angular distributions (IEADs) incident onto the wafer are critical to determining the junction properties. The characteristics of inductively coupled reactors for pulsed plasma doping of semiconductors was computationally investigated. The
IEADs were found to be sensitive functions of the bias voltage waveform and the plasma parameters that determine the sheath properties (e.g. pressure, power, and reactor configuration). The ideal IEAD is angularly symmetric and mono-energetic. Plasma conditions that produce thick sheaths for an extended period during the bias (e.g., low ICP power producing low ion density or large bias voltage) produce low energy tails to the IEADs resulting from ionization that occurs in the sheath by secondary electrons. Since the sheath can extend many cm into the plasma, the uniformity of the plasma far from the substrate is extremely important. Gradients in the thickness of the sheath were found to produce angularly asymmetric IEADs. The angular symmetry can however be controlled through the shape of the reactor or modifications such as the height of the focus ring that decrease the gradient in the sheath thickness across the wafer.

Plasma atomic layer etching (PALE) was investigated as an alternative to reactive ion etching techniques which do not allow for atomic level resolution. Although atomic layer etching techniques have been shown to be feasible they typically utilize a remote plasma source or expensive beam equipment. The integration costs to current fabrication processes are therefore prohibitive. In this work, PALE techniques were computationally investigated using different conventional plasma etching equipments for etching of advanced feature geometries. Although PALE was shown to be feasible in ICP and CCP reactors, the throughput is typically slow and, at this time, serves as a useful complement to conventional RIE techniques. PALE utilizing only a single gas mixture was also investigated by way of achieving extreme control over the IEADs by varying the bias voltage waveform on the substrate. A narrow IEAD with selectable peak allows discrimination between the thresholds of the etching materials resulting in high selectivity.
Wafer-to-wafer process reproducibility during plasma etching often depends on the conditioning of the inside surfaces of the reactor. Passivation of reactor surfaces by plasma generated species change the reactive sticking coefficients for radicals, thereby changing the composition of the radical and ion fluxes to the wafer. Seasoning of plasma reactors was investigated using results from Si etching in a chlorine plasma. The etch rate was found to decrease as the chamber walls are seasoned due to a decrease in sticking coefficient for etch products which increases their gas phase density and increases their redeposition on the wafer as etch blocks. Further, fairly subtle changes in the placement of the coils above the quartz window can have profound effect on the seasoning of the reactor. The height of the coils above the quartz determines the amount of capacitive coupling to the plasma and the ion energies incident onto the quartz. This in turn determines the amount of sputtering of the quartz and the flux of O atoms injected into the plasma. The O atoms are a potential source of etch blocks (e.g., SiOCl) and wall passivation. A feedback control scheme was implemented to maintain a constant etch rate. The control algorithm is a proportional controller which uses the etch rate variation to vary the bias voltage to maintain a constant etch rate on both a real-time and run-to-run basis. Such a scheme can stabilize the process during a single etch while wafer-to-wafer control is sometimes complicated by disparity between the fresh state of a newly inserted wafer compared to the seasoned walls.
APPENDIX A: Si ETCHING IN Ar/Cl₂; SURFACE REACTION MECHANISM

Polysilicon etch mechanism[1] in Ar/Cl₂ plasmas used in the present study is given below:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Probability</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(s) + Cl  →  SiCl(s)</td>
<td>0.99</td>
<td>2</td>
</tr>
<tr>
<td>SiCl(s) + Cl  →  SiCl₂(s)</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>SiCl₂(s) + Cl  →  SiCl₃(s)</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>SiCl₃(s) + Cl  →  SiCl₄(s)</td>
<td>0.0001</td>
<td>2,e</td>
</tr>
<tr>
<td>Si(s) + SiCl₂  →  Si(s) + SiCl₂(s)</td>
<td>0.8</td>
<td>2</td>
</tr>
<tr>
<td>SiCl(s) + SiCl₂  →  SiCl(s) + SiCl₂(s)</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>SiCl₂(s) + SiCl₂  →  SiCl₂(s) + SiCl₂(s)</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>SiCl₃(s) + SiCl₂  →  SiCl₃(s) + SiCl₂(s)</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>SiCl₂(s) + Ar⁺  →  SiCl₂ + Ar</td>
<td>0.16 $\frac{(e - e_o)^{1/2}}{e_o^{1/2}}$</td>
<td>3,f</td>
</tr>
<tr>
<td>SiCl₃(s) + Ar⁺  →  SiCl₃ + Ar</td>
<td>0.16 $\frac{(e - e_o)^{1/2}}{e_o^{1/2}}$</td>
<td>3,f</td>
</tr>
<tr>
<td>SiCl(s) + Cl⁺  →  SiCl₂</td>
<td>0.13 $\frac{(e - e_o)^{1/2}}{e_o^{1/2}}$</td>
<td>3,f</td>
</tr>
<tr>
<td>SiCl₂(s) + Si(s) + Cl⁺  →  SiCl₂ + SiCl(s)</td>
<td>0.16 $\frac{(e - e_o)^{1/2}}{e_o^{1/2}}$</td>
<td>3,f</td>
</tr>
<tr>
<td>SiCl₃(s) + Cl⁺  →  SiCl₄</td>
<td>0.19 $\frac{(e - e_o)^{1/2}}{e_o^{1/2}}$</td>
<td>3,f</td>
</tr>
</tbody>
</table>
Si(s) + Cl₂⁺ → SiCl₂

0.13 \left( \frac{e - e_o}{e_o} \right)^{1/2} 3,f

SiCl(s) + Si(s) + Cl₂⁺ → SiCl₂ + SiCl(s)

0.16 \left( \frac{e - e_o}{e_o} \right)^{1/2} 3,f

SiCl₂(s) + Si(s) + Cl₂⁺ → SiCl₂ + SiCl₂(s)

0.16 \left( \frac{e - e_o}{e_o} \right)^{1/2} 3,f

SiCl₃(s) + Si(s) + Cl₂⁺ → SiCl₄ + SiCl(s)

0.16 \left( \frac{e - e_o}{e_o} \right)^{1/2} 3,f

\(a\) (s) denotes a surface species.

\(b\) Unless otherwise specified, all ions neutralize on surfaces, returning as their neutral counterparts.

\(c\) In reactions with no chemical change, the gas species are reflected off the surface. These reactions are not shown in the table.

\(d\) \(e\) is the ion energy. \(e_o = 10\) eV unless noted otherwise.

\(e\) Thermal etch probability was varied for some cases as noted.

\(f\) Reaction mechanism was derived from the cited reference. The precise values for probabilities have been modified.

A.1 References


Surface reaction mechanism for fluorocarbon etching[1] of SiO$_2$ used in the present study is given below:

Species and symbols definition:

CF$_3^+$ represents all ions,

CF$_x$ and C$_x$F$_y$ radicals represent polymerizing species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorocarbon polymer</td>
<td>P</td>
</tr>
<tr>
<td>Hydrogenated polymer</td>
<td>HP</td>
</tr>
<tr>
<td>Activated Species</td>
<td>*</td>
</tr>
<tr>
<td>Ions</td>
<td>+</td>
</tr>
<tr>
<td>Gas phase species</td>
<td>g</td>
</tr>
<tr>
<td>Hot neutrals</td>
<td>h</td>
</tr>
<tr>
<td>Surface species</td>
<td>s</td>
</tr>
</tbody>
</table>

