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Trifluoroiodomethane as an environmentally friendly gas for water patterning by plasma etching process

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ABSTRACT

TRIFLUOROIODOMETHANE
AS AN ENVIRONMENTALLY FRIENDLY GAS
FOR WAFER PATTERNING BY PLASMA ETCHING PROCESS

by
Krit Aryusook

Trifluoroiodomethane (CF_3I), a non-global warming gas, has been investigated with study as a substitute for typical CFC etchants, such as CF_4 and C_2F_6, used in wafer pattering technology. This investigation was carried out by exposing dielectric films of silicon oxide (SiO_2) and silicon nitride (Si_3N_4) in CF_3I and C_2F_6/O_2 (used as a reference) plasma environments. The etch rate of these films was ascertained as function of applied rf power, etchant gas flow rate, reaction chamber operating pressure, and O_2 to CF_3I ratio.

Upon increasing power, the etch rates of SiO_2 and Si_3N_4 by both CF_3I and C_2F_6/O_2 were increased. The study of flow rate showed various results depending on types of etchants and dielectric film materials. According to the processing conditions, there were two limits in etching with CF_3I. First, at the pressure higher than 50 mTorr, etching of Si_3N_4 can produce polymer film on sample surface. Secondly, at O_2/CF_3I ratio higher than 0.17, etching of both dielectric films can result in generating reddish particles all over the sample and the reaction chamber side wall.

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FOR WAFER PATTERNING BY PLASMA ETCHING PROCESS

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This thesis is dedicated to
my parents

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CHAPTER 1

INTRODUCTION

1.1 Global Warming Concerns

Perfluorinated compounds (PFCs) are widely used for wafer patterning in the microelectronics industry. However, there are rising concerns regarding the environmental safety of these compounds prompting both chemical suppliers and chip manufacturers to examine alternate chemistries. These concerns stem from the fact that, after being released in the air, PFCs have extremely long atmospheric lifetimes. They also absorb infrared radiation in a region of the spectrum where the earth's atmosphere is transparent. As a result, these compounds are suspected of contributing of the atmosphere's green house effect which, in turn, causes the global warming phenomenon [1].

Recently, iodofluorocarbon such as CF_3I and C_2F_5I have been suggested as promising replacements for PFCs since their short lifetimes greatly limit their transport to the stratosphere. In the case of CF_3I, the steady state ozone depletion potential (ODP) for surface releases was determined to be less than 0.0008 and more likely to be below 0.0001. Furthermore, measured infrared absorption data combined with the known lifetime of this specie revealed that the 20-year global warming potential (GWP) of this gas, relative to CFC-11, would be less than 1×10^{-3} and extremely small compared to CO_2 (less than 5) [2].

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1.2 Objective of Study

The studies based on these promising reports are established to develop a wafer patterning technology using non-global warming gas as a substitute for typical etchant CFC's such as CF_4, C_2F_6, SF_6, and CHF_3. An Applied Materials AMP 3300 IIA parallel plate plasma enhanced CVD batch reactor was utilized for the wafer patterning studies. The use of CF_3I was investigated as a C_2F_6/O_2 substitute etchant for wafer patterning. Samples with dielectric films of silicon oxide (SiO_2) and of silicon nitride (Si_3N_4) was sequentially exposed to both CF_3I and C_2F_6/O_2 plasma environments under equivalent processing conditions. The etch rate of these dielectric films was ascertained as a function of applied RF power, total pressure, flow rate, and etchant composition ratio of O_2/CF_3I. Changes in thickness was determined by Nanospec interferometry for film deposited directly on silicon. The generated data base will provide the optimal condition for wafer patterning with CF_3I and assess the relative etching effectiveness of this non-global warming gas with respect to C_2F_6/O_2.

1.3 Wet Etching

Wet etching is purely chemical process that can have serious drawbacks: a lack of anisotrophy, poor process control, and excessive particle contamination. However, wet etching can be highly selective and often does not damage the substrate. As a result, while the process is much less popular than it once was, it continues to be used for wide range of "noncritical" tasks.

Since the reactive species is normally present in the etchant solution, wet chemical etching consists of three processes: movement of the etchant species to the surface of the wafer, a chemical reaction with the exposed film that produces soluble byproducts, and movement of the reaction products away from the substrate of the wafer. Since all three steps must occur, the slowest one, called the rate limiting step, determines the etch rate. Since it is generally desirable to have a large, uniform, well controlled etch rate, the wet etch solution is often agitated in some manner to assist in the movement of etchant to the surface and the removal of the etch product. Some etch wet process use a continuous acid spray to ensure a fresh supply of etchant.

For most wet etch processes, the film to be etched is not directly soluble in the etchant solution. It is usually necessary to change the material to be etched from a solid to a liquid or a gas. If the etching process produces a gas. this gas can form bubbles that can prevent the movement of fresh etchant to the surface. This is an extremely serious problem since the occurrence of the bubbles cannot be predicted. The problem is most pronounced near pattern edges. In addition to assisting the movement of fresh etchant chemicals to the surface of the wafer, agitation in the wet chemical bath will also reduce the ability of the bubbles to adhere to the wafer. Even in the absences of bubbles, however, small geometry features may etch more slowly, due to the difficulty in removing all of the etch products. This phenomenon has been shown to be related to microscopic bubbles of trapped gas [3]. Another common problem for wet etch processes is undetected resist scumming. This occurs when some of the exposed photoresist is not removed in the develop process. Common causes are incorrect or incomplete exposures

and insufficient developing of the pattern. Due to their high selectivity, even a very thin layer of resist residue is sufficient to completely block the wet etch process [4].

1.4 Dry Etching

1.4.1 Introduction

In the microelectronics industry there is a need for etching process in the fabrication of devices with fine line width geometries which maintain the same dimensions as the masking layer. This can be achieved with plasma etching, particularly when assisted with ion bombardment normal to the working surface with negligible lateral removal of material. This is known as "Anisotropic Etching" and enables accurate mask pattern transfer to be obtained. The capability of producing fine line geometries allows the circuit layout designer to pack more devices per single chip area. Thus given devices can now be manufactured in smaller sizes or more complex devices produced.

The initial step of mask preparation down to a few μm in dimension has depended on the development of processes for producing fine line patterns and this has led to UV photolithography and electron beam lithographic techniques with which it is possible to generate a line width pattern of less than 1 μm dimension in organic polymer films.

Larger geometries can use conventional photoresist development to provide the masking layer followed by wet etching of the electronic device. However, these simple techniques have a number of disadvantages which become more evident as the line width dimensions of the devices are reduced. Conventional resist development can be used from

line width down to 2 μm, but generally wet etching cannot be used below 5 μm width for the following reasons:

1) Ragged edges form in the etched material and there is a poor dimensional control where the resist is not adherent to the substrate.

2) Bubbles grow during the etching of the exposed substrate surface thereby acting as localized masks resulting in inadequate substrate removal.

3) Wet etching removes substrate material both perpendicular to the surface and laterally, commonly known as "Isotropic Etching" . The lateral etching component results in substrate material being removed from under the resist mask layer so that the line width loss is difficult to control [6].

By dry etching, film is removed through exposure to reactive plasmas that interact with film atoms to produce volatile by-products that are pumped away. For example, typical dry etchants for Si, SiO_2 and Al are SF_6 + Cl_2, CF_4 + H_2, and BCl_3 + Cl_2 gas mixtures, respectively. Alternatively, inert-gas plasmas are also employed to erode the film surface in a process that resembles the reverse of sputtering deposition. In both cases, positive ion bombardment normal to the surface leads to greater vertical than horizontal etching, i.e., anisotropic etching. Steep sidewall topography and high aspect ratio features are the result of anisotropic material removal.

An important issue in dry etching is the etchant selectivity or ability to preferentially react with one film species relative to others that are present. Simply changing the plasma gas composition can significantly alter etching selectivity. For example, the SiO_2 etch rate exceeds that of poly-Si by only 25% in a pure CF_4 plasma. In

an equimolar mixture of $H_2 + CF_4$, however, the etch rate of poly-Si drops almost to zero; the selectivity or ratio of etch rate of SiO_2 relative to poly-Si exceeds 45 [5].

1.4.2 Technology Overview

Plasma etch processes are used in micro electronics fabrication for pattern transfer. Applying plasma processes to microelectronics is particularly demanding. Controlling the profile of the etched feature, for example, is often required. The profile is controlled with a combination of energetic-ion bombardment and chemical reaction with species produced by the plasma.

The pattern to be etched is defined by a mask layer, often photoresist patterned using standard lithographic techniques. Features may be etched anisotropically, i.e., at different rates in the horizontal and vertical directions; and isotropically-at the same rate in the horizontal and vertical directions (Fig 1.1). Profiles with varying degrees of anisotropy can be obtained by varying the process parameters.

The main requirements for plasma-assisted etching in microelectronics applications are:

1) High etch rate

2) Control of etched profile (by controlling anisotropy)

3) High selectivity of the layer to be etched with respect to both the masking material and to the underlying layers.

4) Low energy or density of ions bombarding the etched surface to minimize damage.
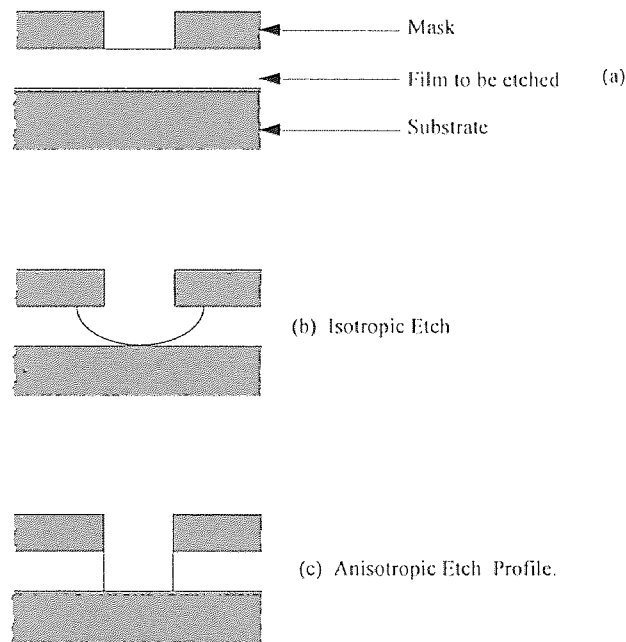
Figure 1.1 In the process of mask-layer definition and subsequent pattern transfer, a wafer must be patterned before plasma etching (a). Features may be etched isotropically (b) or anisotrpically (c).

5) A residue-free surface after etch.

6) Uniformity of etch rate across the surface.

7) Pattern sensitivity (difference in etch rate depending on feature size).

8) Process repeatability.

9) Safety.

The primary consideration in process development will depend on the application; silicon VLSI circuits or submicron III-V optoelectronic devices, for example. In all cases, the effect of the plasma etch on the finished circuit or device must be minimized for reliable operation.

The etch chemistry and the etch tool are the two primary process-design considerations. Plasma-assisted etching uses a variety of gas sets on numerous materials for semiconductor processing (Table1.1). In general, the selection of process gases depends upon the etch requirements, etch rate and selectivity, and the constraints imposed by the material to be etched, such as the existence of volatile products and the nature of native oxides.

Table 1.1 Typical Etch Chemistries

Material	Gases
Silicon	CF_4/O_2, CF_2Cl_2, CF_3Cl, $SF_6/O_2/Cl_2$, $Cl_2/H_2/C_2F_6/CCl_4$, C_2ClF_5/O_2, SiF_4/O_2, NF_3, ClF_3, CCl_4, CCl_3F_5, C_2ClF_5/SF_6, C_2F_6/CF_3Cl, Br_2, CF_3Cl/Br_2
SiO_2	CF_4/H_2, C_2F_6, C_3F_8, CHF_3/O_2
Si_3N_4	$CF_4/O_2/H_2$, C_2F_6, C_3F_8, CHF_3
Organics	O_2, CF_4/O_2, SF_6O_2
Silicides	CF_4/O_2, NF_3, SF_6Cl_2, CF_4/Cl_2
Al	BCl_3, BCl_3/Cl_2, $CCl_4/Cl_2/BCl_3$, $SiCl_4/Cl_2$
Cr	Cl_2, CCl_4/Cl_2
Mo, Nb, Ta, Ti, W	CF_4/O_2, SF_6/O_2, NF_3/H_2
Au	$C_2Cl_2F_4$, Cl_2, $CClF_3$
GaAs	BCl_3/Ar, $Cl_2/O_2/H_2$, $CCl_2F_2/O_2/Ar/He$, CCl_4
InP	CH_4/H_2, C_2H_6/H_2, Cl_2/Ar

The fluorocarbon gas sets used to etch silicon and polysilicon are the most thoroughly understood systems. Gases containing chlorine and bromine have also produced favorable etching characteristics on silicon and polysilicon but they are not as well understood. The same fluorocarbon gases used for etching silicon are used for etching silicon dioxide and silicon nitride. The selectivity of the layer to be etched with respect to an underlying layer, i.e., the ability to selectively etch SiO_2 over Si, for instance, determines which additional process gases are necessary. Including hydrogen in the process gas mixture, for example, tends to reduce the concentration of free radicals and form unwanted polymeric material. The polymer's volatility is greater in the presence of oxygen so the etch rate in SiO_2 is greater than in Si. Including oxygen in the process gas mixture, on the other hand, tends to enhance free-radical concentrations, inhibits the formation of polymers, and increases the silicon etch rate. (At high concentrations, however, oxygen can inhibit etching, either by competing with the etching radicals for surface sites or by forming an involatile oxygenated layer at the surface.) Oxygen containing plasmas can etch organic films, and are often used for photoresist stripping. Fluorocarbon gases are generally used for Silicides.

1.4.3 RF Glow Discharges (Plasmas)

A plasma is a partially ionized gas composed of ions, electrons, and a host of neutral species in both ground and in excited states. In addition, a plasma has approximately equal concentrations of positive and negative charge carriers. Usually, it is formed by

applying a large electric field to a volume of gas. Numerous plasma types exist [7]; they differ primarily in electron concentration (n_e) and in average electron energy (kT_e).

A quantity that is useful in characterizing the average electron energy in a plasma is the ratio of the electric field to the pressure, E/p [7]. As the electric field increases, free electrons, whose velocities increase as a result of acceleration by the field, gain energy. However, they lose this energy by collision processes, so that an increase in pressure, which decrease the mean free path of the electrons, decrease the electron energy.

In thin film processes for micro electronic applications, radio-frequency (rf) glow discharges are used almost exclusively. Typical properties of these plasma are indicated in Table 1.2.

