Study on Surface Kinetics in PECVD Chamber Cleaning using Remote Plasma Source

by

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Abstract

The scope of this research work is to characterize the Transformer Coupled Toroidal Plasma (TCTP); to understand gas phase reactions and surface reactions of neutrals in the cleaning chamber by analyzing the concentration of neutrals in downstream cleaning process chamber; and to make a global model that predicts the partial pressure of active species in the cleaning chamber. The final goal is to set-up an optimal cleaning process using the results from the experiment and the global model.

The first object is to characterize the TCTP and the power consumed by plasma is measured as one approach to the characterization of plasma. MKS Astex plasma source has a very high power density. Compared to a typical industrial plasma source, the power density of the TCTP source is two orders of magnitude higher. The extremely high power density makes the plasma source very unique and its parameters very different from other plasma sources. It is discussed that there are several factors that affect the plasma power consumption. One factor is the flow rate of inlet gas and the elevated pressure due to the high flow rate of inlet gas increases the power consumption. Experimentally it is observed that the plasma power is linearly dependent upon the plasma source pressure, not upon the process chamber pressure. Another factor of controlling the power consumption is the resistivity of gases. For example, the bonding energy of
N-F in NF₃ gas is different from the bonding energy of C-F bonding in C₂F₆. Experimental result shows that C₂F₆ + O₂ gas requires more power than NF₃ gas to dissociate in the plasma due to the different resistivity.

The second object is to understand gas phase reactions and surface reactions among neutrals in the cleaning chamber. The effect of nitric oxide as a silicon nitride etching enhancement factor is discussed. It is shown that only 4.5% of additives (O₂, CO and CO₂) into NF₃ discharge doubles nitride etching rate and the enhancement of etching rate occurs regardless of the additive types. The enhancement results from the production of NO in the discharge of NF₃ gas mixture. As the amount of oxygen containing additive increases, the amount of NO increases. However, atomic fluorine decreases as the amount of oxygen containing additive increases because the additive dilutes NF₃ plasma. At low process chamber pressure, the effect of NO is offset by the dilution effect of atomic fluorine. At high pressure, addition of oxygen enhances the recombination of atomic fluorine and 25% of O₂ in NF₃ discharge decreases 54% of atomic fluorine. Therefore, the effect of a decrease in atomic fluorine is remarkably higher than the effect of increase in the concentration of NO by adding O₂ at high pressure, which leads to a decrease of nitride etching rate at 5torr.

Also, the nitride etching rates of NF₃ plasma and NF₃/C₂F₆/O₂ plasma are compared and it is shown that NF₃/C₂F₆/O₂ plasma brings better performance than NF₃ plasma in increasing the nitride etching rate. The main reason why the nitride etching rate of NF₃/C₂F₆/O₂ plasma is higher than that of NF₃ plasma is because nitric oxide is formed in the gas phase of NF₃/C₂F₆/O₂ plasma and the nitric oxide reacts with the nitrogen atom on the silicon nitride surface producing N₂O or N₂, while nitrogen is substituted by oxygen on the surface by the reaction. Removing nitrogen atom from silicon nitride substrate is assumed to be the rate-limiting step in the fluorine
base etching of silicon nitride film. In summary, the nitric oxide makes it easier to remove the nitrogen atom from silicon nitride surface in the presence of atomic fluorine, which is the rate-limiting step for nitride etching with F base gas, therefore enhancing silicon nitride etching rate.

The last object is to make a global model to predict the partial pressure of neutrals in downstream. It is shown that incorporating kinetics into the global modeling of PECVD chamber cleaning system successfully enables the prediction of the partial pressure of atomic fluorine in NF$_3$/N$_2$ and NF$_3$/O$_2$ discharge, which is crucial in estimating cleaning rate of TEOS film. First of all, effect of nitrogen addition in NF$_3$ discharge is experimentally investigated by measuring the etching rates of TEOS film and the partial pressure of neutral species. Both modeling results and experimental results make a good agreement that the addition of nitrogen in NF$_3$ has advantage in increasing TEOS etching rate at high chamber pressure. In other words, at high chamber pressure, TEOS etching rate is increased by adding nitrogen in NF$_3$ plasma. Then, the effect of oxygen in NF$_3$ discharge is studied. TEOS film etching rates and partial pressure of atomic fluorine in the gas phase shows that adding oxygen in NF$_3$ discharge increases F-F recombination, which lowers TEOS etching rate. By incorporating the above kinetics information in the global model, the partial pressure of neutral species in NF$_3$/O$_2$ discharge is successfully predicted by the global model.

Thesis Advisor: Herbert H. Sawin
Thesis Committee Member: George Stephanopoulos, Karen K. Gleason
Dedication

To my husband, Jung Hoon
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Chapter 1 Introduction

1.1 Integrated Circuits

Integrated circuits are electrical circuits that are manufactured by a sequence of steps that simultaneously build the transistors, capacitors, diodes, resistors, wiring, etc. that compose the circuit. Transistors are the key elements in the integrated circuits. A transistor is a switch which is closed and opened by an isolated control terminal, representing the digital 0 and 1 state.

There are two dominant types of transistors used in silicon integrated circuits today, the Bipolar Junction Transistors (BJTs) and Field-Effect Transistor (FET). The BJTs were first invented by Bardeen, Brattain, and Shockley in 1947 at the Bell Telephone Laboratories[1, 2]. It is a three layer sandwich of differently doped sections, either N-type|P-type|N-type (NPN transistors) or P-type|N-type|P-type (PNP transistors). Although the field effect mechanism on which the Metal Oxide Semiconductor (MOS) device is based was first investigated in the 1930s, the first MOS device was invented at Bell Labs in 1960. It was structured by putting an insulating layer on the surface of the semiconductor and then placing a metallic gate electrode on the insulating layer. It used crystalline silicon for the semiconductor and a thermally oxidized layer of silicon dioxide for the insulator.

The Metal Oxide Semiconductor Field-Effect Transistor (MOSFET) has achieved electronic hegemony over other types of transistors including the BJTs devices. MOSFET not only possesses such technical attractions as low cost of production and ease of integration, but also avoids the problem of generating localized electron traps at the interface between the silicon and its native oxide layer. The localized electron traps had impeded the performance of earlier transistors[3]. This was the case especially after the invention of complementary metal-oxide-
semiconductor (CMOS) by Frank Wanlass at Fairchild Semiconductor in 1963. A CMOS device is usually structured with an NMOS and a PMOS next to each other. CMOS has become the predominant technology in digital integrated circuits. This is essentially the case when the area occupation, operating speed, energy efficiency and manufacturing costs have benefited and continue to benefit from the geometric downsizing that comes with every new generation of semiconductor manufacturing processes. In addition, the simplicity and the comparatively low power dissipation of CMOS circuits have allowed for integration densities not possible on the basis of bipolar junction transistors[4].

![Cross section of a MOS transistor](image)

**Figure 1.1 Cross section of a MOS transistor.**

Figure 1.1 illustrates the simplified cross section of a PMOS transistor. A P-MOSFET consists of an n-doped silicon substrate with two highly p-doped contacts, the source and the drain. The channel region in between is covered by an insulating layer, the gate-oxide, which is in contact with the gate electrode. Without applying a voltage at the gate electrode, no current can flow from source to drain as the pn-junctions between each contact and the substrate act as two opposite diodes. When applying a positive (negative) voltage at the gate electrode, the channel region close to the gate oxide is "inverted" (i.e. from n-(p-) doped to p-(n-)doped), and hence current can flow between source and drain.
The number of MOS transistors on the chip has increased continuously. Therefore the decrease of MOS size and the increase of wafer size have been inevitable in the mass production of microelectronics. The processing power of the state-of-the-art chips will double every 18 months, known as “Moore’s Law”. In the semiconductor industry, decreasing component size is often characterized by the critical feature size, or the minimum line width, which is usually defined as the smallest lateral feature size that is printed on the wafer surface during the fabrication process. Similar trend is to be seen in “Hwang’s Law”. Samsung president Hwang announced that the density of the top-of-the-line flash memory chips will double every 12 months.

Smaller MOSFETs are desirable for three reasons. First, smaller MOSFETs allow more current to pass. Conceptually, MOSFETs are like resistors in the on-state, and shorter resistors have less resistance, hence allow more current for the same voltage. Second, smaller MOSFETs have smaller gates, and thus lower gate capacitance. These first two factors contribute to shorter switching times, and thus higher processing speeds. A third reason for MOSFET scaling is that reduced area leads to reduced cost. Smaller MOSFETs can be packed more densely, resulting in either smaller chips or chips with more computing power in the same area. Since the cost of fabricating a semiconductor wafer is relatively fixed, the cost of an individual chip is mainly related to the number of chips that can be produced per wafer. Hence, smaller MOSFETs allow more chips per wafer, reducing the price per chip[3].

The bottleneck of decreasing the size of the MOSFET has been associated with the semiconductor device fabrication process. The past success was enabled by increasingly sophisticated materials selections and manufacturing techniques.
1.2 Semiconductor Fabrication Processing

The current microelectronics processing originated from the planar process, invented by Jean Hoerni of Fairchild Semiconductor in the late 1950s. Semiconductor fabrication processing consists of a series of several unit processes: lithography by photoresist; plasma etching; wet etching; film deposition; CMP (Chemical Mechanical Polish).

![Diagram of basic semiconductor process steps:](image)

**Figure 1.2** Basic semiconductor process steps. (a) Film to be patterned is deposited on a substrate. b) The film is coated with a light-sensitive polymer known as photoresist. c) The resist is exposed through a mask consisting of transparent and opaque regions defining the desired circuit features. d) After exposure, the photoresist is developed, leaving portions of the film masked by remaining photoresist. e) The film is etched in a plasma process, leaving the areas protected by resist. f) The remaining resist is stripped, leaving a patterned film. These processes are then repeated over and over to build up the circuit layers.

Figure 1.2 shows the typical sequence of several unit processes used in current semiconductor processes[5]. To form a structure of another material on the substrate as in Figure 1.2(f), a film of that material is first deposited on the substrate. The typical deposition methods include thermal oxidation (for SiO₂), Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD) and Plasma-Enhanced Chemical Vapor Deposition (PECVD)[4]. After the
material film is deposited, a light-sensitive polymer material known as photoresist is deposited on top of it. The photoresist is exposed to radiation through a mask. The exposed areas of the resist undergo a change in structure, and are washed away upon development (for a positive-tone resist). The remaining patterned resist on the wafer acts as a mask, protecting the underlying film material. This process is called lithography. With the photoresist film as a mask, the deposited film is then etched away. The typical etching methods are either wet etching or plasma etching. Following the etch process, the remaining resist is stripped, leaving desired features remaining in the film. The steps, film deposition, lithography, and etch as shown in Figure 1.2, are repeated over and over to fabricate all necessary components (transistors, resistors, capacitors etc.) on the chip to build up the complete integrated circuit.

Among unit processes mentioned above, we will focus on the unit processes that use plasma in the next section (section 1.3). In semiconductor fabrication process, plasma is used for various purposes: depositing various kinds of films and for etching those films to make a pattern. In section 1.3.1, we will discuss how plasma is applied for thin film deposition and the application of plasma for etching will be discussed in section 1.3.2

1.3 Application of Plasmas

1.3.1 Thin Film Deposition

One of the important steps in the fabrication of the semiconductor is a film deposition. Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) are the major two categories of methods used for thin film deposition. In each case, the substrate is placed in a deposition chamber, and the components of the deposited film are usually delivered through gas phase to the surface of the substrate and then form the deposited film. In CVD, chemical
reactions happen among the reactant gases to deposit film on the substrate. In PVD, physical methods are used to produce the constituent atoms which pass through a low-pressure gas phase and then condense on the substrate.

Low pressure Plasma Enhanced Chemical Vapor Deposition (PECVD) is the major CVD method currently used in the industry. Although the atmospheric pressure chemical vapor deposition was used, the uniformity of the deposited film was found to be bad due to the gradient of species concentration across the wafer. The industry has hence moved to the low-pressure process at a pressure of about 1torr. Lowering the pressure increases the diffusion, decreases the species gradient across the wafer, and hence improves the wafer uniformity.

For several reasons, plasma helps the deposition process in the lower pressure PECVD method. First, plasma makes the chemical reaction possible in much lower temperature than non-plasma CVD by supplying additional energy from the plasma to the neutrals. This is especially important for film that cannot endure the high temperature (800-1000K) in non-plasma CVD. Second, the ion bombardment from the plasma to the film allows more easily altering the film's properties such as composition, density and stress for particular applications.

The atom fluxes in the PVD process are generated by either evaporation or ion bombardments. In the evaporation method, the solid is heated up to a high temperature which causes evaporation to happen. In the ion bombardment method, plasma is formed in the chamber and the ions bombard the solid to release atoms and molecules into the gas phase. This method is sometimes also called sputtering deposition. Compared to the CVD process, the PVD process is generally more versatile, allowing for the deposition of almost any material. PVD with ion bombardment is another example that plasma is used in semiconductor industry.
One of the key issues for all thin film deposition processes is the cleaning of the deposition chamber. In all the deposition process, the same materials are deposited on the chamber wall as they are deposited on the wafer in the chamber. As the film thickness increases, the mechanical stress at the film-wall interfaces increases. At sufficient thicknesses and stresses, the interface delaminates and produces flaking particles, which then leaves the chamber wall and transit to the surface of the wafer. This is usually called particle contamination and it is the major mechanism for the point defect which causes malfunction of the final products[6]. To avoid the problem, the typical procedure is to clean the chamber wall on a regular basis to remove all deposited film. The chamber cleaning is usually the rate limiting step in the deposition process, and hence faster chamber cleaning increases the overall productivity.

Over the past 20 years, the chamber cleaning procedure has evolved from periodic manual (wet) cleaning of the chamber wall to routine \textit{in situ} plasma cleaning and, finally, to remote (or \textit{ex situ}) plasma cleaning. In wet chamber cleaning, reactive solutions are used to wipe the chamber wall by hand. In both the \textit{in situ} plasma cleaning and the remote plasma cleaning, plasma is used to create reactive radicals to remove the film on the chamber wall. The remote chamber cleaning method is to generate plasma based on fluorine-rich discharges[7-10]. The etching is a combination of spontaneous isotropic chemical etching and ion induced etching. Typically, mixtures of $\text{C}_2\text{F}_6 + \text{O}_2$ have been used to produce the high atomic fluorine concentrations needed for cleaning. $\text{CF}_4 + \text{O}_2$ can be used, but the greater power density needed to break apart the $\text{CF}_4$ has favored the use of larger fluorocarbons that fragment more easily in the plasma. Gases such as $\text{NF}_3$ and $\text{SF}_6$ that produce large atomic fluorine concentrations are also used. We will discuss further the remote plasma etching in section 1.4.
1.3.2 Plasma Etching

There are two main methods used in the semiconductor industry: wet etching and dry, or plasma, etching. In wet etching, the wafers are usually immersed into baths of liquid etchant solution and the exposed materials are etched by pure chemical processes. Wet etches were developed for all steps in the fabrication process. For example, silicon dioxide is commonly etched in hydrofluoric acid (HF) by reaction shown in the equation below.

\[ SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \]  \hspace{1cm} (1.1)

Wet chemical etching is almost entirely superseded by dry plasma etching processes due to the decrease of feature size and the limitation of wet etching. Figure 1.3(a) shows a poor pattern transfer when the sample is wet-etched. Since the etching medium attacks the etched layer isotropically, the materials are removed horizontally under the mask at the same rate as that the etched layer is removed vertically. The process was fine before 1980 when the critical dimension was over 2\( \mu \)m. When the size of the feature gets smaller than 2\( \mu \)m, the process cannot be used anymore because the mask would be entirely undercut by the etching fluid before it reached the substrate when the width of the mask horizontally is less than twice the thickness of the layer to be etched.

![Diagram of plasma etching](image)

Figure 1.3 Plasma etching in integrated circuit manufacture: (a) example of isotropic wet etching; (b) illustrating the role of bombarding ions in anisotropic dry etching.
Plasma etching has become the dominant etching process ever since 1980s due to its great pattern transformation. Figure 1.3(b) shows an example where a substrate with patterned mask is etched in plasma. Usually RF glow discharge plasma generates reactive species (both neutral radicals and ions), which then impinge on the mask and the exposed etched layer. Because the mask is relatively hard to be etched, it remains in place to shield the layer below it from bombardment by active species originating in the plasma. An important feature of the plasma etching process is that the etching occurs vertically due to the enhancement of ion bombardments. Another aspect of plasma etching that should be considered is the selectivity, meaning that the layer intended to be etched is actually etched, not the mask or the substrate.

![Graph](image)

**Figure 1.4 Data of Coburn and Winters on the interaction of 450eV argon ions with silicon, with and without the presence of xenon difluoride gas. The etching rate prior to 200 sec is due to chemical etching by xenon difluoride gas. The 450eV argon ion beam was turned at 200 sec, producing the increased silicon etching rate shown. After the xenon difluoride was pumped out of the system at 650 sec, only the etching rate caused by argon ion sputtering is evident.**

When a surface is exposed to both chemically reactive neutral which can react with a surface to produce a volatile product and ion bombardments, the combined ion and neutral fluxes often
etch more rapidly than surfaces exposed to only the neutral beam or the ion bombardments. Shown in Figure 1.4 is a beam experiment performed by Coburn et al in which the etching rate was monitored when xenon difluoride and argon ion beam were turned on and off[11, 12]. The etching rate prior to 200 sec is due to chemical etching by xenon difluoride gas. The 450eV argon ion beam was turned on at 200 sec, producing the increased silicon etching rate. After the xenon difluoride was pumped out of the system at 650 sec, only the etching rate caused by argon ion sputtering is evident. It can be seen that the combination of both ions and fluorine source results in an etching rate that is quite synergistic and exhibits an etching yield that is an order of magnitude greater than physical sputtering. In plasma, both ions and reactive neutrals are generated and the ion bombardment is directional. The area with exposure to ion bombardment will have much higher etching rate than the area without the exposure, causing a vertical anisotropic etching pattern as in Figure 1.3(b).

Figure 1.5 Inductively coupled plasma etcher with full wafer interferometry (FWI) and optical emission spectroscopy (OES) diagnostics. The pancake coil is powered by a 13.56 MHz rf power supply to generate the plasma, and the bottom electrode is powered by another rf power supply to control the ion bombardment energy.
A typical plasma etcher with some diagnostic capability is shown in Figure 1.5[13]. The plasma is generated by inductive coupling. The AC current passing through the top coil generates time-varying magnetic field, which then causes electric field in the gases. Free electrons are accelerated and then excite and dissociate molecules to form energetic ions and reactive neutrals. Plasma sheath is formed between the plasma and surrounding surface, with electric field which repels electrons and accelerates ions. Ions are accelerated across the plasma sheath with high energy, impinge on the surface with high directionality, and enhance the surface reaction as demonstrated earlier. To further change the ion bombardment energy, another RF power is applied on the bottom electrode, which is usually cooled by helium gases. Full Wafer Interferometry (FWI) is used for etching rate and uniformity study[14] and Optical Emission Spectroscopy (OES) is used to monitor the plasma.

There are two approaches for experimental studies on plasma processing. One is to construct a complete reactor as in Figure 1.5, diagnose the plasma parameters, measure the plasma etching performance and then back out the surface reaction mechanism. A collaborative experimental effort was initiated at a workshop at the 1988 Gaseous Electronics Conference (GEC) to understand the fundamental physics of processing plasma, as well as to give researchers a baseline experiment to develop plasma diagnostics to be used on manufacturing plasma systems[15]. The design was based on the usage of 4 in. diameter, aluminum electrodes in a parallel plate configuration at 13.56 MHz. Many research based on similar etchers was carried out to study the etching of silicon and other materials[16-18]. The drawback of these studies is that it is difficult to resolve so many possible simultaneous reactions on the surface.[19]

The second type of experiments is beam experiments, in which individual neutral and ion beams are generated and the reaction mechanisms are studied. Started from the ion beam etching
in early 1980s[20, 21], beam experiments were set up to study the etching performance of silicon and silicon oxide etching in F/Ar beam or CF$_2$/Ar beam[22-24]. Beam experiments were set up to study the silicon etching in chlorine or bromine beams[25-27], the silicon or silicon oxide etching in more complicated fluorocarbon radical beams[28, 29]. The advantage of beam experiments is that they separate the contribution of different radicals from the plasma. Therefore, the beam experiment data are the best set of data for modeling surface kinetics.

### 1.4 Remote Plasma Processing for ex situ Chamber Cleaning

Remote plasma sources for the production of fluorine atoms are currently widely used for chamber cleaning in the semiconductor processing industry, particularly in the cleaning of chambers used for deposition. The use of remote plasma sources avoids the erosion of the interior chamber materials typical of *in situ* chamber cleans in which ions generated in the discharge sputter the wall surface. While capacitively coupled and inductively coupled Radio Frequency (RF) sources, as well as microwave remote sources have been developed for these sorts of applications, the industry is rapidly moving toward transformer-coupled inductive sources in which the plasma has a toroidal configuration and forms the secondary of the transformer. The use of lower frequency RF power and magnetic cores enhances the inductive coupling; thereby allowing the more efficient transfer of energy to the plasma without excessive ion bombardment which limits the lifetime of the remote plasma source chamber interior.

Figure 1.6 illustrates a typical set up for remote processing with chamber cleaning. The main chamber is used for deposition process. Deposition gases go through the shower head in the deposition cycle. In the cleaning cycle, the valve between the chamber and the deposition gas line is closed and the valve between the remote plasma source and the chamber is open. Then the
radicals from the plasma source enter the main chamber through the showerhead or from the side of the chamber. After the *ex situ* cleaning process, the deposition process happens again.

![Figure 1.6 Schematic drawing of industrial setup of using remote plasma source for chamber cleaning][30].

The plasma sources are used to generate reactive species which are then used to process the material in the downstream chamber. Oxygen atoms are generated to remove photoresist, a process called stripping[31]. Fluorine atoms are generally generated to remove the deposited film in the downstream chamber. And hydrogen atoms are generated to clean the wafer in the downstream chamber. Both nitrogen trifluoride (NF₃) and fluorocarbon gases are used to generate fluorine atoms in remote plasma source. The fluorocarbon gases include tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), octafluoropropane (C₃F₈), and octafluorocyclobutane (C₄F₈). Compared to nitrogen trifluoride, fluorocarbon gases have the advantage of being non-toxic, easier to handle and of lower cost. For several reasons, the
The semiconductor industry has shifted to NF₃ for remote chamber cleaning, away from mixtures of fluorocarbons with oxygen, which initially were the dominant gases used for in situ chamber cleaning.