Surface reaction mechanism

<table>
<thead>
<tr>
<th>Reaction$^{a,b}$</th>
<th>Probability</th>
<th>Footnote</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of complex at polymer-SiO$_2$ interface:</td>
<td>$p_0$</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$s + CF$_x$g $\rightarrow$ SiO$<em>2$CF$</em>{xs}$</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$s + C$_x$F$_y$g $\rightarrow$ SiO$_2$C$<em>x$F$</em>{ys}$</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Low energy ion activation to form polymer, activated complex site</td>
<td>$p_0$</td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{SiO}_2\text{CF}_s + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{CF}_s^* + \text{CF}_3h & 0.1 & c \\
\text{SiO}_2\text{CF}_{2s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{CF}_{2s}^* + \text{CF}_3h & 0.1 & c \\
\text{SiO}_2\text{C}_2\text{F}_{3s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{3s}^* + \text{CF}_3h & 0.1 & c \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s}^* + \text{CF}_3h & 0.1 & c \\
\text{SiO}_2\text{CF}_s + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{CF}_s + \text{Ps} & 0.1 & c \\
\text{SiO}_2\text{CF}_{2s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{CF}_{2s} + \text{Ps} & 0.1 & c \\
\text{SiO}_2\text{C}_2\text{F}_{3s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{3s} + \text{Ps} & 0.1 & c \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3^+ & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{Ps} & 0.1 & c \\
\text{SiO}_2\text{CF}_s + \text{CF}_3g & \rightarrow \text{SiO}_2\text{CF}_s + \text{CF}_g + \text{CF}_3h & 0.08 & d \\
\text{SiO}_2\text{CF}_{2s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{CF}_{2s} + \text{CF}_2g + \text{CF}_3h & 0.08 & d \\
\text{SiO}_2\text{C}_2\text{F}_{3s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{3s} + \text{CO}_g + \text{CF}_3h & 0.90 & d \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CO}_g + \text{CF}_3h & 0.90 & d \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{C}_2\text{F}_3g + \text{CF}_3h & 0.03 & d \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CO}_g + \text{CF}_3h & 0.03 & d \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{C}_2\text{F}_3g + \text{CF}_3h & 0.03 & d \\
\text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{4s} + \text{CO}_g + \text{CF}_3h & 0.03 & d \\
\text{SiO}_2\text{C}_2\text{F}_{3s}^* + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{3s}^* + \text{CF}_3h & 0.08 & d \\
\text{SiO}_2\text{C}_2\text{F}_{2s}^* + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{2s}^* + \text{CF}_3h & 0.08 & d \\
\text{SiO}_2\text{C}_2\text{F}_{3s}^* + \text{CF}_3g & \rightarrow \text{SiO}_2\text{C}_2\text{F}_{3s}^* + \text{CO}_g + \text{CF}_3h & 0.90 & d \\
\end{align*}
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_3* + \text{CF}_3^+ \rightarrow \text{SiO}_2 + \text{C}_2\text{F}_3 + \text{CF}_3$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_4* + \text{CF}_3^+ \rightarrow \text{SiOCF}_4 + \text{CO}_g + \text{CF}_3$</td>
<td>0.90</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_4* + \text{CF}_3^+ \rightarrow \text{SiO}_2 + \text{C}_2\text{F}_4 + \text{CF}_3$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\text{SiOCF}_3* + \text{CF}_3^+ \rightarrow \text{SiF}_2 + \text{COF}_g + \text{CF}_3$</td>
<td>0.01</td>
</tr>
<tr>
<td>$\text{SiOCF}_4* + \text{CF}_3^+ \rightarrow \text{SiF}_3 + \text{COF}_g + \text{CF}_3$</td>
<td>0.01</td>
</tr>
<tr>
<td>$\text{SiF}_3* + \text{CF}_3^+ \rightarrow \text{SiF}_3 + \text{CF}_3$</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Reactions with polymerizing specie ($\text{CF}_x, \text{C}_x\text{F}_y$)  

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_s + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_3$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_2* + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_4$</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_s* + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_s + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_2* + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_2 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_3* + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_3 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_4* + \text{CF}_x \rightarrow \text{SiO}_2\text{C}_2\text{F}_4 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_s* + \text{C}_x\text{F}_y \rightarrow \text{SiO}_2\text{C}_2\text{F}_s + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_2* + \text{C}_x\text{F}_y \rightarrow \text{SiO}_2\text{C}_2\text{F}_2 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_3* + \text{C}_x\text{F}_y \rightarrow \text{SiO}_2\text{C}_2\text{F}_3 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{SiO}_2\text{C}_2\text{F}_4* + \text{C}_x\text{F}_y \rightarrow \text{SiO}_2\text{C}_2\text{F}_4 + \text{P}_s$</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Si}_s + \text{CF}_x \rightarrow \text{Si}_s + \text{P}_s$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{Si}_s + \text{C}_x\text{F}_y \rightarrow \text{Si}_s + \text{P}_s$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{SiF}_s + \text{CF}_x \rightarrow \text{SiF}_s + \text{P}_s$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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SiF_{2s} + CF_{xg} \rightarrow SiF_{2s} + Ps \hspace{1cm} 0.15

SiF_{s} + C_xF_{yg} \rightarrow SiF_{s} + Ps \hspace{1cm} 0.15

SiF_{2s} + C_xF_{yg} \rightarrow SiF_{2s} + Ps \hspace{1cm} 0.15

SiF_{3s} + CF_{xg} \rightarrow SiF_{3s} + Ps \hspace{1cm} 0.15

SiF_{3s} + C_xF_{yg} \rightarrow SiF_{3s} + Ps \hspace{1cm} 0.15

**Fluorination reactions**

Si_{s} + F_{g} \rightarrow SiF_{s} \hspace{1cm} 0.05

SiF_{s} + F_{g} \rightarrow SiF_{2s} \hspace{1cm} 0.05

SiF_{2s} + F_{g} \rightarrow SiF_{3s} \hspace{1cm} 0.05

SiF_{3s} + F_{g} \rightarrow SiF_{4g} \hspace{1cm} 0.10

SiO_2CF_{s} + F_{g} \rightarrow SiF_{2s} + CO_{2g} \hspace{1cm} 0.01

SiO_2CF_{2s} + F_{g} \rightarrow SiF_{3s} + CO_{2g} \hspace{1cm} 0.01

**Reactions on polymer surface**

Ps + F_{g} \rightarrow CF_{2g} \hspace{1cm} 0.03

Ps + H_{g} \rightarrow Ps + HP_{s} \hspace{1cm} 0.90

Ps + C_xF_{yg} \rightarrow Ps + Ps \hspace{1cm} 0.15

Ps + CF_{xg} \rightarrow Ps + Ps \hspace{1cm} 0.15

Ps + CF_{3g}^+ \rightarrow CF_{3h} + CF_{2g} \hspace{1cm} 0.15
\[ \text{HP}_s + \text{F}_g \rightarrow \text{CF}_2g \quad 0.03 \quad \text{f} \]
\[ \text{HP}_s + \text{H}_g \rightarrow \text{HP}_s + \text{HP}_s \quad 0.99 \quad \text{f} \]
\[ \text{HP}_s + \text{C}_x\text{F}_y g \rightarrow \text{HP}_s + \text{HP}_s \quad 0.05 \quad \text{f} \]
\[ \text{HP}_s + \text{CF}_xg \rightarrow \text{HP}_s + \text{HP}_s \quad 0.05 \quad \text{f} \]
\[ \text{HP}_s + \text{CF}_3g^+ \rightarrow \text{CF}_3h + \text{CF}_2g \quad 0.28 \quad \text{e,f} \]

\(^a\) All ions return as a hot neutral. Ions and hot neutrals have the same mechanism.

\(^b\) In reactions with no change chemically, the gas species are reflected of the surface.

\[ p(E_r) = p_0 \max \left( 0,1 - \frac{E_i}{E_c} \right), \quad E_c = 70 \text{ eV}. \quad \text{E}_c \text{ refers to maximum allowable energy (in eV) and p}_0 \text{ is the probability at 0 eV.} \]

\[ p(\theta) = p_0 \left[ \frac{E_i^n - E_{th}^n}{E_r^n - E_{th}^n} \right] f(\theta), \quad E_{th} = 70 \text{ eV, E}_r = 140 \text{ eV and } n = 0.97. \quad \text{E}_\text{th} \text{ refers to threshold energy, E}_r \text{ refers to reference energy, (both energies in eV) and p}_0 \text{ is the probability at E}_r. \]

\[ p(\theta) = p_0 \left[ \frac{E_i^n - E_{th}^n}{E_r^n - E_{th}^n} \right] f(\theta), \quad E_{th} = 125 \text{ eV, E}_r = 175 \text{ eV and } n = 0.98. \]

\(^f\) Reactions on P and HP surfaces are similar with different probabilities.