Table 1.2 Properties of Glow Discharge Used for Plasma Etching

Properties	Magnitude
f	50 kHz - 40 MHz
p	0.02 - 10 Torr
n_e	$10^8 - 10^{12}$ cm^{-3}
N_N	10^{15} cm^{-3}
kTe	1-10 eV
kT_i	0.04 eV

Since the plasma is essentially electrically neutral, the positive ion density is approximately equal to the electron density. However, the neutral species concentration (n_N) is many orders of magnitude higher than the charged particle density. Thus, these plasmas are only weakly ionized. As a result of this concentration difference, the neutral species (atoms, molecules, radicals, etc.) are primarily responsible for etching or deposition. In addition, electron energies are high in such systems (1-10 eV, corresponding to temperature of 10^4 - 10^5 ° K). Because the ion energy is much lower than the electron energy, glow discharges are called non-equilibrium plasmas.

The above characteristics impart glow discharge plasma with unique and useful properties. Energetic electrons are capable of breaking chemical bonds via collisions with gas molecules. In this way, highly reactive chemical species are produced for etching (or deposition) reactions. Since the gas temperature remains near ambient, temperature sensitive materials can be processed in this environment. Also, the surface chemistry occurring in glow discharges is generally modified by the impingement of ions and electrons onto the film being etched. The combination of these physical processes with the strictly chemical reactions (due to atoms or molecules) results in etch rates and etch profiles unattainable with either process individually. Thus the role of the plasma in etching processes is two fold [8]: create chemically reactive species, and provide energetic radiation (principally ions and electrons, but also photons) for alteration of surface chemistry.

Essentially all plasma etching and deposition processes in thin film technology utilize rf rather than dc glow discharges. The reason for this are severalfold [9]. Electrons

gain sufficient energy during oscillation in the alternating field to ionize molecules during impact collisions. Therefore, unlike dc plasmas, the discharge can be sustained even with low secondary electron yield. Electron oscillations also enhance ionization efficiency so that low pressures can be invoked. Finally, since surfaces in contact with plasma are bombarded with electrons and positive ions on alternate half cycles of the rf, insulators can be used as electrode materials.

1.4.4 Physical and Electrical Characteristics

The energy of ions and electrons striking surfaces in a glow discharge is determined by the potentials established within the reaction chamber. Etching of thin films for this study was carried out in an rf plasma generated by capacitively coupling the rf field to the plasma [9]. The potentials of importance in rf glow discharge systems [10,11] are the plasma potential (the potential of the glow region), the floating potential (the potential assumed by a surface within the plasma which is not externally biased or grounded, and thus draws no net current) and the potential of the powered or externally biased electrode. When the plasma contacts a surface, that surface, even if grounded, is at a negative potential with respect to the plasma [10,12,13]. Therefore, positive ion bombardment occurs. The energy of the bombarding ions is established by the difference in potential between the plasma and the surface which the ion strikes. Because these potentials may range from a few volts to a thousand volts, surface bonds can be broken, and in certain instances sputtering of film or electrode material may occur [10].

1.4.5 Chemical Characteristics

Since an etch process is simply a chemical reaction, plasma etching can be broken down into six primary steps:

1) Generation of etchant species

2) Diffusion of etchant to surface

3) Adsorption onto surface

4) Reaction

5) Product desorption

6) Transport of product from surface

If any of these individual processes does not occur, the overall etch cycle terminates. First, reactive species (atoms, molecules, or ions) must be generated by electron/molecule collisions. This step is vital in plasma etching, because many of gases used to etch in thin film materials do not react spontaneously with the film. For instance, carbon tetrafluoride (CF_4) does not etch silicon. However, when CF_4 is dissociated via electron collisions to form fluorine atoms, etching of silicon occurs readily.

1.4.6 Plasma Condition

Low pressure plasma used in process apparatus are generally characterized by low degree of gas ionization, (typical 0.1-1 %) and an absence of thermal equilibrium between the ionized component, the free electrons and the neutral gas molecules. Thus one can consider three separate temperatures (or separate energy distribution systems). The range

of electron energies are between 1-20 eV and the ion densities are normally between 10^9 - 10^{12} cm^{-3}.

The mass difference between electrons and ions results in the electrons being accelerated to higher velocities than the ions, in the presence of electric field. In particular high frequency (hf) and radio frequency (rf) systems the electrons can reach much higher energies than the ions because of their smaller mass and the rapidity of the field change. Ions in the region of the space charge sheath are accelerated towards the electrode surface producing secondary electrons on impact. The secondary electrons are accelerated out into the plasma by the same space charge sheath and may all obtain considerable energy from the sheath.

Ions, because of their larger mass, and smaller mean free path, can more effectively transfer kinetic energy by elastic collision with gas molecules. The average fraction of an electron energy lost in an elastic collision with a gas molecule is $\cong$ m/2M where m is the mass of the electron and M is the mass of the molecule.. Thus only 10^{-5} of the kinetic energy is lost by an elastic collision, and the electron energy may continue to rise between collision.

Typical ratios of ion energy and electron energy in the plasma region of the glow discharge are between 1:10 - 1:1000. This absence of thermal equilibrium makes it possible for the gas temperature (Tg) in the plasma zone to be near ambient, with the ion temperature (Ti) in the plasma region of the glow discharge only slightly higher than Tg, i.e. Ti $\cong$ Tg.

However, some of the electrons have enough energy to excite, or ionize molecules or atoms and even rupture molecular bonds during inelastic collisions. Compounds exposed to high temperature (e.g. flames) are composed mainly of radicals and molecules that are incompletely dissociated. However, in glow discharge or plasma the larger average electron energy produces many more molecular and atomic fragments, which may also be ionized. It is such species produced in an rf discharge with an excitation frequency between 5 kHz and 5.6 GHz which are used in the fabrication of semiconductor devices.

However, as discussed here, an ion sheath may form adjacent to the wafer resting on the electrode surface. Ions from the plasma zone enter the ion sheath and are accelerated towards the electrode, gaining considerable energy. If an inert gas is used the ions are accelerated and bombard the wafer surface removing material by physical sputtering.

Examples of physical sputtering methods to remove material are the rf diode sputter-etcher [14] and the ion beam miller [15].

Physical sputtering methods are generally not applicable to etching silicon and many other semiconductor materials. This is due to the slow sputtering rates and poor selectivity between the layer to be etched and substrate. However, the addition of reactive gases (halogenated hydrocarbon, e.g. CF_4) to a gas discharge can release chemically active gases for surface etching at high rates and increases the selectivity. By careful choice of plasma chemistry and conditions a volatile compound is formed between the

active gas and the material being etched. This volatile compound can be removed from the reaction vessel by pumping.

This is the basis of the plasma etching process, which requires a chamber for plasma reaction, a flow meter to monitor the rate of gas flow into the chamber and a mechanical vacuum pump to maintain a vacuum in the chamber. The pump should rough out and maintain a pressure in the region 0.01-1.0 torr and at the same time remove the reacted compounds. The plasma can be sustained by dc or ac supplies, but it is more useful to use rf excitation because of the charging that occurs on dielectric films when etching is dc plasmas. At low rf frequencies the coupling through insulated layers such as a quartz vessel starts to become difficult and electrodes have to be located with in the plasma volume. There may also be other advantages of using rf excitation, such as sustaining plasmas at lower pressure. A typical plasma process system layout is shown in Figure 1.2 [6].
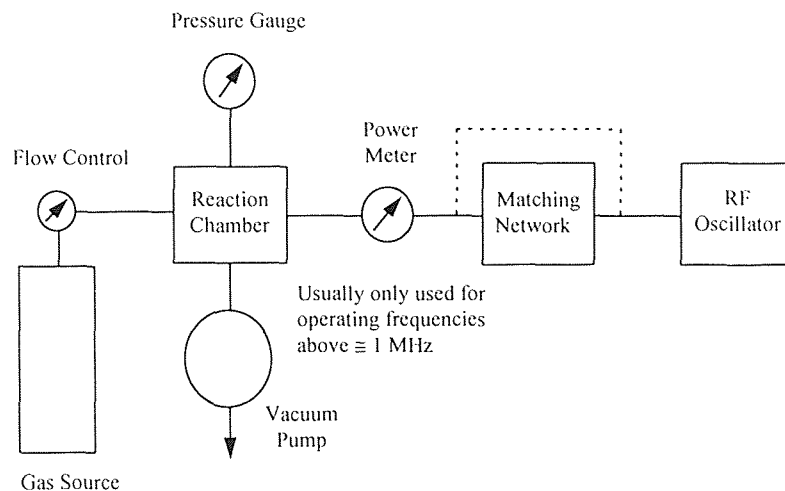
Figure 1.2 Typical Plasma Processing Arrangement

1.4.7 The Role of Ion Bombardment

The etching process depends on the chemical reaction of etchant species and film or substance to be etched. For example, the etch rate of silicon by the etchant of fluorine atoms are predicted as follows:[16]

$$\text{Etch Rate (Å/min)} = 2.91 \times 10^{-12} \, n_F \, T^{1/2} \exp(-E_a/kT) \tag{1.1}$$

Where n_F is the neutral fluorine atom concentration $= 10^{15} \, cm^{-3}$

                 E_a is an activation energy $= 0.108 \, eV$

                 T is room temperature $= 298 \, K$

                 k is Boltzmann constant

According to the above equation, the yielded etch rate $\cong 1,300$ Å/min.

This equation has been experimentally verified by exposing a clean silicon wafer surface to a gas of fluorine atoms. When silicon is exposed to a fluorine-containing plasma, however, rather than just a neutral fluorine atom flux, the etch rate can easily be larger by an order of magnitude [17, 18, 19, 20, 21]. The enhancement results from ion bombardment and is often referred to as an ion-neutral synergy. In the example of silicon etching given above, the principal role of ion bombardment is to remove fluorocarbon surface film and expose reactive sites for fluorine adsorption.

Ion bombardment also assists silicon etching in other halogens such as chlorine and bromine. The activation energy for silicon etched in chlorine is about five times larger than for fluorine. This helps to reduce the spontaneous lateral or isotropic etch

component, but lowers the etch rate. The etch rate in chlorine plasmas is enhanced by ion bombardment in two ways: first, by altering or damaging a surface layer on the substrate to increase activity and product formation, and second, by promoting the desorption of etch product like $SiCl_2$ and $SiCl_4$. The ion-neutral synergy can produce an etch rate that is much larger than the sum of the neutral atom chemical etch rate and the energetic ion sputtering rate [22].

1.4.8 Etching of SiO_2 and Si_3N_4 Films

The vast majority of dry etching processes for silicon oxide are based on fluorocarbon (Freon) discharges; the chemical end products of the reaction are silicon tetrafluoride and carbon monoxide or dioxide. Patterning is done mostly with hard-baked photoresist. Crucial factor in all processes, apart from the evident anisotropy requirements, is selectivity to the silicon. Since the reaction of silicon dioxide and silicon with Freon discharges is the best understandable system of dry etching, the explanation here will be focused on this system. However, in terms of fundamentals, this will also turn out to be useful in other process [23, 24, 25].

Fluorocarbon molecules in the ground state are inert towards both silicon and silicon oxide surfaces. Sticking coefficients are in the 10^{-6}- 10^{-7} range; even on ion bombarded surfaces no reaction occurs. Etching only starts after the reaction gas has been fragmented and ionized, for example by striking a glow discharge. Particles relevant to the reaction are charged and uncharged C_nF_m fragments (n,m = 0,1,...). The simplest

fluorocarbon is CF_4 (Freon-14). The fragmentation and subsequent etching of SiO_2 and Si in a CF_4 plasma can be described according to the following scheme:

$$CF_4 \rightarrow 2F + CF_2 \tag{1.2}$$

$$SiO_2 + 4F \rightarrow SiF_4 + 2O \tag{1.3}$$

$$Si + 4F \rightarrow SiF_4 \tag{1.4}$$

$$SiO_2 + 2CF_2 \rightarrow SiF_4 + 2CO \tag{1.5}$$

$$Si + 2CF_2 \rightarrow SiF_4 + 2C \tag{1.6}$$

For simplicity, atomic fluorine and difluorocarbene have been assumed to be the only intermediates, with carbon monoxide and silicon tetrafluoride as the volatile endproducts. The relative importance of the four idealized etch reaction will be discussed first. Next, it will be shown how equilibria can be shifted to obtain the required behavior for a given system.

Atomic fluorine, the reagent in the equation (1.3) and (1.4) is a long-lived species in the pressure regime of glow discharges. Even in the absence of ion bombardment , it reacts rapidly with silicon; the reaction rate with SiO_2 is 1-2 orders of magnitude lower. Ion bombardment enhances the reaction rate between F and Si only slightly. This is the reason why silicon etchs isotropically in most plasma systems based on fluorine. Adding an oxidizing agent such as O_2 to a CF_4 glow discharge increases the amount of free F through the formation of oxyfluorides from fluorocarbons, e.g.,

$$CF_4 + O \rightarrow COF_2 + 2F \tag{1.7}$$
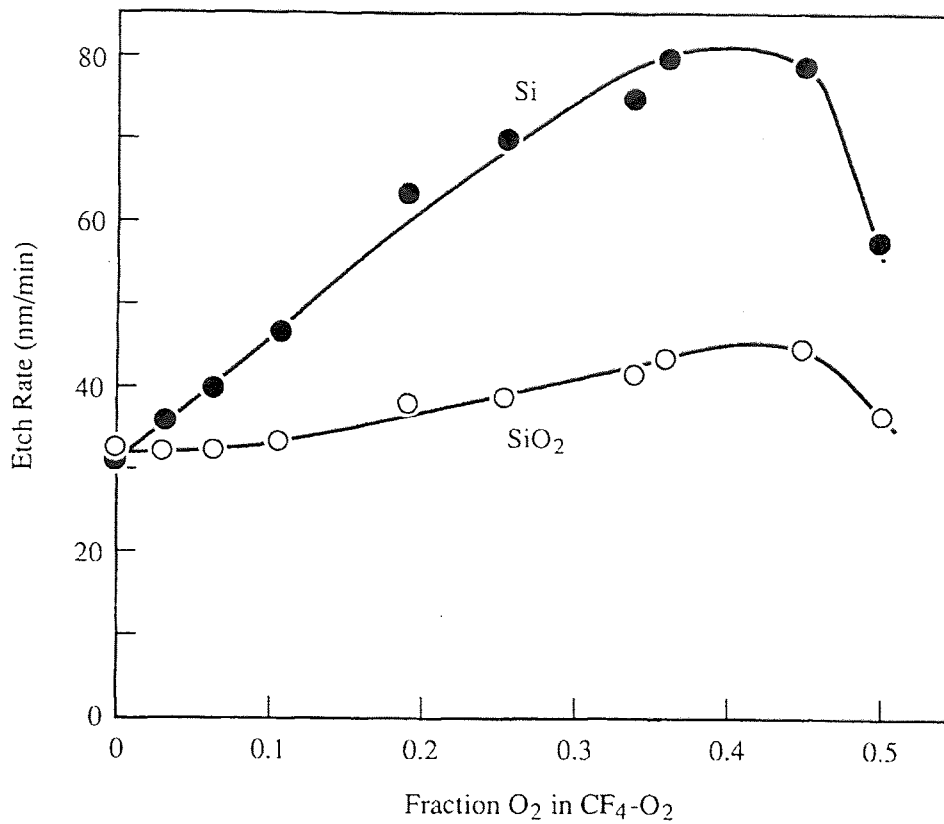
Figure 1.3 Etch rate of Si and SiO_2 in a CF_4-O_2 planar discharge

Figure 1.3 shows that the silicon etch rate in a CF_4 discharge is increased by such an addition, in agreement with equation (1.4). At higher oxygen concentrations, the etch rate drops again. this can be ascribed in part to a lowering in free F because of gas-phase recombination,

$$O_2 + F \rightarrow FO_2 \qquad (1.8)$$

$$FO_2 + F \rightarrow F_2 + O_2 \qquad (1.9)$$

However, the largest F atom density in CF_4-O_2 occurs at different - and higher - oxygen concentration than the maximum Si etch rate. The explanation for this behavior lies in surface oxidation competing with the fluorine-based etch reaction.