First, the emissions of global warming gases from such processes were commonly much higher than that of nitrogen trifluoride (NF₃) processes. NF₃ dissociates more easily in a discharge and is not significantly formed by recombination of the product species. Therefore, low levels of global warming emissions can be achieved more easily. In contrast, fluorocarbons are more difficult to breakdown in a discharge and recombine to form species such as tetrafluoromethane (CF₄) which are even more difficult to break down than other fluorocarbons.

Second, it was usually observed that the etching rate or cleaning rate when using fluorocarbon discharges is much smaller than that when using NF₃ discharges. This was ascribed to incomplete dissociation of the fluorocarbon gases.

Third, it was commonly found that fluorocarbon discharges produced “polymer” depositions that require more frequent wet cleans to remove these deposits that build up after repetitive dry cleans[32]. The propensity of fluorocarbon cleans to deposit “polymers” occurs to a greater extent in remote cleans in which no ion bombardment occurs during the cleaning. These observations dissuaded the industry from developing industrial processes based on fluorocarbon feed gases. In fact, the PECVD equipment manufacturers tested remote cleans based on fluorocarbon in glow RF discharges, but to date have been unsuccessful because of low cleaning rate and polymer deposition in the process chambers[33, 34].

Recent research is focusing on shifting NF₃ cleaning process into point-of-use F₂ cleaning process because F₂ does not have global warming issue unlike NF₃ or other fluorocarbon gases and at the same time F₂ is comparable to NF₃ in cleaning deposition chambers. However, due to
the high toxicity and corrosive property of F₂, F₂ cleaning process has limited applications in semiconductor industry. This is why industry wants to drive the cleaning process into point-of-use F₂ cleaning process.

1.5 Global Modeling of Cleaning Chamber

Accurate modeling of the downstream cleaning chamber is very important in semiconductor fabrication industry because the needs for process optimization and integration for new tools at low cost are growing very fast. The global model predicts the partial pressure of reaction products in the cleaning chamber at a given pressure. The partial pressure of atomic fluorine allows the prediction of the cleaning rate for silicon dioxide and silicon film by the following[35, 36].

\[
ER_{SiO_2} = 6.14 \times 10^{-13} n_F T^{3/2} \exp(-0.163eV / k_b T) A / \text{min}, \tag{1.2}
\]

\[
ER_{Si} = 2.91 \times 10^{-12} n_F T^{3/2} \exp(-0.108eV / k_b T) A / \text{min}, \tag{1.3}
\]

where \(n_F\) (cm\(^{-3}\)) is the atom concentration, \(T\) (K) is the wafer temperature.

The entire cleaning system consists of three different sections: plasma source, transfer tube and cleaning chamber. In the plasma source, it is assumed that inlet gases such as NF₃, N₂ and O₂ are completely dissociated into elementary atoms. This assumption is based upon high power density property of transformer-coupled toroidal plasma source (20W/cm\(^3\))[30]. Temperature of neutrals in the plasma source ranges from 450K to 2000K[37, 38]. This assumption eliminated the uncertainty in the plasma source. Therefore, global model of cleaning chamber includes only two parts: transfer tube and downstream chamber.

Input parameters for the global model are wall temperature, surface area of transfer tube and cleaning chamber, volume of transfer tube and cleaning chamber, flow rate of cleaning gas,
pressure at the plasma source and pressure in the cleaning chamber. And the partial pressures of reaction products predicted by the global model are finally validated by comparing them to the experimental results such as the partial pressure of atomic fluorine measured by mass spectrometer. Global model shows in good agreement with the experimental results. In addition, global model predicts the relative importance of surface reaction over gas phase reaction over the range of process chamber from 0.5torr to 10torr as well as the effect of the length of the transfer tube on the partial pressure of atomic fluorine in downstream chamber.

1.6 Goal of this work

The scope of this research work is basically to characterize the Transformer Coupled Toroidal Plasma (TCTP); to understand gas phase reactions and surface reactions by neutrals in the cleaning chamber by analyzing the concentration of neutrals in downstream cleaning process chamber; and to make a global modeling that predicts the partial pressure of active species in the cleaning chamber. The final goal is to set-up an optimal cleaning process using the results from the experiment and the global model.

The first object is to characterize the TCTP. Previously, Bai[30] worked on characterizing the TCTP source. In addition to his work, power consumption by plasma is measured with \( \text{C}_2\text{F}_6/\text{O}_2 \) condition and with \( \text{NF}_3 \) condition. The experimental apparatus will be discussed in Chapter 2. In Chapter 3, the factors that affect the power consumption will be discussed in detail as one approach to the characterization of plasma.

The second object is to understand gas phase reactions and surface reactions by neutrals in the cleaning chamber. The concentration of neutrals in downstream cleaning process chamber is successfully measured by line-of-sight mass spectrometer and FT-IR is measured in the exhaust.
line. The enhancement of nitride etching rate by different additives will be discussed in Chapter 4.

The last object is to make a global model to predict the partial pressure of neutrals in downstream. This subject will be discussed in Chapter 5. Bai[37] measured the neutral gas temperature, the electron temperature and the electron density. Temperature of neutrals which is required as one of the model input is taken by his results. This model consists of two parts: PFR (Plug Flow Reactor) and CSTR (Continuously Stirred Tank Reactor). The validation of this model is confirmed by comparing the modeling results with the partial pressure of neutrals measured by mass spectrometer. Beginning with NF₃ system, the effect of adding N₂ or O₂ in NF₃ is illustrated in Chapter 5. The ultimate goal of the global model is finally to predict the partial pressure of neutrals in C₂F₆/O₂/N₂/NF₃ system.
Chapter 2 Experimental Set-Up

2.1 Overall System

Figure 2.1 illustrates the schematic drawing of the experimental apparatus. It is composed of a main process system and a diagnostic system. Most of the basic set-up was accomplished by Bai[30] and a couple of minor modifications were done afterwards.

Figure 2.1 Detailed schematic drawing of experimental apparatus.

The main process system is composed of a transformer coupled toroidal plasma source, a four way cross, a transfer tube with water cooling, a process chamber and pumps. Capacitance manometers right after the plasma source and on the process chamber are used to measure the
pressure at each point. The butterfly valve between the transfer tube and the process chamber, and the throttle valve between the process chamber and the pumps, are adjusted for relatively independent control of the pressure in the plasma source and the process chamber. The vacuum system is sealed by Klamp-Flange® fittings[39], and Kalrez® or Chemraz® O-rings are used to reduce the corrosion of O-ring in the fluorine-rich environment. Except for the plasma source and the pumps, all other components are home-designed and fabricated.

The standard etching process in the system is as follows. Gas molecules such as nitrogen trifluoride enter the toroidal source chamber, in which plasma is formed and the gas molecules are dissociated to form electrons, ions and radicals such as fluorine atoms. The electrons and ions are annihilated in the transfer tube and the reactive radicals are transferred to the downstream process chamber after being cooled down in the transfer tube. The radicals undergo recombination reactions both on the transfer tube wall and in the gas phase. Then the remaining radicals move to the process chamber to etch the semiconductor materials on the electrode of the process chamber. Typical samples studied in this thesis are polycrystalline silicon, silicon dioxide and silicon nitride. Finally all the gaseous particles are taken away by vacuum pump.

The diagnostic system is used to measure the properties of both the plasma source and the downstream system. Mass Spectrometer is used to measure the radical concentration in the process chamber. Fourier Transformed Infrared spectroscopy (FTIR) is used to measure the stable species concentration in the exhaust. Laser interferometer is used for real-time etching rate measurements. Outside the system, an X-ray Photon Electron Spectroscopy (XPS) is used for surface species concentration measurements.
The toroidal transformer-coupled plasma source is discussed in section 2.2 and the method of preparing the sample is introduced in section 2.3. Different diagnostic methods mentioned above are discussed in section 2.4-2.7.

### 2.2 Toroidal Transformer-Coupled Plasma Source

Different types of plasma sources were developed for remote plasma process. Microwave plasma generator was one of the earliest developed tool for remote chamber cleaning\[40-43\]. However, the input power and coupling efficiency of the microwave reactor were limited. RF plasma source similar to a plasma etcher was developed for remote processing\[44\], but the low power coupling efficiency makes it less usable. Recently, Transformer-Coupled Toroidal Plasma (TCTP) source was developed as an emerging tool for such semiconductor processes as etching, cleaning and stripping\[45\].

#### 2.2.1 Introduction of MKS ASTEX Plasma Source

Figure 2.2 shows the most widely used equipment fabricated by MKS ASTEX\[46\]. The plasma is contained in a donut-shaped toroidal chamber. An H-bridge of MOSFET’s forms the power section. RF voltage is generated by the switching action of these paired MOSFETs’ (A & B) alternate ON and OFF cycles. Then the output of the MOSFETs is connected to the primary winding of the transformer. Then the RF power is transferred to the plasma via a transformer core with the plasma serving as the secondary loop.
Figure 2.2 Diagram of the Transformer Coupled Toroidal Plasma made by MKS ASTEX. Left: Schematic diagram. Right: Schematic of the power unit.

The plasma source used in this experiment is an ASTRON hf+ unit (Model Number: Ax7635-02) made by MKS ASTEX[45]. This plasma source is so compact that all components including a plasma vacuum chamber, electronics and a water cooling system are in a single enclosure, unlike microwave-based system that requires several individual components to be assembled into a subsystem. The source has an integrated electronic control and power supply system, and it is rated for continuous operation at the frequency of 400 kHz. The outlet pressure is measured at ports immediately downstream of the source utilizing a capacitance manometer gauge. Plasma is produced by transformer coupling between the ferrite core and gases flowing inside. The plasma source is operated on the basis of a constant current, and the voltage of the plasma is changed automatically according to the dissociation rate and resistivity of the added gases.

2.2.2 Comparison: Transformer Coupled Toroidal Plasma VS. Other Plasma Sources

The high power density TCTP plasma is different from other low-temperature plasma, such as DC glow discharge, DC arc discharge, inductively coupled RF discharge, capacitively coupled
RF discharge and microwave discharge. TCTP source operates with AC power, similar to industrial RF discharges and different from DC discharges. The power density of TCTP is as high as 20W/cm$^3$, making it much higher than the typical power density of less than 0.2 W/cm$^3$ of other discharge. The neutral gas temperature in TCTP is as high as a couple of thousand Kelvin, which can only be matched by DC arc discharge and which is much higher than the neutral gas temperature in other discharges. In the toroidal chamber of TCTP, no electrode exists and hence no thermionic electron emission is involved, which makes it very different from DC arc discharge where electron emission is important for plasma formation[47, 48]. The plasma in TCTP source is of glow discharge property, with smooth spatial profile of plasma parameters. The glowing discharge property of TCTP is similar to the DC glow discharge used in cylindrical normal glow discharge for lighting devices[48], parallel plate source[49], and beam plasma sources[47].

Pure inductive coupling is guaranteed[6] in TCTP, quite different from both capacitively-coupled RF discharge and inductively-coupled RF discharge in which the capacitive coupling is an important component of the plasma formation. In TCTP, no electrode exists in the system and pure inductive coupling is possible in TCTP[6]. The power used in the RF discharge is usually less than 1kW, causing a power density less than 0.1W/cm$^3$, significantly smaller than the power density of TCTP.

### 2.2.3 Measurement of Power Consumption by Plasma

The commercial plasma source is modified to allow measuring plasma loop voltage and current. The plasma loop voltage and current are calculated from that measured across the ferrite core based on negligible (<5%) loss of magnetic flux. Voltage is directly measured by Lecroy Oscilloscope (model: 9414) and the current was measured by a Pearson Current Sensor (model:
Plasma power and resistivity can be calculated based on the voltage and current waveform. Figure 2.3 shows an example of the measured waveform of current and voltage for the plasma from the gas mixture of 1250sccm C₂F₆, 3750sccm O₂ and 2000sccm Ar at the source pressure of 3.9torr. The power is calculated to be 7.14kW.

![Figure 2.3 Waveform of current and voltage for plasma at conditions 1250sccm C₂F₆ + 3750sccm O₂ + 2000sccm Ar at source pressure 3.9torr. The total power calculated to be 7.14 kW.](image)

Another power measurement method is to measure the total power that goes into the plasma source, which includes the power coupled into the plasma and the power consumed by the electronic circuit boards. The plasma source operates with a three-phase 208 V electrical power outlet. By measuring the current going through each phase, the total power can be easily calculated. Current through one phase of the wiring is measured by Craftsman current meter (model: 82014). For the same condition as shown in Figure 2.3, the current is measured to be 22.6 A and the total power consumed by the whole plasma source is 8.14 kW. Therefore, the efficiency of power usage for plasma generation is as high as 87.8%. The power utilization efficiency is much higher than typical inductively coupled plasma apparatus. Once the
correlation between the total power consumption calculated by this method and the power consumption of plasma calculated by the first method at the same gas condition is known, the plasma power can be easily obtained by measuring the current through one phase of the wiring only and this method of calculating the plasma power is used in Chapter 3.

The current plasma source also has a very high power density. The volume of the plasma chamber is 360 cm$^3$ and for a power of 7.15 kW, the power density is 20 W/cm$^3$. Compared to a typical industrial plasma source (power density <0.1 W/cm$^3$), the power density of the TCTP source is two orders of magnitude higher. The extremely high power density makes the plasma source very unique and its parameters very different from other plasma sources.

2.2.4 Plasma Chamber Wall

The plasma source chamber wall is made of aluminum with inner surface coated with a thick Al$_2$O$_3$ layer to prevent Al from being eroded by strong fluorine plasma. Four dielectric breakers are designed in the chamber wall to avoid inductive current in the chamber wall during the transfer coupling between the primary circuit and the plasma. A patented special gas nozzle mixes gases before sending them into the plasma chamber. Water cooling system is incorporated in the chamber wall to allow high power operation of the plasma source. Water flow rate through the plasma source is 3 gpm.

2.3 Sample Preparation

The ultimate goal of using samples is to measure the cleaning rate inside the process chamber. The tool for measuring the cleaning rate is He-Ne laser interferometer. Typical samples that are used for this experiment are silicon dioxide, silicon nitride and poly silicon. A wafer (silicon dioxide, silicon nitride and poly silicon) is cut into several one inch square samples. This sample
is usually placed on a mounting in the process chamber at the temperature controlled by thermocouple placed on the bottom of the process chamber. Grease (Apiezon Products) is used for better thermal contact between the wafer and the bottom stage.

However, in reality, deposits are everywhere inside the process chamber, which means cleaning reactant such as atomic fluorine can be depleted by larger cleaning area. The cleaning rate in a larger cleaning area can be different from the cleaning rate of one inch square sample although the processing conditions such as flow rate of inlet gas, pressure and temperature are the same for both cases. It is because the number of atomic fluorine is easily decreased with larger cleaning area, which is called “loading”. Therefore, a silicon nitride block (5 inch*5 inch*0.25 inch) is used for silicon nitride etching and a quartz disc (5 inch in diameter, 1/16 inch in thickness) is used for silicon dioxide etching to simulate the cleaning system with large cleaning area in a small lab-base experiment (see Figure 2.4). For example, 1 inch$^2$ silicon nitride sample is placed on top of silicon nitride block and silicon nitride block is placed on the sample mounting for silicon nitride etching. Grease (Apiezon Products) is also used for better thermal contact between the block and the bottom stage and between the block and the sample.
Figure 2.4 The position of a sample inside the process chamber. A thin silicon nitride block is placed in between sample mounting and silicon nitride sample. Grease is used for better thermal contact.

Most of the etching reactions are highly exothermic reactions. Therefore the temperature of a sample keeps increasing as etching processing time increases. Temperature control becomes more difficult when the nitride block is placed between a sample and sample mounting because exothermic surface reaction will occur on the entire nitride block which has more surface area (25 inch$^2$) than a sample (1 inch$^2$). Moreover, cooling by air outside the process chamber is the only way to cool down the sample mounting because there is no water circulation system on the backside. If temperature is not controlled, the etching rate data taken by interferometry become unreliable. Hence, it is very important to prevent the elevation of sample temperature.

$$Si(s) + 4 F(g) \rightarrow SiF_4(g)$$
$$SiO_2(s) + 4 F(g) \rightarrow SiF_4(g) + O_2(g)$$

(2.1)

There are two solutions to minimize the elevation of the temperature within a sample. First way is to minimize the thickness of the nitride block or the quartz disc. Assuming the heat released by exothermic reactions (see equation (2.1)) is only transferred by the conduction through the quartz disc, temperature rise by the heat ($\Delta T$) can be calculated by the equation below
\[ Q = k_{\text{quartz}} \times \frac{\Delta T}{\text{thickness of quartz}} \]  \hspace{1cm} (2.2)

where \( Q \) is the heat flux released by exothermic reaction, \( k_{\text{quartz}} \) is heat conductivity of quartz (~0.014 J/s/cm/K at 298K) and \( \Delta T \) is the temperature difference between top and bottom of the quartz. Therefore, the thinner the thickness of quartz becomes, the less the temperature difference becomes.

Another method to prevent the temperature elevation is to cover the edge of a sample with grease which is inert to atomic fluorine. When active neutral such as atomic fluorine exists, the edge of a sample is also etched by atomic fluorine. In the edge of a silicon dioxide sample, silicon substrate as well as thin silicon dioxide layer is exposed to the atomic fluorine. The abrupt rise in sample temperature stems from high etching rate of silicon substrate and high heat of reaction between silicon substrate and atomic fluorine. Order of magnitude of the heat flux \( (Q) \) by silicon etching reaction in the edge of the sample wafer is calculated in equation (2.3)

\[ Q = \frac{ER_{\text{silicon}} \times \text{Heats}_{\text{silicon Reaction}} \times \rho_{\text{Si}}}{MW_{\text{Silicon}}} \approx 1 \text{ J/s/cm}^2 \]  \hspace{1cm} (2.3)

where \( ER_{\text{silicon}} \) is the etching rate of silicon (A/min), \( \text{Heats}_{\text{silicon Reaction}} \) is the heat of reaction by silicon and atomic fluorine (kJ/mol), \( \rho_{\text{Si}} \) is the density of silicon (g/cm\(^3\)) and \( MW_{\text{Silicon}} \) is the molecular weight of silicon (g/mol). In addition, the heat flux by Si-F reaction can be expressed as equation (2.4)

\[ Q = \rho_{\text{Si}} \times C_{P,\text{Si}} \times \frac{d(\Delta T)}{dt} \times \frac{\text{Volume}_{\text{Sample}}}{\text{Surface}_{\text{reaction}}} \]  \hspace{1cm} (2.4)

where \( C_{P,\text{Si}} \) is the heat capacity of silicon (~0.7 J/g/K), \( \text{Surface}_{\text{reaction}} \) is the surface area of sample edge, \( \text{Volume}_{\text{Sample}} \) is the volume of a sampler. Combining equation (2.3) and (2.4)
determines the order of magnitude of the temperature rise rate \( \frac{d(\Delta T)}{dt} \approx 1 \text{ K/sec} \), which is quite high. In fact, very rapid etching due to high temperature of one square inch wafer sample on top of a quartz disc was experimentally observed when the edge of the sample was not covered by grease.

### 2.4 Mass Spectrometer

#### 2.4.1 Overall Design of Mass Spectrometer System

The mass spectrometer system is used to measure the concentration of neutral particles in the process chamber in our system. It is composed of a mass spec chamber, two turbo pumps and the mass spectrometer. The schematic drawing of the mass spectrometer system and its connection to the main chamber and the pumps are shown in Figure 2.5.

![Schematic drawing of the mass spectrometer system and its connection to the main chamber and the pump set.](image)

Figure 2.5 schematic drawing of the mass spectrometer system and its connection to the main chamber and the pump set.
The mass spectrometer chamber is attached right on the process chamber, with only an aluminum valve between the process chamber and the mass spectrometer chamber. There are two mass spec valves related to the mass spec system: one is between the process chamber and the mass spectrometer chamber and the other is between the mass spectrometer chamber and the pumps. These two valves are closed to make the mass spectrometer isolated when the mass spec is not sampling. During the mass spectrometer experiments, the valve between the process chamber and the main pumps are closed and the two mass spec valves are open. This procedure guarantees a strong convection flow outside the orifice entrance of the mass spectrometer chamber. Strong convection helps to reduce the residence time of gas passing through so that fluorine will have less chance to recombine on the tube wall.

The mass spectrometer chamber consists of two sections to hold the mass spectrometer in a differentially pumped system. The gas from the process (around 1-10torr) is sampled through a 0.002" diameter orifice into the front section. The section is pumped through a Leybold corrosive service 360 l/sec turbo pump (model: TurboVac 361c). The abstracted beam is then channeled through a beam skimmer cone (Ni with 1/16" orifice; Model 1 manufactured by Beam Dynamics, Inc.) into the second section with the mass spectrometer. The second section chamber is pumped by another Leybold turbo pump (model: TurboVac 361c). The two turbo pumps are supported by an Edward E2M40 roughing pump. The mass spectrometer chamber is equipped with an ionization gauge (model: MKS HPS) for measuring the pressure. The diffusion pumping system makes the pressure in the first chamber around $10^{-5} - 10^{-4}$torr and the pressure in the second chamber $10^{-8} - 10^{-7}$torr during measurements. A chopper (EOPC Model CH10, frequency 400Hz) is used in the mass spec chamber to eliminate the background signal such as HF, H$_2$O and N$_2$ from the original mass spec signal.
2.4.2 Mass Spectrometer

The mass spectrometer used in the system is a quadrupole model made by UTI (model: UTI 100C)[50]. It is composed of three major components of ionizer, mass filter and detector. The electrons are emitted from the filaments within the ionizer and energy of -40eV is applied to electrons in this work. The filament current was maintained to about 0.15mA. Gas molecules are dissociated and ionized by electrons when passing through the ionizer to become positively charged ions that are then injected into the filter section. A combined radio-frequency and electrostatic field is formed by two pairs of metal rods in the filter section. A charged substance with a specific mass-to-charge ratio has a dynamically stable trajectory within the field formed by the voltages on the rods. All other substances are filtered out. Then the species coming out of the filter are detected by an electron multiplier that amplifies the single charge of the ion into a current. The applied voltages on the filter rods are continuously changed to allow different ions to pass through and the output current of the multiplier is referenced against the scan voltage, thereby producing a spectrum of peaks.