\section*{B.1 References}

APPENDIX C: LIST OF REACTIONS OF Ar/NF₃

The reaction chemistry[1] for an Ar/NF₃ gas mixture used in the present study is given below:

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>Rate Coefficienta</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>e + Ar → Ar + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>Ar</td>
<td>e + Ar ↔ Ar* + e</td>
<td>b,c,d</td>
<td>3</td>
</tr>
<tr>
<td>Ar*</td>
<td>e + Ar → Ar⁺ + e + e</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>e + Ar⁺ → Ar⁺ + e + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>N₂</td>
<td>e + NFₓ → NFₓ + e</td>
<td>b,e</td>
<td>6</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>e + NFₓ → NFₓ⁺(v) + e</td>
<td>b,e,f</td>
<td>7</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>e + NF₃ → NF₂ + F + e</td>
<td>b</td>
<td>6</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>e + NF₃ → NF + F + F + e</td>
<td>b</td>
<td>6</td>
</tr>
</tbody>
</table>

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\begin{align*}
&\text{e} + \text{NF}_3 \rightarrow \text{NF}_2 + \text{F}^- \quad \text{b} \quad 8 \\
&\text{e} + \text{NF}_3 \rightarrow \text{NF}_3^+ + \text{e} + \text{e} \quad \text{b} \quad 9 \\
&\text{e} + \text{NF}_3 \rightarrow \text{NF}_2^+ + \text{F} + \text{e} + \text{e} \quad \text{b} \quad 9 \\
&\text{e} + \text{NF}_3 \rightarrow \text{NF}^+ + \text{F} + \text{F} + \text{e} + \text{e} \quad \text{b} \quad 9 \\
&\text{e} + \text{NF}_2 \rightarrow \text{NF} + \text{F} + \text{e} \quad \text{b} \quad 7 \\
&\text{e} + \text{NF}_2 \rightarrow \text{N} + \text{F} + \text{F} + \text{e} \quad \text{b} \quad 7 \\
&\text{e} + \text{NF}_2 \rightarrow \text{NF}_2^+ + \text{e} + \text{e} \quad \text{b} \quad 9 \\
&\text{e} + \text{NF}_2 \rightarrow \text{NF} + \text{F}^- \quad \text{b} \quad 7, 8, g \\
&\text{e} + \text{NF} \rightarrow \text{N} + \text{F} + \text{e} \quad \text{b} \quad 7 \\
&\text{e} + \text{NF} \rightarrow \text{NF}^+ + \text{e} + \text{e} \quad \text{b} \quad 9 \\
&\text{e} + \text{NF}_3^+ \rightarrow \text{NF}_2 + \text{F} \quad 1 \times 10^{-7} T_e^{-0.5} \quad 10 \\
&\text{e} + \text{NF}_2^+ \rightarrow \text{NF} + \text{F} \quad 1 \times 10^{-7} T_e^{-0.5} \quad 10 \\
&\text{e} + \text{NF}^+ \rightarrow \text{N} + \text{F} \quad 1 \times 10^{-7} T_e^{-0.5} \quad 10 \\
&\text{e} + \text{F}_2 \rightarrow \text{F}_2^+ + \text{e} \quad \text{b} \quad 11 \\
&\text{e} + \text{F}_2 \rightarrow \text{F}_2(v) + \text{e} \quad \text{b, f} \quad 11 \\
&\text{e} + \text{F}_2 \rightarrow \text{F}^+ + \text{F} \quad \text{b} \quad 11 \\
&\text{e} + \text{F}_2 \rightarrow \text{F} + \text{F} + \text{e} \quad \text{b} \quad 11 \\
&\text{e} + \text{F}_2 \rightarrow \text{F}_2^+ + \text{e} + \text{e} \quad \text{b} \quad 11 \\
&\text{e} + \text{F}_2^+ \rightarrow \text{F} + \text{F} \quad 1 \times 10^{-7} T_e^{-0.5} \quad 11 \\
&\text{e} + \text{F} \rightarrow \text{F}^+ + \text{e} \quad \text{b} \quad 12 \\
&\text{e} + \text{F} \rightarrow \text{F}^* + \text{e} \quad \text{b, f} \quad 12 \\
&\text{e} + \text{F} \rightarrow \text{F}^+ + \text{e} + \text{e} \quad \text{b} \quad 13
\end{align*}
\[ e + N_2 \rightarrow N_2 + e \] 14
\[ e + N_2 \rightarrow N_2(v) + e \] b,f
\[ e + N_2 \leftrightarrow N_2^* + e \] b,c,h 15,16,17
\[ e + N_2 \rightarrow N + N + e \] b 14
\[ e + N_2 \rightarrow N_2^+ + e + e \] b 4
\[ e + N_2^* \rightarrow N_2^+ + e + e \] b 18
\[ e + N_2^+ \rightarrow N^* + N \] \(1 \times 10^{-7} T_c^{-0.5}\) 19
\[ e + N \rightarrow N + e \] b 20
\[ e + N \leftrightarrow N^* + e \] b,c,i 21
\[ e + N \rightarrow N^+ + e + e \] b 22
\[ e + N^* \rightarrow N^+ + e + e \] b 18
\[ Ar^* + Ar^* \rightarrow Ar^+ + Ar + e \] \(5 \times 10^{-10}\) 23
\[ Ar^* + N^* \rightarrow N^+ + Ar + e \] \(5 \times 10^{-10}\) j
\[ Ar^* + N \rightarrow N^* + Ar \] \(1 \times 10^{-12}\) j
\[ Ar^* + N_2^* \rightarrow N_2^+ + Ar + e \] \(5 \times 10^{-10}\) j
\[ Ar^* + N_2 \rightarrow N_2 + Ar \] \(3.6 \times 10^{-11}\) 24
\[ Ar^* + NF_3 \rightarrow NF_2 + F + Ar \] \(1 \times 10^{-10}\) 25
\[ Ar^+ + N_2 \rightarrow N_2^+ + Ar \] \(1 \times 10^{-11}\) 26
\[ Ar^+ + N_2 \rightarrow N_2^+ + Ar \] \(1 \times 10^{-11}\) 26
\[ Ar^+ + N \rightarrow N^+ + Ar \] \(1 \times 10^{-11}\) j
\[ Ar^+ + N^* \rightarrow N^+ + Ar \] \(1 \times 10^{-11}\) j
\[ Ar^+ + NF_3 \rightarrow NF_2^+ + F + Ar \] \(1 \times 10^{-11}\) 27
\[
\begin{align*}
  \text{Ar}^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{Ar} & 1 \times 10^{-11} & \text{j} \\
  \text{Ar}^+ + \text{NF} & \rightarrow \text{NF}^+ + \text{Ar} & 5 \times 10^{-12} & \text{j} \\
  \text{F}^+ + \text{NF}_3 & \rightarrow \text{NF}_2^+ + \text{F} + \text{F} & 1 \times 10^{-11} & \text{j} \\
  \text{F}^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{F} & 1 \times 10^{-11} & 28,k \\
  \text{F}^+ + \text{NF} & \rightarrow \text{NF}^+ + \text{F} & 1 \times 10^{-11} & \text{j} \\
  \text{F}^+ + \text{N}_2 & \rightarrow \text{N}_2^+ + \text{F} & 1 \times 10^{-11} & 29 \\
  \text{F}^+ + \text{N} & \rightarrow \text{N}^+ + \text{F} & 1 \times 10^{-11} & 28,l \\
  \text{F}_2^+ + \text{NF}_3 & \rightarrow \text{NF}_2^+ + \text{F} + \text{F}_2 & 1 \times 10^{-11} & \text{j} \\
  \text{F}_2^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{F}_2 & 1 \times 10^{-11} & \text{j} \\
  \text{F}_2^+ + \text{NF} & \rightarrow \text{NF}^+ + \text{F}_2 & 1 \times 10^{-11} & \text{j} \\
  \text{F}_2^+ + \text{N}_2 & \rightarrow \text{N}_2^+ + \text{F}_2 & 5 \times 10^{-12} & \text{j} \\
  \text{F}_2^+ + \text{N} & \rightarrow \text{N}^+ + \text{F}_2 & 1 \times 10^{-11} & \text{j} \\
  \text{N}^+ + \text{NF}_3 & \rightarrow \text{NF}_3^+ + \text{N} & 1 \times 10^{-11} & 30,m \\
  \text{N}^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{N} & 1 \times 10^{-11} & 30,g \\
  \text{N}_2^+ + \text{N} & \rightarrow \text{N}^+ + \text{N}_2 & 5 \times 10^{-12} & 31 \\
  \text{N}_2^+ + \text{N}^* & \rightarrow \text{N}^+ + \text{N}_2 & 1 \times 10^{-10} & 31,n \\
  \text{N}_2^+ + \text{NF}_3 & \rightarrow \text{NF}_2^+ + \text{F} + \text{N}_2 & 1 \times 10^{-11} & 30 \\
  \text{N}_2^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{N}_2 & 1 \times 10^{-11} & 30 \\
  \text{NF}_2^+ + \text{NF}_3 & \rightarrow \text{NF}_3^+ + \text{NF}_2 & 1 \times 10^{-9} & 32,o \\
  \text{NF}^+ + \text{NF}_3 & \rightarrow \text{NF}_3^+ + \text{NF} & 1 \times 10^{-11} & 33 \\
  \text{NF}^+ + \text{NF}_2 & \rightarrow \text{NF}_2^+ + \text{NF} & 1 \times 10^{-11} & 33 \\
  \text{F}^- + \text{Ar}^+ & \rightarrow \text{F} + \text{Ar} & 1 \times 10^{-7} & 34 \\
\end{align*}
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F^- + F_2^+ \rightarrow F + F_2$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + F^+ \rightarrow F + F$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + NF_3^+ \rightarrow F + NF_3$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + NF_2^+ \rightarrow F + NF_2$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + NF^+ \rightarrow F + NF$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + N_2^+ \rightarrow F + N_2$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F^- + N^+ \rightarrow F + N$</td>
<td>$1 \times 10^{-7}$</td>
<td>28</td>
</tr>
<tr>
<td>$F + F + M \rightarrow F_2 + M$</td>
<td>$6.77 \times 10^{-28}$ cm$^6$ s$^{-1}$</td>
<td>35</td>
</tr>
<tr>
<td>$NF_2 + F + M \rightarrow NF_3 + M$</td>
<td>$5 \times 10^{-31}$ cm$^6$ s$^{-1}$</td>
<td>36</td>
</tr>
<tr>
<td>$NF + NF \rightarrow N_2 + F + F$</td>
<td>$6.88 \times 10^{-11} e^{-1251/T}$</td>
<td>37</td>
</tr>
<tr>
<td>$NF + NF \rightarrow F_2 + N_2$</td>
<td>$4 \times 10^{-12}$</td>
<td>37,38</td>
</tr>
<tr>
<td>$NF_2 + N \rightarrow NF + NF$</td>
<td>$3 \times 10^{-12}$</td>
<td>39</td>
</tr>
<tr>
<td>$NF_2 + N \rightarrow F + F + N_2$</td>
<td>$1.4 \times 10^{-11} e^{-95/T}$</td>
<td>40</td>
</tr>
<tr>
<td>$N_2^* + NF_3 \rightarrow NF_2 + F + N_2$</td>
<td>$1 \times 10^{-11}$</td>
<td>41,m</td>
</tr>
<tr>
<td>$N_2^* + N_2 \rightarrow N_2 + N_2$</td>
<td>$1.9 \times 10^{-13}$</td>
<td>42</td>
</tr>
<tr>
<td>$N_2^* + N \rightarrow N_2 + N$</td>
<td>$1 \times 10^{-13}$</td>
<td>j</td>
</tr>
<tr>
<td>$N_2^* + N^* \rightarrow N_2 + N$</td>
<td>$1 \times 10^{-13}$</td>
<td>j</td>
</tr>
<tr>
<td>$N^* + N_2 \rightarrow N + N_2$</td>
<td>$2 \times 10^{-14}$</td>
<td>43</td>
</tr>
<tr>
<td>$N^* + N + M \rightarrow N_2^* + M$</td>
<td>$2 \times 10^{-32}$ cm$^6$ s$^{-1}$</td>
<td>44,n</td>
</tr>
<tr>
<td>$N + N + M \rightarrow N_2^* + M$</td>
<td>$1 \times 10^{-32}$ cm$^6$ s$^{-1}$</td>
<td>44</td>
</tr>
<tr>
<td>$N + N + M \rightarrow N_2 + M$</td>
<td>$1 \times 10^{-32}$ cm$^6$ s$^{-1}$</td>
<td>44</td>
</tr>
<tr>
<td>$N_2^* + N_2^* \rightarrow N_2 + N_2^*$</td>
<td>$1.36 \times 10^{-9}$</td>
<td>42,45</td>
</tr>
</tbody>
</table>
a Rate coefficients have units of cm$^3$·s$^{-1}$ unless noted otherwise.