Free fluorine radicals in aglow discharge can be scavenged by adding hydrogen,

$$H_2 \rightarrow 2H \qquad\qquad (1.10)$$

$$H + F \rightarrow HF \qquad\qquad (1.11)$$

The resulting hydrogen fluoride can be consider as an effective thermodynamic sink, owing to its high bond strength; the HF molecule dissociates at a much lower rate than its parents H_2 and CF_4. Figure 1.4 demonstrates that adding H_2 to a CF_4 discharge lowers the Si etch rate. It appears, therefore, that etching of silicon in fluorocarbon plasma can be described conveniently by equation (1.4), i.e., through interaction with free F [26, 27].
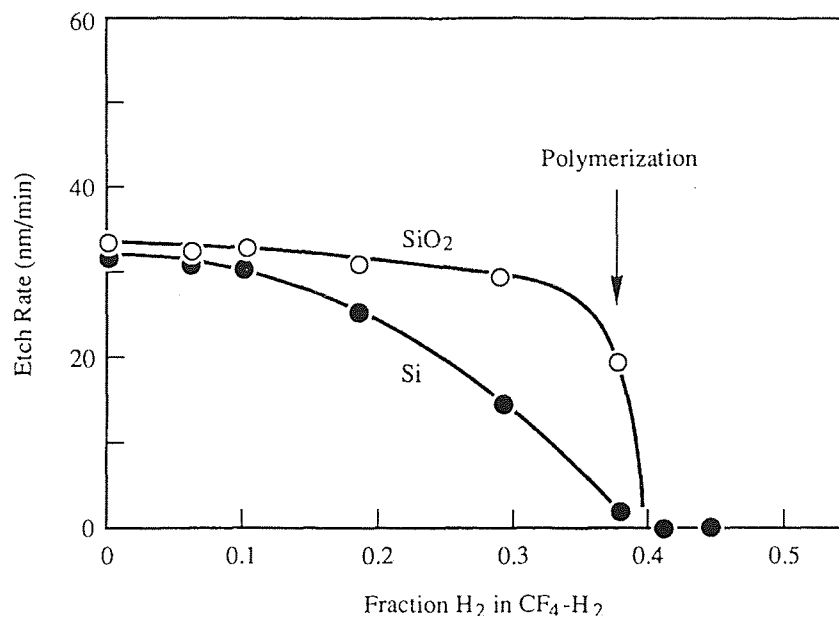
Figure 1.4 Etch rate of Si and SiO_2 in CF_4-H_2. Same condition as in Figure 1.3

Meanwhile, the etch rate of silicon is virtually unaffected by the moderate additions of either O_2 or H_2. From the same argument as given above for silicon, this means that free F does not contribute significantly to the etching of SiO_2 in the presence of ion bombardment. Instead, carbon-containing compounds have to be taken into account, see equation (1.5) and (1.6). Fluorocarbon fragments are strongly chemisorbed on both bare silicon and oxide surfaces, but react only slowly without ion bombardment. In the presence of enough free fluorine, the adsorbate is readily removed by back-formation of CF_4. Hence with CF_4-O_2 plasma, it is possible to etch silicon and, at a low rate, silicon oxide, even if ions are not allowed to reach the surface. Making the discharge fluorine deficient by, for example, adding hydrogen, suppress this recombination, and a polymer film is formed that will eventually stop the etch reactions,

$$n\,CF_2 \rightarrow [CF_2]_n \qquad\qquad (1.12)$$

Whether surface inhibition occurs for a given gas phase or not depends on two factors: the chemical composition of the surface and the intensity of the local ion bombardment. Pattern sidewalls are not hit by ions, and lateral etching of both silicon and silicon oxide stops at relatively low concentrations. In CF_4, A few percent is typically sufficient to obtain a perfectly anisotropic process. At a sufficiently high flux density and energy level, impinging ions will damage the surface layers, and the fluorocarbon adsorbate can react with the substrate. If the substrate is silicon oxide, oxygen from the lattice is available to form volatile carbon oxides with carbon-containing species, see equation (1.5). At the same time, F is released to remove the remaining Si atoms. This explanation

is supported by the fact that there exists a positive relation between silicon oxide etch rate and gas-phase difluorocarbene concentration. A similar mechanism is not available for silicon, and a carbon-rich film will e formed there, see equation (1.6). Carbon is a material with a low sputter yield, which suppresses further Si removal.
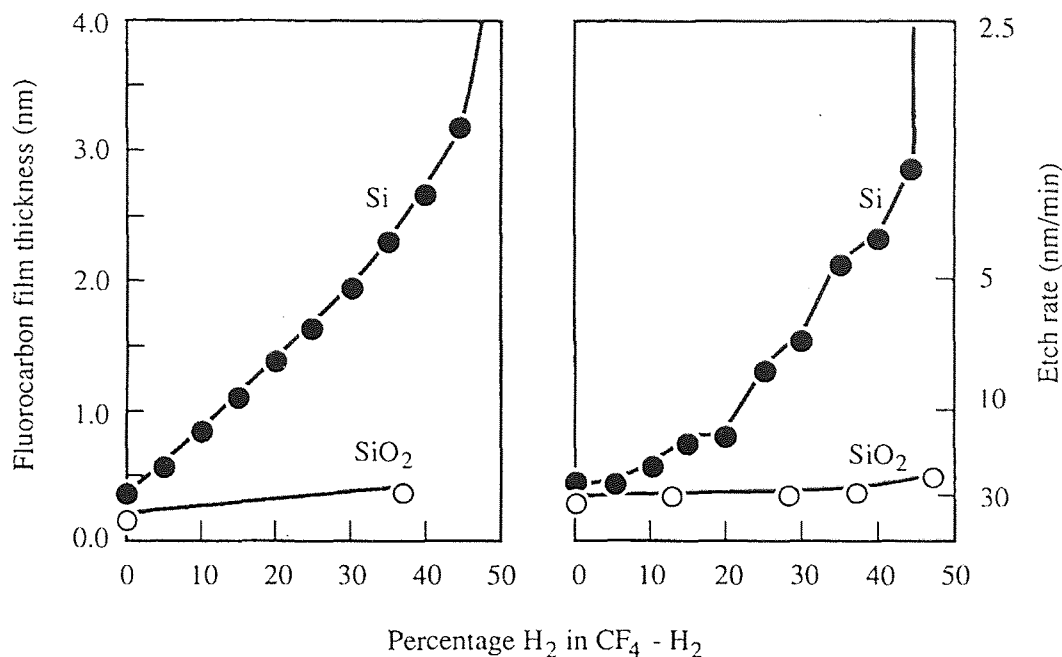
Figure 1.5 Fluorocarbon film thickness (left) and inverse etch rate (right) for Si and SiO$_2$ as a function of hydrogen concentration in a CF$_4$-H$_2$ discharge.

The silicon etch mechanism explained above is also applicable to organic layers, such as photoresist. Silicon nitride takes an intermediate position between silicon and silicon oxide. Nitride reacts faster with atomic F than the oxide because of the intrinsically weaker Si-N bond, although not as fast as silicon. It also appears to react with CF$_2$ species, as it is etched in CF$_4$-H$_2$ at roughly the same rates as silicon oxide. By analogy with equation (1.3), the surface carbon may be removed as CN.

1.4.9 The Planar Reactor

The planar reactor, now widely used for etching, is one type of plasma reactors for which this study used. The system using parallel plate electrodes was an important development because it provided the capability under some conditions for anisotropic etching. A typical reactor consists of a top electrode connected via an insulated feed through to an rf supply and a bottom electrode which is normally grounded, Figure 1.6. The wafers rest on the ground electrode and are immersed in the plasma. The top electrode is normally capacitively coupled via a blocking capacitor to the rf supply. In this system each electrode is negatively biased to the plasma and generally the negative bias is higher on the top electrode, as shown in the experimental studies.
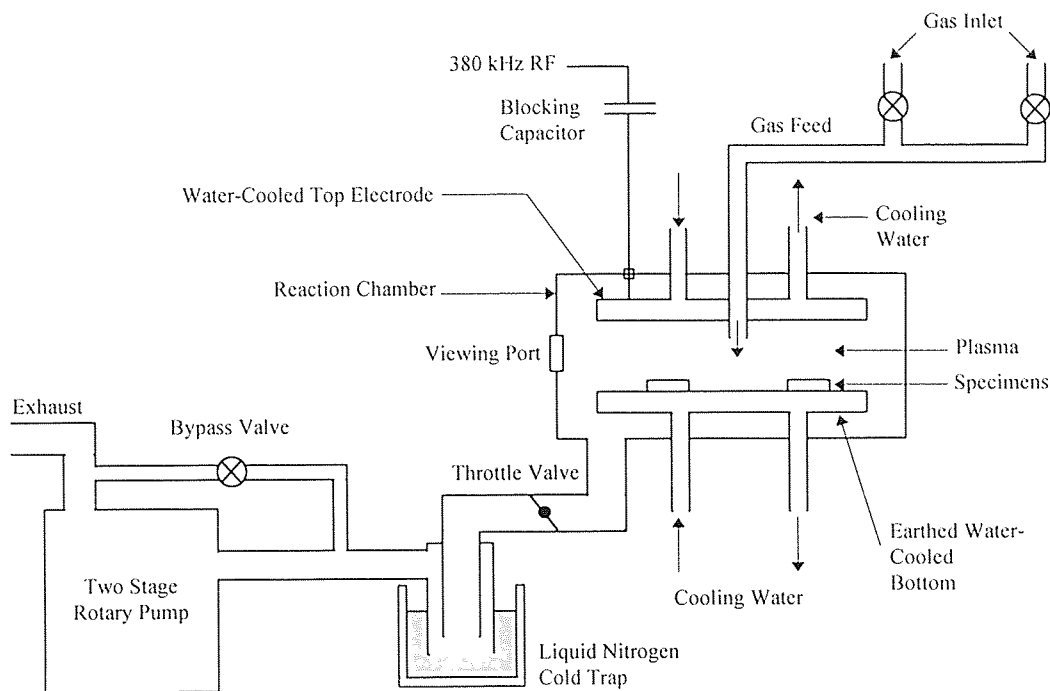
Figure 1.6 A typical planar reactor system

It is noted here that a planar reactor will etch wafers located on either electrode surface and in some cases will etch wafers faster on the top rf electrode due to the larger negative bias developed on the top electrode.

In the planar system considered here, the work surface is the grounded electrode which forms an adjacent ion sheath because of the negative bias developed with respect to the plasma potential. Thus the wafers placed on the ground electrode are bombarded by atomic and molecular ions which have been accelerated in the ion sheath as well as low energy electrons. The wafers are also exposed to free radicals and molecular fragments produced in the plasma volume.

Planar reactors have some disadvantages such as high cost, low selectivity, and small wafer throughput. The poor selectivity is because of physical sputtering from the ion bombardment contribution which also produces heating effects that can result in poor etching uniformity, rapid removal of photoresist, and resist flow if heating is too excessive. However, to improve the uniformity and increase the photoresist life time during etching, the planar reactor electrodes have been designed to have water cooling.

A problem arising in the large planar reactors is obtaining uniform etching. Thus, if the etching selectivity in a particular process is poor, then serious etching can occur in the substrate of some wafers before others have had the layer to be etched removed. For this reason, some manufacturers have made a planar machine for production use holding and etching a single wafer at a time. These machines have a fast pump down and fast etch rates because the chamber is small and the power density can be high. Although the throughput of these machines is obviously smaller than that of the large capacity plants,

they give better uniformity. End point detectors are used on plasma etching machines to avoid over-etching. End point systems work particularly well on single wafer machines since there is a smaller volume for observation. Also, laser interference can be used to monitor the single wafer in the reaction chamber.

With all plasma process machines, it is necessary to precondition the reaction chamber by running the process before the wafers are etched, thus improving etching uniformity and reproducibility. The preconditioning of the chamber (before wafers are placed and etched in the chamber) warms the chamber and reduces the wafer contamination. Water vapor is considered one of the contaminants. Prevention of water vapor or atmospheric contamination in the plasma reaction chamber can improve the uniformity and reproducibility of the etching process.

1.4.10 General Plasma Parameters

The key parameters effecting to plasma etching result are gas operating pressure, rf power input, gas flow rate, loading quantity, and temperature. The followings are some significant characteristics of each parameter in plasma etching.

1.4.10.1 Gas Pressure: The manner in which etching depends on plasma pressure is complex as many effects occur simultaneously. As the gas pressure is raised there is generally a reduction in the mean free path of the plasma components producing more radicals and ions, (depending on the electron temperature and the species in the system). The increase in free radical and ion production can have several effects. For example it

can increase the etch rate of the wafer by raising the ion or free radical concentration at the surface of the wafer. On the other hand, free radicals can recombine with each other forming higher molecular weight species, e.g. from fragmented CF_4 molecule one can obtain:

$$CF_3^{\bullet} + CF_3^{\bullet} \rightarrow C_2F_6 \text{ (dimer)} \qquad (1.13)$$
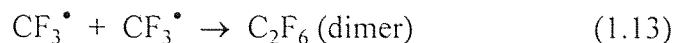
The dimer can also fragment and recombine eventually forming high molecular weight condensed polymers on surfaces. Such an event is more probable at higher pressures, and with long resident times for free radicals of heavy mass.