Figure 2.6 shows a block diagram of mass spec when a chopper is used in the mass spec system for eliminating the background signal from the original signal. Among many cables that connect the information in the quadrupole to the RF box, only one cable (electron multiplier) is diverted from the quadrupole to the low noise preamplifier (SRS SR570) and the lock-in-amplifier (EG&G Model 5204). A chopper signal (400 Hz) is being used as a reference signal in the lock-in-amplifier.
2.4.3 Cracking Pattern of Gases

Cracking of gas occurs within the mass spec when molecules collide with electrons with very high energy (40–70eV) in the ionizer. It is sometimes difficult to accurately analyze the concentration of each species in the system just by looking at the original mass spec results. It is because the original mass spec signal contains the signals both from the cracked species and from non-cracked species. For example, atomic fluorine (F) signal stems from the atomic fluorine that is available in the system as well as the atomic fluorine that is cracked from F$_2$. The former atomic fluorine is the only signal that we want to retrieve from the original mass spec signal and the latter is the signal that we want to eliminate from the original signal. To analyze the accurate concentration of atomic fluorine which is available in the system, it is necessary to figure out how much atomic fluorine is generated from the cracking of F$_2$. Therefore, it is important to know the cracking patterns of the gases of interest before analyzing the concentration of gases in the system.
Figure 2.7 Ion current of NO+, N2+, O2+, F2+ (no plasma). Ion current of each gas is measured separately at the flow rate of 500 sccm without plasma. (a) represents molecules with negligible cracking pattern whereas F2+ in (b) has significant portion of cracking by electron impact. Ion current data of Ar+ is used for only reference. Ion current is not corrected by ionization efficiency (a combination of ionization cross-section and ionization potential), multiplier gain, and quadrupole transmission efficiency.

Figure 2.7 shows the cracking patterns of NO, N2, O2 and F2. Each gas is separately flown into the process chamber with plasma off and sample of each gas is taken from the process chamber to the mass spec chamber to measure the mass spec signal. For example, to analyze the cracking pattern of NO, only NO is flown to the process chamber and the mass spec signal is taken by manipulating the process chamber from 0.4 torr to 10 torr, which finally brings a linear curve like in Figure 2.7. Ion current is calculated by integrating the peak intensity. AMU 14 (N) and AMU 16 (O) are rarely observed when the sample of NO gas is measured in the mass spec chamber, which means almost no cracking of NO occurs when NO is ionized in the mass spec.

Not only the cracking pattern of NO, but also the cracking pattern of N2, O2 and F2 are measured and Figure 2.7 shows the cracking pattern of each gas at different process chamber. Unlike other gases, F2 molecules are partially cracked into atomic fluorine in the mass spec with ease (see Figure 2.7(b)). Argon gas is used for comparing the relative signal intensity.
Figure 2.7 contains important information, i.e. the correlation between the ion current and the chamber pressure, which is the key for the quantitative analysis. Assuming NO, Ar, N\textsubscript{2} and O\textsubscript{2} gases are mixed in the system and the partial pressure of each gas is unknown, then the partial pressure of each gas is calculated by the correlation between the ion current and the chamber pressure in Figure 2.7. Once the peak intensity data (or ion current) of NO, Ar, N\textsubscript{2} and O\textsubscript{2} in the system are obtained by the mass spec, it means the values in the y-axis of Figure 2.7(a) are known for each gas. Then, the partial pressure of each gas is finally calculated by reading the value in the x-axis at the intersection point where the linear curve in Figure 2.7 meets the value in y-axis that is obtained by taking mass spec data. For example, if the ion current of N\textsubscript{2} in the system is measured to be 5 a.u., the partial pressure of N\textsubscript{2} is calculated by the slope \( \frac{5.000}{5.628} = 0.888 \ \text{torr} \) in the Figure 2.7(a). For accurate quantitative analysis, it is believed that the measured peak intensities should be corrected by ionization efficiency (a combination of ionization cross-section and ionization potential), multiplier gain, and quadrupole transmission efficiency for each species. However, by using the method introduced in Figure 2.7, the partial pressures of gases in the system are calculated without correction by ionization efficiency, multiplier gain and quadrupole transmission efficiency.

2.4.4 Trouble shooting: Mass Spec Signal Attenuation

An interesting fact was observed when mass spec signal was continuously taken from the process chamber for a couple of hours. Initially the mass spec signal was very clear and sharp. However, after several hours of data sampling from the mass spec, the signal became broad and the intensity of the signal kept decreasing. It is either because the filament in front of the quadrupole is contaminated by atomic fluorine or because quadrupole itself is contaminated by
atomic fluorine, hence the charged surface by atomic fluorine might affect the mass spec signal processing. Therefore, the key to preventing signal attenuating is to minimize the exposure to the atomic fluorine in the mass spec.

There are many ways to partially avoid the attenuation in the mass spec signal so that data sampling time can be extended to the reasonable extent. The first way is to minimize the size of the orifice between the mass spec chamber and the process chamber so that the flow rate of sample gas can be as small as possible. The second way is to strip the contaminated fluorine in the quadrupole and the filament by methanol. This method requires a frequent breakdown of the equipment. The third way to prevent the attenuation of the signal is keep the chamber surface temperature high while the filament is kept on (0.15 mA) and nitrogen gas is continuously circulated in the mass spec chamber so that atomic fluorine is spontaneously volatilized from the contaminated surface with ease. Experimentally it takes three to four days for the attenuated signal to return to the original.

2.5 Fourier Transform InfraRed Spectroscopy

Fourier Transform InfraRed (FTIR) spectroscopy is a tool for measuring the concentration of the species coming out of the plasma source using the principle of the resonant interaction between the infrared light and the vibration mode of molecules. FT-IR is attached in the exhaust of the pump, therefore sampling all the stable species that come out of the pump.
Figure 2.8 Schematic setup of Fourier Transformed InfraRed spectroscopy. The top mirror is fixed and the right mirror is moving.

FTIR spectrometry uses Michelson interferometry, as illustrated in Figure 2.8. A beam of IR radiation from the source is focused on a beam splitter, where half the beam is reflected to a fixed mirror and the other half of the beam is transmitted to a moving mirror which reflects the beam back to the beam splitter from where it travels, recombined with the original half beam, to the detector. The IR intensity variation with optical path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. The IR absorption spectrum can be obtained by measuring an interferogram with and without a sample in the beam and transforming the interferograms into spectra.

The molecules have different vibrational energy levels, since the bond between the atoms can bend or stretch. If the bond is subjected to infrared radiation of a specific frequency (between 300 - 4000 cm\(^{-1}\)), it will absorb the energy, and the bond will move from the lowest vibrational state, to the next highest. The energy corresponding to these transitions between molecular vibrational states is generally 1-10 Kcal/mole which corresponds to the infrared portion of the electromagnetic spectrum.
In a simple diatomic molecule, there is only one direction of vibrating, stretching. This means there is only one band of infrared absorption. If there are more atoms, there will be more bonds, and therefore more modes of vibrations. This will produce a more complicated spectrum. Homo-nuclear diatomic molecules (N₂, F₂) do not have an infrared absorption spectrum because they have no dipole moment and hence do not interact with electromagnetic wave.

Different types of bonds have characteristic regions of the spectrum where they absorb. Every molecule has a unique pattern. Therefore, if an unknown sample produces a spectrum which matches that of a known compound, the sample can be confirmed to be that compound. If no radiation is absorbed at a particular frequency, the fraction of absorbed light is zero at the corresponding wave number. Because the strength of the absorption is proportional to the concentration of the corresponding species, FTIR can be used for quantitative analyses.

The FTIR system in this experiment is I Series FTIRs fabricated by MIDAC, Inc. A 1650K silicon carbide IR source is mounted. The detector is made of Mercury Cadmium Telluride which requires continuous cooling by liquid nitrogen. The gas cell body is constructed of nickel-coated aluminum with windows made of moisture and chemical resistant ZnSe. And all other interface optics are gold coated for high throughput. Gases are sampled from the exhaust of the pump, and passing through the gas cell of the FTIR and are pumped away by an aspirator with water operation in a vented hood.

FTIR has the advantage of being non-destructive and molecules are not cracked for the measurements compared to the mass spectrometer. Therefore it is easier for a quantitative analysis than the mass spectrometer. However, FTIR cannot measure the homonuclear diatomic atoms such as F₂ and O₂, which can be measured by the mass spectrometer. Another disadvantage of FTIR in this system is fact that it is placed after the pump. This means it cannot
capture the reactive radicals which recombine easily when passing through the pump. Therefore, both FTIR and mass spec should be used together for better analysis.

### 2.6 Laser Interferometry

A simple home-made laser interferometry is used to measure the etching rate of different films. 0.95mW He-Ne laser (632.8nm wavelength) is used as the incident light, and a photometer (model: Metrologic Photometer) is used to detect the light reflected from the sample surface. Then the signal is collected by the data acquisition board on a PC. The interference between the beam reflecting from the top of the film and from the film substrate interface, give rise to a sinusoidal signal which can be used to calculate the etching rate.

Using standard interferometry analysis[51], the etching rate can be calculated as:

\[
ER = \frac{\lambda}{2\Delta t \sqrt{n^2 - \sin^2 \theta}},
\]  

where \( \lambda \) is wavelength in Å, \( ER \) is the etching rate in Å/min, \( n \) is the refractive index of the film, \( \theta \) is the angle of the laser from the normal, and \( \Delta t \) is the time period of the observed waveform in minutes. The refractive index is 1.45 for silicon dioxide, 3.85 for silicon and 2.05 for silicon nitride. A simpler way to calculate the etching rate is to realize that one full period in the interferometry data represents 1905 Å for silicon dioxide, 808 Å for silicon, and 1348 Å for silicon nitride.
Figure 2.9 Interferometry signal for etching rate measurements. The gas mixture is composed of 4000sccm NF₃ and 2000sccm Ar. The plasma source pressure is 3.9torr and the process chamber pressure is 2torr. Silicon dioxide sample is put on the electrode with temperature 50°C. The peak distance is used to calculate the etching rate.

Figure 2.9 shows the interferometry signal for etching rate measurements. The gas mixture was composed of 4000sccm NF₃ and 2000sccm Ar. The plasma source pressure was 3.9torr and the process chamber pressure was 2torr. The silicon dioxide sample was put on the electrode with the temperature controlled at 50°C. The measured period is about 52 second, which is corresponding to the etching rate of 2180 Å/min.

2.7 X-ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is used to characterize the surface concentration of a given sample. Because XPS is not connected in the main system, in situ measurement of XPS is impossible. The exposure time to the air should be minimized for more accurate data analysis. A typical XPS setup is shown in Figure 2.10. In the XPS operation, X-rays are irradiated on the material surface and the photoelectrons emitted from the surface are analyzed. The kinetic energy is related to the binding energy by
in which $K.E.$ is the measured kinetic energy of the photoelectrons, $B.E.$ is the binding energy of the photoelectrons in the material, and $h\nu$ is the energy of the incident X–rays. The binding energy can be derived with known X-rays energy and measured kinetics energy, therefore indicate the type of atom it is attached to and then the chemical identity of the surface species is identified[52].

![Diagram of XPS operation](image)

**Figure 2.10 Schematic of typical XPS operation.** X – rays impinge on a sample surface, releasing photoelectrons that are detected by an electron energy analyzer. By measuring the kinetic energy of the electrons, the chemical composition of the surface can be determined.

The X-ray source used in this work is a Mg Kα with energy 1256.6eV (model Specs 865). The electron energy analyzer usually scans across a range of energies and plots the photoelectron numbers at each energy step. Each peak is identified to be corresponding to a specific atom. For example, the fluorine 1s peak is located at 684.5eV of binding energy.
Chapter 3 Control of Power Consumption of Plasma

MKS Astex plasma source has a very high power density. The volume of the plasma chamber is 360 cm$^3$ and for a power of 7.15kW, the power density is 20 W/cm$^3$. Compared to a typical industrial plasma source (power density <0.1W/cm$^3$), the power density of the TCTP source is two orders of magnitude higher. The extremely high power density makes the plasma source very unique and its parameters very different from other plasma sources. In this chapter, the power consumed by plasma is measured as one approach to the characterization of plasma.

As discussed in Chapter 2, the commercial plasma source is modified to allow measuring plasma loop voltage and current. The plasma loop voltage and current are calculated from that measured across the ferrite core based on negligible (<5%) loss of magnetic flux. Voltage is directly measured by Lecroy Oscilloscope (model: 9414) and the current is measured by a Pearson Current Sensor (model: 3972). Plasma power and resistivity can be calculated based on the voltage and current waveform.

Another power measurement method is to measure the total power that goes into the plasma source, which includes the power coupled into the plasma and the power consumed by the electronic circuit boards. The plasma source operates with a three-phase 208 V electrical power outlet. By measuring the current going through each phase, the total power can be easily calculated. Current through one phase of the wiring is measured by Craftsman current meter (model: 82014). The method of calculating plasma power in this chapter is to correlate the first method to the second one so that the plasma power is calculated by measuring the current through one phase of the wiring (Craftsman, model: 82014) only. The correlation between the total power and the plasma power reveals that around 70~80% of the total power is consumed by plasma.
There are several factors that affect the plasma power consumption. One of them stems from the different resistivity of gases, which means each gas has different dissociation energy. For example, N-F bonding in NF₃ gas is different from C-F bonding in C₂F₆. Other factor for power control is the flow rate of inlet gas and the elevated pressure due to the high flow rate of inlet gas increases the power consumption. In section 3.1, we will discuss it in detail, and the flow restricting device (orifice) will be introduced in section 3.2 as an efficient power enhancement tool.

### 3.1 Control Factors of Plasma Power

#### 3.1.1 Pressure Dependence

Figure 3.1 shows the dependence of plasma source pressure and process chamber pressure on the plasma power consumption. Gas condition is 1000sccm NF₃ + 500sccm C₂F₆ + 500sccm O₂ + 4200 N₂. Plasma source pressure is measured by the manometer located after the plasma source chamber and process chamber pressure is measured by the manometer located at the process chamber. While the process chamber pressure increases up to 4torr, the plasma source pressure remains at around 12.2kW. Figure 3.1(b) shows that the plasma power is linearly dependent upon the plasma source pressure, not the process chamber pressure.
Figure 3.1 Dependence of plasma source pressure and chamber pressure on the plasma power consumption. Chamber pressure is measured in the process chamber and plasma source pressure is measured after the plasma source chamber. Gas condition is 1000sccm NF3/500sccm C2F6/500sccm O2/4200sccm N2. Plasma source is linearly dependent upon the plasma power consumption.

3.1.2 Resistivity of Cleaning Gas Dependence

In Figure 3.2 is shown the linear dependence of the plasma power consumption on the plasma source pressure with three different gas conditions. The difference between Figure 3.2(a) and (c) is nitrogen flow rate and the difference between Figure 3.2(b) and (c) is oxygen flow rate.
The slope in Figure 3.2(a) is different from the slope in Figure 3.2(b) and (c) because oxygen has resistivity different from nitrogen gas.

![Graphs (a), (b), and (c)](image)

Figure 3.2 Plasma power consumption as a linear function of the plasma source pressure. (a) 1300sccm C₂F₆/1300sccm O₂/2000sccm N₂ (b) 1300sccm C₂F₆/2000sccm O₂/1300sccm N₂ (c) 1300sccm C₂F₆/2000sccm O₂/2000sccm N₂.
Another example of different gas giving different power consumption is shown in Figure 3.3. 2000sccm of NF$_3$ gas is used for reference and it consumes 6kW of power. The same flow rate but different composition of gas (1000sccm NF$_3$ + 500sccm C$_2$F$_6$ + 500sccm O$_2$) is used to compare the power consumption. Compared to 2000sccm NF$_3$, the power consumption of 1000sccm NF$_3$ + 500sccm C$_2$F$_6$ + 500sccm O$_2$ is 45% higher. In addition, as nitrogen gas is added in NF$_3$ + 500sccm C$_2$F$_6$ + 500sccm O$_2$ gas, plasma power increases up to 100%. This result shows that C$_2$F$_6$ + O$_2$ gas requires more power than NF$_3$ gas to dissociate in the plasma due to the different resistivity and that nitrogen is very useful to increase the plasma power because it is cheaper and does not affect the cleaning process significantly. Adding nitrogen helps to increase the cleaning rate of TEOS film in C$_2$F$_6$ + O$_2$ or CF$_4$ + O$_2$ gas[53] and we will discuss it in the following section.

![Power consumptions at different conditions](image)

Figure 3.3 Effect of nitrogen on plasma power consumption. Chamber pressure is maintained at 4torr. 2000sccm NF$_3$ results in 6kW of power consumption and 2000sccm NF$_3$/C$_2$F$_6$/O$_2$ increases power by 45%. As the flow rate of nitrogen increases, plasma power also increases up to 100% compared to pure NF$_3$. 

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Figure 3.4 shows the effect of adding N₂O in 1300sccm C₂F₆ + 1300sccm O₂ on the plasma source pressure and the power consumption. N₂O is shown to be very similar to N₂ in increasing power consumption, but the effect of N₂O on the etching rate is different from that of nitrogen.

![Graph showing the effect of N₂O on plasma source pressure and power consumption.](image)

Figure 3.4 Dependence of plasma power and plasma source pressure on N₂O flow rate. 1300sccm C₂F₆ + 1300sccm O₂ is used and N₂O is added in it. Process chamber is maintained at 4torr. Ps represents plasma source pressure.

3.1.3 Effect of Nitrogen

Figure 3.5 is an example that shows the effect of adding nitrogen in 1300sccm C₂F₆ + 1300sccm O₂ discharge. As nitrogen is added up to 1300sccm, TEOS etching rate begins to increase and power consumption is also increased. Enhancement of TEOS etching rate by adding nitrogen in perfluorocarbon gas has been reported[53] and the reason why nitrogen enhances TEOS etching rate is because nitrogen selectively blocks the active site on the surface for producing COF₂ which is the key product of the loss of atomic F. Bai[53] showed by FT-IR
measurements that the concentration of COF$_2$ is decreased and the concentration of CO$_2$ is increased by adding nitrogen in CF$_6$/O$_2$ discharge to prove the selective blocking of COF$_2$ active site by nitrogen.

However, as the flow rate increases above 1300sccm of N$_2$, TEOS etching rate gradually decreases because atomic fluorine is diluted by nitrogen. Instead, power consumption continuously increases as nitrogen is added in C$_2$F$_6$/O$_2$ discharge as expected.

![Graph showing the effect of nitrogen on TEOS etching rate and power consumption.](image)

**Figure 3.5** Effect of nitrogen on TEOS etching rate and power consumption. Nitrogen is added in 1300sccm C$_2$F$_6$ + 1300sccm O$_2$ discharge. Process chamber pressure is 4torr and sample mounting temperature is 250°C.

In Figure 3.6 is shown the TEOS etching rate and plasma power consumption of C$_2$F$_6$ + O$_2$ + N$_2$ gas. The flow rate of C$_2$F$_6$ is fixed at 1300sccm and the flow rates of oxygen and nitrogen gases are changed. Process chamber pressure is maintained at 4torr and plasma source pressure is not controlled by the butterfly between the transfer tube and the process chamber. As total flow rate is increased, the plasma source pressure is also increased because the process chamber pressure is maintained at 4torr. Sample mounting temperature is 250°C.

TEOS etching rate of 1300sccm C$_2$F$_6$ + 1300sccm O$_2$ in Figure 3.6 is around 1300 A/min. As 1300sccm of nitrogen is added in 1300sccm C$_2$F$_6$ + 1300sccm O$_2$, TEOS etching rate is
increased by 2.5 times. This result confirms that adding nitrogen in $\text{C}_2\text{F}_6/\text{O}_2$ increases TEOS etching rate. However, increasing the flow rate of nitrogen does not increase TEOS etching rate further and etching rate is decreased because atomic fluorine which plays a major role in increasing TEOS etching rate is diluted by nitrogen. Instead, it helps increase power consumption by plasma.

Figure 3.6 TEOS etching rate and plasma power consumption of 1300sccm $\text{C}_2\text{F}_6 + \text{O}_2 + \text{N}_2$. The flow rates of oxygen and nitrogen are changed. $P_s$ represents plasma source pressure and chamber pressure is maintained at 4torr. $P_s$ changes according to the flow rate of inlet gas. Temperature of sample mounting is maintained at 250°C.

Unlike nitrogen, adding excessive oxygen in $\text{C}_2\text{F}_6/\text{O}_2/\text{N}_2$ decreases TEOS etching rate (see Figure 3.6). It is consistent with the result in the literature that shows 50% of oxygen mole percent brings the fastest cleaning rate[54]. And compared to 1300sccm $\text{C}_2\text{F}_6 + 2000$ sccm $\text{O}_2 + 1300$ sccm $\text{N}_2$, 1300sccm $\text{C}_2\text{F}_6 + 1300$ sccm $\text{O}_2 + 2000$ sccm $\text{N}_2$ consumes more power, which means oxygen is less efficient than nitrogen in consuming power.

Although nitrogen is effective in increasing plasma power consumption, there is a limitation because too much nitrogen addition in discharge eventually dilutes the cleaning system, which
leads to lowering the overall cleaning rate. Therefore, a flow restricting device is adopted to increase the power consumption effectively and it will be discussed in section 3.2.

### 3.2 Introduction of an Orifice for Power Enhancement

#### 3.2.1 Effect of an Orifice on Power Consumption and Etching Rate

Figure 3.7 Illustration of PECVD chamber cleaning system. A water-cooled orifice is attached in between the plasma source and the transfer tube.