b The rate coefficient was obtained by solving Boltzmann’s equation for the electron energy distribution. Cross sections for the process are from the indicated reference.

c Cross section or rate coefficient for inverse process obtained by detailed balance.

d Ar$^*$ nominally represents Ar(4s) and includes excitation to that and higher lying states.

e Cross section for NF$_3$. Analogous cross sections used for NF$_x$ ($x < 3$).

f Inelastic loss included in calculation of electron energy distributions however excited state is not included in the model.

g Estimated by analogy to NF$_3$.

h N$_2^*$ nominally represents N$_2$(A) and includes excitation to that and higher lying states.

i N$^*$ nominally represents N($^2$D) and includes excitation to that and higher lying states.

j Estimated.

k Estimated by analogy to CF$_2$.

l Estimated by analogy to C.

m Estimated by analogy to NH$_3$.

n Estimated by analogy to N.

o Estimated by analogy to PF$_3$.

C.1 References


18. L. Vriens, “Calculation of absolute ionization cross sections of He, He⁺, Ne, Ne⁺, Ar, Ar⁺, Hg, Hg⁺,” *Phys. Lett.* 8, 260 (1964).


**APPENDIX D: LIST OF REACTIONS OF Ar/Cl₂**

The reaction chemistry[1] for an Ar/Cl₂ gas mixture used in the present study is given below:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + Ar → Ar⁺ + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + Ar → Ar⁺ + e + e</td>
<td>b</td>
<td>3</td>
</tr>
<tr>
<td>e + Ar⁺ → Ar⁺ + e + e</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>e + Ar⁺ → Ar + e</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>Ar⁺ + Ar⁺ → Ar⁺ + Ar + e</td>
<td>$5 \times 10^{-10}$</td>
<td>c</td>
</tr>
<tr>
<td>Ar⁺ + Ar → Ar + Ar⁺</td>
<td>$5.7 \times 10^{-10}$</td>
<td>c</td>
</tr>
<tr>
<td>e + Cl₂ → Cl + Cl⁻</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl₂ → Cl + Cl + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl₂ → Cl₂⁺ + e + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl → Cl⁺ + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl → Cl⁺ + e + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl⁺ → Cl⁺ + e + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>Cl⁺ → Cl</td>
<td>$1 \times 10^5 \text{s}^{-1}$</td>
<td>c</td>
</tr>
<tr>
<td>e + Cl⁻ → Cl + e + e</td>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>e + Cl₂⁺ → Cl + Cl</td>
<td>$1 \times 10^{-7}T_e^{-0.5}$</td>
<td>c</td>
</tr>
<tr>
<td>Cl⁻ + Cl⁺ → Cl + Cl</td>
<td>$1 \times 10^{-7}$</td>
<td>c</td>
</tr>
<tr>
<td>Cl⁻ + Cl₂⁺ → Cl + Cl + Cl</td>
<td>$1 \times 10^{-7}$</td>
<td>c</td>
</tr>
<tr>
<td>Cl⁻ + Ar⁺ → Cl + Ar</td>
<td>$7.1 \times 10^{-10}$</td>
<td>c</td>
</tr>
<tr>
<td>Ar⁺ + Cl₂ → Cl₂⁺ + Ar + e</td>
<td>$1 \times 10^{-7}$</td>
<td>c</td>
</tr>
</tbody>
</table>
\begin{align*}
\text{Ar}^* + \text{Cl} & \rightarrow \text{Cl}^* + \text{Ar} & 7 \times 10^{-10} & \text{c} \\
\text{Ar}^* + \text{Cl}_2 & \rightarrow \text{Cl}_2^* + \text{Ar} & 8.4 \times 10^{-9} & \text{6} \\
\text{Ar}^* + \text{Cl}_2 & \rightarrow \text{Cl}^* + \text{Cl} + \text{Ar} & 6.4 \times 10^{-9} & \text{6} \\
\text{Ar}^* + \text{Cl} & \rightarrow \text{Cl}^* + \text{Ar} & 2 \times 10^{-10} & \text{6} \\
\text{Cl} + \text{Cl} + \text{Ar} & \rightarrow \text{Cl}_2 + \text{Ar} & 1.28 \times 10^{-32} \text{ cm}^6 \text{s}^{-1} & \text{6} \\
\text{Cl} + \text{Cl} + \text{Cl} & \rightarrow \text{Cl}_2 + \text{Cl} & 1.28 \times 10^{-32} \text{ cm}^6 \text{s}^{-1} & \text{7} \\
\text{Cl} + \text{Cl} + \text{Cl}_2 & \rightarrow \text{Cl}_2 + \text{Cl}_2 & 5.4 \times 10^{-32} \text{ cm}^6 \text{s}^{-1} & \text{7} \\
\text{Cl}^* + \text{Cl}_2 & \rightarrow \text{Cl}_2^* + \text{Cl} & 5.4 \times 10^{-10} & \text{6, c} \\
\text{Cl}^* + \text{Cl} & \rightarrow \text{Cl} + \text{Cl}^* & 1 \times 10^{-9} & \text{c} \\
\text{Cl}_2^* + \text{Cl}_2 & \rightarrow \text{Cl}_2 + \text{Cl}_2^* & 8 \times 10^{-10} & \text{c}
\end{align*}

\text{a} \quad \text{Rate coefficients have units of cm}^3 \cdot \text{s}^{-1} \text{ unless noted otherwise.}

\text{b} \quad \text{The rate coefficient was obtained by solving Boltzmann’s equation for the electron energy}
\text{distribution. Cross sections for the process are from the indicated reference.}

\text{c} \quad \text{Estimated.}

\text{d} \quad \text{Cross section or rate coefficient for inverse process obtained by detailed balance.}

\textbf{D.1 References}

\text{Transients in Inductively Coupled Plasmas using Moderate Computational Parallelism.}
\text{II. ArCl}_2 \text{ Pulsed Plasmas,” J. Vac. Sci. Technol. A 20, 325 (2002).}