When increasing the pressure, the ion concentration may initially increase and thus the impedance of the plasma may fall thereby resulting in a lower applied potential at a given power input. At the ion sheath, the ion bombardment energy will fall with the decrease in sheath potential caused by the reduction of applied potential to the plasma. Thus polymer may glow on an exposed surface if the ions arriving have an energy below the sputtering threshold to remove the polymer from the surface. Also the ion energy may be too low to induce chemical reactions which need ion bombardment.

The increase in ion density at a given power input with a rise in pressure is due to the increase in collision rates between the electrons and gas molecules and between ions and neutrals. The pressure rise will also increase the ionization events and recombination events in the plasma. It may also increase the collisions between ions and neutrals whilst traversing the dark space, thus reducing the ion energy on impact with the electrode surface. Increasing the operating pressures of plasmas may also increase the rate and type

of species that could physically or chemically absorb on the wafer surface. This could then change the rate-controlling step in wafer etching processes.

1.4.10.2 RF Power Input: At constant pressure the plasma density can be raised by increasing the power input into the plasma. This increase in power will cause a rise in the applied potential particularly at the lower pressures [28]. It will also increase the potential across the ion sheath, thus raising the ion bombardment energy. Any increase in power will also increase the rate of formation of other plasma products such as free radicals. However, any polymer condensation from heavy free radicals will be offset by the higher ion bombardment energy.

The increase in ion bombardment energy by increasing rf power input could make the ion bombardment, at the surface, a more probable reaction for inducing chemical change by bond rupture or damage. There will also be an increase in ion density, which will increase the rate of material being removed from the surface. Alternatively, if the reaction rate is limited by a free radical process, an increase in ion energy or density alone may not be significant. Thus, etching will be enhanced by a rise in free radical concentration in the plasma. An increase in ion bombardment energy may also have an effect on surrounding atoms in the area of bombardment which could lower the activation energy and increase the rate of reaction thus increasing the etch rate.

System design may also have an effect on the relation of etch rate with rf power input since the applied rf frequency and type of matching network can vary from one system to another.

1.4.10.3 Gas Flow Rate: The dependence of gas flow rate on the etching rate of specific wafer surface material varies from plasma reactor to plasma reactor. However, below a critical flow rate, there is an inadequate supply of reactant to etch the wafer material and thus a small increase in flow rate can rapidly increase the wafer etch rate.

As the flow rate is raised, the product species are flushed away and thus subjected to less dissociation and recombination reaction in the plasma but at the same time the initial reactant gas is less utilized [29]. Use of the etchant gas will increase as the rf power input is increased [29]. If the flow rate is further increased with accompanying increase in pumping speed to maintain a constant pressure of operation, then it is possible that the active species produced in plasma can be pumped away before they have the opportunity to react. The foregoing effects are illustrated in Figure 1.7 in relation to the etch rate observed.

According to the Figure 1.7, the utilization (U), supply rate limited etching (E_S), and pumping rate limited etching (E_p) are defined as:

$$U = \frac{\text{etch rate of atoms}}{\text{input flux of reactive molecules}} \tag{1.14}$$

$$E_S = E_L \left[1 - f \left(EA_s / Q \right) \right] \tag{1.15}$$

$$E_P = \frac{E_L}{\left[1 + 4Q / PCR_s A_s \right]} \tag{1.16}$$

Figure 1.7 Theoretical model for etch rate vs flow rate.
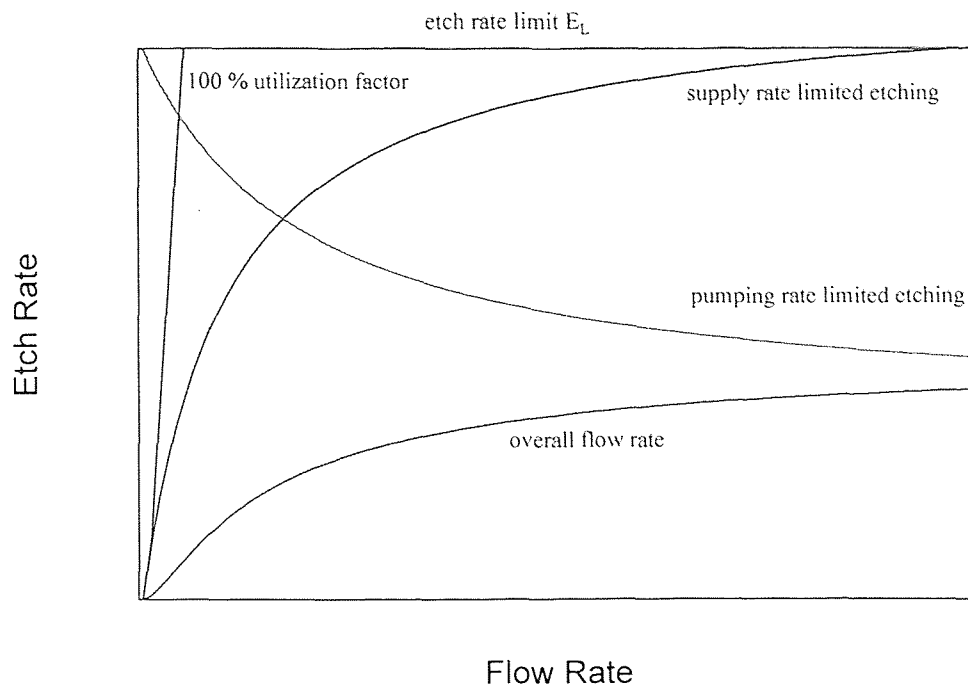
where E_L =   etch rate limit

          E_s =   supply rate limited etching

          E_p =   pumping rate limited etching

          A_s =   substrate area

          R_s =   reaction probability at the wafer

          P =   system pressure

          Q =   flow rate

          C =   mean speed of gas molecules

The time which a plasma species spends in the system chamber before being pumped away is known as the residence time (τ). This is related to the volume of the chamber (V) and the pumping rate (S), and is directly related to the flow rate.

$$\tau = V/S \quad \text{(liters/liters per sec)} \quad (1.17)$$

The pumping rate is related to the system geometry and pressure, and in many processes the resident time will not be reached by an active species because it is reacting and being consumed thereby producing other products. Residence times for molecules in process systems can vary between 0.5 to 50 seconds providing they are not consumed.

1.4.10.4 Loading Effects: Loading effects result from having a limited supply of etching species produced in the plasma. As the free radical species are more effectively consumed with rise in the wafer load, the contribution of the free radical species to the etch rate can fall to a level where ion bombardment is the main component determining the etch rate.

Also, the loading effects can vary depending on the pressure, species present and their resident time in the plasma. Changes which occur in the gas phase may also cause changes in any surface compound formation which ions may activate or physically sputter. If the active free radicals in the plasma have a high recombination rate and react before they have a chance to etch the wafer, then the active free radical concentration will be low. A low concentration of active free radical species in plasma compared with the ion etching component will result in a smaller loading effect in a system. A low

concentration of active free radical species will also reduce the lateral etch component in a plasma etching process resulting in an increase of anisotropy.

1.4.10.5 Temperature: The rate of etching may be dependent on temperature because the chemical reaction involved is subject to an activation energy and also because the surface coverage of chemisorbed species is temperature dependent. Substrate cooling is usually necessary to protect the photoresist mask during etching against thermal deterioration and flow. Substrate cooling can also give consistent etch rates during etching since the wafer temperature can be kept constant.

Many researches on plasma etching involving a large free radical etching component exhibit an Arrhenius type temperature dependence for the etch rate with activation energies lying in the range of 0.05-0.5 eV. The Arrhenius relation is usually written as follows:

$$K = A\exp(-\Delta E/RT) \qquad (1.18)$$

where

R   is the gas constant (J mol^{-1} K^{-1})

T   is the reaction temperature ($^\circ$ K)

ΔE is the activation energy (J mol^{-1})

A   is the frequency factor (sec^{-1})

K   is the reaction rate (sec^{-1})

The activation energy is a measurement of the energy barrier which must be crossed in order for reaction to proceed and the frequency factor is the probability for the reaction. Both A and ΔE are independent of temperature to a first approximation.

The dependence of etch rate on temperature will be less in processes where the etching proceeds mainly by ion bombardment in the presence of the active species such as planar reactors, where the ion impact supplies the activation energy.

Much of the rf power dissipated in the plasma ultimately appears as heat and is the major source of temperature rise [30]. In planar reactors, the electrodes should be water cooled and have good thermal contact with wafers thus providing temperature control, reproducibility in etching and an improvement in uniformity, particularly where there is a large free radical etching component.

1.4.11 Plasma Etch Tools

Plasma etch tools may be categorized according to the etch mechanism each of them employs. This helps to elucidate similarities and differences between the types of etch equipment that are commercially available (Table 1.3). Each etch tool uses a particular combination of pressure, electrode configuration and type, source frequency, and gas set to control the two primary etch mechanisms: chemical and physical. The number of electrode configurations in plasma-assisted etch equipment are illustrated in Figure 1.8 [31]

Table 1.3 Processes and Types of Etching Equipment

Etch tool Configuration	Etching Mechanism	Pressure Range (torr)	Electrode Arrangement	Wafer Location	Excitation
Barrel Etching or Tunnel Etching	Chemical	10^{-1} - 10^{0}	Coil or electrodes outside vessel	In rack in plasma; wafer electrically floating	RF
Downstream or Effluent Plasma Etching	Chemical	10^{-1} - 10^{1}	Coil or electrodes outside vessel	In rack downstream of plasma	RF
Plasma Etching	Chemical or Chemical/Physical	10^{-1} - 10^{0}	Planar diode	On grounded (anode) electrode	RF
Ion Etching or Sputter Etching	Physical	10^{-2} - 10^{-1}	Planar diode or cylindrical (hexagonal) diode	On cathode	RF
Reactive Ion Etching	Chemical/Physical	10^{-3} - 10^{-2}	Planar diode or cylindrical (hexagonal) diode	On cathode	RF
Magnetic Confinement Ion Etching	Physical	10^{-3} - 10^{-2}	Planar diode or cylindrical (hexagonal) diode with magnetic field confinement near cathode	On cathode	RF
Magnetic Confinement Reactive Ion Etching	Chemical/Physical	10^{-3} - 10^{-2}	Planar diode or cylindrical (hexagonal) diode with magnetic field confinement near cathode	On cathode	RF
Triode Etching	Chemical/Physical	10^{-3} - 10^{-2}	Triode	On platform electrode	RF or DC
Ion Beam Etching or Ion Beam Milling	Physical	10^{-4}	Planar diode	On grounded (cathode) electrode	DC
Reactive Ion Beam Etching	Chemical/Physical	10^{-4}	Planar diode	On grounded (cathode) electrode	DC
Electron Cyclotron Resonance Sources	Chemical/Physical	10^{-4}	External	On either	Microwave
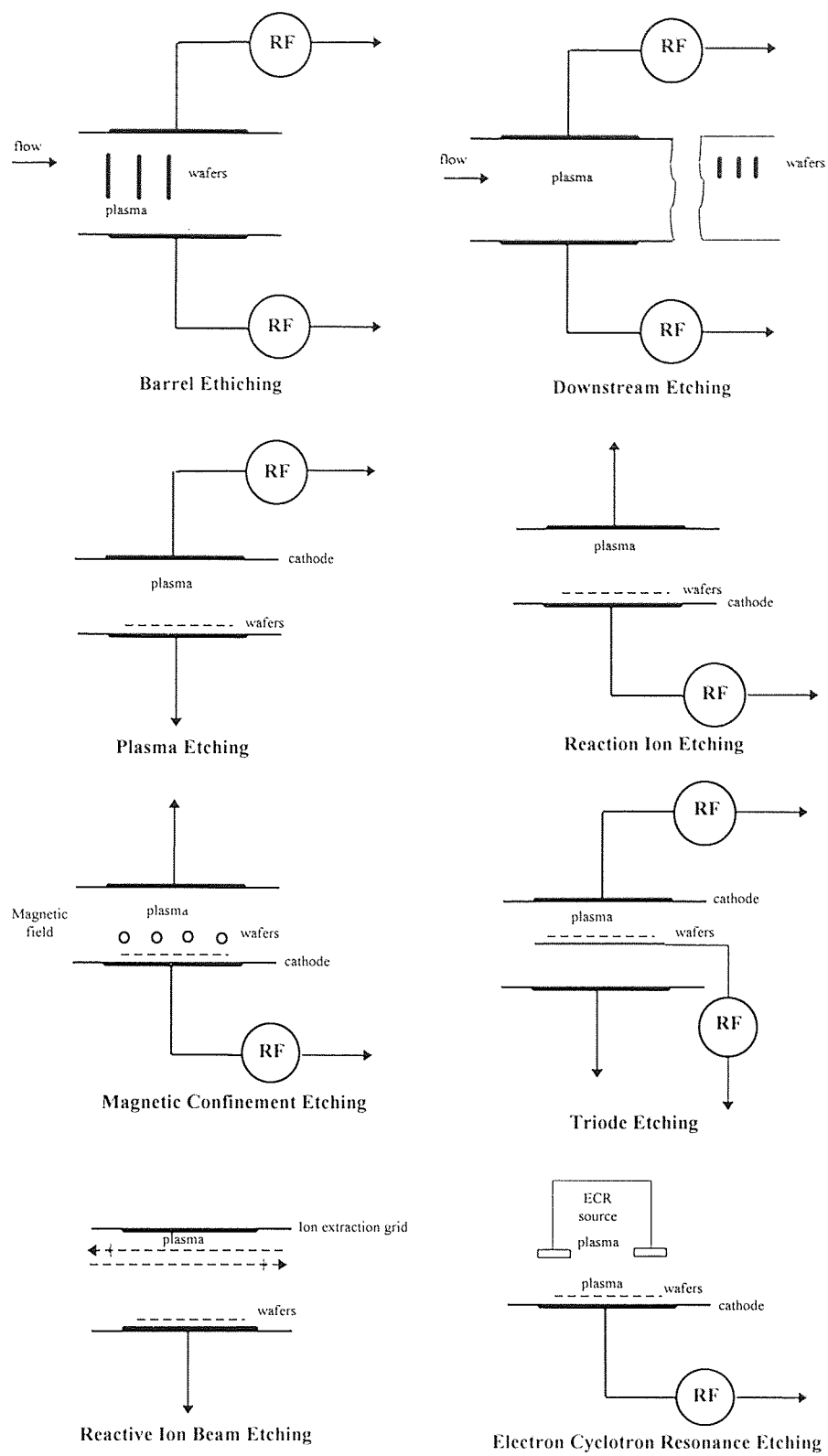
Figure 1.8 A wide variety of electrode configurations in plasma-assisted etch equipment

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Set-up of Plasma Etching Reactor

The plasma etching was carried out using an Applied Material AMP 3300 IIA PECVD system. The scheme of the reactor is illustrated in the Figure 2.1. The reaction chamber is an aluminum cylinder with aluminum plates on both the top and the bottom, as upper electrode and susceptor, respectively. The diameter of the electrode and susceptor are about 26 inches and the distance between the upper electrode and susceptor is 2 inches.