As mentioned in the previous section, although nitrogen is effective in increasing plasma power consumption, there is a certain limitation because too much nitrogen addition in discharge eventually dilutes the cleaning system, which leads to lowering the overall cleaning rate. Moreover, the capacity of the dry pump also limits the total flow rate of cleaning gas. Therefore, a flow restricting device (orifice) is adopted in the cleaning system to increase the power consumption effectively (see Figure 3.1). Because the ions, neutrals and electrons coming out of the plasma source are very hot, water circulation is required inside the orifice to prevent melting...
down the orifice itself which is made of aluminum. The specific drawings are shown in Figure 3.8.
Figure 3.9 shows the TEOS etching rate at 250°C and the power consumption of 1300sccm C₂F₆ + 1300sccm O₂ + 450sccm NF₃ + 450sccm N₂ with the orifice (hole diameter: 0.43 inch) in the cleaning system. Power consumption and plasma source pressure are constant regardless of the process chamber pressure. It is because the mixture of gas coming out of the plasma source becomes choked flow after flowing through the small hole of the orifice.

Figure 3.9 TEOS etching rate and power consumption of 1300sccm C₂F₆ + 1300sccm O₂ + 450sccm NF₃ + 450sccm N₂. Sample mounting temperature is 250°C. Plasma source pressure is 11.6kW regardless of the process chamber pressure

When a flowing fluid at a certain pressure and temperature flows through a restriction (such as the hole in an orifice plate) into a lower pressure environment, under the conservation of mass the fluid velocity must increase for initially subsonic upstream conditions as it flows through the smaller cross-sectional area of the restriction. At the same time, the venturi effect causes the pressure to decrease. Choked flow is a limiting condition which occurs when the mass flux will not increase with a further decrease in the downstream pressure environment[55]. The choked flow of gases is useful in many engineering applications because the mass flow rate is
independent of the downstream pressure, depending only on the temperature and pressure on the upstream side of the restriction.

![Graph showing the effect of orifice on TEOS etching rate.](image)

**Figure 3.10** Effect of the orifice on TEOS etching rate. (1) represents TEOS etching rate without an orifice in the cleaning system and (2) represents the orifice with a diameter of 0.43 inch located at the place where the butterfly valve was previously located. TEOS etching rate is measured at 250°C and inlet gas conditions are 1300 sccm C₂F₆ + 1300 sccm O₂ + 450 sccm NF₃ + 450 sccm N₂ and 2000 sccm NF₃.

Figure 3.10 illustrates TEOS etching rate measured at 250°C with an orifice in the cleaning system and without an orifice in the system. (1) represents TEOS etching rate without an orifice in the cleaning system and (2) represents the orifice with a diameter of 0.43 inch located at the place where the butterfly valve was previously located. With an orifice in the cleaning system, 28% of TEOS etching rate is decreased compared to the etching rate without an orifice in the entire system when 2000 sccm NF₃ is used. And 53% of TEOS etching rate is decreased compared to the etching rate without an orifice in the entire system when 1300 sccm C₂F₆ + 1300 sccm O₂ + 450 sccm NF₃ + 450 sccm N₂ is used. Therefore, Figure 3.10 shows that using an
orifice decreases TEOS etching rate because high pressure in the plasma source caused by flow restriction decreases the available atomic fluorine due to the higher F-F recombination. The reason by the degree of decreasing TEOS etching rate is different according to the gas condition is because gases with different composition have different recombination properties.

Figure 3.11 Effect of the hole size of an orifice on TEOS etching rate. Gas condition is 1000sccm SF$_6$ + 1000sccm O$_2$ + 1400sccm N$_2$ + 650sccm NF$_3$ and sample mounting temperature is 250°C. Plasma source pressure and power consumption of two different hole sizes are shown in the figure.

Figure 3.11 shows the TEOS etching rates of two different orifice hole sizes. The orifice is placed in between the plasma source and the transfer tube (see Figure 3.7). Inlet gas condition is 1000sccm SF$_6$ + 1000sccm O$_2$ + 1400sccm N$_2$ + 650sccm N$_2$ and sample temperature is 250°C. Figure 3.11 illustrates that attaching a smaller orifice lowers TEOS etching rate and enhances plasma power and plasma source pressure. It is because smaller orifice plays a role as a flow-restricting device that makes the plasma source pressure higher, which leads to higher F-F
recombination in the plasma source. Of course, TEOS etching rate is optimal when the flow-restricting device is not placed in the cleaning system. For certain circumstances, it is necessary to control plasma power consumption and installing an orifice in the cleaning system is a good alternative to increasing nitrogen flow rate for controlling plasma power although the presence of an orifice in the cleaning system decreases the etching rate.

### 3.2.2 Location of an Orifice and its Effect

![Graph showing the effect of the location of an orifice. The bars on the right side represent the power consumption and TEOS etching rate when the orifice is in the original place (between the plasma source and the transfer tube) and those on the left side represent the power consumption and TEOS etching rate when the orifice is moved to the place where the butterfly valve was located previously. Gas condition is 1300sccm C\textsubscript{2}F\textsubscript{6} + 1300sccm O\textsubscript{2}, sample mounting temperature is 250°C and process chamber pressure is 4torr.](image)

Figure 3.12 shows the importance of the location of an orifice. The bars on the right side represent the power consumption and TEOS etching rate when the orifice is in the original place (between the plasma source and the transfer tube) and those on the left side represent the power consumption and TEOS etching rate when the orifice is moved to the place where the butterfly valve was located previously. Gas condition is 1300sccm C\textsubscript{2}F\textsubscript{6} + 1300sccm O\textsubscript{2}, sample mounting temperature is 250°C and process chamber pressure is 4torr.
valve was previously located. Gas condition is 1300sccm C₂F₆ + 1300sccm O₂, sample mounting temperature is 250°C and process chamber pressure is 4torr. If the orifice is placed near to the downstream chamber, plasma source pressure becomes lower and etching rate is decreased. The reason why the plasma source pressure becomes lower when the orifice is placed near to the downstream chamber is because the total volume restricted by the orifice becomes larger, hence the plasma source pressure becomes lower by the ideal gas law which explains that pressure is proportional to the reciprocal of volume at constant temperature. And the reason why TEOS etching rate becomes lower when the orifice is placed near to the downstream chamber is because the surface of the inner transfer tube is all exposed to the relatively high pressure, which causes higher F-F recombination. If the F-F recombination reaction occurs actively, the available atomic fluorine that crucially affects TEOS etching rate is diminished, therefore TEOS etching rate is decreased when the orifice is placed near to the downstream chamber.

3.3 Summary

In this chapter, the power consumed by plasma is measured as one approach to the characterization of plasma. Compared to a typical industrial plasma source, the power density of the TCTP source is two orders of magnitude higher. The extremely high power density makes the plasma source very unique and its parameters very different from other plasma sources.

In section Chapter 3, we discussed that there are several factors that affect the plasma power consumption. One factor is the flow rate of inlet gas and the elevated pressure due to the high flow rate of inlet gas increases the power consumption. Experimentally it is observed that the plasma power is linearly dependent upon the plasma source pressure, not the process chamber pressure.
Another factor of the power control is the resistivity of gases. It means each gas has different dissociation energy. For example, N-F bonding in NF₃ gas is different from C-F bonding in C₂F₆. Experimental result shows that C₂F₆ + O₂ gas requires more power than NF₃ gas to dissociate in the plasma due to the different resistivity and that nitrogen is very useful to increase the plasma power because it is cheaper and does not affect the cleaning process significantly.

Adding nitrogen helps to increase the cleaning rate of TEOS film in C₂F₆ + O₂ or CF₄ + O₂ gas[53]. Enhancement of TEOS etching rate by adding nitrogen in perfluorocarbon gas has been reported[53] and the reason why nitrogen enhances TEOS etching rate is because nitrogen selectively blocks the active site on the surface for producing COF₂ which is the key product of the loss of atomic F. Bai[53] showed by FT-IR measurements that the concentration of COF₂ is decreased and the concentration of CO₂ is increased by adding nitrogen in CF₄/O₂ discharge to prove the selective blocking of COF₂ active site by nitrogen. However, as the flow rate increases above a certain limit, TEOS etching rate gradually decreases because atomic fluorine is diluted by nitrogen. Instead, power consumption continuously increases as nitrogen is added in C₂F₆/O₂ discharge as expected.

In section 3.2, a flow restricting device (orifice) is introduced to increase the power consumption effectively. Although nitrogen is effective in increasing the plasma power consumption, there is a certain limitation because too much nitrogen addition in discharge eventually dilutes the cleaning system, which leads to lowering the overall cleaning rate. Moreover, the capacity of the dry pump also limits the total flow rate of cleaning gas. Because the ions, neutrals and electrons coming out of the plasma source are very hot, water circulation is required inside the orifice to prevent melting down the orifice itself which is made of aluminum.
It is observed that power consumption and plasma source pressure are constant regardless of the process chamber pressure. It is because the mixture of gas coming out of the plasma source becomes choked flow after flowing through the small hole of the orifice. Choked flow is a limiting condition which occurs when the mass flux will not increase with a further decrease in the downstream pressure environment[55].

With an orifice in the cleaning system, TEOS etching rate is decreased compared to the etching rate without an orifice in the entire system. It is because the high pressure in the plasma source caused by flow restriction decreases the available atomic fluorine due to the higher F-F recombination. The degree of decreasing TEOS etching rate is different according to the gas condition is because gases with different composition have different recombination properties.

Also, different orifice size affects TEOS etching rate. Attaching a smaller orifice lowers TEOS etching rate and enhances plasma power and plasma source pressure. It is because smaller orifice plays a role as a flow-restricting device that makes the plasma source pressure higher, which leads to higher F-F recombination in the plasma source. Of course, TEOS etching rate is optimal when the flow-restricting device is not placed in the cleaning system. For certain circumstances, it is necessary to control plasma power consumption and installing an orifice in the cleaning system is a good alternative to increasing nitrogen flow rate for controlling plasma power.

Finally, different location of an orifice leads to different TEOS etching rate and different plasma source pressure. If the orifice is placed near to the downstream chamber, plasma source pressure becomes lower and etching rate is decreased. The reason why the plasma source pressure becomes lower when the orifice is placed near to the downstream chamber is because the total volume that is restricted by the orifice becomes larger, hence the plasma source pressure
becomes lower by the ideal gas law which explains that pressure is proportional to the reciprocal of volume at constant temperature. And the reason why TEOS etching rate becomes lower when the orifice is placed near to the downstream chamber is because the surface of the inner transfer tube is all exposed to the relatively high pressure, which causes higher F-F recombination. If the F-F recombination reaction occurs actively, the available atomic fluorine that crucially affects TEOS etching rate is diminished, therefore TEOS etching rate is decreased when the orifice is placed near to the downstream chamber.
Chapter 4 Enhancement of Silicon Nitride Cleaning Rate by Nitric Oxide

Reactors for plasma enhanced chemical vapor deposition (PECVD) need to be cleaned periodically in order to ensure a constant high quality of the thin films deposited. Currently, PECVD chambers are often cleaned *ex situ* by remote plasmas to minimize tool downtime and chamber damage. The etching characteristics of various reactive gases such as perfluorocarbon (PFC) and NF₃ have been widely studied.

In several papers, it was already studied that adding oxygen into NF₃ plasma enhances etching rate of silicon nitride by forming NO which replaces the nitrogen atom on the silicon nitride substrate with oxygen[56-59]. Because the removal of nitrogen atom in silicon nitride is considered to be the rate limiting step in the removal of silicon nitride film, the formation of NO (nitric oxide) makes it possible to enhance the nitride film etching rates.

In this chapter, the main topic is on the enhancement of silicon nitride etching rate by NO. In section 4.1, it will be discussed that addition of O₂ in NF₃ discharge doubles nitride etching rate as a result of NO formation. In addition, Not only oxygen but also CO and CO₂ shows the same enhancement effect on the nitride etching rate because of the production of NO. In section 4.2, the enhancement of etching rate in silicon nitride in NF₃/C₂F₆/O₂ system will be discussed.
4.1 Role of $O_2$, $CO$ and $CO_2$ Gas Additives on Silicon Nitride Etching Rate in $NF_3$ Remote Plasmas

4.1.1 Experimental Set-up

The experimental apparatus is shown in Figure 4.1. The remote plasma source is an Astron®ex reactive gas generator made by MKS Astex. The feed gases are introduced into the plasma source and dissociated to form an activated gas mixture, which then pass through a one meter long water-cooled aluminum heat exchanger before entering the process chamber. A one inch square silicon nitride sample is placed on a mounting in the process chamber with its temperature controlled at 50°C. Grease (Apiezon Products) is used for better thermal contact between the wafer and the bottom stage. Process chamber pressure is maintained at around 1~10torr by throttle valve.

![Figure 4.1 Illustration of the chemical downstream etch reactor.](image)
Plasma is first ignited by Ar and then NF₃, O₂, CO and CO₂ are added sequentially. Argon gas is only used at the ignition time and is removed as another gas such as NF₃ and O₂ are introduced in the plasma source. Total flow rate of gas is always maintained at 1700sccm, therefore the flow rate of inlet flow rate of NF₃ is decreased by the same amount of additives such as O₂, CO₂ and CO that is introduced in the plasma source. The etching rate of nitride film is measured by He-Ne laser interferometry. A quadrupole line-of-sight mass spectrometry is mounted on the process chamber and the electron ionization energy is reduced to 40 eV to minimize the dissociative ionization of the chemical species such as F₂. The mass spec chamber is maintained by two stage differential turbo pumps and the pressure of the mass spec chamber is maintained at 10⁻⁸~10⁻⁷torr. A Chopper with a lock-in-amplifier is installed in the mass spectrometry chamber to remove the background signal from the original signal. FT-IR (MIDAC, I series) analysis is done to figure out the chemical species at the exhaust of the dry pump.

4.1.2 Effect of Additives on Nitride Etching Rate in NF₃ Remote Plasmas

Figure 4.2 shows that 4.5% of O₂, CO₂ and CO in NF₃ plasma doubles nitride etching rates both at low pressure (1torr) and at high pressure (5torr). At 1torr (see Figure 4.2(a)), the increased nitride etching rate is kept constant as the mole fraction of inlet additive gas is increased up to 25%. However, at 5torr (see Figure 4.2(b)), the overshoot behavior of the nitride etching rate is found when 4.5% of additive gas is introduced in the NF₃ discharge, and then the nitride etching rate decreases as the amount of additive is increased. Among three additives (O₂, CO and CO₂), the decrease in etching rate is great when O₂ was added in NF₃ plasma.
Figure 4.2 Enhancement of nitride etching rate by additives in NF₃ discharge.

This etching rate enhancement cannot be simply explained by the amount of atomic fluorine because nitride etching rate remains almost constant although 25% of additive dilutes the concentration of atomic fluorine in the gas phase (see Figure 4.2(a)). Instead, the enhancement of
the nitride etching rate by addition of oxygen containing molecules in NF$_3$ discharge can be explained by creation of nitric oxide (NO). Previously, Blain[60] proposed the mechanism of enhanced nitrogen atom removal by NO in the presence of atomic fluorine in the gas phase and experimentally proved this mechanism by directly injecting NO in the downstream chamber. The nitric oxide that is made by the reaction of dissociated nitrogen and oxygen molecule in the plasma (N + O$_2$ → NO + O) breaks the bond between nitrogen atom and substrate silicon atom, therefore N$_2$, N$_2$O are released in the gas phase as reaction products (see reaction 4.1 ~ 4.4). In addition, Kastenmeier et al[59] showed that reaction (4.3) is dominant over reaction (4.2).

\[
\begin{align*}
2\text{NO}(g) + 2\text{N}(s) & \rightarrow 2\text{N}_2(g) + \text{O}_2(g) & (4.1) \\
\text{NO}(g) + \text{N}(s) & \rightarrow \text{N}_2\text{O}(g) & (4.2) \\
\text{NO}(g) + \text{N}(s) & \rightarrow 2\text{N}_2(g) + \text{O}(s) & (4.3) \\
2\text{O}(s) & \rightarrow \text{O}_2(g) & (4.4)
\end{align*}
\]

4.1.3 The Formation of NO and its Analysis by Mass Spec and FT-IR

The formation of NO is proven by FT-IR that is located at the exhaust of the dry pump. In Figure 4.3(a), NO, N$_2$O and NF$_3$ are found in NF$_3$+O$_2$ plasma. When nitride block (5inch * 5inch * 0.25 inch) is placed on top of the stage (Figure 4.3(b)), NO is completely consumed by the nitride block in the process chamber and SiF$_4$ appears as an etching product. Consequently, N$_2$O concentration is also slightly increased when nitride block is placed inside the process chamber because NO reacts with nitrogen atom on the surface of the nitride block producing N$_2$O by reaction (4.2). NO$_2$ is not found in the FT-IR analysis because NO$_2$ was consumed very fast by the NO regeneration reaction (see reaction (4.5))[61] as long as atomic oxygen exists.
Figure 4.3 FT-IR analysis. Total flow rate of gas mixture (NF$_3$ + O$_2$) is 1700 sccm.

NO can be also regenerated by N$_2$O (reaction (4.6) – (4.8))[62]. However, the regeneration of NO by N$_2$O (reaction (4.6) – (4.8)) is almost impossible at the pump exhaust where FT-IR is located because the concentration of atomic oxygen at the pump exhaust is almost negligible by the recombination of atomic oxygen throughout the transfer tube and the reactor. Therefore N$_2$O that is produced by surface reaction on the nitride block (see reaction (4.2)) can be observed in FT-IR without being reacted with atomic oxygen.
NO\(_2\) (g) + O(g) → NO(g) + O\(_2\) (g) \hspace{1cm} (4.5)

N\(_2\)O(g) + O(g) → 2NO(g) : consumption of N\(_2\)O \hspace{1cm} (4.6)

N\(_2\)O(g) + O(g) → N\(_2\)(g) + O\(_2\)(g) : consumption of N\(_2\)O, very fast \hspace{1cm} (4.7)

N\(_2\)(g) + O(g) → NO(g) + N(g) : regeneration of nitric oxide \hspace{1cm} (4.8)

Silicon nitride etching rate is limited by two factors: the concentration of NO and the concentration of atomic fluorine. At pressure of 1torr, nitride etching rate is almost constant regardless of the flow rate of the inlet additive. As the amount of additive increases, the concentration of NO gradually increases (see Figure 4.3(a)). If NO is the only limiting factor to control the nitride etching rate, nitride etching rate should be dependent on the amount of the additive because the amount of NO is proportional to the flow rate of the inlet additive. This can be explained by considering the amount of atomic fluorine. The amount of atomic fluorine also affects the nitride etching rates. In the mass spectrometer results (see Figure 4.4(a)), partial pressure of atomic fluorine decreases by 25% as the ratio of additive increases by 25% at 1torr of chamber pressure. The reason why the nitride etching rate is maintained at the same level at 1torr of chamber pressure regardless of the amount of the additive is because the decrease in atomic fluorine is totally offset by the increase in the concentration of NO.
Figure 4.4 Line-of-sight mass spectrometer results at chamber pressure 1torr with three different additives in NF$_3$ discharge (O$_2$, CO$_2$ and CO). Total flow rate of gas mixture is 1700sccm. Nitride block is put on the stage of the process chamber. The intensities of mass spec peaks are adjusted by the sensitivity of mass filter and multiplier, but not for the difference of the ionization cross section.

However, at high pressure, adding oxygen in NF$_3$ discharge accelerates the production of molecular fluorine (see Figure 4.5(a)), which means that the recombination rate of atomic fluorine is increased significantly. Mass spec results (see Table 4.1) support this argument by showing that 25% of O$_2$ addition decreases the partial pressure of atomic fluorine by 54% which is more than the dilution by the additive. Compared to 25% of decrease in atomic fluorine at low
pressure (1torr), 54% of decrease in atomic fluorine at high pressure significantly decreases
nitride etching rate. In other words, addition of oxygen decreases the amount of atomic fluorine
not only by dilution but also by the enhancement in the recombination rate of atomic fluorine.

For more accurate analysis of atomic fluorine concentration in the mass spec, the cracking
pattern information of molecular fluorine is required because not only the atomic fluorine that is
dissociated in the plasma source but also the cracked molecular fluorine contributes to the signal
of the atomic fluorine. If the cracking pattern of molecular fluorine is taken into account in the
calculation in Table 4.1, the decrease percentage of atomic fluorine with O₂ addition will be
more remarkable than with CO or CO₂ because molecular fluorine signal in the presence of
oxygen (see Figure 4.5(a)) is stronger than those with CO and CO₂ (see Figure 4.5(b) and Figure
4.5(c)). This strengthens the hypothesis of higher recombination rate with oxygen in NF₃
discharge.

**Table 4.1 Decrease in atomic fluorine (%) at three different levels of additives in NF₃
discharge¹ at 5torr. Atomic fluorine signal in 1700sccm NF₃ discharge is used as a reference. For
detailed calculation, see foot note.**

<table>
<thead>
<tr>
<th>Additive Percentage</th>
<th>4.5%</th>
<th>13.5%</th>
<th>25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>30.4</td>
<td>51.1</td>
<td>54.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>20.7</td>
<td>45.3</td>
<td>59.4</td>
</tr>
<tr>
<td>CO</td>
<td>14.3</td>
<td>23.0</td>
<td>39.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additive Percentage</th>
<th>4.5%</th>
<th>13.5%</th>
<th>25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>31.7</td>
<td>51.7</td>
<td>54.7</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.6</td>
<td>39.3</td>
<td>55.6</td>
</tr>
<tr>
<td>CO</td>
<td>12.5</td>
<td>24.1</td>
<td>38.0</td>
</tr>
</tbody>
</table>

¹ Partial pressure data of atomic fluorine were retrieved from mass spectrometer. Decrease in atomic fluorine with
addition of O₂, CO and CO₂ was calculated by this equation. \( \text{Decrease(%) = } 100 \times \left( \frac{P_{F,0} - P_F}{P_{F,0}} \right) \), where \( P_{F,0} \)
is the partial pressure of atomic fluorine without any additive in 1700 sccm of NF₃ discharge and \( P_F \) is the partial
pressure of atomic fluorine with specified percentage of additive in NF₃ discharge.
If there is no nitric oxide in the system, etching rate will be only affected by the number of atomic fluorine. But, as oxygen is introduced in NF₃ discharge, NO also significantly affects the etching rate by removing nitrogen atom from silicon nitride substrate, which explains the overshoot of the nitride etching rate at 4.5% of oxygen addition in NF₃ discharge. As the amount of oxygen increases, atomic fluorine decreases by the enhanced recombination of atomic fluorine as well as by dilution, which lowers nitride etching rate remarkably. This explains the silicon nitride etching rate trend at high chamber pressure.

