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Reactive ion etching of SiO₂ using CHF₃/CO₂ gas mixture

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REACTIVE ION ETCHING OF SiO_2 USING CHF_3/CO_2 GAS MIXTURE

**A Thesis Presented to
The faculty of the Department of Materials Engineering
San Jose State University**

**In Partial Fulfillment of
the Requirements for the Degree
Master of Science**

**By
ANTHONY HYUNWOO CHUNG**

December 1997

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ABSTRACT

Reactive Ion Etching of SiO₂ Using CHF₃/CO₂ Gas Mixture

By Anthony Hyunwoo Chung

The reactive ion etching of silicon dioxide with CHF₃/CO₂ gas mixture was investigated using an AME-8110 RIE etcher. Five etch process parameters were varied: power, pressure and flow rates of CHF₃, CO₂ and O₂. The etch rates of Si, SiO₂, and photoresist were measured. The etch rate ratios of SiO₂-to-Si and SiO₂-to-photoresist were analyzed to determine the optimum etch process condition. It was found that CO₂ addition to CHF₃ was sufficient to achieve high SiO₂/Si and SiO₂/resist etch rate ratios: the maximum etch ratios obtained were 18 and 3.2, respectively. The effects of the process variables were obtained by a second order regression analysis of the data. The observed trends are consistent with the analysis based on published reports.

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1. INTRODUCTION

The driving force for the rapid development of plasma etch processing over the past 20 years has been the microelectronic industry and in particular, the fabrication of silicon integrated circuits (IC's). There has been a consistent annual doubling of the complexity of these circuits: today, memory chips containing over 16 million transistors have been in production for a few years, chips with 64 million transistors are beginning production, chips comprised of over 256 million transistors are being developed, and there is on-going research work involving circuits with 4 times that number of active devices. This increased complexity is driven by the need to provide more functionality and to reduce the cost of providing it. The large increase in the number of transistors has been accomplished primarily by reducing their size. In the early 1970's, the feature size (i.e. transistor gate length) was 20 μm . Today, feature size of 0.25 μm is in production, with smaller sizes on the horizon.

Many IC fabrication processes involve the sequential formation of patterned layers of materials on the wafer surface. To form sub-half-micron features requires anisotropic pattern delineation. Wet etching cannot be used, since its isotropic etch results in larger hole patterns than the originally intended size. Anisotropy is achieved by plasma etching by exposing the wafer directly to the electric field, known as reactive ion etching (RIE).

RIE and other plasma etching processes have been discussed in detail in many books^[1,2] and articles.^[3,4] Chapter 2 provides a review of plasma etching.

The major application of plasma etching in IC fabrication processes is the anisotropic patterning of contact holes to silicon, and of via holes between various levels of interconnect in multilevel metallization, as shown in Figure 1. This involves dry etching processes for silicon dioxide, which are based on fluorocarbon (Freon) discharges. The chemical endproducts of the reaction are silicon tetrafluoride and carbon monoxide or dioxide. Plasma etching of silicon (Si) and silicon dioxide (SiO_2) by Freons is well documented.^[5,6] Aside from anisotropy, high SiO_2/Si and $\text{SiO}_2/\text{photoresist}$ etch rate ratios is another crucial factor in oxide etching. Chapter 3 provides a review of silicon and its oxide etching in fluorocarbon plasmas.

Figure 1: Schematic cross section of 2-level metal interconnect

To meet today's SiO_2 plasma etching requirements, the most commonly used gas is Freon-23 (trifluoromethane) in addition to other gases, such as Ar, He, N_2 , H_2 , CO, and other variants of Freon gases. The effect of adding carbon dioxide (CO_2) to trifluoromethane (CHF_3) on the etch rates and selectivity for oxide etching relative to silicon in the reactive ion etching was examined in this study. From the review of relevant literature in Chapter 3, as well as previously unpublished work by the author, it was hypothesized* that CHF_3/CO_2 plasma would lead to high etch rates for SiO_2 while maintaining low etch rates for Si, and resulting in high SiO_2/Si etch rate ratio. CO_2 was found to be sufficient to prevent polymerization on the wafer surface and on the walls of the reaction chamber.