Figure 2.1 Schematic Diagram of Plasma Etching Reactor

2.2 Pre-experiment Procedure

2.2.1 Leakage Test

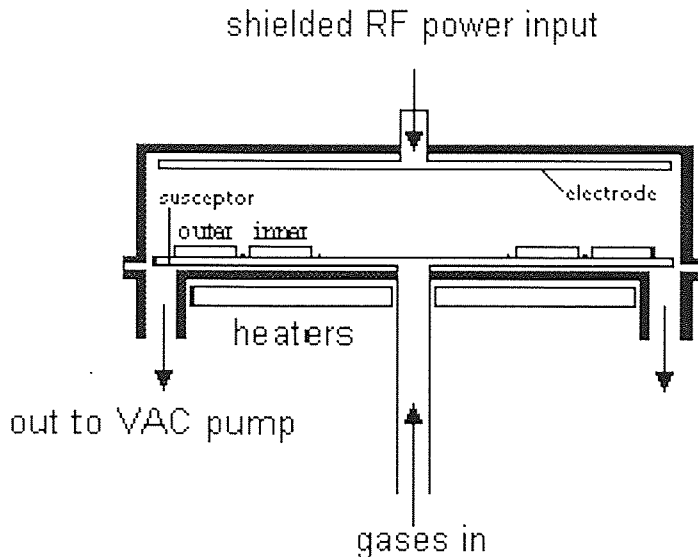A routine leakage test was conducted every time before operating by shutting off the source supply valves and then evacuating all gases trapped in the chamber. Switched on the flow control valves and observed the chamber pressure from the control panel. The maximum leakage rate was found to be 6 mtorr/min.

2.2.2 Calibration of Gas Flow System

All gas flows were controlled by Applied Materials model AFC 550 automatic N_2 mass flow controllers. The N_2 calibration of the AFC was checked by delivering a fix volume of gas (product of the metered flow rate and the time) into the known reaction chamber volume. After closing gas outlet valve of chamber, the internal pressure is built up. With the certain differential pressure, the corresponding time consumed is measured. The obtained results are utilized in calculation for actual flow rate according to the gas law-based formula. To standardize the flow rate in sccm unit, however, the formula is adjusted to the standard condition (0°C, 1 atm). The final formula is shown below as a result.

$$\text{Flow Rate (sccm)} = 60(\Delta P/\Delta t)(T_0 V/P_0 T) \qquad (2.1)$$

where

ΔP = differential pressure in torr,

$T_0 = 273$ K

$P_0 = 760$ torr

V = volume of the chamber = 42000 cm^3

Δt = time of delivering gas, sec.

The calibration was carried out at various set points (at the control panel) of flow rate of CF_3I and C_2F_6/O_2 to determine gas correction factors. The actual flow rates were first computed according to the above equation. The gas correction factors for CF_3I and C_2F_6/O_2 were then calculated. The results of calibration are depicted in Figure 2.2-2.5.
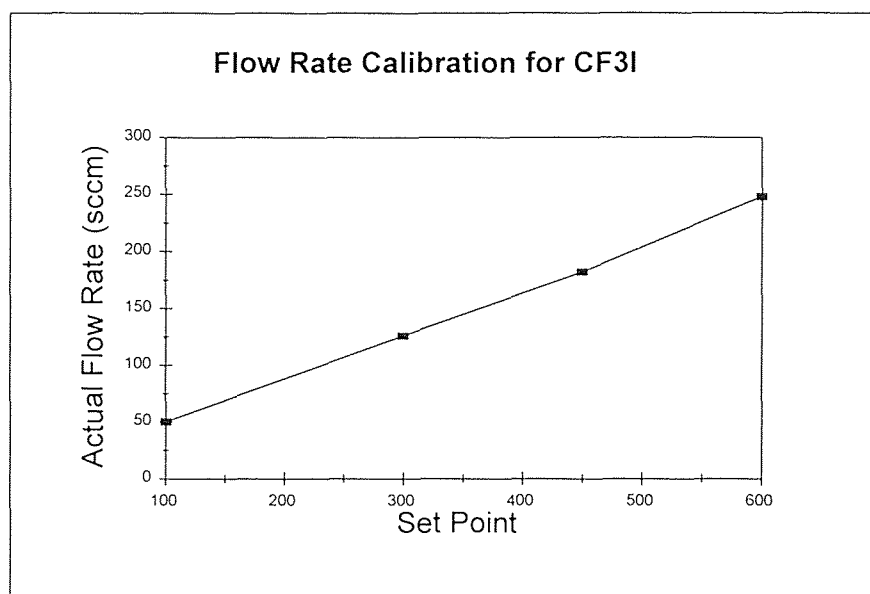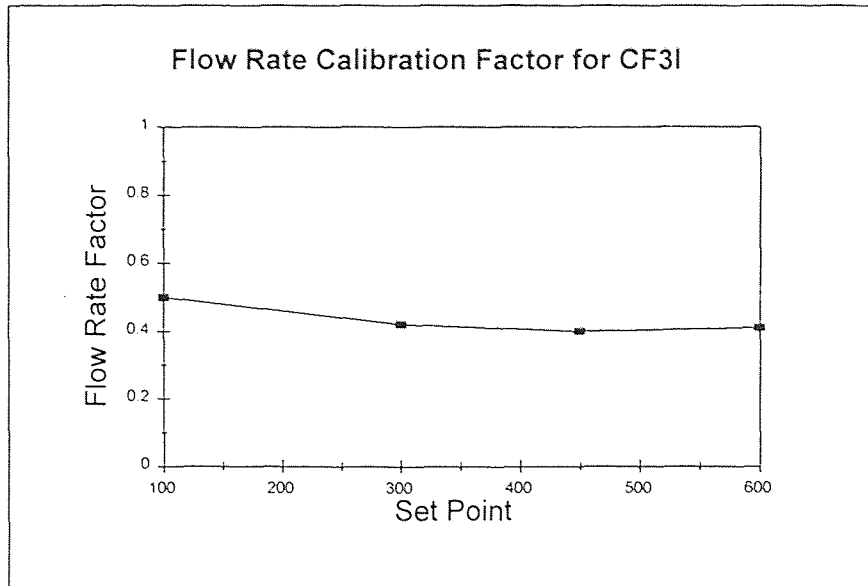

Figure 2.2 Flow Rate Calibration for CF_3I

Figure 2.3 Flow Rate Calibration Factor for CF_3I
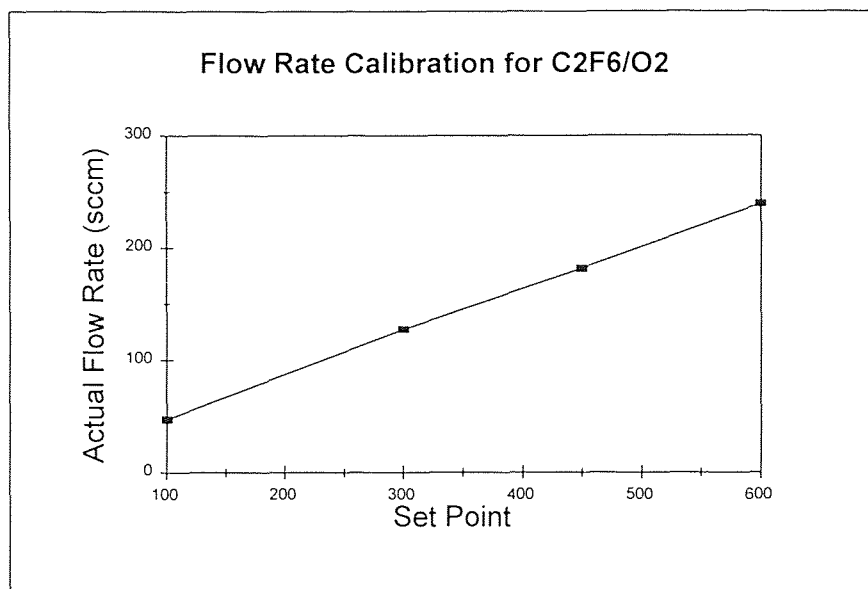
Figure 2.4 Flow Rate Calibration for C_2F_6/O_2
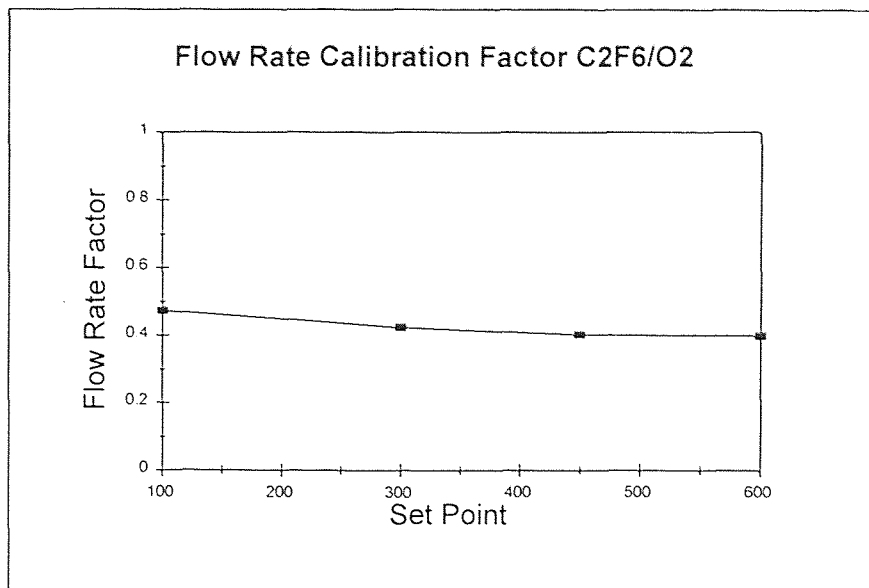
Figure 2.5 Flow Rate Calibration Factor for

2.2.3 Deposition Condition of SiO_2 and Si_3N_4 Thin Films

Dielectric films employed in this study are silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). Both of them are synthesized by means of plasma enhanced chemical vapor deposition (PECVD) using an Applied Materials AMP 3300 IIA parallel plate plasma enhanced CVD batch reactor. The films are deposited on 4" $\varnothing$ silicon substrate [32]. For SiO_2 film, diethylsilane (DES) and nitrous oxide (N_2O) are utilized as the precursor and the oxidant, respectively. The deposition condition was as follow: at pressure = 300 mtorr, temperature = 300° C, flow rate ratio N_2O/DES = 240 sccm/15sccm, and RF power = 500 watt @ 100 kHz. For Si_3N_4 film, DES ,NH_3 ,and N_2 are used as precursors with the deposition condition set as follow: at pressure = 300 mtorr, temperature = 250° C, flow rate ratio NH_3/DES = 270 sccm/15sccm, and RF power = 500 watt @ 100 kHz.

2.2.4 Wafer Loading and Deposition Condition Setting

One side polished single crystal silicon wafers, 10 cm in diameter and 525 μm thick, were placed horizontally on the susceptor. The reaction chamber and the precursor delivery lines were evacuated. The temperature controller was set to the desired point, and the susceptor was heated for an hour under vacuum to ensure an uniform temperature. At the same time, the cooling water was turned on. The flow rate of precursors, pressure, deposition time, plasma power and frequency were set at the engineering panel.

2.2.5 Film Deposition

When a constant temperature was reached, the deposition was started by pressing the START button in deposition mode. Then, the chamber was pumped down to the base pressure. The sequential steps included: high purging, prepurging, and processing gas. At the processing gas step, the precursors in gas state were introduced to the reaction chamber at their set flow rates automatically. The deposition pressure, however, was adjusted to the set value manually at the processing gas step by controlling blower speed. This is because in automatic mode for pressure controlling, the pressure oscillates with the wide range around the setting point.

2.2.6 Post-deposition Procedure

When the deposition was advanced to the set time, the rf power will be shut off automatically. The chamber was pumped down and cooled down under vacuum to below 100°C with the cooling water to avoid any undesired reactions. The chamber was back-

filled with nitrogen. After the reaction chamber cover was opened, the wafers were taken out for the next step, sample preparation. Finally, the chamber was evacuated and kept under vacuum.

2.2.7 Reactor Etching

During the deposition reactions, films were observed to deposit on the upper electrode and susceptor. The reactor had to be cleaned in order to remove the deposits in the reaction chamber, which may peel off and effect the subsequent wafer etching process or even succeeding deposition process. Therefore, after finishing deposition, the reaction chamber was cleaned under the following condition: time = 30-40 minutes, pressure = 300 mtorr, $C_2F_6+O_2$ (1:1) flow rate = 500 sccm, rf power = 1.5 kW, with the heater off.

2.2.8 Sample Preparation

After depositing dielectric films of SiO_2 and Si_3N_4, the wafers, by diamond tip pen, were dissected into 4 pieces and marked with a small circle to locate the point of thickness measurement. The film thickness measurement was conducted using Nanospec Interferometer. Importantly, during measuring, the monochromatic light emitted from the Nanospec Interferometer is required to locate within the circumference of the marked small circle in order to minimize an error from misplacing. The resulting thickness was recorded as thickness before making experiment (plasma etching).