2. K. Tachibana, “Excitation of the 1s_5, 1s_4, 1s_3, and 1s_2 levels of argon by low-energy


APPENDIX E: LIST OF REACTIONS OF Ar/C₄F₈

The reaction chemistry[1] for an Ar/C₄F₈ gas mixture used in the present study is given below:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + Ar → Ar + e</td>
<td>c</td>
<td>2</td>
</tr>
<tr>
<td>e + Ar → Ar⁺ + e</td>
<td>c</td>
<td>3</td>
</tr>
<tr>
<td>e + Ar → Ar** + e</td>
<td>c</td>
<td>4</td>
</tr>
<tr>
<td>e + Ar → Ar⁺ + e + e</td>
<td>c</td>
<td>5</td>
</tr>
<tr>
<td>e + Ar⁺ → Ar** + e</td>
<td>c</td>
<td>6</td>
</tr>
<tr>
<td>e + Ar⁺ → Ar⁺ + e + e</td>
<td>c</td>
<td>6d</td>
</tr>
<tr>
<td>e + Ar** → Ar + e</td>
<td>c</td>
<td>3d</td>
</tr>
<tr>
<td>e + Ar** → Ar⁺ + e + e</td>
<td>c</td>
<td>7</td>
</tr>
<tr>
<td>e + Ar** → Ar⁺ + e</td>
<td>c</td>
<td>6d</td>
</tr>
<tr>
<td>e + F → F + e</td>
<td>c</td>
<td>8</td>
</tr>
<tr>
<td>e + F → F (ex) + e</td>
<td>c</td>
<td>8</td>
</tr>
<tr>
<td>e + F → F⁺ + e + e</td>
<td>c</td>
<td>8</td>
</tr>
<tr>
<td>e + F₂ → F₂ + e</td>
<td>c</td>
<td>9</td>
</tr>
<tr>
<td>e + F₂ → F₂ (v) + e</td>
<td>c</td>
<td>9</td>
</tr>
<tr>
<td>e + F₂ → F₂ (ex) + e</td>
<td>c</td>
<td>9</td>
</tr>
<tr>
<td>e + F₂ → F₂ + e</td>
<td>c</td>
<td>9</td>
</tr>
<tr>
<td>e + F₂ → F⁺ + F⁻</td>
<td>c</td>
<td>9</td>
</tr>
</tbody>
</table>
\[
\begin{aligned}
e + F_2 &\rightarrow F_2^+ + e + e & c & 9 \\
e + CF &\rightarrow CF + e & c & 10^e \\
e + CF &\rightarrow CF (v) + e & c & 10^e \\
e + CF &\rightarrow \text{c + F + e} & c & 10^e \\
e + CF &\rightarrow CF^+ + e + e & c & 11 \\
e + CF_2 &\rightarrow CF_2 + e & c & 12^f \\
e + CF_2 &\rightarrow CF_2 (v) + e & c & 12^f \\
e + CF_2 &\rightarrow CF + F^- & c & 12^f \\
e + CF_2 &\rightarrow CF + F + e & c & 12^f \\
e + CF_2 &\rightarrow CF_2^- + F + e + e & c & 13 \\
e + CF_2 &\rightarrow CF^+ + F + e + e & c & 13 \\
e + CF_3 &\rightarrow CF_3 + e & c & 12^f \\
e + CF_3 &\rightarrow CF_3 (v) + e & c & 12^f \\
e + CF_3 &\rightarrow CF_2 + F + e & c & 12^f \\
e + CF_3 &\rightarrow CF_3^+ + e + e & c & 13 \\
e + CF_3 &\rightarrow CF_2 + F^- & c & 12^f \\
e + CF_4 &\rightarrow CF_4 + e & c & 12 \\
e + CF_4 &\rightarrow CF_4 (v) + e & c & 12 \\
e + CF_4 &\rightarrow CF_3 + F^- & c & 12 \\
e + CF_4 &\rightarrow CF_3^- + F & c & 12 \\
e + CF_4 &\rightarrow CF_3 + F + e & c & 12 
\end{aligned}
\]
\[ e + CF_4 \rightarrow CF_3^+ + F + e + e \] c 12
\[ e + CF_4 \rightarrow CF_2 + F + F + e \] c 12
\[ e + CF_4 \rightarrow CF_3^+ + F^- + e \] c 12
\[ e + CF_4 \rightarrow CF + F + F_2 + e \] c 12
\[ e + C_2F_3 \rightarrow CF + CF_2 + e \] 15\[ \times 10^{-8} T_e^{0.91} \exp(-5.0/T_e) \] 14^g
\[ e + C_2F_4 \rightarrow C_2F_4 + e \] c 15,16
\[ e + C_2F_4 \rightarrow C_2F_4 (v) + e \] c 15,16
\[ e + C_2F_4 \rightarrow CF_2 + CF_2 + e \] c 15,16
\[ e + C_2F_4 \rightarrow C_2F_4^+ + e + e \] c 15,16
\[ e + C_2F_4 \rightarrow C_2F_3^+ + F + e \] c 15,16
\[ e + C_2F_4 \rightarrow CF^+ + CF_3^+ + e \] c 15,16
\[ e + C_2F_5 \rightarrow C_2F_5 + e \] c 17^h
\[ e + C_2F_5 \rightarrow C_2F_5 (v) + e \] c 17^h
\[ e + C_2F_5 \rightarrow CF_3^- + CF_2 \] c 17^h
\[ e + C_2F_5 \rightarrow CF_3 + CF_2 + e \] c 17^h
\[ e + C_2F_5 \rightarrow CF_3^- + CF_2 + e + e \] c 18
\[ e + C_2F_5 \rightarrow C_2F_5^+ + e + e \] c 18
\[ e + C_2F_6 \rightarrow CF_3^+ + CF_3 + e + e \] c 17
\[ e + C_2F_6 \rightarrow C_2F_6 + e \] c 17
\[ e + C_2F_6 \rightarrow C_2F_6 (v) + e \] c 17
\[ e + C_2F_6 \rightarrow CF_3 + CF_3^- \] c 17
\[ e + C_2F_6 \rightarrow C_2F_5 + F^- \] c 17
\begin{align*}
\text{e} + \text{C}_2\text{F}_6 & \rightarrow \text{CF}_3 + \text{CF}_3 + \text{e} & c & 17 \\
\text{e} + \text{C}_3\text{F}_5 & \rightarrow \text{C}_2\text{F}_3 + \text{CF}_2 + \text{e} & 1.8 \times 10^{-8} T_e^{0.52} \exp(-12.3 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_3\text{F}_5 & \rightarrow \text{C}_2\text{F}_4 + \text{CF} + \text{e} & 1.8 \times 10^{-8} T_e^{0.52} \exp(-12.3 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_3\text{F}_6 & \rightarrow \text{C}_2\text{F}_6^+ + \text{e} & 1.4 \times 10^{-8} T_e^{0.68} \exp(-10.6 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_3\text{F}_6 & \rightarrow \text{C}_2\text{F}_3 + \text{CF}_3 + \text{e} & 1.8 \times 10^{-8} T_e^{0.52} \exp(-12.3 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_3\text{F}_6 & \rightarrow \text{C}_2\text{F}_4 + \text{CF}_2 + \text{e} & 1.8 \times 10^{-8} T_e^{0.52} \exp(-12.3 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_3\text{F}_7 & \rightarrow \text{C}_2\text{F}_4 + \text{CF}_3 + \text{e} & 1.8 \times 10^{-8} T_e^{0.52} \exp(-12.3 / T_e) & 15,16^{g,i} \\
\text{e} + \text{C}_4\text{F}_7 & \rightarrow \text{C}_2\text{F}_4 + \text{C}_2\text{F}_3 + \text{e} & 5.7 \times 10^{-8} T_e^{0.28} \exp(-8.0 / T_e) & 17^{g,h} \\