Chapter 4 describes the experimental procedures for wafer preparation, RIE etching, and etch rates and selectivity measurements. Decision was made to use the screening matrix to do initial characterization and then use factorial experiments to optimize the process. The process variables were set within the range of the machine capability. Since the maximum SiO_2/Si etch rate ratio occurs when the etching and polymerization on silicon surface is at equilibrium, data could not be collected under some conditions close to the equilibrium point. The design of experiments (DOE) is discussed in Chapter 4.

* The author was unaware of the work of Choe et al.⁷ and Shanfield et al.⁸ when the effect of addition of CO_2 to CHF_3 was hypothesized. The results obtained in this study not only are consistent with the articles, but also explored a much wider process window.

The process variables were power, pressure, and flow rates of trifluoromethane, oxygen, and carbon dioxide.

The results and discussion are presented in Chapters 5 and 6, respectively. The hypothesis that CO_2 addition to CHF_3 leads to high SiO_2/Si etch rate ratio was confirmed.

2. OVERVIEW OF PLASMA ETCHING

Wet etching processes has been replaced by plasma assisted etching procedures in many semiconductor manufacturing processes . The most important driving force behind the rapid introduction of plasma-based etching technology into current semiconductor manufacturing has been the achievement of etch directionality and the ability to faithfully transfer lithographically defined photoresist patterns into underlying layers. In addition, plasma based dry etching processes are superior to wet etching because of cleanliness, compatibility with automation and vacuum processing technologies. Plasma-based etching techniques include ion milling, sputter etching, reactive ion beam etching, plasma etching, and reactive ion etching.

Reactive ion etching (RIE) is a plasma-based dry etching technique characterized by a combination of physical sputtering and the chemical activity of reactive species. This enables the achievement of material selective etch anisotropy.

2.1 Plasma

A plasma is a gas containing charged and neutral species, including some or all of the following; electrons, positive ions, negative ions, atoms, and molecules. On average a plasma is electrically neutral, because any charge imbalance would result in electric fields that would tend to move the charges in such a way as to eliminate the imbalance.

As a result, the density of electrons plus the density of negative ions will be equal to the density of positively charged ions.

An important parameter of a plasma is the degree of ionization of the gas, which is the fraction of the original neutral species which have become ionized. Plasmas with a degree of ionization much less than unity are referred to as weakly ionized, and the relatively large population of neutral species dominate the behavior of the plasma. In fully ionized plasmas, the degree of ionization approaches unity, and neutral particles play little or no role.

To form and sustain a plasma requires some energy source to produce the required ionization. Under steady state conditions, the rate of ionization must balance the losses of ions and electrons from the plasma volume by recombination and diffusion or convection to the boundary. Plasma is often referred to as the fourth state of matter, since it occurs by adding energy (heat) to a gas. There is not, however, a distinct phase change in going from a neutral gas to a plasma. The process is more continuous.

A plasma is initiated and sustained by electric fields which are produced by either direct current (dc) or alternating current (ac) power supplies. Typical ac frequencies of excitation are 100 kHz, at the low end of the spectrum, 13.56 MHz in the radio frequency (rf) portion of the spectrum, and 2.45 GHz in the microwave region. These plasma are

also referred to as electric discharges, gaseous discharges, or glow discharges (the latter because they emit light). These terms are often used interchangeably.

2.2 Plasma Etching

Plasma etching is defined as the process of removal of material by interaction with glow discharge. Of all the species produced in the discharge, two classes have special importance for etching.

One type of species are reactive neutrals, hitting the surface at random, without any impact directionality. The reactive neutrals: (a) react chemically to form volatile compounds, resulting in transportation of surface material to the system exhaust, and (b) produce surface coatings by polymerization, either directly, from the source gas, or indirectly, from the product formed in the reaction with the substrate.