2.3 Experiment Procedure

2.3.1 Wafer Loading

After finishing wafer preparation, the small piece of wafer called "quarter" was placed horizontally on the susceptor at the position and orientation shown in the schematic below.
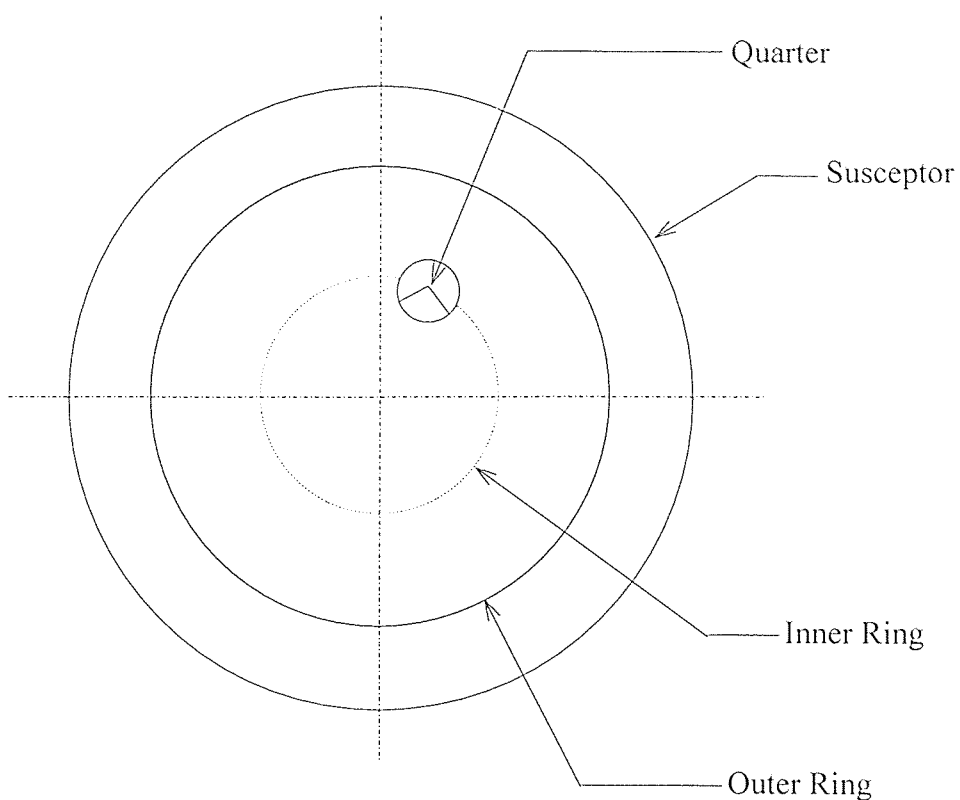

Figure 2.6 Position and Orientation of Quarter Placed on Susceptor

Since different position and orientation in placing the quarter may influence the plasma etching result, therefore to keep constant these parameters, the quarter be placed at the same position and orientation every experiment.

2.3.2 Etching Condition Setting

After loading wafer, the gate valve of etchant cylinder was opened manually to be ready for delivering to the reaction chamber. Then, the cooling water was turned on. At the engineering panel, etch mode was selected. The etchant flow rate, etching time, rf power, and etching pressure were also set at this panel according to the desired conditions.

2.3.3 Etching Process

After closing the reaction chamber, the etching process was started by pressing the START button. The chamber was pumped down to the base pressure. Then sequential steps -high purging, prepurging, and processing gas- were carried out automatically. At the processing gas step, the etchant was introduced to the reaction chamber with the set flow rate. After the flow rate of etchant was steady at the desired level, the etching pressure was adjusted to the set value manually by controlling blower speed. When pressure was steady, by pressing ADVANCE button, the rf power was applied to generate plasma for etching process. In a very short period, plasma will be steady. Concurrently, rf power will attain the setting level. Immediately after being steady, the ADVANCE button was pressed again to activate counting clock.

There are two points to be noted at this step. First, in automatic mode for pressure controlling, the pressure oscillates with a wide range around the setting point. Consequently, the etching pressure was adjusted and controlled manually. Secondly, after applying rf power, pressure will be built up higher than setting point as a result of etching

reaction. Therefore, controlling the blower speed to bring down the pressure at the beginning of etching process was required.

2.3.4 Post-etching Procedure

When etching process was advanced to the set time, the rf power would shut off automatically. The chamber was pumped down, post purged, and then back-filled with nitrogen to open the chamber cover. The quarter can be taken out to evaluate for etching rate.

Due to the fact that there is residue depositing on the susceptor and the side wall of reaction chamber. This could affect the subsequent etching reaction. Consequently, reactor cleaning to remove this residue with O_2 plasma etching was practiced every time after finishing etching process.

2.3.5 Etch Rate Evaluation

After finishing etching process, the etched quarter was taken to Nanospec interferometry for after-etch thickness measurement. The etch rate can then be calculated according to the formula below.

$$\text{Etch Rate (Å/min)} \quad = \quad (X_1-X_2)/t \qquad (2.2)$$

Where X_1 is thickness before etching (Å)

X_2 is thickness after etching (Å)

t   is etching time (minute)

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Power Study

RF power supply effects on the etch rate of SiO_2 and Si_3N_4 films were studied over a series of rf powers ranging from 500 W to 1500 W for CF_3I etching on SiO_2 and Si_3N_4 films, from 300 W to 1400 W for C_2F_6/O_2 etching on SiO_2 film, and from 300 W to 1200 W for C_2F_6/O_2 etching on Si_3N_4 film. The flow rate of both CF_3I and C_2F_6/O_2 were set at 50 sccm. Total pressures inside the reaction chamber were maintained at 50 mtorr for case of etching with CF_3I, and at 150 mtorr for case of etching with C_2F_6/O_2. The frequency was kept at 100 kHz throughout the power study series.

In the range of study using CF_3I as the etchant, the etch rate of SiO_2 film increased from 285 Å/min to 631 Å/min as the rf powers increased from 500 W to 1500 W, as shown in Figure 3.1.

For Si_3N_4 film etched by CF_3I, similarly, the etch rate increased from 255 Å/min to 1026 Å/min as the rf power increased from 500 W to 1500 W, as shown in Figure 3.2.

For the case of C_2F_6/O_2 used as the etchant, the SiO_2 film etch rates increased from 2066 Å/min to 6723 Å/min as the rf powers increased from 300 W to 1400 W, as shown in Figure 3.3. The Si_3N_4 film etch rates increased from 153 Å/min to 1890 Å/min as the rf powers increased from 300 W to 1200 W, as shown in Figure 3.4.

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Figure 3.1 The etch rate dependence on rf power of SiO_2 film etched with CF_3I at flow rate = 50 sccm, pressure = 50 mTorr, rf = 100 kHz, no oxygen content

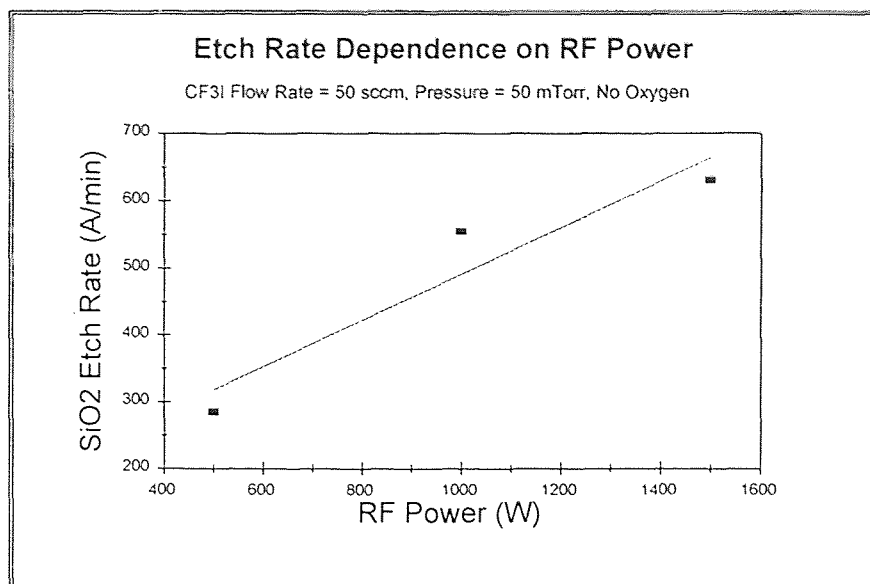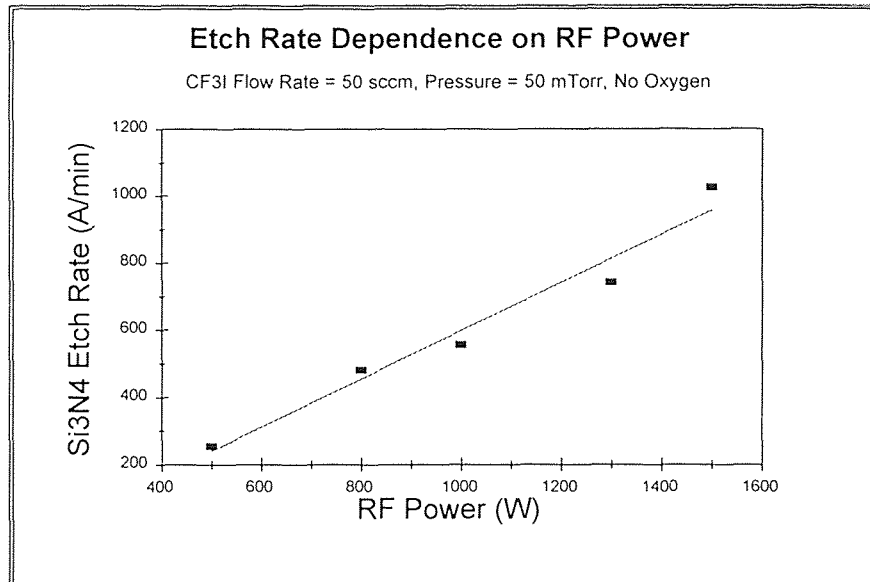**Figure 3.2** The etch rate dependence on rf power of Si_3N_4 film etched with CF_3I at flow rate = 50 sccm, pressure = 50 mTorr, rf = 100 kHz, no oxygen content

Figure 3.3 The etch rate dependence on rf power of SiO_2 film etched with C_2F_6/O_2 (ratio 1:1) at flow rate = 50 sccm, pressure = 150 mTorr, rf = 100 kHz

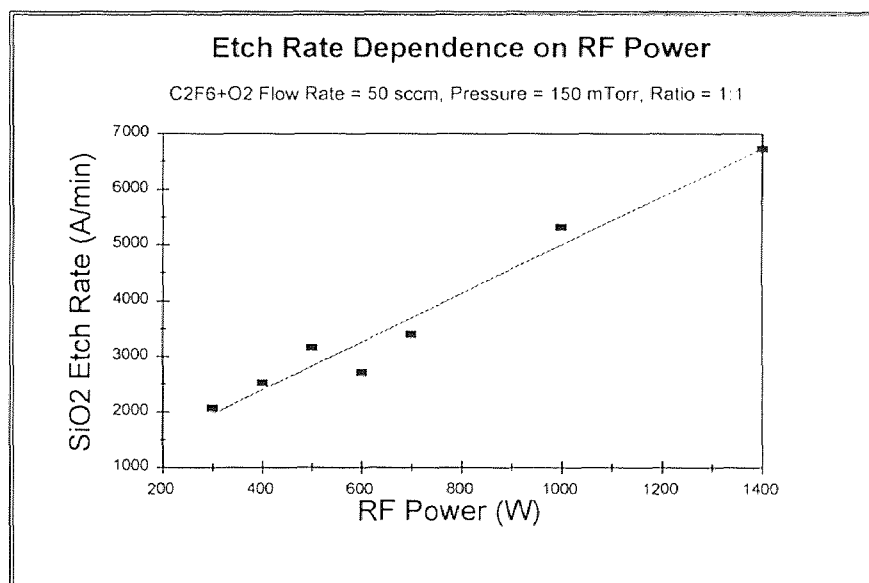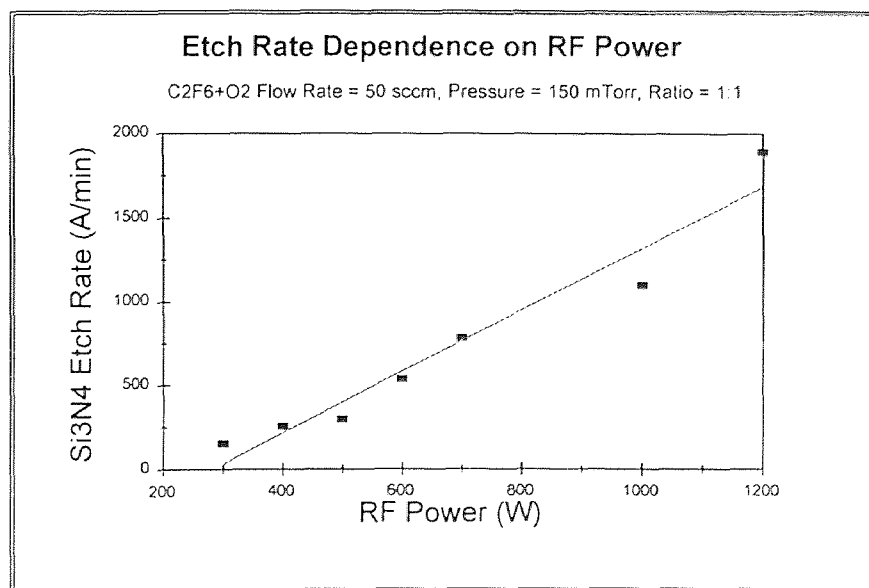**Figure 3.4** The etch rate dependence on rf power of Si_3N_4 film etched with C_2F_6/O_2 (ratio 1:1) at flow rate = 50 sccm, pressure = 150 mTorr, rf = 100 kHz

In power study, the increase in rf power resulted in the higher etch rates for the films etched by both CF_3I and C_2F_6/O_2. The increase in power will result in the following effects which play the major roles in the plasma etching process:

1) Increase the potential across the ion sheath thus raising the ion bombardment energy.

2) Increase the electron energy thus raising the ion density

3) Increase the rate of formation of plasma products such as free radicals.

The increase in ion bombardment energy by increasing rf power input could make the ion bombardment, at the surface, a more probable reaction for inducing chemical change by bond rupture or damage. Also, it could lower the activation energy on surrounding atoms in the area of bombardment thus increasing the rate of reaction. The increase in ion density will increase the rate of material being removed from the surface. Both can result in an increase of etch rate. However, an increase in ion energy or density alone may not be significant if the reaction is rate limited by a free radical process, i.e., the third effect as mentioned above will be limited and play the major role in controlling the reaction rate. Consequently, to avoid this event, the etching will be enhanced by a rise in free radicals concentration in plasma. When considering the effect of the third factor, according to the rf power study results illustrated in Figure 3.1-3.4, these etching processes would not be limited by a free radical process because the etch rates kept increasing linearly as the pressure and the flow rate were maintained constantly. However, beyond the range of the study, this factor possibly became effective thus slowing the increasing etch rates.