\text{e} + \text{C}_4\text{F}_7 & \rightarrow \text{C}_4\text{F}_7^+ + \text{e} + \text{e} & 1.4 \times 10^{-8} T_e^{0.68} \exp(-10.6 / T_e) & 17^{g,h} \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_4\text{F}_8 + \text{e} & c & 19 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_4\text{F}_8 \text{(v)} + \text{e} & c & 19 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_2\text{F}_4 + \text{C}_2\text{F}_4 + \text{e} & c & 19 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_4\text{F}_8^* & c & 19 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{F}^+ + \text{C}_4\text{F}_7 & c & 19 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_3\text{F}_5^+ + \text{CF}_3 + \text{e} + \text{e} & c & 20 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{C}_2\text{F}_4^+ + \text{C}_2\text{F}_4 + \text{e} + \text{e} & c & 20 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{F}^+ + \text{C}_4\text{F}_7 + \text{e} + \text{e} & c & 20 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{CF}_3^+ + \text{C}_3\text{F}_5 + \text{e} + \text{e} & c & 20 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{CF}_2^+ + \text{C}_3\text{F}_6 + \text{e} + \text{e} & c & 20 \\
\text{e} + \text{C}_4\text{F}_8 & \rightarrow \text{CF}^+ + \text{C}_3\text{F}_7 + \text{e} + \text{e} & c & 20 \\
\end{align*}
Only reactions directly affecting species densities are included in the FKM. The additional electron impact collisions such as momentum transfer and excitation of vibrational and electronic states are included in the EETM to account for the transport and energy loses of the electron.

Rate coefficients have units of cm³/s unless noted otherwise.

Rate coefficient is calculated from electron energy distribution obtained in the EETM using the cross section from the cited reference.

Cross section was obtained by detailed balance.

Estimated by analogy to NF.

Estimated by analogy to CF₄.

Estimated using Maxwellian distribution.

Estimated by analogy to C₂F₆.

Estimated by analogy to C₂F₄.

E.1 References


3. K. Tachibana, “Excitation of the 1s₅, 1s₄, 1s₃, and 1s₂ levels of argon by low-energy electrons,” Phys. Rev. A 34, 1007 (1986).


7. L. Vriens, “Calculation of absolute ionization cross sections of He, He^{+}, He^{++}, Ne, Ne^{+}, Ar, Ar^{+}, Hg, and Hg^{+},” Phys. Lett. 8, 260 (1964).


APPENDIX F: Si ETCHING IN Ar/Cl$_2$; SURFACE REACTION MECHANISM

The surface reactions for polysilicon etch mechanism[1] used in the present study is given below and is based on the works of Cheng et al.[2] and Meeks and Shon[3]. The plasma-surface reaction mechanism on non-wafer surfaces is based on the work of Cuneg et al.[4]:

Species definitions:
- $X$  Gas phase species
- $X(s)$  Surface site
- $W(s)$  Reactor wall surface site

<table>
<thead>
<tr>
<th>Reaction$^{a,b,c}$</th>
<th>Probability</th>
<th>Footnote</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of passivation layer:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cl} + \text{Si}(s) \rightarrow \text{SiCl}(s)$</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl} + \text{SiCl}(s) \rightarrow \text{SiCl}_2(s)$</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl} + \text{SiCl}_2(s) \rightarrow \text{SiCl}_3(s)$</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}^+ + \text{Si}(s) \rightarrow \text{SiCl}(s)$</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}^+ + \text{Si}(s) \rightarrow \text{SiCl}(s)$</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Formation of etch blocks:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiCl}_2 + \text{Si}(s) \rightarrow \text{Si}_2\text{Cl}_2(s)$</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>$\text{SiCl}_2 + \text{SiCl}(s) \rightarrow \text{Si}_2\text{Cl}_3(s)$</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>$\text{SiCl}_2 + \text{SiCl}_2(s) \rightarrow \text{Si}_2\text{Cl}_4(s)$</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>
Consumption of passivation layer/etch blocks:

\[ \text{Cl} + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{Cl}_2 \] 0.02

\[ \text{Cl} + \text{SiCl}_3(s) \rightarrow \text{SiCl}_4 + \text{Si}(s) \] 0.001

\[ \text{Cl} + \text{SiCl}_3(s) \rightarrow \text{SiCl}_2(s) + \text{Cl}_2 \] 0.08

\[ \text{Cl} + \text{Si}_2\text{Cl}_2(s) \rightarrow \text{SiCl}(s) + \text{SiCl}_2 \] 0.008

\[ \text{Cl} + \text{Si}_2\text{Cl}_3(s) \rightarrow \text{SiCl}(s) + \text{SiCl}_2 + \text{Cl} \] 0.008

\[ \text{Cl} + \text{Si}_2\text{Cl}_4(s) \rightarrow \text{SiCl}_2(s) + \text{SiCl}_2 + \text{Cl} \] 0.008

\[ \text{Cl}^+ + \text{SiCl}(s) \rightarrow \text{SiCl}_2 + \text{Si}(s) \] 0.25

\[ \text{Cl}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2 + \text{Cl} + \text{Si}(s) \] 0.5

\[ \text{Cl}^+ + \text{SiCl}_3(s) \rightarrow \text{SiCl}_4 + \text{Si}(s) \] 0.5