The other type are the positive ions, which hit the wafers perpendicularly as a result of the dark space electric field. These accelerated ions can: (a) remove material by physical sputtering; (b) locally enhance the surface reaction with reactive neutrals; (c) suppress surface polymerization.

The four most important parameters in dry etching processes are etch rate, non-uniformity, anisotropy and selectivity. The etch rate is the measure of how fast a material is removed, and is usually measured in angstrom per minute ($\text{\AA}/\text{min}$). The etch

non-uniformity is defined as a measure of how uniform a material is removed from the wafer surface.

The degree of anisotropy of an etch process is expressed as

$$A = 1 - V_h / V_v \quad \text{Equation (1),}$$

where A is the degree of anisotropy, V_h is the horizontal etch rate, and V_v is the vertical etch rate. Isotropic etching ($A = 0$) is represented schematically in Figure 2a, and anisotropic etching ($A \sim 1$) in Figure 2b. Since the horizontal etch rate will never be eliminated from the etch process, the anisotropic etch with $A=1$ will never be true.

Fig. 2: Schematic cross section of (a) isotropic and (b) anisotropic etch conditions

The selectivity of a process (S_{AB}) is a measure of the etch rate of the layer to be etched (E_A) relative to other material (E_B) on the wafer surface, and is normally expressed as the ratio of these two rates; $S_{AB} = E_A / E_B$. The selectivity of the material of interest to the masking material and to the layer immediately under the layer to be etched are two

important process parameters. The former usually determines the initial height of resist necessary to accurately transfer a pattern into a layer.

High selectivity requires E_A to be much higher than E_B , and necessary whenever a process requires an overetch. Overetching is essential in most cases because all etch processes have some degree of etch rate non-uniformity. In addition, the deposited film to be etched starts with a nonuniform thickness due to inherent deposition conditions. Figure 3 is an example of contacts landing on varied depths of 1 and 2, where field oxide isolation introduces a step height. In order to etch through contact A, enough selectivity to polycrystalline silicon (Poly) underlayer of contact B is required. If an etch process is not selective, there is a good chance that contact B will “punch-through” the Poly underlayer before Contact A is completely etched. Therefore, it is a common practice to etch with a highly selective process for a certain percentage time longer than is necessary to ensure complete removal of the film.

Fig. 3: Schematic cross-section of plasma etch on topography.

It is because of this overetch that the selectivity to the exposed underlying layer is important, as illustrated in Figure 4. In Figure 4(a), a high selectivity process will remove very little silicon during overetch to ensure complete removal of SiO_2 from the bottom of the contact. In Figure 4(b), low selectivity etch results in excessive silicon gouging during overetch, which is not desirable.

Fig. 4: Schematic cross-section of plasma etch with (a) high selectivity and (b) low selectivity ratio

2.3 Effect of Process Variables

Numerous process parameters can be varied during plasma etching, such as pressure, temperature, power, and flow rates of different gases. The types of gases used are determined by the type of material that is to be removed. Pressure and power are considered among the biggest contributors to the variability of plasma etching processes.

2.3.1 Effect of Pressure

One of the most important process parameters is pressure. It affects the etch rate, dc bias, and etch profile. At low pressures (< 5 mTorr), the etching is done primarily by

ions. As the pressure is increased, the concentration of neutral species increases and therefore, so does chemical etching rate and the overall etch rate. Figure 5 shows the effect of pressure on etch rate for Si_3N_4 , Si, and SiO_2 , at 150 Watts etched in a barrel etcher with $\text{CF}_4\text{-O}_2$ chemistry.^[9]

Figure 5: Film average etch rates as a function of total pressure.