In addition, etching rate of TEOS film is also measured at different levels of oxygen in NF₃ discharge to confirm higher recombination rate of atomic fluorine in the presence of oxygen in NF₃ discharge because the etching rate of silicon dioxide film is proportional to the concentration of atomic fluorine in the system[63]. As oxygen amount increases, the etching rate of TEOS is decreased significantly, which is consistent with the mass spec result in Figure 4.5.

In the literature[64, 65], oxygen is only shown to increase the atomic fluorine by reaction (4.9)–(4.12). It is not certain how oxygen additive enhances the recombination rate of atomic fluorine. One of the possible pathways is that the oxygen absorbed on the surface attracts atomic fluorine stronger than the adsorbed fluorine on the surface attracts atomic fluorine because bond strength between oxygen and fluorine (45 kcal/mol) is stronger than the one between atomic fluorine (38 kcal/mol). Therefore, the crowd of atomic fluorine exists near the oxygen atom absorbed on the surface, which may leads to higher F-F surface recombination rate.

\[
\begin{align*}
O(g) + NF_2(g) &\rightarrow NF(g) + OF(g) \\ O(g) + NF(g) &\rightarrow NO(g) + F(g) \\ 2OF(g) &\rightarrow 2F(g) + O_2(g) \\ O(g) + OF(g) &\rightarrow O_2(g) + F(g)
\end{align*}
\]
Figure 4.5 Line-of-sight mass spectrometer results at chamber pressure 5torr without placing nitride block on the stage of the process chamber.

Another important aspect of Figure 4.2 is that NO is created not only by adding O$_2$ in NF$_3$ plasma but also by adding oxygen-containing gas such as CO and CO$_2$ in NF$_3$ plasma. It is
proven by FT-IR analysis that adding oxygen-containing gas into NF$_3$ discharge results in the formation of NO although those additives contain carbon source (see Figure 4.6(a)). Similar to the case of NF$_3$+O$_2$ discharge, NO disappears completely when the nitride block is placed in the process chamber producing N$_2$O and SiF$_4$ (see Figure 4.6(b)). SiF$_4$ concentration slightly increases when additives are introduced in NF$_3$ discharge, which indirectly shows that the addition of oxygen containing molecules in NF$_3$ discharge leads to higher etching rate. Other carbon containing by-products such as CF$_4$, C$_2$F$_6$, CO$_2$ and COF$_2$ are also produced because CO and CO$_2$ additive gas contain carbon source.
4.1.4 Carbon to Oxygen Ratio

The ratio of carbon to oxygen (C/O) in the additive molecule determines the nitride etching rate. At 1torr of chamber pressure, lower C/O ratio brings higher nitride etching rate and the nitride etching rate is independent upon the flow rate of the additive. In Figure 4.7, it is observed that the average concentration of NO is proportional to the nitride etching rate at 1torr when 9% CO₂.

Figure 4.6 FT-IR analysis. Total flow rate of gas mixture (NF₃ + CO₂) is 1700 sccm².

---

² The same experiment with CO was done and the results were very similar to the one with CO₂.
of O₂, CO₂ and CO are introduced each in NF₃ discharge. In other words, lower C/O ratio produces higher concentration of NO, which results in higher nitride etching rate at low pressure. At low pressure (see Figure 4.4), the recombination of the atomic fluorine is relatively low compared to the recombination at high pressure. Moreover, the concentration of atomic fluorine at 1torr is almost identical regardless of additive type (see Figure 4.4(a), (b) and (c)). Therefore, it is possible to exclude the effect of atomic fluorine concentration on the nitride etching rate at low pressure. In result, only C/O ratio determines the amount of produced NO and the nitride etching rate.

\[
\begin{align*}
\text{Additive} & \quad \text{Total Flow Rate} = 1700 \text{ sccm} \\
\text{Pressure} & = 1 \text{ torr}
\end{align*}
\]

**Figure 4.7** Average concentration of NO retrieved from FT-IR. Nitride etching rate data are taken at 1torr.

However, at 5torr of process chamber pressure, etching rate with higher C/O ratio is higher than with low C/O ratio. At high pressure (5torr), recombination of atomic fluorine is more important. Table 4.1 shows that 25% dilution of oxygen in NF₃ plasma results in 54% of decrease in atomic fluorine while 25% dilution of CO caused 39.1% of decrease in atomic fluorine. It is not certain how carbon source inhibits the recombination of atomic fluorine. One
probable explanation is that the active carbon radical in NF₃ discharge recombines with oxygen and fluorine to produce CO, CO₂ and COF₂, which makes the plasma more in an oxygen deficient state. Therefore, additives with high C/O ratio consume more oxygen that contributes to an enhancement of recombination among atomic fluorine.

4.2 Enhancement of Nitride Etching Rate in NF₃/C₂F₆/O₂ gas system

4.2.1 Comparison of Nitride Etching Rate: NF₃ VS. NF₃+C₂F₆+O₂

In Figure 4.8, it is shown that nitride etching rate is increased by adding both C₂F₆ and O₂ in NF₃ plasma. Compared to the nitride etching rate with pure NF₃ plasma, nitride etching rate is increased by adding 3.5% O₂ in NF₃, however etching rate is decreased by adding 2.3% C₂F₆. When both C₂F₆ and O₂ gases are equally added in NF₃ (i.e. the ratio of C₂F₆:O₂ is 1:1), nitride etching rate has increased by four times. An interesting observation in Figure 4.8 is that the nitride etching rate remains constant as the composition of NF₃ in the mixture decreases from 94.2% to 50%. This result is remarkable because the processing cost and time for cleaning PECVD chamber can be minimized to 25% by adding small amount of C₂F₆+O₂ in NF₃ plasma.
Figure 4.8 Enhancement of nitride etching rate by adding C₂F₆/O₂ in NF₃ plasma. Process chamber pressure is 5torr and Sample Temperature is 50 °C. Total flow rate is 1700sccm.

Figure 4.9 shows the nitride etching rates with three different gas mixtures at four different stage temperatures. NF₃ only in Figure 4.9 means 100% NF₃ plasma, Blend-1 represents 91% NF₃ + 4.5% C₂F₆ + 4.5% O₂ and Blend-2 represents 82% NF₃ + 9% C₂F₆ + 9% O₂. At low temperature such as 50°C, difference in the nitride etching rate between pure NF₃ plasma and other two blends are more drastic than the difference in the nitride etching at higher stage temperature. And there is no difference between two gas mixtures in the etching rate, which is similar to the results in Figure 4.8. Hence the advantage of using NF₃/C₂F₆/O₂ gas mixture is maximized at lower temperature. In fact, within the cleaning chamber, spot at lower temperature is harder to clean, which means that the overall cleaning rate is determined by a “cool” place instead of a “hot” place. Because the blends are particularly good for the cold spot, they can contribute to lowering the processing cost very effectively by increasing the cleaning rate in the cold place which is rate-limiting.
Other useful information in Figure 4.9 is that the apparent activation energy \( E_{\text{act, apparent}} \) of NF\(_3\) etching and NF\(_3\)/C\(_2\)F\(_6\)/O\(_2\) etching is calculated by equation (4.13). Apparent activation energy is composed of activation energy of adsorption on the surface, activation energy of surface reaction and activation energy of desorption from the surface, which is expressed in equation (4.14)

\[
\log k = \log A - \frac{E_{\text{act, apparent}}}{RT}, \quad (4.13)
\]

\[
E_{\text{act, apparent}} = E_{\text{act, adsorption}} + E_{\text{act, reaction}} + E_{\text{act, desorption}}, \quad (4.14)
\]

where \( k \) is kinetic rate constant, \( A \) is Arrhenius constant, \( R \) is gas constant and \( T \) is temperature. Obviously, the apparent activation of the reaction of NF\(_3\) gas is greater than that of the blends. \( E_{\text{act, apparent}} \) is different from the value published by Flamm[63] because Flamm’s result represents the activation energy of F-F reaction( \( E_{\text{act, reaction}} \)), not the apparent activation energy ( \( E_{\text{act, apparent}} \)).
Figure 4.9 Nitride etching rate at four different stage temperatures. Blend-1 represents 91% NF$_3$ + 4.5% C$_2$F$_6$ + 4.5% O$_2$ and blend-2 represents 82% NF$_3$ + 9% C$_2$F$_6$ + 9% O$_2$. Process chamber is 2torr and total flow rate is 1700 sccm.

In Figure 4.10, the nitride etching rates are measured at two different chamber pressures (2torr for Figure 4.10(a) and 5torr for Figure 4.10(b)). At low chamber pressure (2torr), the nitride etching rates of NF$_3$ plasma with O$_2$ (second bar), with C$_2$F$_6$/O$_2$=1:1 (third bar) and with C$_2$F$_6$/O$_2$=1:2 (fourth bar) are almost identical. However, at high chamber pressure (5torr), an equal amount of C$_2$F$_6$ and O$_2$ in NF$_3$ plasma still remains at highest etching rate while higher flow rate of O$_2$ in NF$_3$ plasma brings lower etching rate. This observation implies that oxygen in NF$_3$ induces more F-F recombination on the surface, consuming available atomic fluorine and hence causing lower etching rate. Also, it implies that the proper amount of carbon helps prevent F-F recombination caused by the excessive oxygen in NF$_3$. However, it has not been clearly understood why oxygen causes more F-F recombination on the aluminum surface and why carbon helps to prevent the recombination caused by oxygen. One of the possible pathways
described in section 4.2 is that the oxygen absorbed on the surface attracts atomic fluorine stronger than the adsorbed fluorine on the surface attracts atomic fluorine because bond strength between oxygen and fluorine (45 kcal/mol) is stronger than the one between atomic fluorine (38 kcal/mol). Therefore, the crowd of atomic fluorine exists near the oxygen atom absorbed on the surface, which may leads to higher F-F surface recombination rate. Also, a possible scenario of the way carbon helps to prevent the recombination caused by oxygen is that the active carbon radical in NF$_3$ discharge recombines with oxygen and fluorine to produce CO, CO$_2$ and COF$_2$, which makes the plasma more in an oxygen deficient state. Therefore, additives with high C/O ratio consume more oxygen that contributes to an enhancement of recombination among atomic fluorine.
Figure 4.10 Nitride etching rate with four different gas condition. (a) chamber pressure = 2torr. (b) chamber pressure = 5torr. Ps represents the pressure at plasma source. Source pressure is controlled by the butterfly valve between the plasma source and the process chamber.

The main reason why the nitride etching rate of NF$_3$/C$_2$F$_6$/O$_2$ plasma is higher than that of NF$_3$ plasma is believed to be because nitric oxide is formed in the gas phase and the nitric oxide reacts with the nitrogen atom on the silicon nitride surface producing N$_2$O or N$_2$, while nitrogen is substituted by oxygen on the surface by the reaction. Removing nitrogen atom from silicon
nitride substrate is assumed to be the rate-limiting step in the fluorine base etching of silicon nitride film. In summary, the nitric oxide makes it easier to remove the nitrogen atom from silicon nitride surface, which is the rate-limiting step for nitride etching in the presence of F, therefore enhancing silicon nitride etching rate.

4.2.2 Mass Spec Analysis

Mass spec is used to support the enhancement of nitride etching rate by nitric oxide. Total flow rate of inlet gas is 1700sccm and chamber pressure is maintained at 5torr. In Figure 4.11, five mass spec results are illustrated according to the inlet gas conditions. There are many factors that cause experimental error in the mass spec analysis. Background signal, such as HF, H₂O, CO₂ and etc. needs to be eliminated from signal for accurate quantitative analysis. And the cracking patterns of F₂, CF₄ and SiF₄ should also be included in the analysis. Although these two factors are not taken into account in the analysis, a general trend can be learned from the Figure 4.11.

In Figure 4.11(a), a silicon nitride block is put inside the process chamber and a silicon nitride block is not used in Figure 4.11(b) to understand the effect of the reaction by silicon nitride film. Compared to the concentration of atomic fluorine in (b), atomic fluorine concentration in (a) is decreased because considerable amount of atomic fluorine is consumed by the silicon nitride block. Other observation is that, compared to the F₂ concentration of pure NF₃ plasma, 3.5% O₂ + 96.5% NF₃ has higher concentration of F₂ in both (a) and (b), which supports that higher F-F recombination occurs on the aluminum surface when oxygen is added in NF₃ plasma. In addition, 82% NF₃+6% C₂F₆+12% O₂ plasma that has higher O₂/C₂F₆ ratio also has higher concentration of F₂, which is consistent with the trend of silicon nitride etching rate in Figure 4.10(b).
Figure 4.11 Measurement of mass spec (a) with a 5 inch*5 inch*0.25 inch silicon nitride block in the process chamber and (b) without a silicon nitride block in the process chamber. Total flow rate is 1700sccm, chamber pressure is 5torr. Electron ionization energy is 30eV and filament current is 1.3mA. Peak intensities are adjusted by the sensitivity of mass filter and multiplier. No background signal is eliminated by a chopper and no cracking pattern is taken into account in this analysis.

As C\textsubscript{2}F\textsubscript{6}+O\textsubscript{2} is added in NF\textsubscript{3} plasma, the general trends are that F\textsubscript{2} concentration is decreased compared to NF\textsubscript{3}/O\textsubscript{2} plasma and that other by-products, such as CO, CO\textsubscript{2} and COF\textsubscript{2} are formed.
by reactions among C, O and F. However, the mechanism of the role of carbon as an inhibitor of F-F recombination is not fully understood in Figure 4.11.

Although the peak intensity of SiF$_3^+$ is miniscule, SiF$_3^+$ intensity has a very strong correlation with nitride etching rate. Figure 4.12 illustrates the correlation between the nitride etching rate that is taken from Figure 4.10(b) and the SiF$_3^+$ signal from Figure 4.11(a). This graph strongly supports that the quantitative analysis of the mass spec is quite accurate.

![Graph showing the correlation between SiF$_3^+$ peak intensity and nitride etching rate at 5torr of process chamber pressure. Total flow rate is 1700sccm.](image)

**Figure 4.12** Correlation between SiF$_3^+$ peak intensity and nitride etching rate at 5torr of process chamber pressure. Total flow rate is 1700sccm.

### 4.3 Summary

The main topic of this chapter is the effect of nitric oxide as a silicon nitride etching enhancement factor. In section 4.1, it is shown that only 4.5% of additives (O$_2$, CO and CO$_2$) into NF$_3$ discharge doubles nitride etching rate and this enhancement of etching rate occurs regardless of additive types. The enhancement results from the production of NO in the discharge of NF$_3$.
gas mixture. As the amount of oxygen containing additive increases, the amount of NO increases. However, atomic fluorine decreases as the amount of oxygen containing additive increases because the additive dilutes NF₃ plasma. At low process chamber pressure, the effect of NO is offset by the dilution effect of atomic fluorine, which maintains nitride etching rate constant up to 25% addition of O₂, CO₂ and CO. C/O ratio is also important because this ratio determines the amount of the produced NO. Low C/O ratio produces more NO, which explains why nitride etching rate with addition of oxygen is higher than the one with addition of CO and CO₂ at low pressure. At high pressure, addition of oxygen enhances the recombination of atomic fluorine and 25% of O₂ in NF₃ discharge decreases 54% of atomic fluorine. Therefore, the effect of a decrease in atomic fluorine is remarkably higher than the effect of increase in the concentration of NO by adding O₂ at high pressure, which leads to a decrease of nitride etching rate at 5torr. Additive with higher C/O ratio such as CO, however, decreases the recombination of atomic fluorine because only 39% of atomic fluorine decreases with 25% addition of CO. This explains the reason why additive with a high C/O ratio brings higher nitride etching rate at 5torr. One possible explanation why additives with high C/O ratio brings high etching rate at high pressure is that higher carbon source consumes more oxygen which will contribute to a higher recombination rate of atomic fluorine.

In section 4.2, the nitride etching rates of NF₃ plasma and NF₃/C₂F₆/O₂ plasma are compared and it is shown that NF₃/C₂F₆/O₂ plasma has better performance in nitride etching rate over NF₃ plasma. The main reason why the nitride etching rate of NF₃/C₂F₆/O₂ plasma is higher than that of NF₃ plasma is believed to be because nitric oxide is formed in the gas phase and the nitric oxide reacts with the nitrogen atom on the silicon nitride surface producing N₂O or N₂, while nitrogen is substituted by oxygen on the surface by the reaction. Removing nitrogen atom from
silicon nitride substrate is assumed to be the rate-limiting step in the fluorine base etching of silicon nitride film. In summary, the nitric oxide makes it easier to remove the nitrogen atom from silicon nitride surface, which is the rate-limiting step for nitride etching with F base gas, therefore enhancing silicon nitride etching rate. The advantage of using NF$_3$/C$_2$F$_6$/O$_2$ gas mixture is maximized at lower temperature and at higher process chamber. In fact, within the cleaning chamber, spots of lower temperature is harder to clean, which means that the overall cleaning rate is determined by a “cool” place instead of a “hot” place. Because NF$_3$/C$_2$F$_6$/O$_2$ gas mixtures are particularly good for the cold spot, they can contribute to lowering the processing cost very effectively by increasing the cleaning rate in the cold place which is rate-limiting. Finally, mass spec is used to confirm the existence of nitric oxide, higher F-F recombination with higher flow rate of O$_2$ in NF$_3$ plasma and the role of carbon as an inhibitor of F-F recombination in NF$_3$/C$_2$F$_6$/O$_2$ plasma. This chapter will be very useful in semiconductor fabrication industry because this new gas composition can save both cleaning cost and cleaning time tremendously.
Chapter 5 Global Modeling of PECVD Cleaning Chamber

5.1 Introduction of Global Model

Accurate modeling of a downstream cleaning chamber is very important in semiconductor fabrication industry because the needs for process optimization and integration for new tools at low cost are growing very fast. Prediction of the partial pressure of atomic fluorine at a given process chamber pressure is the main goal of the global modeling because it allows the prediction of the cleaning rate for silicon dioxide and silicon film[35, 36]. Partial pressures of reaction products predicted by the global model are finally validated by comparing them to the experimental results such as the partial pressure of atomic fluorine measured by mass spectrometer. In addition, global model predicts the relative importance of surface reaction over gas phase reaction over the range of process chamber from 0.5torr to 10torr as well as the effect of the length of the transfer tube on the partial pressure of atomic fluorine in downstream chamber.

Input parameters for the global model are wall temperature, surface area of transfer tube and cleaning chamber, volume of transfer tube and cleaning chamber, flow rate of cleaning gas, pressure at the plasma source and pressure in the cleaning chamber.

The entire cleaning system consists of three different sections: plasma source, transfer tube and cleaning chamber. In the plasma source, it is assumed that inlet gases such as NF₃, N₂ and O₂ are completely dissociated into elementary atoms. This assumption is based upon high power density property of transformer-coupled toroidal plasma source (20W/cm³)[30]. Temperature of neutrals in the plasma source ranges from 450K to 2000K[37, 38]. This assumption eliminates
the uncertainty in the plasma source. Therefore, global model of cleaning chamber includes only two parts: transfer tube and downstream chamber.

![Diagram of the entire cleaning system for global modeling of PECVD cleaning chamber](image)

**Figure 5.1** Description of the entire cleaning system for global modeling of PECVD cleaning chamber. It consists of three different sections: plasma source, transfer tube and cleaning chamber.

### 5.1.1 Modeling of Transfer Tube

Second part is the transfer tube with 2.8 liter of volume and 1773 cm² of surface area. Hot neutrals are introduced at the entrance of aluminum transfer tube, and quickly cooled down to 300K by outer water circulation tube. Therefore, it is assumed that the entire system is maintained at 300K. While electrons and ions are annihilated, neutrals undergo surface reactions such as F-F recombination and N-N recombination as well as three body volume recombination reactions in this region. In NF₃/N₂ discharge, N-N recombination rate is faster than F-F recombination and it is experimentally observed by the line-of-sight mass spec which is attached to the cleaning process chamber. Mass spec results shows that the only chemical species
detectable in the cleaning process chamber are N₂, F₂ and F in NF₃ plasma. Therefore, it is appropriate to assume that the conversion of atomic nitrogen into molecular nitrogen is 100% and recombination reaction of atomic fluorine (i.e. reaction (5.1) and (5.5) in Table 5.2) needs to be incorporated in the global model to predict the partial pressure of F and F₂.