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_2(s) \rightarrow \text{Si}(s) + \text{SiCl}_2 + \text{Cl} \] 0.8

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_3(s) \rightarrow \text{SiCl}(s) + \text{SiCl}_2 + \text{Cl} \] 0.9

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_4(s) \rightarrow \text{SiCl}_2(s) + \text{SiCl}_2 + \text{Cl} \] 0.9

\[ \text{Cl}^+ + \text{SiCl}(s) \rightarrow \text{SiCl}_2 + \text{Si}(s) \] 0.3  

\[ \text{Cl}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2 + \text{Cl} + \text{Si}(s) \] 0.6  

\[ \text{Cl}^+ + \text{SiCl}_3(s) \rightarrow \text{SiCl}_4 + \text{Si}(s) \] 0.6  

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_2(s) \rightarrow \text{Si}(s) + \text{SiCl}_2 + \text{Cl} \] 0.9  

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_3(s) \rightarrow \text{SiCl}(s) + \text{SiCl}_2 + \text{Cl} \] 0.99  

\[ \text{Cl}^+ + \text{Si}_2\text{Cl}_4(s) \rightarrow \text{SiCl}_2(s) + \text{SiCl}_2 + \text{Cl} \] 0.99  

\[ \text{Cl}_2^+ + \text{Si}(s) \rightarrow \text{SiCl}_2 + \text{Si}(s) \] 0.002  

\[ \text{Cl}_2^+ + \text{SiCl}(s) \rightarrow \text{SiCl}_2 + \text{Cl} + \text{Si}(s) \] 0.25
Cl\(_2^+\) + SiCl\(_2\)(s) → SiCl\(_2^+\) + Cl\(_2\) + Si(s) 0.6 d
Cl\(_2^+\) + SiCl\(_3\)(s) → SiCl\(_4\) + Cl\(^+\) + Si(s) 0.6 d
Cl\(_2^+\) + Si\(_2\)Cl\(_2\)(s) → Si(s) + SiCl\(_2\) + Cl\(_2\) 0.9 d
Cl\(_2^+\) + Si\(_2\)Cl\(_3\)(s) → SiCl(s) + SiCl\(_2\) + Cl\(_2\) 0.99 d
Cl\(_2^+\) + Si\(_2\)Cl\(_4\)(s) → SiCl\(_2\)(s) + SiCl\(_2\) + Cl\(_2\) 0.99 d
Ar\(^*\) + SiCl\(_2\)(s) → SiCl\(_2\) + Ar + Si(s) 0.3
Ar\(^*\) + Si\(_2\)Cl\(_2\)(s) → Si(s) + SiCl\(_2\) + Ar 0.8
Ar\(^*\) + Si\(_2\)Cl\(_3\)(s) → SiCl(s) + SiCl\(_2\) + Ar 0.9
Ar\(^*\) + Si\(_2\)Cl\(_4\)(s) → SiCl\(_2\)(s) + SiCl\(_2\) + Ar 0.9
Ar\(^+\) + SiCl\(_2\)(s) → SiCl\(_2\) + Ar + Si(s) 0.4 d
Ar\(^+\) + SiCl\(_2\)(s) → SiCl\(_2\)(s) + Ar 0.6 d
Ar\(^+\) + Si\(_2\)Cl\(_2\)(s) → Si(s) + SiCl\(_2\) + Ar 0.9 d
Ar\(^+\) + Si\(_2\)Cl\(_3\)(s) → SiCl(s) + SiCl\(_2\) + Ar 0.99 d
Ar\(^+\) + Si\(_2\)Cl\(_4\)(s) → SiCl\(_2\)(s) + SiCl\(_2\) + Ar 0.99 d
SiCl\(_2^+\) + SiCl\(_2\)(s) → SiCl\(_2\)(s) + SiCl\(_2\) + Si(s) + E 0.6 d
SiCl\(_2^+\) + Si\(_2\)Cl\(_2\)(s) → Si(s) + SiCl\(_2\) + SiCl\(_2\) 0.9 d
SiCl\(_2^+\) + Si\(_2\)Cl\(_3\)(s) → SiCl(s) + SiCl\(_2\) + SiCl\(_2\) 0.99 d
SiCl\(_2^+\) + Si\(_2\)Cl\(_4\)(s) → SiCl\(_2\)(s) + SiCl\(_2\) + SiCl\(_2\) 0.99 d

On non-wafer surfaces:

Cl + W(s) → Cl(s) 0.02
Cl + Cl(s) → W(s) + Cl\(_2\) 0.02
\[ \text{Cl}^* + \text{W(s)} \rightarrow \text{Cl(s)} \quad 0.06 \]
\[ \text{Cl} + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2(s) + \text{Cl} \quad 1 \]
\[ \text{Cl}^* + \text{Cl}(s) \rightarrow \text{W(s)} + \text{Cl}_2 \quad 0.16 \]
\[ \text{Cl}^* + \text{SiCl}_2(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{Cl} \quad 0.04 \]
\[ \text{Cl}^* + \text{Cl}(s) \rightarrow \text{W(s)} + \text{Cl}_2 \quad 0.8 \]
\[ \text{Cl} + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2(s) + \text{Cl} \quad 0.8 \]
\[ \text{Cl}^* + \text{SiCl}_2(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{Cl} \quad 0.5 \quad d \]
\[ \text{Cl}^* + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{Cl}_2 \quad 0.1 \quad e \]
\[ \text{Cl}^+ + \text{Cl}(s) \rightarrow \text{W(s)} + \text{Cl}_2 + \text{Cl} \quad 0.8 \]
\[ \text{Cl}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2(s) + \text{Cl}_2 \quad 0.84 \quad d \]
\[ \text{Cl}^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{Cl}_2 + \text{Cl} \quad 0.1 \quad e \]
\[ \text{Ar}^* + \text{Cl}(s) \rightarrow \text{W(s)} + \text{Cl}^+ \text{ Ar} \quad 0.06 \]
\[ \text{Ar}^* + \text{SiCl}_2(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{Cl} \quad 0.8 \quad d \]
\[ \text{Ar}^* + \text{Cl}(s) \rightarrow \text{W(s)} + \text{Cl}^+ \text{ Ar} \quad 0.4 \]
\[ \text{Ar}^* + \text{SiCl}_2(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{Cl} \quad 0.8 \quad d \]
\[ \text{Ar}^* + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{Cl}^+ \text{ Ar} \quad 0.1 \quad e \]
\[ \text{SiCl}_2 + \text{W(s)} \rightarrow \text{SiCl}_2(s) \quad 0.2 \]
\[ \text{SiCl}_2 + \text{Cl}(s) \rightarrow \text{Cl}(s) + \text{SiCl}_2 \quad 1 \]
\[ \text{SiCl}_2 + \text{SiCl}_2(s) \rightarrow \text{SiCl}_2(s) + \text{SiCl}_2 \quad 1 \]
\[ \text{SiCl}_2^+ + \text{W(s)} \rightarrow \text{W(s)} + \text{SiCl}_2 \quad 1 \]
\[ \text{SiCl}_2^+ + \text{Cl}(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{Cl} \quad 0.8 \quad d \]
\[ \text{SiCl}_2^+ + \text{SiCl}_2(s) \rightarrow \text{W(s)} + \text{SiCl}_2 + \text{SiCl}_2 \quad 0.04 \quad d \]
\[ \text{SiCl}_2^+ + \text{SiCl}_2(s) \rightarrow \text{SiCl}(s) + \text{SiCl}_2 + \text{Cl} \quad 0.1 \quad e \]
a Unless otherwise specified, all ions neutralize on surfaces, returning as their neutral counterparts.

b All gas phase species have units of flux (cm\(^{-2}\).s\(^{-1}\)). All surface species have units of fractional coverage.

c In reactions with no chemical change, the gas species are reflected off the surface. These reactions are not shown in the table.

d See Eq. (3). \(E_r = 150\) eV, \(E_t = 20\) eV.

e See Eq. (s). \(E_r = 150\) eV, \(E_t = 30\) eV.