3.2 Flow Rate Study

The etch rate dependence on flow rate of SiO_2 and Si_3N_4 films was studied over a series of flow rates ranging from 50 sccm to 250 sccm for films etched by CF_3I; the pressure and power were set constantly at 50 mtorr and 1500 W, respectively. For SiO_2 and Si_3N_4 films etched by C_2F_6/O_2, the flow rates were varied from 50 sccm to 300 sccm while the pressure and power were maintained at 150 mtorr and 500 W, respectively.

It should be noted that the differences in pressures and rf powers between the case of CF_3I etchant and of C_2F_6/O_2 etchant were resulted from which the plasma condition was required to be steady and bright. For the study of etching with CF_3I, the high power (1500 W) and low pressure (50 mtorr), one of the conditions providing good plasma, were selected.

The etch rate dependence on flow rate of SiO_2 film etched by CF_3I was studied over a series of the flow rates ranging from 50 sccm to 250 sccm. The results showed almost constant etch rates over the entire range of study. In the other words, for this case, the etch rates were independent to the CF_3I flow rates, as shown in Figure 3.5.

Unlike SiO_2 film, etch rates of Si_3N_4 film etched by CF_3I increased from 1026 Å/min to 1425 Å/min with increasing flow rates from 50 sccm to 250 sccm, as shown in Figure 3.6.

In the case of C_2F_6/O_2 used as the etchant, the SiO_2 film etch rates decreased exponentially from 3061 Å/min to 235 Å/min while the flow rates increased from 50 sccm to 300 sccm, as shown in Figure 3.7. The Si_3N_4 film etch rates increased from 295 Å/min to 1026 Å/min as the flow rates increased from 50 sccm to 300 sccm, as shown in Figure3.8.
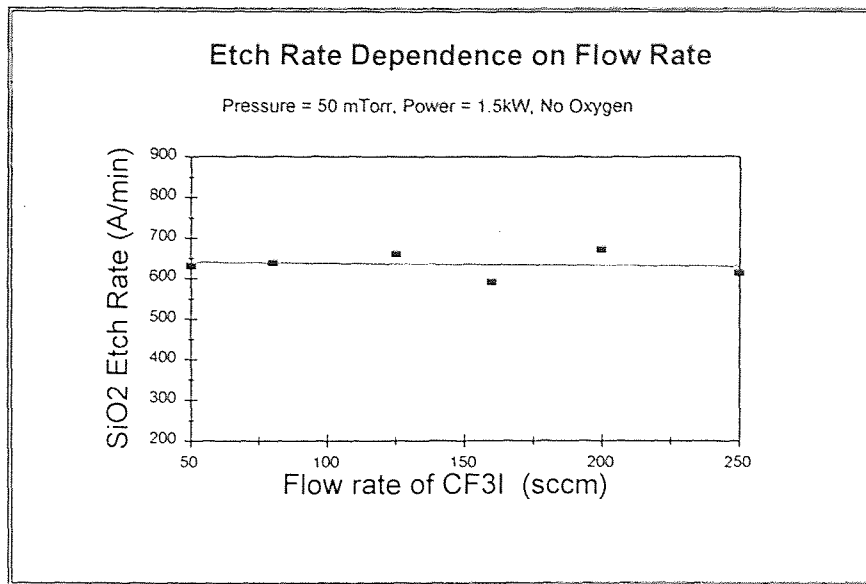
Figure 3.5 The etch rate dependence on flow rate of SiO_2 film etched with CF_3I at pressure = 50 mTorr, power = 1500 W, rf = 100 kHz, no oxygen content
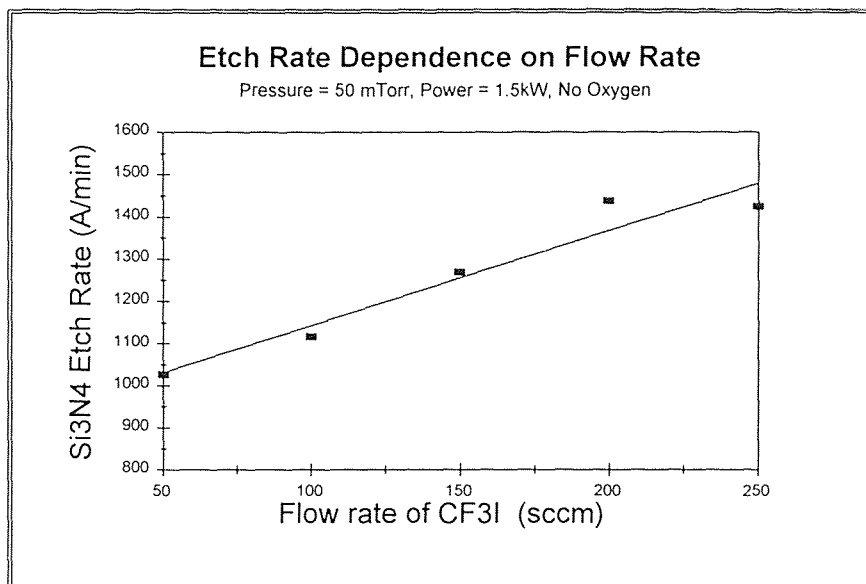
Figure 3.6 The etch rate dependence on flow rate of Si_3N_4 film etched with CF_3I at pressure = 50 mTorr, power = 1500 W, rf = 100 kHz, no oxygen content

Figure 3.7   The etch rate dependence on flow rate of SiO_2 film etched with C_2F_6/O_2 (ratio 1:1) at pressure = 150 mTorr, power = 500 W, rf = 100 kHz

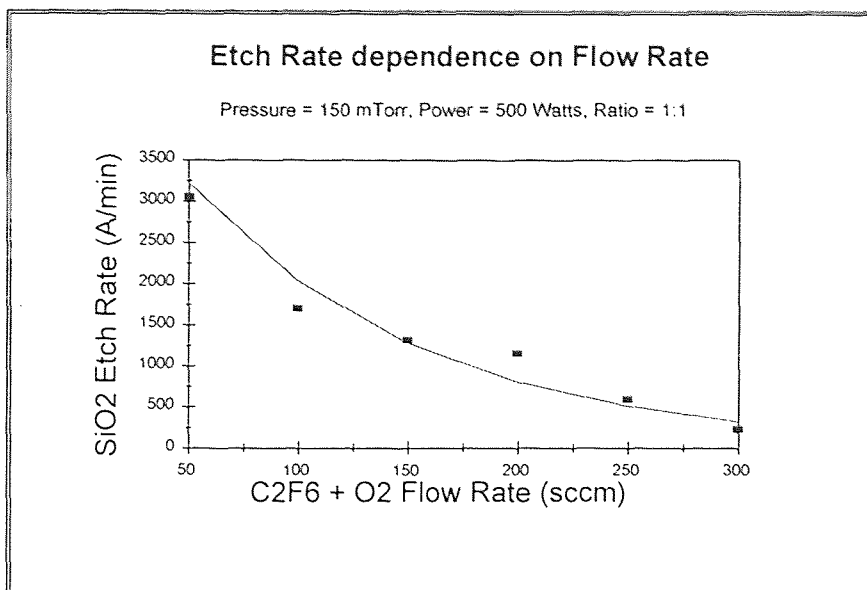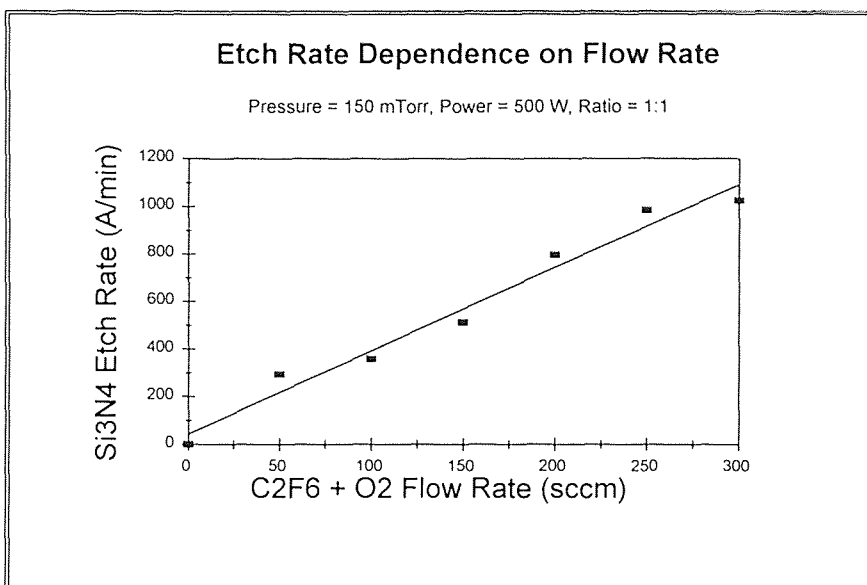**Figure 3.8**   The etch rate dependence on flow rate of Si_3N_4 film etched with C_2F_6/O_2 (ratio 1:1) at pressure = 150 mTorr, power = 500 W, rf = 100 kHz

As shown in Figure 3.5-3.8, the etch rate dependence on flow rate varied from etchant to etchant and from material to material. This flow rate dependence occured because of a superposition of two different effects: supply rate limited etching and pumping rate limited etching, as shown diagramatically in Figure 1.7. For some systems, either supply rate limited etching or pumping rate limited etching controls the etching process as one can see in this study.

For supply rate limited etching, there is a large flow rate effect for low flow regime. In other words, this low flow rate effect is simply due to an inadequate supply of etchant gas. Evidently, this effect displayed in Figure 3.6 and Figure 3.8. As illustrated, the increase in flow rate resulted in the increase in etch rates over the entire rage of study.

It is noticeable that the supply rate limited etching had a considerable effect particularly on Si_3N_4 film for both etchants. This may be attributed to high utilization factor[9] of Si_3N_4 film etching when compared to that of SiO_2 film etching. The utilization factor, U, is defined as:

$$U = \frac{\text{Etch rate of atoms}}{\text{Input flux of reactive molecules}} \qquad (3.1)$$

The limiting case, unexpected to attain, would be 100% utilization, i.e., all of the input etchant was converted to etching products. The schematic presentation for this case was shown in Figure 1.7.

For pumping rate limited etching, as the flow rates increase, the accompanying increase in pumping speed (for constant pressure operation) will eventually produce a situation where active species can be pumped away before they have the opportunity to

react. Additionally, at the same time the initial etchant gas is less utilized. The aforementioned effects were shown diagramatically in Figure 1.7 as well as in Figure 3.5 and Figure 3.7 for the results from experiments.

According to the Figure 3.5 and Figure 3.7, the etching of SiO_2 with CF_3I displayed this effect on etch rate less obviously than that of SiO_2 with C_2F_6/O_2. This could be resulted from much higher pumping rate for the case of etching SiO_2 with CF_3I in which the system was required to keep pressure constant as low as 50 mtorr. As a result, at the larger flow rate, the pumping rate had to be very large in order to maintain pressure at the desired level. This can make speed of gas molecules ($\overline{C}$) very high and reaction probability at the wafer (R_s) low while the flow rate (Q) was high. According to the formular of pumping rate limited etching shown in Figure 1.7.

$$E = E_L \left[\cfrac{1}{1 + \cfrac{4Q}{P\overline{C}} \cdot \cfrac{1}{R_s A_s}} \right] \tag{3.2}$$

The competition among these 3 factors may result in etch rate as shown in Figure 3.5 where the mean speed of the gas molecules was high enough to keep the etch rate constant. For the etching of SiO_2 with C_2F_6/O_2, the mean speed of the gas molecules was not too high to dominate the etching process because of lower pumping rate. In the other words, both flow rate and reaction probability had the stronger effect on etching process resulting in exponential decrease in etch rate.

3.3 Pressure Study

The etch rate dependence on pressure of SiO_2 and Si_3N_4 films was studied over a series of pressures ranging from 50 mtorr to 300 mtorr. For SiO_2 film etched by CF_3I, the flow rate and power were maintained at 105 sccm and 1500 W, respectively. It should be advised that etching of Si_3N_4 film was not achievable at the pressure over 50 mtorr because of polymer forming on the surface of the film resulting in ceasing of etching process. As a result, the study of Si_3N_4 films etched by CF_3I was waived. For SiO_2 and Si_3N_4 films etched by C_2F_6/O_2, the flow rate and power were maintained at 150 sccm and 500 W, respectively.

The SiO_2 film etched by CF_3I, when varying pressure from 50 mtorr to 250 mtorr, provided the etch rates decreasing from 1563 Å/min (at 50 mtorr) to 1209 Å/min (at 100 mtorr) and then increasing to 1833 Å/min (at 250 mtorr), as shown in Figure 3.9.

In the case of C_2F_6/O_2 used as the etchant, the SiO_2 film etch rates decreased from 1449 Å/min to 299 Å/min with the increase of pressure from 50 mtorr to 300 mtorr, as shown in Figure 3.10. Similarly, the etch rates of Si_3N_4 film decreased from 642 Å/min to 225 Å/min while increasing the pressure from 50 mtorr to 300 mtorr, as shown in Figure 3.11.

When increasing the plasma pressure, many effects can occur simultaneously as followings:

1) The increase in rate and type of free radicals and ion products because of the increase in collision rates (reductions in the mean free path of the plasma species)

between the electrons and gas molecules and between ions and neutrals. These species could physically or chemically absorb on the wafer surface.

2) The increase in recombination reactions in the plasma forming high molecular weight condensed polymers on wafer surfaces. Such recombination reactions are more probable at higher pressure, and with long resident time for free radicals of heavy mass.

3) The decrease in ion energy on impact with the electrode surface due to the increase in collision rates resulting in inadequacy in the ion energy to induce chemical reactions which need ion bombardment. The polymer may grow on an exposed surface if the ion arriving have an energy below the sputtering threshold to remove polymer from the surface.
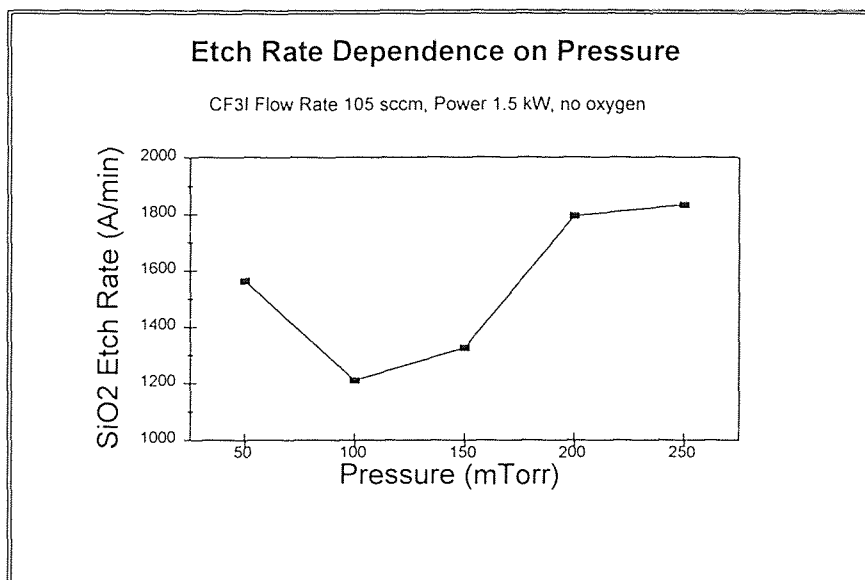
Figure 3.9   The etch rate dependence on pressure of SiO_2 film etched with CF_3I at flow rate = 105 sccm, power = 1500 W, rf = 100 kHz, no oxygen content.