Dimensionless number (Peclet number, Pe) is adopted to rationalize the assumption that transfer tube region is a plug flow reactor because Peclet number represents the relative importance of forced convection to diffusion. Pe is calculated as

\[
Pe = \frac{UL}{D}, \quad (5.1)
\]

where U is a total mass bulk flow rate (cm/sec); L is the length of transfer tube (cm); D is the diffusion coefficient of neutrals in the transfer tube (cm²/s). Diffusion coefficient of oxygen atom \( \frac{4.4 \times 10^{-2} T^{4.5}}{P} \) in cm²/s, where T in Kelvin and P in torr) is adopted to figure out the order of magnitude of Peclet number[38]. Large Pe number supports the idea that it is appropriate to assume transfer tube is a plug flow rate (see Pe in Table 5.1). It should be noted that this model does not work properly at low flow rate regime where Pe is very low (i.e. diffusion control regime). In the case of low Pe, diffusion term should be included in the mass balance equation and therefore the next step will be solving second order ordinary differential equation.
Table 5.1 Parameters used for global modeling.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Volumetric flow rate</td>
<td>3000-6000</td>
<td>sccm</td>
</tr>
<tr>
<td>L</td>
<td>Length of transfer tube</td>
<td>88.9</td>
<td>cm</td>
</tr>
<tr>
<td>R</td>
<td>Radius of transfer tube</td>
<td>3.2</td>
<td>cm</td>
</tr>
<tr>
<td>Tn</td>
<td>Temperature of neutrals in plasma source</td>
<td>450-2000</td>
<td>K</td>
</tr>
<tr>
<td>Ts</td>
<td>Standard temperature</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>Pc</td>
<td>Cleaning chamber pressure</td>
<td>0.5-10</td>
<td>torr</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>42-7871</td>
<td>cm²/sec</td>
</tr>
<tr>
<td>U</td>
<td>Total mass bulk flow rate</td>
<td>117-15758</td>
<td>cm³/sec</td>
</tr>
</tbody>
</table>

\[ P_{e} = \frac{UL}{D} \]

Peclent number (transfer tube) 178-375 dimensionless

Figure 5.2 illustrates the mole balance in the differential (control) volume of transfer tube. Surface reactions \( R_{\text{surface}} \) and gas phase reactions \( R_{\text{volume}} \) are involved in the mole balance. In addition, equation (5.2) \( \sim \) (5.7) lists all of the required calculation for the steady-state plug flow where \( n_{F,0} \) is the inlet molar flow rate of atomic fluorine; \( n_{F}, n_{F2} \) and \( n_{N2} \) are the molar flow rate of F, F₂ and N₂ (mol/s); \( X_{F} \) is the conversion of atomic fluorine into molecular fluorine;

\( R_{\text{surface}} \) is the surface reaction rate by F-F recombination \( \text{(mol/cm}^2/\text{s)} \); \( R_{\text{volume}} \) is the volume recombination rate \( \text{(mol/cm}^3/\text{s)} \); \( dA_{1}, dV_{1} \) is the differential form of the surface area and the volume of a transfer tube; \( R \) is the radius of transfer tube; \( \Gamma_{F,\text{inc}} \) is the incident molar flux of atomic fluorine on the transfer tube surface \( \text{(mol/cm}^2/\text{s)} \); \( N_{F} \) is the molar density of atomic fluorine \( \left( \frac{P_{F}}{R_{\text{ideal,gas}}T} \right) \) based upon the assumption that the neutrals in the system are ideal \( \text{(mol/cm}^3) \); \( P_{F} \) is the partial pressure of atomic fluorine \( \text{(torr)} \); \( R_{\text{ideal,gas}} \) is ideal gas constant; \( c \) is the mean thermal velocity of atomic fluorine \( \left( \sqrt{\frac{8kT}{m}}, \text{cm/s} \right) \); \( k \) is Boltzmann constant \( \text{(J/K)} \).
Equation (5.2a-5.2c) shows the molar flow rate of F, F₂ and N₂ as a function of initial molar flow rate and conversion. Equation (5.3) represents the mole balance in the control volume shown in Figure 5.2. Equation (5.4) is a surface recombination rate and equation (5.5) is a volume recombination rate. Equation (5.7) is the complete form of the mole balance and the conversion of atomic fluorine \( X_F \) at different position in the transfer tube can be obtained by numerically integrating the equation (5.7).

\[
n_F = n_{F,0}(1 - X_F) \quad (5.2a)
\]

\[
n_{F_2} = 0.5n_{F,0}X_F \quad (5.2b)
\]

\[
n_{N_2} = 0.5n_{N,0} \quad \text{(Assumption: 100% conversion of N)} \quad (5.2c)
\]

\[
dn_F = d[n_{F,0}(1 - X_F)] = -n_{F,0}dX_F = R_{\text{surface}}dA + R_{\text{volume}}dV \quad (5.3)
\]

\[
= R_{\text{surface}} \times 2\pi R d\ell + R_{\text{volume}} \times \pi R^2 d\ell
\]

\[
R_{\text{surface}} = -k_{F_2} \times \Gamma_{F,loc} = -k_{F_2} \times (N_F \times \frac{C}{4})^2 \quad (5.4)
\]
\[ R_{\text{volume}} = -2k_{S_F} \times P_F^2 \times P \]  

(5.5)

\[ P_F = \frac{P \times n_F}{n_F + n_{F_2} + n_{N_2}} = \frac{P \times n_{F,0} (1 - X_F)}{n_{F,0} (1 - X_F) + 0.5 n_{F,0} X_F + n_{N_2}} \]  

(5.6)

\[ \frac{dX_F}{d\ell} = -\frac{R_{\text{surface}} \times 2\pi R + R_{\text{volume}} \times \pi R^2}{n_{F,0}} \]  

(5.7)

A major assumption in the surface recombination of atomic fluorine is if it is the first order reaction of atomic fluorine or the second order reaction. It is still controversial if the recombination of atomic fluorine on the surface is a first order reaction or a second order reaction\[66\]. If the surface reaction rate is a first order reaction, aluminum surface is assumed to be saturated with atomic fluorine, forming an Al-F bond on the aluminum surface. Then the incident fluorine atoms from the gas phase are diffused on the surface and reacts with one of the fluorine atoms that are very weakly bound to the aluminum surface. Incident molar flux of atomic fluorine was calculated by \( \frac{N_F c}{4} \) where \( N_F \) is the molar density of atomic fluorine and \( c \) represents the average thermal velocity of fluorine atom. \( N_F \) is equal to \( \frac{P_F}{R_{\text{ideal gas}} T} \) by ideal gas law. However, if the surface reaction rate is a second order reaction, then the two physisorbed atoms that are weakly bound on the surface react together leaving products in the gas phase.

Surface recombination of oxygen and nitrogen is experimentally turned out to be the first order reaction\[66, 67\], and the other surface reactions are all treated as second order reactions in this global model. For fluorine, both first order and second order reaction are tested in the global
model, and it is found that the second order reaction explains the experimental results more accurately, which will be discussed in section 5.3 in detail.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>F</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>F(s) + F(s) → F₂(g)</td>
<td>-kₛF₂ * (rₑ/inc)²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>N(s) + N(s) → N₂(g)</td>
<td>-kₛN₂ * rₑ/inc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>O(s) + O(s) → O₂(g)</td>
<td>-kₛO₂ * rₒ/inc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>N(s) + O(s) → NO(g)</td>
<td>-kₛNO * rₑ/inc * rₒ/inc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>F(g) + F(g) + M → F₂(g)</td>
<td>-2kᵥF₂ * P_F² P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>N(g) + N(g) + M → N₂(g)</td>
<td>-2kᵥN₂ * P_N² P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(7)</td>
<td>O(g) + O(g) + M → O₂(g)</td>
<td>-2kᵥO₂ * P_O² P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(8)</td>
<td>N(g) + O(g) + M → NO(g)</td>
<td>-kᵥNO * P_N P_O P</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2 Surface reactions and volume reactions involved in the global cleaning model of NF₃/N₂/O₂ plasma.

Volume reaction in the gas phase is assumed to be a three body reaction because radicals are very hot and it is more probable for three atoms to collide together. M represents the collision medium and surface recombination rate with different medium has different recombination rate[68]. However, one lumped volume recombination rate (kᵥF₂) is used in this model for simplicity.

**5.1.2 Modeling of Process Chamber**

The last part in the global cleaning model is the cleaning process chamber. The surface area (A₂) of the cleaning chamber is 2402 cm² and the volume (V₂) is 6.8 liter. Because the cleaning chamber is geometrically very different from the transfer tube, it is assumed that the cleaning chamber is a steady state CSTR (Continuously Stirred Tank Reactor).
Figure 5.3 Illustration of the cleaning process chamber. $N_{F,1}$ is the molar flow rate of inlet and $N_{F,2}$ is the molar flow rate of outlet. $X_{F,1}$ is the conversion of atomic fluorine at the exit of the transfer tube and $X_{F,2}$ is the conversion of atomic fluorine in the outlet of the process chamber.

Equation (5.10) represents the mole balance in the cleaning process chamber, where $n_{F,1}$ and $n_{F,2}$ are the molar flow rate of inlet and outlet in the process chamber; $X_{F,1}$ and $X_{F,2}$ are the conversion of atomic fluorine into molecular fluorine in the inlet and outlet (see Figure 5.3). Conversion of atomic fluorine in the inlet of the cleaning process chamber ($X_{F,1}$) equals to the conversion at the end of the transfer tube and is calculated by numerically integrating the equation (5.7) and then $X_{F,2}$ can be obtained by solving equation (5.10). Once the conversion of $F$, $F_2$ and $N_2$ is obtained by (5.10), partial pressure of $F$, $F_2$ and $N_2$ is calculated by equation (5.11a).

In equation (5.10), the only unknown parameters are the reaction constants for the surface and volume reaction ($k_{S,F_2}$ and $k_{V,F_2}$). F-F recombination reaction constants are initially adopted from the literature[66, 68, 69] and then modified to fit the partial pressure of $N_2$, $F_2$ and
F that are experimentally obtained by the mass spec. The fitted reaction constants (\( k_{S,F2} \) and \( k_{V,F2} \)) are shown in Table 5.3 and it is confirmed that the fitted recombination rate values are close to the actual value from the literature[66, 68, 69].

\[
\begin{align*}
n_{F,1} &= n_{F,0}(1 - X_{F,1}) \quad (5.8) \\
n_{F,2} &= n_{F,0}(1 - X_{F,2}) \quad (5.9) \\
\frac{dn_F}{dt} &= n_{F,1} - n_{F,2} + R_{\text{surface}} A_2 + R_{\text{volume}} dV_2 \quad (5.10) \\
&= n_{F,0} (X_{F,2} - X_{F,1}) + R_{\text{surface}} A_2 + R_{\text{volume}} dV_2 = 0 \quad \text{(steady state)}
\end{align*}
\]

\[
P_i = \frac{P \times n_i}{\sum_j n_j} \quad (i, j = F, F_2, N_2) \quad (5.11a)
\]

\[
\sum_j n_j = n_{F,0} (1 - 0.5 X_F) + 0.5 n_{N,0} \quad (5.12a)
\]

**Table 5.3 Parameters used for global modeling.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{S,F2} )</td>
<td>Reaction constant for F-F surface recombination</td>
<td>0.67</td>
<td>( \text{cm}^2 \cdot \text{s/mol} )</td>
</tr>
<tr>
<td>( k_{S,N2} )</td>
<td>Reaction constant for N-N surface recombination</td>
<td>( 1.0 \times 10^3 )</td>
<td>dimensionless</td>
</tr>
<tr>
<td>( k_{S,O2} )</td>
<td>Reaction constant for O-O surface recombination</td>
<td>( 2.1 \times 10^3 )</td>
<td>dimensionless</td>
</tr>
<tr>
<td>( k_{S,NO} )</td>
<td>Reaction constant for O-N surface recombination</td>
<td>0.2</td>
<td>( \text{cm}^2 \cdot \text{s/mol} )</td>
</tr>
<tr>
<td>( k_{V,F2} )</td>
<td>Reaction constant for F-F volume recombination</td>
<td>( 1.3 \times 10^{13} )</td>
<td>( \text{cm}^6 / \text{mol}^2 / \text{s} )</td>
</tr>
<tr>
<td>( k_{V,N2} )</td>
<td>Reaction constant for N-N volume recombination</td>
<td>( 8.2 \times 10^{15} )</td>
<td>( \text{cm}^6 / \text{mol}^2 / \text{s} )</td>
</tr>
<tr>
<td>( k_{V,O2} )</td>
<td>Reaction constant for O-O volume recombination</td>
<td>( 5.4 \times 10^{14} )</td>
<td>( \text{cm}^6 / \text{mol}^2 / \text{s} )</td>
</tr>
<tr>
<td>( k_{V,NO} )</td>
<td>Reaction constant for O-N volume recombination</td>
<td>( 1.0 \times 10^{10} )</td>
<td>( \text{cm}^6 / \text{mol}^2 / \text{s} )</td>
</tr>
</tbody>
</table>
5.2 Experimental Set-up

5.2.1 Overall Set-up

Figure 5.4 Schematic illustration of the chemical downstream etching reactor.

Figure 5.4 shows the entire experimental system that consists of plasma source, transfer tube, process chamber and mass spec chamber. Active chemical species that are formed in the plasma source (ASTeX) move through the 35 inch long transfer tube which is made of aluminum with the surface coated by aluminum oxide film. Inner transfer tube is always cooled by outer water circulation tube which provides 2.7 gal/min of water through the entire outer tube. Inlet gas is NF₃, N₂, O₂ and C₂F₆ and these gases are dissociated in the plasma source. Electrons and ions are annihilated in the transfer tube, and active radicals that are formed in the plasma source experience surface reactions on transfer tube wall and volume reactions in gas phase. Active radicals that do not go through the reaction in the transfer tube region finally react with a 1cm² TEOS wafer piece on the stage in the process chamber. Stage temperature is controlled from the
room temperature to 315°C which is limited by the o-ring (Kalrez K8085). Cleaning chamber pressure is maintained between 1torr to 10torr by a 1000 ℓ/s blower and dry pump.

5.2.2 Set-up of Mass Spec

The basic objective of using mass spec is to quantitatively analyze the chemical species in the gas phase. Quadrupole mass spectrometry (UTi Model 100C) is used to measure the partial pressure of radical species in the process chamber. Sample wafer is not put on the stage when the mass spec is operated because the purpose of the experiment is to analyze the reactants of reactions. 40eV is used for ionization electron energy, and filament current is 15mA.

It is difficult to measure the reproducible result of atomic fluorine partial pressure in gas phase by using quadrupole mass spectrometer because the filament and quadrupole in the mass spectrometer are contaminated by fluorine with ease, which leads to degrading the mass spec signal except for atomic fluorine (amu 19). Therefore, it is critical to minimize the flow rate through the mass spec chamber by decreasing the orifice diameter between mass spec chamber and process chamber. Also, it is required to keep the mass spec turned on and baked even in the idle time for the fast desorption of fluorine on the quadrupole and filament surface.

In addition, large background signals due to the multiple wall collisions make it difficult to retrieve the quantitative information on the gas phase. Therefore, two stages of differential pumping are adopted to obtain relatively large beam to background signal radio. Pressure of the first stage is an order of 10^-5 torr and the second stage is maintained at 10^-7 ~ 10^-8 torr. The orifice size between the process chamber and the first stage is 0.002 inch in diameter and the diameter of the skimmer cone between the first stage and the second stage is 0.0625 inch. A chopper (EOPC Model CH10, frequency 400Hz) is used to remove background signal such as H₂O and N₂.
5.2.3 Sensitivity Factors (Cracking Pattern)

As mentioned previously, the basic objective of using mass spec is to quantitatively analyze the chemical species in the gas phase. Sensitivity factors of molecules are required to get the partial pressure information in the gas phase. Sensitivity factor is determined by various parameters: ionization efficiency, electron multiplier gain and transmission. Ionization efficiency of molecule is a function of number of electrons in a molecule. Electron multiplier gain and transmission of any ion through the quadrupole filter is a function of molecular weight. Usually sensitivity factors of molecules at 70eV of electron voltage are available in the literature. However, because 40eV of electron voltage is used in this experiment to minimize the cracking of molecules, it is necessary to get the customized sensitivity factor of each gas molecule for quantitative analysis, and it will be discussed in the next paragraph how to get the customized sensitivity factor of each gas molecule at 40eV of electron ionization energy.

Figure 5.5 shows the ion current of NO, N₂, O₂ and F₂ over the pressure range from 0.5torr to 9torr without turning on the plasma. In other words, the ion current of NO is measured by turning on 500sccm of NO gas in the cleaning system while another gas line is shut down. Other gases, such as N₂, O₂ and F₂ follow the same method as NO. NO, N₂ and O₂ are shown to have negligible portion of cracking by electron impact in Figure 5.5(a) whereas the cracking portion of F₂ is quite significant (Figure 5.5b). Ion current of each molecule is linearly dependent upon the chamber pressure, which means each molecule has a constant and unique “slope”. The slope of each molecule in Figure 5.5 is calculated by linear regression with zero intercept. Once ion current data are retrieved from the mass spec, the partial pressure of molecule is calculated based upon this linear dependence of ion current versus chamber pressure

\[ P_i = \frac{\text{Ion current}}{\text{Slope}_i} \quad (i = \text{NO, N}_2, \text{O}_2 \text{ and F}_2) \]  

(5.13)
where \( P_i \) is the partial pressure of species \( i \); \( \text{Slope}_i \) is the slope retrieved from Figure 5.5; \( \text{Ion}_i \) \( \text{Current} \) is the ion current of species \( i \) measured by the mass spec.

![Figure 5.5](image)

**Figure 5.5** Ion current of NO\(^+\), N\(_2\)\(^+\), O\(_2\), F\(_2\)\(^+\) with plasma off. Ion current of each gas is measured separately with the flow rate of 500sccm without plasma. (a) represents molecules with negligible cracking pattern whereas F\(_2\)\(^+\) in (b) has significant portion of cracking by electron impact. Ion current data of Ar\(^+\) is used for only reference.

This method can be applied to measure the partial pressure of various chemical species that are generated in the plasma. The simplest example is the quantitative analysis of F\(_2\) discharge because there are only two species in the F\(_2\) discharge: F and F\(_2\). When F\(_2\) plasma is running in the cleaning system, the ion current of F (amu 19) and F\(_2\) (amu 38) are obtained from the mass spec. If F\(_2\) is completely dissociated into F atoms in the plasma source, F\(_2\) detected in the process chamber originates from the recombination of atomic fluorine in the cleaning system. If F\(_2\) is completely dissociated in the plasma source and F-F recombination does not occur in the system, only atomic fluorine should be detected in the mass spec. In reality, significant amount of F-F recombination takes place on the surface of the transfer tube making contribution to the \( P_{F_2} \) (partial pressure of F\(_2\)) in equation (5.14). The atomic fluorine that is detected in the mass spec \((\text{Ion}_\text{Current}_{F, \text{total}})\) stems from two sources: atomic fluorine that is cracked from F\(_2\) by electron impact in the mass spec \((\text{Ion}_\text{Current}_{F, \text{cracked from } F_2 \text{ by mass spec}})\) and atomic fluorine that is formed
in the plasma source and then does not go through the recombination in the transfer tube (Ion_Current_{F, plasma}). The latter is the target for quantitative analysis.

\[ P_{\text{chamber}} = P_F + P_{F_2} \]  
\[ \text{Ion\_Current}_{F, \text{total}} = \text{Ion\_Current}_{F, \text{cracked from F2 by mass spec}} + \text{Ion\_Current}_{F, \text{plasma}} \]  

Figure 5.6 (a) Cracking pattern of F\(_2\) (b) estimated plot of ion current of F versus P\(_F\).

Once the ion current of F and F\(_2\) are taken from the mass spec, then the partial pressure of F\(_2\) (P\(_{F2}\)) is calculated from equation (5.13) with ease. However, equation (5.13) is not applicable to calculate the partial pressure of F (P\(_F\)) because the sensitivity plot which is similar to Figure 5.5(a) is not available for F due to the unstable property of F radical. Although it is physically impossible to obtain the slope in Figure 5.5 for atomic fluorine, it is possible to calculate the slope for atomic F indirectly. P\(_F\) is obtained by rearranging equation (5.14) because the chamber pressure (P\(_{\text{chamber}}\)) and the partial pressure of F\(_2\) (P\(_{F2}\)) are already known. In addition, the ion current of the atomic fluorine (Ion_Current\(_{F, \text{plasma}}\)) that contributes to the partial pressure of F (P\(_F\)) is obtained by rearranging equation (5.15). The value of Ion_Current\(_{F, \text{cracked from F2 by mass spec}}\) is required to calculate Ion_Current\(_{F, \text{plasma}}\) in equation (5.15). The way how Ion_Current\(_{F, \text{cracked from F2 by mass spec}}\) is calculated from Ion_Current\(_{F2}\) is sequentially described in Figure 5.6(a) and its
result is shown in Figure 5.5(b). By plotting the values of $P_F$ in (5.14) and the values of \text{Ion\_Current}_{F,\text{plasma}}$ in (5.15) together, the slope of the sensitivity plot ($\text{Ion\_Current}_{F,\text{plasma}}$ vs. $P_F$) for atomic fluorine is finally determined to be 2.924 (see Figure 5.6(b)) by linear regression and data are scattered in a broad range because it is calculated from indirect method.

![Image of Figure 5.7](image)

**Figure 5.7** Partial pressure of atomic fluorine in the process chamber measured by mass spec. (a)3000 sccm $F_2$ and 4500 sccm $F_2$, (b)3000 sccm $NF_3$ and 4800 sccm $NF_3$. Original mass spec data is corrected by the cracking pattern of $F_2$. The detailed method is described in this section.

Quantitative analysis of $NF_3/N_2$ plasma is also possible using the same method as described in the previous paragraph. $F$, $F_2$ and $N_2$ are detected in the mass spec. Detection of atomic nitrogen is negligible because the recombination rate of $N$ is very fast and because the cracking from $N_2$ is infinitesimally small. Now, it is possible to calculate $P_{N_2}$ by using the slope in Figure 5.5(a), $P_{F_2}$ by the slope in Figure 5.5(b) and $P_F$ by the slope in Figure 5.6(b). Finally, bell shaped trends of partial pressure of atomic fluorine (see Figure 5.7) is obtained by using the above method and the trends are very similar to those of TEOS etching rates.
5.3 Result and Discussion: Model Prediction VS. Experimental Results

5.3.1 NF$_3$/N$_2$ Discharge

![Graphs showing partial pressure of F, F$_2$, and N$_2$ predicted by the global model and measured by mass spec at two different gas conditions (a) 3000sccm NF$_3$, (b) 3000sccm NF$_3$ + 3000sccm N$_2$.]

Figure 5.8 Partial pressure of F, F$_2$, and N$_2$ predicted by the global model and measured by mass spec at two different gas conditions (a) 3000sccm NF$_3$, (b) 3000sccm NF$_3$ + 3000sccm N$_2$.

Partial pressure of each species at the pressure range from 0.5torr to 10torr is available in Figure 5.8. Also, Figure 5.8 illustrates that global model can successfully predict the partial pressure of F, F$_2$, and N$_2$ which is measured by mass spec at the flow rate of 3000sccm NF$_3$ and
3000sccm NF$_3$ + 3000sccm N$_2$ discharge. It is notable that the partial pressure of atomic fluorine in the downstream is very low due to the high surface recombination in the transfer tube.

![Surface Recombination vs. Volume Recombination](image_url)

**Figure 5.9** Modeling Results: comparison between surface recombination term and volume recombination term in the transfer tube. Surface recombination is more important over volume recombination. However, the ratio of surface to volume is decreased as pressure is increased because volume reaction is third order of pressure whereas surface reaction is second (or first) order of pressure.