F.1 References


APPENDIX G: Si ETCHING IN Ar/Cl₂; OXYGEN SPUTTER REACTIONS

The polysilicon etch surface reactions including oxygen atoms used in the present study is given below:

Species definitions:

- X Gas phase species
- X(s) Surface site
- Q(s) Quartz window surface site

<table>
<thead>
<tr>
<th>Reaction&lt;sup&gt;a,b,c&lt;/sup&gt;</th>
<th>Probability</th>
<th>Footnote</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen Sputter from Quartz Window:</strong></td>
<td>p₀</td>
<td></td>
</tr>
<tr>
<td>( O^+ + Q(s) \rightarrow Q(s) + O + O )</td>
<td>1.0</td>
<td>d</td>
</tr>
<tr>
<td>( Cl^+ + Q(s) \rightarrow Q(s) + Cl + O )</td>
<td>1.0</td>
<td>d</td>
</tr>
<tr>
<td>( Cl_2^+ + Q(s) \rightarrow Q(s) + Cl_2 + O )</td>
<td>1.0</td>
<td>d</td>
</tr>
<tr>
<td>( Ar^+ + Q(s) \rightarrow Q(s) + Ar + O )</td>
<td>1.0</td>
<td>d</td>
</tr>
<tr>
<td>( SiCl_2^+ + Q(s) \rightarrow Q(s) + SiCl_2 + O )</td>
<td>1.0</td>
<td>d</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction&lt;sup&gt;a,b,c&lt;/sup&gt;</th>
<th>Probability</th>
<th>Footnote</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formation of etch blocks:</strong></td>
<td>p₀</td>
<td></td>
</tr>
<tr>
<td>( O + SiCl(s) \rightarrow SiOCl(s) )</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>( O + SiCl_2(s) \rightarrow SiOCl(s) )</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>( O + SiCl_3(s) \rightarrow SiOCl(s) )</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>( O + Si_2Cl_2(s) \rightarrow SiOCl(s) )</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>( O + Si_2Cl_3(s) \rightarrow SiOCl(s) )</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
\[
O + \text{Si}_2\text{Cl}_4(\text{s}) \rightarrow \text{SiOCl}(\text{s})
\]

**Removal of etch blocks:**

\[
\text{p}_0
\]

\[
\text{Cl}^+ + \text{SiOCl}(\text{s}) \rightarrow \text{SiCl}(\text{s}) + \text{Cl} + \text{O}
\]

\[
\text{Cl}_2^+ + \text{SiOCl}(\text{s}) \rightarrow \text{SiCl}(\text{s}) + \text{Cl}_2 + \text{O}
\]

\[
\text{Ar}^+ + \text{SiOCl}(\text{s}) \rightarrow \text{SiCl}(\text{s}) + \text{Ar} + \text{O}
\]

\[
\text{SiCl}_2^+ + \text{SiOCl}(\text{s}) \rightarrow \text{SiCl}(\text{s}) + \text{SiCl}_2 + \text{O}
\]

\[
\text{O}^+ + \text{SiOCl}(\text{s}) \rightarrow \text{SiCl}(\text{s}) + \text{O} + \text{O}
\]

\[a\] Unless otherwise specified, all ions neutralize on surfaces, returning as their neutral counterparts.

\[b\] All gas phase species have units of flux (cm\(^{-2}.s^{-1}\)). All surface species have units of fractional coverage.

\[c\] In reactions with no chemical change, the gas species are reflected off the surface. These reactions are not shown in the table.

\[d\] See Eq. (3). \(E_r = 150 \text{ eV}, E_t = 50 \text{ eV}\).

\[e\] See Eq. (3). \(E_r = 150 \text{ eV}, E_t = 60 \text{ eV}\).
APPENDIX H: LIST OF REACTIONS OF OXYGEN IN Ar/Cl₂/O

The reaction chemistry for an Ar/Cl₂/O gas mixture used in the present study is given below. The Ar/Cl₂ reactions are summarized in Appendix D. Only the reactions of oxygen are summarized here:

<table>
<thead>
<tr>
<th>Species</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>O</td>
<td>Cl₂</td>
</tr>
<tr>
<td>Ar</td>
<td>O⁺</td>
<td>Cl</td>
</tr>
<tr>
<td>Ar⁺(4s)</td>
<td>O*</td>
<td>M</td>
</tr>
<tr>
<td>Ar⁺</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient⁺</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + O → O⁺ + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + O → O⁺ + e + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + O⁺ → O⁺ + e + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + O⁺ → O⁺ + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + O⁺ → O⁺</td>
<td>5.3 × 10⁻¹⁰</td>
<td>2</td>
</tr>
<tr>
<td>e + e + O⁺ → O⁺ + e</td>
<td>5.12 × 10⁻²⁷</td>
<td>2</td>
</tr>
<tr>
<td>O + O⁺ → O + O⁺</td>
<td>1 × 10⁻⁹</td>
<td>3</td>
</tr>
<tr>
<td>O + O⁺ + M → O + O⁺ + M</td>
<td>1 × 10⁻²⁹</td>
<td>3</td>
</tr>
<tr>
<td>O⁺ + O → O + O</td>
<td>8 × 10⁻¹²</td>
<td>3</td>
</tr>
</tbody>
</table>
\[ \text{Ar}^* + \text{O} \rightarrow \text{O}^* + \text{Ar} \quad 4.1 \times 10^{-11}, \text{c} \quad 4 \]

\[ \text{Ar}^+ + \text{O}^* \rightarrow \text{O}^+ + \text{Ar} \quad 1 \times 10^{-11} \quad 5 \]

\[ \text{O}^* + \text{Ar} \rightarrow \text{O} + \text{Ar} \quad 5 \times 10^{-13} \quad 6 \]

\[ \text{Ar}^+ + \text{O} \rightarrow \text{O}^+ + \text{Ar} \quad 1 \times 10^{-11} \quad 7 \]

\[ \text{O}^+ + \text{Cl} \rightarrow \text{Cl}^+ + \text{O} \quad 1 \times 10^{-11} \quad \text{d} \]

\[ \text{O}^+ + \text{Cl}_2 \rightarrow \text{Cl}_2^+ + \text{O} \quad 1 \times 10^{-11} \quad \text{d} \]

\(^a\) Rate coefficients have units of cm\(^3\).s\(^{-1}\) unless noted otherwise.

\(^b\) The rate coefficient was obtained by solving Boltzmann’s equation for the electron energy distribution. Cross sections for the process are from the indicated reference.

\(^c\) \text{Ar}^* nominally represents \text{Ar}(4s) and includes excitation to that and higher lying states.

\(^d\) Estimated.

### H.1 References


AUTHOR’S BIOGRAPHY

Ankur Agarwal was born in Secunderabad, India, in 1982. He received his B.Tech. degree in Chemical Engineering from the Indian Institute of Technology Bombay, India in 2003, and his M.S. in Chemical Engineering from the University of Illinois at Urbana-Champaign in 2005. Under the guidance of Professor Mark J. Kushner, he has studied low pressure plasma sources for processing of advanced materials for use in sub-60 nm technologies since 2004. His work has resulted in 3 refereed journal publications, 17 conference presentations, including 2 invited talks and 2 Best Paper Awards. Upon graduation in December 2007 with his Ph.D. from University of Illinois at Urbana-Champaign, he will work with Applied Materials, Inc. in Santa Clara, CA as a plasma etch modeling engineer.