Figure 3.10 The etch rate dependence on pressure of SiO_2 film etched with C_2F_6/O_2 (ratio 1:1) at flow rate = 150 sccm, power = 500 W, rf = 100 kHz

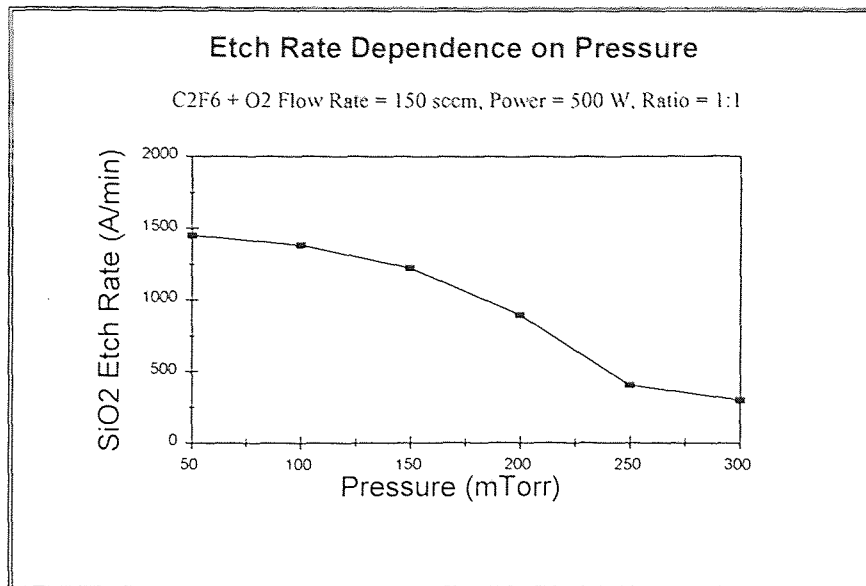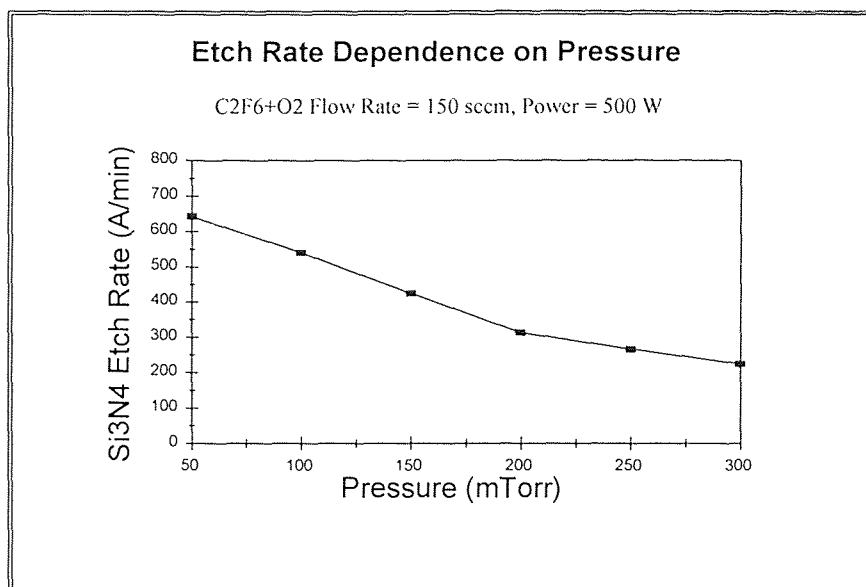**Figure 3.11** The etch rate dependence on pressure of Si_3N_4 film etched with C_2F_6/O_2 (ratio 1:1) at flow rate = 150 sccm, power = 500 W, rf = 100 kHz

Any of these aforementioned effects could be the rate-controlling step for wafer etching process. According to the above results as illustrated in Figure 3.9-3.11, the third effect would play the major role in etching process with insufficiently high pressure to induce polymer forming. However, for SiO_2 etched with CF_3I at the pressure higher than 100 mTorr, the collision resulting in enhancing physical or chemical absorption maybe dominate the etching process. Therefore, at the pressure range 100 mTorr - 250 mTorr, the etch rate increased. As discussed above, the Si_3N_4 film etched with CF_3I, reportedly, was not achievable because of undergoing with polymer formation. The second effect as well as the third effect can explain this.

3.4 Gas Composition Study

Etch rate dependence on gas composition of SiO_2 and Si_3N_4 films was studied over a series of ratio of O_2 to CF_3I ranging from 0 to 0.6 for SiO_2 film etching and from 0 to 0.48 for Si_3N_4 film etching. In this study, the flow rate of CF_3I , pressure, and power were maintained at 105 sccm, 50 mTorr, and 1500 W, respectively, for each experiment.

It should be noted that for SiO_2 film etched with the O_2 to CF_3I ratio over 0.35, the slight reddish particles covering throughout the sample were visually initially observed as well as at the reactor side wall, electrode, and susceptor. Like SiO_2 film etching, the etching of Si_3N_4 film with the O_2 to CF_3I ratio over 0.35 produced by product of reddish particles.

The etch rate of SiO_2 film increased from 640 Å/min to 3290 Å/min while increasing ratios from 0 to 0.6, as shown in Figure 3.12. The etch rate of Si_3N_4 film increased from 1117 Å/min to 4268 Å/min while increasing ratios from 0 to 0.35.

increased from 1117 Å/min to 4268 Å/min while increasing ratios from 0 to 0.35. However, the more O_2 content added to the gas composition, over the ratio of 0.35, resulted in decreasing of etch rate. As a result, the etch rate of Si_3N_4 film decreased from 4268 Å/min to 3909 Å/min with the increase of ratio from 0.35 to 0.48, as shown in Figure 3.13.

The increase in etch rates of SiO_2 and Si_3N_4 with the addition of O_2 to CF_3I could be resulted from which oxygen can react with dissociated CF_3I plasma species and can inhibit following recombination reactions [6]:

$$CF_3^{\bullet} + I^{\bullet} \rightarrow CF_3I \qquad (3.3)$$

$$CF_3^{\bullet} + CF_3^{\bullet} \rightarrow C_2F_6 \qquad (3.4)$$
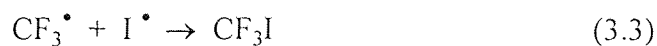
The role of oxygen (both O_2 and $O^{\bullet}$) may be to scavenge the $CF_3^{\bullet}$ radicals thus preventing recombination with $I^{\bullet}$ and $CF_3^{\bullet}$ itself. In addition, it can result in producing fluorine rich plasma according to the following reactions:

$$CF_3^{\bullet} + O_2 \rightarrow COF^{\bullet} + OF^{*} \qquad (3.5)$$

$$CF_3^{\bullet} + O^{\bullet} \rightarrow COF_2 + F^{\bullet} \qquad (3.6)$$
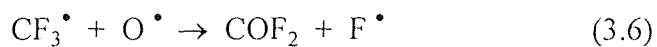
However, OF^{*} is unstable and decomposed either by the process. Therefore, the following reaction will be proceeded:

Figure 3.12 The etch rate dependence on gas composition of SiO_2 film etched with CF_3I at flow rate = 105 sccm, pressure = 50 mTorr, power = 1500 W, rf = 100 kHz
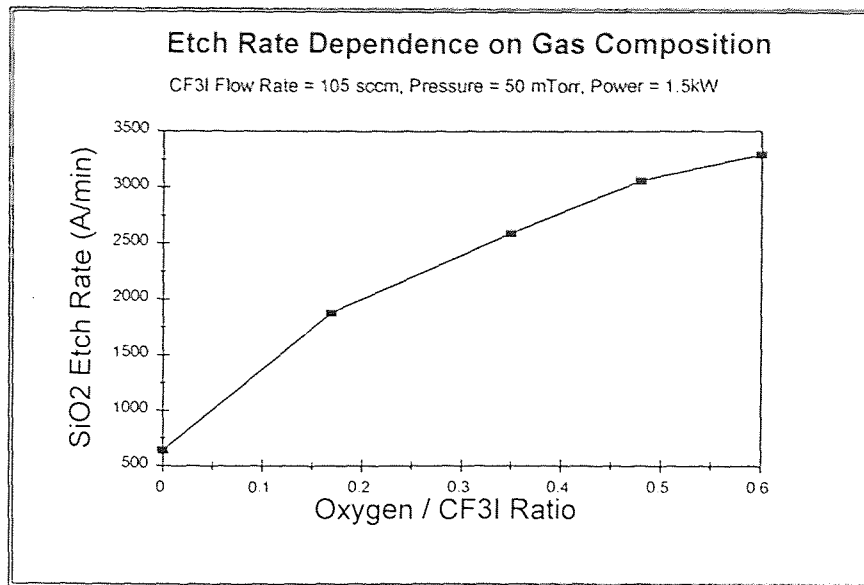

Figure 3.13 The etch rate dependence on gas composition of Si_3N_4 film etched with CF_3I at flow rate = 105 sccm, pressure = 50 mTorr, power = 1500 W, rf = 100 kHz
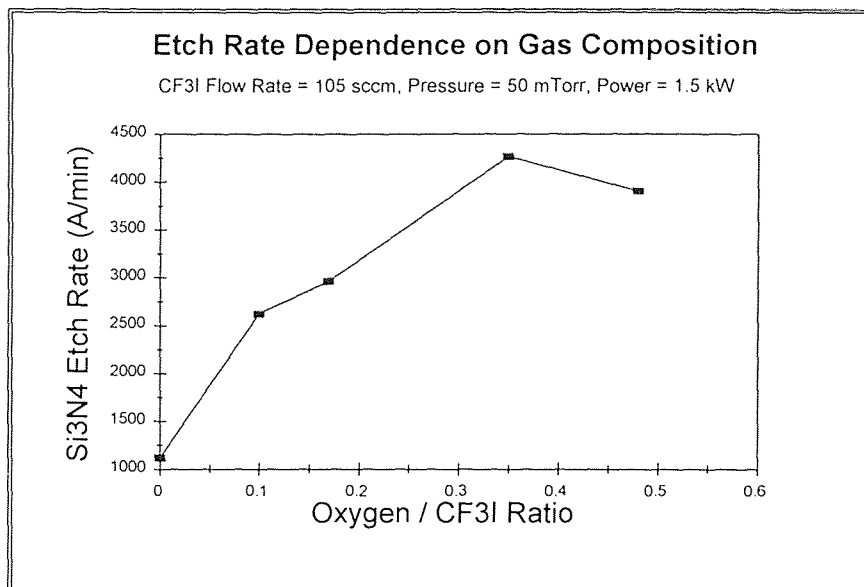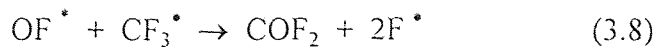
$$2OF^{\bullet} \rightarrow 2F^{\bullet} + O_2 \qquad \text{or} \qquad (3.7)$$

$$OF^{\bullet} + CF_3^{\bullet} \rightarrow COF_2 + 2F^{\bullet} \qquad (3.8)$$

The active plasma species, $COF^{\bullet}$ and $F^{\bullet}$, as a result of O_2 addition to CF_3I, could provide the high etching rate of both SiO_2 and Si_3N_4. At the same oxygen/CF_3I ratio, the Si_3N_4 etch rates were generally observed to be higher than that of SiO_2. This may be because of the weaker bond between Si and N when compared to the bond between Si and O. Consequently, Si and N atoms from the surface of Si_3N_4 film can be dissociated easier.

However, when increasing oxygen/CF_3I ratios the rate of etch rate will be decreasing. Obviously, it can be seen in Figure 3.13 in which the etch rate increased rapidly at the early stage and then slower increased until reached the highest etch rate. Subsequently, the etch rate decreased. This can be explained by which the more increase in oxygen will result in more chemisorption of $O^{\bullet}$ on the film surface thereby reducing the etch rate. Thus, one can consider that with the increase in oxygen/CF_3I ratios, there will be the competition between plasma etch active species and $O^{\bullet}$ atoms where the greater one will present the stronger effect.

The observed reddish particles inside the chamber could be due to the compound of iodine generated from the recombination of $I^{\bullet}$ with some plasma species or with $I^{\bullet}$ itself. At the higher ratios of O_2/CF_3I, the more $I^{\bullet}$ was inhibited to recombine with $CF_3^{\bullet}$ according to the above equation. In addition, the more $CF_3^{\bullet}$, when increasing the ratios, was reacted with both O_2 and $O^{\bullet}$ leaving rich $I^{\bullet}$ to produce iodine compound as a result.

CHAPTER 4

CONCLUSIONS

The etching performance of Trifluoroiodomethane (CF_3I) when compared to of C_2F_6/O_2 generally brought about the same characteristics in power and flow rate for both types of dielectric films, SiO_2 and Si_3N_4. The etch rates was increased upon increasing power because of the increases in ion bombardment energy, ion density, and free radicals. The etch rate dependence on flow rate was caused by the superposition of two different effects: supply rate limited etching and pumping rate limited etching. The etching of Si_3N_4 was controlled by supply rate limited etching attributed to high utilization factor. With regard to that of SiO_2, pumping rate limited etching played the major role in etching process resulted from which the accompanying increase in pumping speed for constant pressure operation will eventually produce a situation where active species can be pumped away before they have the opportunity to react.

There were two restricted conditions in etching with CF_3I. First, etching of Si_3N_4 at the pressure higher than 50 mTorr can result in polymer film forming. This may be caused by the increase in recombination reactions in the plasma forming high molecular weight condensed polymer on wafer surface. Secondly, with the higher composition of oxygen to CF_3I, the reddish particles forming all over the sample including reactor side wall can be observed. It was believed one of the iodine compounds. Therefore, the potential CF_3I as a substitute for C_2F_6/O_2 was limited to the pressure less than 50 mTorr and O_2/CF_3I ratio less than 0.17 if same operating conditions set for study were utilized.

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