In addition, global model predicts that surface recombination term ($\int_0^l R_{\text{surface}} \times 2\pi R\,dl$, integral form of equation 4) is greater than volume recombination term ($\int_0^l R_{\text{volume}} \times \pi R^2 \,dl$, integral form of equation 5) through the operating chamber pressure (0.5torr~10torr), but the ratio between two terms ($\frac{\int_0^l R_{\text{surface}} \times 2\pi R\,dl}{\int_0^l R_{\text{volume}} \times \pi R^2 \,dl}$) decreases as process chamber increases up to 10torr, which means volume recombination becomes more important at high pressure. This is because volume recombination of atomic fluorine is a third order reaction of pressure whereas
surface recombination of atomic fluorine is a first order (or second order) reaction of pressure. In consequence, third order term becomes more important as chamber pressure is increased.

Another example to validate this model is shown in Figure 5.10 illustrating that the trend of TEOS film etching rates are similar to that of $P_F$ predicted by the global model. In the literature, it was published that etching rates of silicon dioxide film is proportional to the concentration of atomic fluorine in the gas phase[63]. In addition, this model predicts the effect of adding nitrogen in NF$_3$ discharge. The advantage of adding nitrogen in NF$_3$ over pure NF$_3$ discharge exists only at high pressure. It is probable that another reaction kinetics besides F-F recombination and N-N recombination is involved in NF$_3$+N$_2$ discharge because TEOS etching rate of 3000sccm NF$_3$ + 3000sccm N$_2$ is a little bit higher than the $P_F$ predicted by the model. However, the effect of TEOS etching rate enhancement with addition of N$_2$ is not significant.

![Figure 5.10 Effect of N$_2$ addition in NF$_3$ discharge. (a) Partial pressure of atomic fluorine predicted by global model at two gas conditions and (b) Etching rate of TEOS film at 125 °C.](image)

The reaction order of F-F recombination on the surface is determined by the global model. As explained previously, it is still controversial if the recombination of atomic fluorine on the surface is a first order reaction or a second order reaction[66]. In Figure 5.11(a), each solid line
represents the partial pressure of atomic fluorine predicted by the global modeling based upon the assumption that the reaction order of F-F recombination on the surface is a first order reaction. And Figure 5.11(b) shows the partial pressure of atomic fluorine predicted by the global modeling based upon the assumption that the reaction order of F-F recombination on the surface is a second order reaction. It is obvious that second order kinetics in the surface reaction of the global model fits the experimentally measured partial pressure of atomic fluorine. And the fitted reaction constant for F-F recombination on the surface \( k_{s,F2} \) and in the gas phase \( k_{v,F2} \) are shown in Table 5.2.

Figure 5.11 Partial pressure of atomic fluorine measured by mass spec (dot) and predicted by global model (solid). The solid line in (a) represents the modeling results based upon the assumption that F-F recombination on the surface is first order and the solid line in (b) represents the modeling results based upon the assumption that F-F recombination on the surface is second order.

5.3.2 NF₃/O₂ Discharge

In NF₃/O₂ plasma, the major molecules that are detected in mass spec are F, F₂, N₂, O₂ and NO. N and O are negligibly small because cracking of N₂ and O₂ is not significant and the recombination of nitrogen and oxygen is very fast. The partial pressure of N₂, O₂ and NO are calculated by using the slope in Figure 5.5(a), \( P_{F2} \) is calculated by the slope in Figure 5.5 (b) and \( P_F \) is by the slope in Figure 5.6(b). Finally, the partial pressure of each species in the process...
chamber using 3000sccm NF$_3$+500sccm O$_2$ discharge is shown in Figure 5.12. At high chamber pressure, the partial pressure of atomic fluorine measured by mass spec is lower than the partial pressure of atomic fluorine predicted by the global model. The error may come either from the measurement of the mass spec or from the over simplification in the kinetics incorporated in the global model.

Figure 5.12 Partial pressure of F, F$_2$, N$_2$, O$_2$ and NO predicted by global model and measured by mass spec. Gas condition is 3000sccm NF$_3$ + 500sccm O$_2$.

Figure 5.13 shows the percentage of the atomic fluorine that does not go through the recombination reaction either on the wall or in the gas phase. At low chamber pressure, for example at 1torr, around 70% of atomic fluorine remains without going through the recombination reaction. However, at high chamber, around 90% of atomic fluorine is vanished in the form of F$_2$ by recombination reaction. In addition, as O$_2$ is introduced in NF$_3$ discharge, the survival percentage becomes lower because oxygen induces F-F recombination more rapidly on
the Al surface. It will be discussed how the major modifications of the global model is made to switch the cleaning gas from NF₃/N₂ base to NF₃/O₂ base and the comparison between the modeling results and the experimental results will be introduced in the following paragraphs.

![Graph showing survival percentage of atomic fluorine](image)

**Figure 5.13** Percentage of atomic fluorine that remains active after going through the transfer tube. Survival % of atomic fluorine is calculated by the formula: \( \frac{P_F}{(P_F+2*P_{F_2})} \times 100 \). Partial pressure of F and F₂ are measured by mass spec.

The same equations are used for modeling a cleaning chamber in NF₃/O₂ discharge. Equation (5.3) is the major mole balance equation for the transfer tube and equation (5.10) is the mole balance equation for the cleaning process chamber. In NF₃/N₂ system, these two mole balance equations are based upon only atomic fluorine. However, in NF₃/O₂ system, additional balance equations for O, N and NO are required. Table 5.4 lists complete set of equations for modeling NF₃/O₂ system. Equations below are also used in the global model to calculate the partial pressure of each chemical species. Four mole balance equations are used to calculate the conversion factor of F, N, O and NO (\( X_F, X_N, X_O \) and \( X_{NO} \)) whereas the conversion factor of atomic fluorine (\( X_F \)) is the only variable in NF₃/N₂ system. In NF₃/N₂ system, the conversion factor of nitrogen was assumed to be 100% because the recombination of nitrogen is so much
faster than that of fluorine. This is also true for NF₃/O₂ discharge, but the formation of NO should be considered in NF₃/O₂ system. This is the reason why mole balance of nitrogen is included in NF₃/O₂ system. It is already verified that method of using 100% of Xₙ and method of solving mole balance of nitrogen in NF₃/N₂ led to the same result in the global modeling.

\[ n_N = n_{N,0}(1 - X_N) \]  \hspace{1cm} (5.2d)

\[ n_{N2} = 0.5n_{N,0}X_N \]  \hspace{1cm} (5.2e)

\[ n_O = n_{O,0}(1 - X_O) \]  \hspace{1cm} (5.2f)

\[ n_{O2} = 0.5n_{O,0}X_O \]  \hspace{1cm} (5.2g)

\[ n_{NO} = n_{N,0}X_{NO} \]  \hspace{1cm} (5.2h)

\[ P_i = \frac{P \times n_i}{\sum_j n_j} \quad (i, j = F, F_2, N, N_2, O, O_2 \text{ and NO}) \]  \hspace{1cm} (5.11b)

\[ \sum_j n_j = n_{F,0}(1 - 0.5X_F) + n_{N,0}(1 - 0.5X_N) + n_{O,0}(1 - 0.5X_O) + n_{N,0}X_{NO} \]  \hspace{1cm} (5.12b)
Table 5.4 Equation set of global modeling for NF₃/O₂ discharge.

<table>
<thead>
<tr>
<th>Basis</th>
<th>Transfer tube</th>
<th>Process Chamber</th>
</tr>
</thead>
</table>
| F     | \[
\frac{dX_F}{dt} = - \frac{R_{\text{surface}} \times 2 \pi R + R_{\text{volume}} \times \pi R^2}{n_{F,0}}
\] | \[
\frac{dn_F}{dt} = n_{F,1} - n_{F,2} + R_{\text{surface}} A_F + R_{\text{volume}} dV_2
\] |
| N     | \[
R_{\text{surface},N} = -k_{S_F} \times \Gamma_{N,0} - k_{S_N} \times \Gamma_{N,0} \times \Gamma_{O,0}
\] | \[
= n_{F,1} \times (X_{F,2} - X_{F,3}) + R_{\text{surface}} A_N + R_{\text{volume}} dV_2 = 0
\] |
| O     | \[
R_{\text{surface},O} = -k_{S_O} \times \Gamma_{O,0} - k_{S_NO} \times \Gamma_{N,0} \times \Gamma_{O,0}
\] | \[
= n_{F,1} \times (X_{F,3} - X_{F,4}) + R_{\text{surface}} A_O + R_{\text{volume}} dV_2 = 0
\] |
| NO    | \[
R_{\text{surface},NO} = k_{S_NO} \times \Gamma_{N,0} \times \Gamma_{O,0}
\] | \[
= n_{F,1} \times (X_{NO,1} - X_{NO,2}) + R_{\text{surface}} A_{NO} + R_{\text{volume}} dV_2 = 0
\] |

variables \(X_F, X_N, X_O\) and \(X_{NO}\)

Once four conversion factors \((X_F, X_N, X_O\) and \(X_{NO}\)) are calculated, partial pressure of each species is obtained by equation (5.11b) which is exactly the same equation as in NF₃/N₂ system.

Partial pressure information obtained by mass spec is used to fit the rate constants in Table 5.3.

Rate constants in Table 5.3 except for the F-F surface recombination rate constant \((k_{S-F_2})\) are the fitted results from the global modeling. \(k_{S-F_2}\) is modified according to the flow rate of oxygen because the surface recombination rate of atomic fluorine is increased as the flow rate of oxygen is increased in NF₃ discharge as discussed in the previous chapter. In Figure 5.14(a) is shown the partial pressure of atomic fluorine in the cleaning process chamber using different \(k_{S-F_2}\) at different flow rate of oxygen. The surface reaction constant \((k_{S-F_2})\) is multiplied by 1.2
at 150sccm of O₂ and it is multiplied by 1.4 at 500sccm of O₂. Figure 5.12 shows that the partial pressure of chemical species in the process chamber which is predicted by global model is very close to the partial pressure which is measured by mass spec. Also, in Figure 5.14, the trend of the partial pressure of atomic fluorine predicted by the global model is very similar to the trend of the etching rate of TEOS film measured at 250°C particularly at low process chamber.

![Graphs](image)

**Figure 5.14** Effect of O₂ addition in NF₃ discharge. (a) Partial pressure of atomic fluorine predicted by global model at three gas conditions and (b) Etching rate of TEOS film at 250°C.

### 5.4 Summary

Incorporating kinetics into the global modeling of PECVD chamber cleaning system successfully enables the prediction of the partial pressure of atomic fluorine in NF₃/N₂ and NF₃/O₂ discharge, which is crucial in estimating cleaning rate of TEOS film. First of all, effect of nitrogen addition in NF₃ discharge is experimentally investigated by measuring the etching rates of TEOS film and the partial pressure of neutral species. Both modeling results and experimental results make a good agreement that nitrogen addition in NF₃ has advantage at high chamber pressure. In other words, at high chamber pressure, TEOS etching rate is increased by adding
nitrogen in NF₃ plasma. In addition, it is shown that the order of F-F recombination on the surface is second order by comparing the experimental result with modeling result in NF₃/N₂ discharge. Then, the effect of oxygen in NF₃ discharge is studied. TEOS film etching rates and partial pressure of atomic fluorine in the gas phase shows that adding oxygen in NF₃ discharge increases F-F recombination. By incorporating the above kinetics information in the global model, we can successfully predict the partial pressure of neutral species in NF₃/O₂ discharge.

5.5 Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_c</td>
<td>Cleaning chamber pressure (torr)</td>
</tr>
<tr>
<td>Q</td>
<td>Volumetric flow rate (sccm)</td>
</tr>
<tr>
<td>P_i</td>
<td>Partial pressure of species i</td>
</tr>
<tr>
<td>Ion_current</td>
<td>Ion current of species i measured by the mass spec (a.u.)</td>
</tr>
<tr>
<td>Slope_i</td>
<td>Slope of the plot (Ion_current, vs. P_c) for species i by linear regression</td>
</tr>
<tr>
<td>L</td>
<td>Transfer tube length (cm)</td>
</tr>
<tr>
<td>U</td>
<td>Total mass bulk rate (cm/s)</td>
</tr>
<tr>
<td>R</td>
<td>Transfer tube diameter (cm)</td>
</tr>
<tr>
<td>A_1</td>
<td>Surface area of transfer tube (cm)</td>
</tr>
<tr>
<td>A_2</td>
<td>Surface area of cleaning reactor (cm)</td>
</tr>
<tr>
<td>V_1</td>
<td>Volume of transfer tube (cm³)</td>
</tr>
<tr>
<td>V_2</td>
<td>Volume of cleaning reactor (cm³)</td>
</tr>
<tr>
<td>dℓ</td>
<td>Differential form of tube length</td>
</tr>
<tr>
<td>dA_1</td>
<td>Differential form of tube area</td>
</tr>
<tr>
<td>dV_1</td>
<td>Differential form of tube area</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>$R_{\text{surface}}$</td>
<td>Surface recombination rate</td>
</tr>
<tr>
<td>$R_{\text{volume}}$</td>
<td>Volume recombination rate</td>
</tr>
<tr>
<td>$n_{F,0}$</td>
<td>Initial molar flow rate of F (mol/s)</td>
</tr>
<tr>
<td>$n_{N,0}$</td>
<td>Initial molar flow rate of N (mol/s)</td>
</tr>
<tr>
<td>$n_{O,0}$</td>
<td>Initial molar flow rate of O (mol/s)</td>
</tr>
<tr>
<td>$n_F$</td>
<td>Molar flow rate of F (mol/s)</td>
</tr>
<tr>
<td>$n_N$</td>
<td>Molar flow rate of N ($n_N = n_{N,0}(1 - X_N)$, mol/s)</td>
</tr>
<tr>
<td>$n_O$</td>
<td>Molar flow rate of O ($n_O = n_{O,0}(1 - X_O)$, mol/s)</td>
</tr>
<tr>
<td>$n_{NO}$</td>
<td>Molar flow rate of O ($n_{NO} = n_{N,0}X_{NO}$, mol/s)</td>
</tr>
<tr>
<td>$n_{F_2}$</td>
<td>Molar flow rate of F$_2$ (mol/s)</td>
</tr>
<tr>
<td>$n_{N_2}$</td>
<td>Molar flow rate of N$_2$ (mol/s)</td>
</tr>
<tr>
<td>$X_F$</td>
<td>Conversion factor of F into F$_2$</td>
</tr>
<tr>
<td>$X_{F,1}$</td>
<td>Conversion factor of F into F$_2$ at the exit of transfer tube</td>
</tr>
<tr>
<td>$X_{F,2}$</td>
<td>Conversion factor of F into F$_2$ in the outlet of cleaning chamber</td>
</tr>
<tr>
<td>$X_N$</td>
<td>Conversion factor of N into N$_2$</td>
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<tr>
<td>$X_O$</td>
<td>Conversion factor of O into O$_2$</td>
</tr>
<tr>
<td>$X_{NO}$</td>
<td>Conversion factor of N into NO</td>
</tr>
<tr>
<td>$N_F$</td>
<td>Molar density (mol/cm$^3$)</td>
</tr>
<tr>
<td>$R_{\text{ideal \ gas}}$</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>$\Gamma_{F, \text{inc}}$</td>
<td>Incident flux of atomic fluorine (mol/cm$^2$/s)</td>
</tr>
<tr>
<td>$\Gamma_{N, \text{inc}}$</td>
<td>Incident flux of atomic nitrogen (mol/cm$^2$/s)</td>
</tr>
<tr>
<td>$\Gamma_{O, \text{inc}}$</td>
<td>Incident flux of atomic oxygen (mol/cm$^2$/s)</td>
</tr>
</tbody>
</table>
\( c \) \hspace{1cm} \text{Thermal velocity of atoms in the gas phase (cm/s)}

\( Pe \) \hspace{1cm} \text{Peclet number}

\( D \) \hspace{1cm} \text{Diffusion coefficient (cm}^2\text{/s)}
Chapter 6 Summary

6.1 Conclusions

The scope of this research work is basically to characterize the Transformer Coupled Toroidal Plasma (TCTP); to understand gas phase reactions and surface reactions by neutrals in the cleaning chamber by analyzing the concentration of neutrals in downstream cleaning process chamber; and to make a global modeling that predicts the partial pressure of active species in the cleaning chamber. The final goal is to set-up an optimal cleaning process using the results from the experiment and the global model.

The first object is to characterize the TCTP. Previously, Bai[30] worked on characterizing the TCTP source. In addition to his work, power consumption by plasma is measured with C$_2$F$_6$/O$_2$ condition and with NF$_3$ condition. The experimental apparatus is discussed in Chapter 2 and the factors that control the power consumption is discussed in detail in Chapter 3.

The second object is to understand gas phase reactions and surface reactions by neutrals in the cleaning chamber. The concentration of neutrals in downstream cleaning process chamber is successfully measured by line-of-sight mass spectrometer and FT-IR is measured in the exhaust line. The enhancement of nitride etching rate by different additives is discussed in Chapter 4.

The last object is to make a global model that enables the prediction of the partial pressure of neutrals in downstream and it is discussed in Chapter 5. Bai[37] measured the neutral gas temperature, the electron temperature and the electron density. Temperature of neutrals which is required as one of the model input is taken by his results. This model consists of two parts: PFR (Plug Flow Reactor) and CSTR (Continuously Stirred Tank Reactor). The validation of this model is accomplished by comparing the modeling results with the partial pressure of neutrals.
measured by mass spectrometer. Beginning with NF3 system, the effect of adding N2 or O2 in NF3 is illustrated in Chapter 5. The final goal of the global modeling is to predict the partial pressure of neutrals in C2F6/O2/N2/NF3 system.

In Chapter 3, the power consumed by plasma is measured as one approach to the characterization of plasma. MKS Astex plasma source has a very high power density. Compared to a typical industrial plasma source, the power density of the TCTP source is two orders of magnitude higher. The extremely high power density makes the plasma source very unique and its parameters very different from other plasma sources.

In section 3.1, we discussed that there are several factors that affect the plasma power consumption. One factor is the flow rate of inlet gas and the elevated pressure due to the high flow rate of inlet gas increases the power consumption. Experimentally it is observed that the plasma power is linearly dependent upon the plasma source pressure, not upon the process chamber pressure. Another factor of the power control is the resistivity of gases. It means each gas has different dissociation energy. For example, N-F bonding in NF3 gas is different from C-F bonding in C2F6. Experimental result shows that C2F6 + O2 gas requires more power than NF3 gas to dissociate in the plasma due to the different resistivity and that nitrogen is very useful to increase the plasma power because it is cheaper and does not affect the cleaning process significantly.

Adding nitrogen helps to increase the cleaning rate of TEOS film in C2F6 + O2 or CF4 + O2 gas[53]. Enhancement of TEOS etching rate by adding nitrogen in perfluorocarbon gas has been reported[53] and the reason why nitrogen enhances TEOS etching rate is because nitrogen selectively blocks the active site on the surface for producing COF2 which is the key product of the loss of atomic F. Bai[53] showed by FT-IR measurements that the concentration of COF2 is
decreased and the concentration of CO$_2$ is increased by adding nitrogen in CF$_4$/O$_2$ discharge to prove the selective blocking of COF$_2$ active site by nitrogen. However, as the flow rate increases above a certain limit, TEOS etching rate gradually decreases because atomic fluorine is diluted by nitrogen. Instead, power consumption continuously increases as nitrogen is added in C$_2$F$_6$/O$_2$ discharge as expected.

In section 3.2, a flow restricting device (orifice) is introduced to increase the power consumption effectively. Although nitrogen is effective in increasing plasma power consumption, there is a certain limitation because too much nitrogen addition in plasma eventually dilutes the cleaning system, which leads to lowering the overall cleaning rate. Moreover, the capacity of the dry pump also limits the total flow rate of cleaning gas. Because the ions, neutrals and electrons coming out of the plasma source are very hot, water circulation is required inside the orifice to prevent melting down the orifice which is made of aluminum.

It is observed that power consumption and plasma source pressure are constant regardless of the process chamber pressure. It is because the mixture of gas coming out of the plasma source becomes choked flow after flowing through the small hole of the orifice. Choked flow is a limiting condition which occurs when the mass flux will not increase with a further decrease in the downstream pressure environment[55].

With an orifice in the cleaning system, TEOS etching rate is decreased compared to the etching rate without the orifice in the entire system. It is because the high pressure in the plasma source caused by flow restriction decreases the available atomic fluorine due to the higher F-F recombination. The degree of decreasing TEOS etching rate is different according to the gas condition is because gases with different composition have different recombination properties.
Also, different orifice size affects TEOS etching rate. Attaching a smaller orifice lowers TEOS etching rate and enhances plasma power and plasma source pressure. It is because smaller orifice plays a role as a flow-restricting device that makes the plasma source pressure higher, which leads to higher F-F recombination in the plasma source. Of course, TEOS etching rate is optimal when the flow-restricting device is not placed in the cleaning system. For certain circumstances, it is necessary to control plasma power consumption and installing an orifice in the cleaning system is a good alternative to increasing nitrogen flow rate for controlling plasma power.

Finally, different location of an orifice leads to different TEOS etching rate and different plasma source pressure. If the orifice is placed near to the downstream chamber, plasma source pressure becomes lower and etching rate is decreased. The reason why the plasma source pressure becomes lower when the orifice is placed near to the downstream chamber is because the total volume that is restricted by the orifice becomes larger, hence the plasma source pressure becomes lower by the ideal gas law which explains that pressure is proportional to the reciprocal of volume at constant temperature. And the reason why TEOS etching rate becomes lower when the orifice is placed near to the downstream chamber is because the larger surface area of the inner transfer tube is exposed to the relatively high pressure, which causes higher F-F recombination. If the F-F recombination reaction occurs actively, the available atomic fluorine that crucially affects TEOS etching rate is diminished, therefore TEOS etching rate is decreased when the orifice is placed near to the downstream chamber.

The main topic of Chapter 4 is the effect of nitric oxide as a silicon nitride etching enhancement factor. In section 4.1, it is shown that only 4.5% of additives (O₂, CO and CO₂) into NF₃ discharge doubles nitride etching rate and this enhancement of etching rate occurs regardless
of additive types. The enhancement results from the production of NO in the discharge of NF₃ gas mixture. As the amount of oxygen containing additive increases, the amount of NO increases. However, atomic fluorine decreases as the amount of oxygen containing additive increases because the additive dilutes NF₃ plasma. At low process chamber pressure, the effect of NO is offset by the dilution effect of atomic fluorine, which maintains nitride etching rate constant up to 25% addition of O₂, CO₂ and CO. C/O ratio is also important because this ratio determines the amount of the produced NO. Low C/O ratio produces more NO, which explains why nitride etching rate with addition of oxygen is higher than the one with addition of CO and CO₂ at low pressure. At high pressure, addition of oxygen enhances the recombination of atomic fluorine and 25% of O₂ in NF₃ discharge decreases 54% of atomic fluorine. Therefore, the effect of a decrease in atomic fluorine is remarkably higher than the effect of increase in the concentration of NO by adding O₂ at high pressure, which leads to a decrease of nitride etching rate at 5torr.

Additive with higher C/O ratio such as CO, however, decreases the recombination of atomic fluorine because only 39% of atomic fluorine decreases with 25% addition of CO. This explains the reason why additive with a high C/O ratio brings higher nitride etching rate at 5torr. One possible explanation why additives with high C/O ratio brings high etching rate at high pressure is that higher carbon source consumes more oxygen which will contribute to a higher recombination rate of atomic fluorine.

In section 4.2, the nitride etching rates of NF₃ plasma and NF₃/C₂F₆/O₂ plasma are compared and it is shown that NF₃/C₂F₆/O₂ plasma brings better performance in nitride etching rate over NF₃ plasma. The main reason why the nitride etching rate of NF₃/C₂F₆/O₂ plasma is higher than that of NF₃ plasma is believed to be because nitric oxide is formed in the gas phase and the nitric oxide reacts with the nitrogen atom on the silicon nitride surface producing N₂O or N₂, while
nitrogen is substituted by oxygen on the surface by the reaction. Removing nitrogen atom from silicon nitride substrate is assumed to be the rate-limiting step in the fluorine base etching of silicon nitride film. In summary, the nitric oxide makes it easier to remove the nitrogen atom from silicon nitride surface, which is the rate-limiting step for nitride etching with F base gas, therefore enhancing silicon nitride etching rate. The advantage of using NF$_3$/C$_2$F$_6$/O$_2$ gas mixture is maximized at lower temperature and at higher process chamber. In fact, within the cleaning chamber, spots of lower temperature are harder to clean, which means that the overall cleaning rate is determined by a “cool” place instead of a “hot” place. Because the NF$_3$/C$_2$F$_6$/O$_2$ blends are particularly good for the cold spot, they can contribute to lowering the processing cost very effectively by increasing the cleaning rate in the cold place which is rate-limiting. Finally, mass spec is used to confirm the existence of nitric oxide, higher F-F recombination with higher flow rate of O$_2$ in NF$_3$ plasma and the role of carbon as an inhibitor of F-F recombination in NF$_3$/C$_2$F$_6$/O$_2$ plasma. This chapter will be very useful in semiconductor production industry because this new gas composition can save both cleaning cost and cleaning time tremendously.

In Chapter 5, it is shown that incorporating kinetics into the global modeling of PECVD chamber cleaning system successfully enables the prediction of the partial pressure of atomic fluorine in NF$_3$/N$_2$ and NF$_3$/O$_2$ discharge, which is crucial in estimating cleaning rate of TEOS film. First of all, effect of nitrogen addition in NF$_3$ discharge is experimentally investigated by measuring the etching rates of TEOS film and the partial pressure of neutral species. Both modeling results and experimental results make a good agreement that the addition of nitrogen in NF$_3$ has advantage at high chamber pressure. In other words, at high chamber pressure, TEOS etching rate is increased by adding nitrogen in NF$_3$ plasma. Then, the effect of oxygen in NF$_3$ discharge is studied. TEOS film etching rates and partial pressure of atomic fluorine in the gas
phase shows that adding oxygen in NF$_3$ discharge increases F-F recombination, therefore lowering TEOS etching rate. By incorporating the above kinetics information in the global model, the partial pressure of neutral species in NF$_3$/O$_2$ discharge is successfully predicted.

### 6.2 Suggestions for Future Work

Modeling the cleaning system of NF$_3$/C$_2$F$_6$/O$_2$/N$_2$ discharge remains as a future work. Incorporating the kinetics of NF$_3$/C$_2$F$_6$/O$_2$/N$_2$ discharge is very complicated because the reaction mechanism of this plasma has not clearly discovered. One starting point of designing a global modeling for NF$_3$/C$_2$F$_6$/O$_2$/N$_2$ cleaning system is to set-up a lumped set of chemical equations for C$_2$F$_6$/O$_2$ discharge based upon literature search[70-76] and the possible reactions are listed in Table 5.1. The basic assumption of this lumped set of reaction is that CF$_2$ is dominant among CF$_x$ radicals. If the global modeling of C$_2$F$_6$/O$_2$ discharge is successfully accomplished, the next step is to set up a modified lumped set of reactions for C$_2$F$_6$/O$_2$/N$_2$ cleaning system. Adding N$_2$ will increase the total number of reactions, but the basic frame of the lumped reaction set will not change.

**Table 6.1 A possible pathway for C$_2$F$_6$/O$_2$ cleaning system.**

<table>
<thead>
<tr>
<th>No;</th>
<th>Surface Reaction</th>
<th>Rate Expression</th>
<th>Gas Phase Reaction</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>F(s) + F(s) → F$_2$(g)</td>
<td>$k_{8.1} \cdot \Gamma_{\text{F,inc}}^2$</td>
<td>F(g) + F(g) + M → F$_2$(g)</td>
<td>$k_{7.1} \cdot (P_F)^2P$</td>
</tr>
<tr>
<td>(2)</td>
<td>O(s) + O(s) → O$_2$(g)</td>
<td>$k_{8.2} \cdot \Gamma_{\text{O,inc}}$</td>
<td>O(g) + O(g) + M → O$_2$(g)</td>
<td>$k_{7.2} \cdot (P_O)^2P$</td>
</tr>
<tr>
<td>(3)</td>
<td>C(s) + 2F(s) → CF$_2$(g)</td>
<td>$k_{8.3} \cdot \Gamma_{\text{C,inc}} \cdot \Gamma_{\text{F,inc}}$</td>
<td>C(g) + 2F(g) → CF$_2$(g)</td>
<td>$k_{7.3} \cdot (P_C)^2F^2$</td>
</tr>
<tr>
<td>(4)</td>
<td>CF$_2$(s) + O(s) → COF(g) + F(g)</td>
<td>$k_{8.4} \cdot \Gamma_{\text{CF2,inc}} \cdot \Gamma_{\text{O,inc}}$</td>
<td>CF$_2$(g) + O(g) → COF(g) + F(g)</td>
<td>$k_{7.4} \cdot P_{\text{CF2}}P_O$</td>
</tr>
<tr>
<td>(5)</td>
<td>CF$_2$(s) + O(s) → CO(g) + 2F(g)</td>
<td>$k_{8.5} \cdot \Gamma_{\text{CF2,inc}} \cdot \Gamma_{\text{O,inc}}$</td>
<td>CF$_2$(g) + O(g) → CO(g) + 2F(g)</td>
<td>$k_{7.5} \cdot P_{\text{CF2}}P_O$</td>
</tr>
<tr>
<td>(6)</td>
<td>CF$_2$(s) + 2F(s) → CF$_4$(g)</td>
<td>$k_{8.6} \cdot \Gamma_{\text{CF2,inc}} \cdot \Gamma_{\text{F,inc}}$</td>
<td>CF$_2$(g) + 2F(g) → CF$_4$(g)</td>
<td>$k_{7.6} \cdot P_{\text{CF2}}F^2$</td>
</tr>
<tr>
<td>(7)</td>
<td>COF(s) + O(s) → CO$_2$(g) + F(g)</td>
<td>$k_{8.7} \cdot \Gamma_{\text{COF,inc}} \cdot \Gamma_{\text{O,inc}}$</td>
<td>COF(g) + O(g) → CO$_2$(g) + F(g)</td>
<td>$k_{7.7} \cdot P_{\text{COF}}P_O$</td>
</tr>
<tr>
<td>(8)</td>
<td>COF(s) + F(s) → COF$_2$(g)</td>
<td>$k_{8.8} \cdot \Gamma_{\text{COF,inc}} \cdot \Gamma_{\text{F,inc}}$</td>
<td>COF(g) + F(g) → COF$_2$(g)</td>
<td>$k_{7.8} \cdot P_{\text{COF}}F$</td>
</tr>
</tbody>
</table>

The effect of nitrogen in C$_2$F$_6$/O$_2$ discharge should be incorporated in the kinetics because experimental work shows that adding nitrogen in C$_2$F$_6$/O$_2$ discharge increases TEOS etching rate.
tremendously. It is because nitrogen selectively blocks the active site on the surface for producing COF₂ which is the key product of the loss of atomic F. FT-IR measurements reveals that the concentration of COF₂ is decreased and the concentration of CO₂ is increased by adding nitrogen in CF₄/O₂ discharge to prove the selective blocking of COF₂ active site by nitrogen. This kinetic mechanism should be incorporated in the global modeling of C₂F₆/O₂/N₂ discharge so that we can predict the partial pressure of atomic fluorine in the cleaning system.

The advantage of this model exists in the fact that surface reactions and gas phase reactions are identical and hence it is convenient to compare the relative importance of surface reaction and gas phase reaction. In addition, by comparing the reaction (7) and (8) of Table 6.1, it is easily incorporated in the global modeling that nitrogen selectively blocks the active site on the surface for producing COF₂ which is the key product of the loss of atomic F. Validation of the model can be done by comparing the predicted partial pressure of each species in the cleaning system to the experimental results. However, the drawback of this model is that the mechanism for this model was not proven by experiment although most of the reactions are taken from the literature[70-76]. And it is also possible to miss some of the important insights due to the oversimplification of the complex chemical mechanism in the modeling.
Reference


[46] ASTEX, ASTEX is Applied Science and Technology which is a division of MKS Instruments.


Appendix A. Design Drawings
O-Ring groove for standard size 2.048 with I.D. 4.739, O.D. 4.828 and depth 0.054.

Twelve DIA 0.43" Clearance Holes on Bolt Circle of 10.24".

Eight DIA 0.265" Clearance Holes on Bolt Circle of 4".

ISO LF NW200 Flange With Bolt Style

D (1.5:1)

O-Ring Groove Fillet R 0.005

Fillet Radius R 0.050

D 0.630

0.090

0.500

MIT Sawin Group

Bottom Flange

ANODIZED 6061 T6 ALUMINUM
Six 3/8 Blind Clearance holes with depth 1.55" on bolts circle of 2".

Six 10/32 blind tapped holes with depth 0.25" on bolts circle of 2".

Eight 1/4-20 blind tapped holes with depth 3/4" on bolts circle of 4".

O-Ring Groove for standard size 2-048 with I.D. 4.739, O.D. 4.828 and depth 0.054.

One 1/16" holes with depth 1".

1/4-20 blind tapped holes with depth 3/4" on bolts circle of 4".

1/16" holes with depth 1".
Six 0.25" clearance holes on bolts circle of DIA 2", and set 60 degrees from each other.

Six 0.2" clearance holes on bolts circle of DIA 2".

Stainless Steel

Heat Cover
Twelve 0.43" Clearance Holes on a bolt circle of DIA 10.24".

Top, LF NW200, bolt style flange

Bottom, KF NW40 Flange
Three KF NW40 Flange, 45 Degree to Horizon, 90 Degree between each others.

Four KF NW40 Flange, 90 Degree between each others.

Two KF NW40 Flange, 180 Degree to each others.

Twelve Dia 0.43" clearance Holes on a bolt circle of 10.24"

KF NW80 Flange

LF NW200 Bolt Style Flange

Main Chamber
Back View

MIT Sawin Group

ALUMINUM

6061 T6

ANODEED

0.50

1.50

2.00

7.55

(6.85)

11.22

8.00

9.26

143
Three NW40 flanges with 45 degree to horizontal and 90 degree to each other.

Twelve DIA 0.43" clearance holes

Four KF NW40 flanges with 90 degree to each other.

Three NW40 flanges with 45 degree to horizontal and 90 degree to each other.

Twelve DIA 0.43" clearance holes

Two KF NW40 flanges with 180 degree to each other.

Support rods

Twelve DIA 0.43" clearance holes

LF NW200 flanges

Flange with O-ring groove with welded hinged viewport door. O-ring groove is not specified and hence decided by manufacturer.

MIT Sawin Group

Main Chamber

Front View
Twelve DIA 0.43" Clearance Holes on a bolt circle of 10.24".
Outer tubing, O.D. 3.5", L.D. 3".
Inner tubing, O.D. 2.5", L.D. 2.37",
McMaster # 89965K871"
Outer Tube: OD 1", ID 0.93", McMaster #89965K15
Inner Tube: OD 0.75", ID 0.62", McMaster #89965K641

NW 63 Flange
Six 6-32 tapped holes on a bolt circle of Dia 4.25” with depth 0.2”

Three 1/8” clearance hole on bolt circle of dia 5.3”

\( \phi 0.125 \)

\( \phi 4.500 \)

\( \phi 4.000 \)

\( (0.875) \)

\( (5.500) \)

\( 0.125 \)

SHOWER HEAD -- PART 1

Quantity: 1

MATERIAL: 6061 T6 ALUMINUM
UNIT: INCH
TOLERANCE: 0.01”

MIT PLASMA PROCESSING GROUP
BO BAI, 617-253-6586
Holes on a 5" 0.125 are of size: 1/8"

Six 6-32 Clearance Holes on a bolt circle of Dia 4.25"

All holes are of the same size: 1/8"

SHOWER HEAD -- PART 2

Quantity: 1

MATERIAL: 6061 T6 ALUMINUM
UNIT: INCH
TOLERANCE: 0.01"

MIT PLASMA PROCESSING GROUP
BO BAL 617-253-6586
Orifice in Mass Spec

Material: Anodized 6061 T6 Aluminum
Unit: inch
Tolerance: 0.01 inch
Orifice between Transfer Tube and Plasma Source

Material: Anodized 6061 T6 Aluminum
Unit: inch
Tolerance: 0.01 inch
Appendix B. Matlab Code for Global Modeling (NF$_3$/N$_2$ System)

function [t, X] = PFRCSRTR48NF3()

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% PFR TERM %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

global radius constant constant2 Q0_NF3 Q1_N2 Q1_F Q1_F2 n1_N2 n1_F n1_F2 x1_N2 x1_F x1_F2 T R k_boltzmann c k_volume Area_1 Volume_1 Pc Ps P_F N_F I;

global Area_2 Volume_2 X1;

Area_2 = (372.3412)*2.54^2; % Surface area of Process chamber [Unit = cm$^2$]
Volume_2 = (416.1599)*2.54^3; % Volume of Process chamber [Unit= cm$^3$]

Pc = 0.5:0.1:10;
Ps = 0.0000624*Pc.^5 - 0.0007777*Pc.^4 - 0.0080181*Pc.^3 + 0.1865423*Pc.^2 - 0.2170354*Pc + 3.9698857;

constant = 0.67;
constant2 = 0.5;

Q0_NF3 = 4.8; % volumetric flow rate of inlet NF3 [UNIT : liter/min]
Q1_N2 = 0.5*Q0_NF3; % volumetric flow rate of outlet N2 [UNIT : liter/min]
Q1_F = 3*Q0_NF3; % volumetric flow rate of outlet F [UNIT : liter/min]
Q1_F2 = 0*Q0_NF3; % volumetric flow rate of outlet F2 [UNIT : liter/min]

n1_N2 = Q1_N2/22.4/60; % molar flow rate of outlet N2 [UNIT : mol/sec]
n1_F = Q1_F/22.4/60; % molar flow rate of outlet F [UNIT : mol/sec]
n1_F2 = Q1_F2/22.4/60; % molar flow rate of outlet F2 [UNIT : mol/sec]

x1_N2 = Q1_N2/(Q1_N2+Q1_F+Q1_F2); %mole fraction of N2 [Unit : N/A]
x1_F = Q1_F/(Q1_N2+Q1_F+Q1_F2); %mole fraction of F [Unit : N/A]
x1_F2 = Q1_F2/(Q1_N2+Q1_F+Q1_F2); %mole fraction of F2 [Unit : N/A]

radius = 1.25*2.54; % inner radius of transfer tube [cm]
T = 300; % Temperature[UNIT : K]
R = 62.3637*10^3; % gas constant [UNIT : cm$^3$. Torr. K$^{-1}$. mol$^{-1}$]
k_boltzmann = 1.38065*10^-23; % boltzmann constant [Unit : m2 kg s$^{-2}$ K$^{-1}$]
c = sqrt(3*k_boltzmann*T/(18.9984*10^-3/6.02/10^23))*100; %Velocity of atomic fluorine gas [Unit : cm s$^{-1}$]
k_volume = 1.6*10^16/T; %[UNIT : cm$^6$/mol$^2$/s]
X00 = zeros(1, length(Pc));
X0 = [X00 Ps X00 X00];
1=35*2.54; %You need to modify 35 to change the length of the tube (35 inch long)
[t, X] = ode45(@(x, function,[0 1], X0)
X1=X(length(t), 1:length(Pc)); %Conversion at tube terminal
X5=X(length(t), 2*length(Pc)+1:3*length(Pc)); %integration of recombination by surface
X6=X(length(t), 3*length(Pc)+1:4*length(Pc)); %integration of recombination by volume
for j=1:length(t)
Pc_column(j,:)=Pc;
end

P_F =Pc_column(length(t,:))*n1_F.*(1-X)./(n1_F*(1-X1/2)+n1_N2); %Partial Pressure of atomic fluorine [UNIT : torr]
P_F2=Pc_column(length(t,:))*n1_F*0.5.*X1./(n1_F*(1-X1/2)+n1_N2);
P_N2=Pc_column(length(t,:)-P_F-P_F2;

X2=zeros(length(Pc));
options = optimset('Display','off); % Turn off Display
X2=fsolve(@(zero_function, X00, options);
P2_F =Pc*n1_F.*(1-X2)./(n1_F*(1-X2/2)+n1_N2); %Partial Pressure of atomic fluorine [UNIT : torr]
P2_F2=Pc*n1_F*0.5.*X2./(n1_F*(1-X2/2)+n1_N2);
P2_N2=Pc-P2_F-P2_F2;

expt=[9.326 0.416128497 9.284 0.236162563 9.282 0.487404427
8.055 0.501662522 8 0.301921649 8 0.595663689
7 0.578181188 7 0.453170007 7 0.775587108
6 0.689416481 6 0.55099638 6.062 0.827403602
5 0.78187593 5 0.718256006 5.015 0.886504611
4.034 0.83580891 4.049 0.827399127 4.044 0.992267859
3 0.846960374 3.02 0.91416496 3.019 1.03725291
2 0.723893682 2 0.860437541 2 0.89636248
1 0.484384763 1 0.617442414 1.02 0.586559945
0.832 0.411907232 0.654 0.456104641 0.935 0.563740727
0 0 0 0 0
];

figure;
plot(expt(:,1), expt(:,2), 'o', expt(:,3), expt(:,4), 'x', expt(:,5), expt(:,6), '.', Pc, P2_F, 'r')
ylim([0 1.5]);
xlabel('Chamber Pressure, Pc (torr)');
ylabel('Partial Pressure of Each Species (torr) at Process Chamber Outlet');
legend('Experimental P_F (3slm NF3+3slm N2)','Experimental P_F (3slm NF3)','Experimental P_F (4.8slm NF3)','P_F from Modeling(4.8slm NF3)');

return

function dX=x_function(t, X)
global radius constant constant2 Q0_NF3 Q1_N2 Q1_F Q1_F2 n1_N2 n1_F n1_F2 x1_N2 x1_F x1_F2 T R k_boltzmann c k_volume Area_1 Volume_1 Pc Ps P_F N_F l;

for u=1:length(Pc)
    P_F(u) = n1_F*(1-X(u))*X(u+length(Pc))/(nl_F*(1-X(u)/2)+nl_N2); % Partial Pressure of atomic fluorine [UNIT : torr]
    N_F(u) = P_F(u)/4/R/T*c; % Rate of impingement of atomic fluorine N_F = n*c/4=n/4*sqrt(3kT/m)=P/4RT*sqrt(3kT/m) [UNIT : mol cm-2 s-1]

    f(u)=constant*N_F(u).^2*2*pi*radius + constant2*X(u+length(Pc))*k_volume*P_F(u)^2/(R*T)^3*pi*radius^2; % 2nd
    % f(u)=constant*N_F(u)*2*pi*radius + constant2*X(u+length(Pc))*k_volume*P_F(u)^2/(R*T)^3*pi*radius^2; % 1st
    dX(u)=f(u)/nl_F*l;
end

for q=1:length(Pc)
    dX(length(Pc)+q)=(-Ps(q)+Pc(q)); % dP/dl
end

for h=1:length(Pc)
    dX(2*length(Pc)+h) = constant*N_F(h)*2*pi*radius*l;
end

for w=1:length(Pc)
    dX(3*length(Pc)+w)=
    constant2*X(w+length(Pc))^2*k_volume*P_F(w)^2/(R*T)^3*pi*radius^2*l; % 2nd
    % dX(3*length(Pc)+w)=
    constant2*X(w+length(Pc))^2*k_volume*P_F(w)^2/(R*T)^3*pi*radius^2*l; % 1st
end

dX=dX';
function f=zerofunction(X2)

global constant constant2 T R k_boltzmann c k_volume Area_2 Volume_2 Pc P_F P_F2 P_N2 
N_F n1_F n1_N2;
global Area_2 Volume_2 X1;

P2_F = n1_F*(1-X2).*Pc./(n1_F*(1-X2/2)+n1_N2);  %Partial Pressure of atomic fluorine 
[UNIT : torr]
N2_F=P2_F/4/R/T*c;  %Rate of impingement of atomic fluorine N_F =
n*c/4=n/4*sqrt(3kT/m)=P/4RT*sqrt(3kT/m) [UNIT : mol cm-2 s-1]

f=n1_F*(1-X1)- n1_F*(1-X2) - constant*N2_F.^2*Area_2 -
constant2*Pc.*k_volume.*P2_F.^2/(R*T)^3*Volume_2; %2nd
%f=n1_F*(1-X1)- n1_F*(1-X2) - constant*N2_F*Area_2 -
constant2*Pc.*k_volume.*P2_F.^2/(R*T)^3*Volume_2; 1st

return