The highest increase in the etch rate due to pressure increase is achieved by Si_3N_4 which is mostly chemical etching. The etching of SiO_2 is more of a physical etching process and it changes very little as pressure is increased. In addition to increasing the etch rate, increasing the pressure also results in the reduction of dc bias. Increasing the pressure lowers the electron temperature, and correspondingly causes the decrease in dc bias.

Lastly, the higher pressure promotes chemical etching, which results in undercutting, or a sloped etch profile.

2.3.2 Effect of RF Power

Another important process parameter is the rf power, which affects the etch rate, dc bias, etch profile, and etch selectivity. At the higher power levels, the concentration of radicals and the etch rate are both higher. Photoresist erosion will also increase with rf power due to more ion bombardment. The effect of power on the etch rate for Si_3N_4 , Si, and SiO_2 , and photoresist is shown in Figure 6 for the case where pressure is at 0.6 Torr etched in a barrel etcher with $\text{CF}_4\text{-O}_2$ chemistry.^[10]

Figure 6: Film average etch rates as a function of RF Power Density for Si_3N_4 , Si, and SiO_2 , and photoresist .

The advantages of using higher rf power levels are: faster throughput by increased etch rate, more anisotropic profile, and better uniformity. The disadvantages are that the increased ion energies cause a decrease in selectivity between oxide and silicon, and reticulation of the photoresist. DC bias will also increase with power, which will increase the etch rate of ion-enhanced processes.

2.4 Plasma Etching Equipment

There are many different types of plasma etching equipment available today. They are generally categorized as batch and single wafer processing. The latter type of etchers are becoming the norm for many etching applications due to the trend towards smaller geometry and larger silicon wafers. The most common type of plasma source is the capacitively coupled rf discharge. This is considered a low-density plasma source, where density refers to the electron density. Currently, there is a great effort in developing high density plasma (HDP) sources for semiconductor processing.^[11] In such sources, magnetron, electron cyclotron resonance (ECR), and helicon wave produce plasma by using a relatively high magnetic field, which has been linked to gate oxide breakdown issues. On the other hand, inductively coupled plasma (ICP)^[12] is gaining popularity because a high electron density is obtained without an additional magnetic field.

For many existing fabrication lines, the cost of upgrading to such technology can be prohibitive, therefore requiring the use of conventional batch etch systems. In the following chapter, a survey of different types of etchers will be presented with respect to

SiO₂ etching. A proposal will be made to achieve similar trends as observed from the literature survey using a conventional RIE batch system with CHF₃/CO₂ chemistry.

3. SiO₂ ETCH

High SiO₂/Si and SiO₂/photoresist etch rate ratios can be achieved by utilizing fluorocarbon plasma based on CHF₃, CF₄/H₂, or related gas mixtures in capacitively coupled rf diode plasmas. Different reactive species exist simultaneously in the gas phase of these discharges and impinge on the surface of the substrate. By varying the gas mixtures, the fluorine atom concentration in the plasma discharge can be increased or decreased. A lower fluorine atom concentration decreases the importance of recombination of fluorine with CF₃ radicals and a discharge rich with unsaturated fluorocarbons, such as CF₂, is produced.^[13] These species are precursors of polymeric fluorocarbon films. High etch ratio results because a thin layer of fluorocarbon film forms on non-oxidized surfaces that prevent their etching. The SiO₂ surface often remains free of fluorocarbon films and it is etched.

Heinecke discovered that by the addition of H₂ to CF₄, the etching of Si can be minimized relative to the etching of SiO₂.^[14] Lehmann and Widmer used CHF₃ to obtain similar results.^[15] The hydrogen reduces the Si etch rate in two ways. First, the atomic H scavenges atomic F in the gas phase to form HF molecules and the Si etch rate, which depends on the F concentration, is consequently reduced. Second, a partially fluorinated, highly crosslinked fluorocarbon film selectively forms on the Si surface which again

reduces the Si etch rate. Thus, SiO_2/Si etch ratio is dramatically increased, achieving a highly selective oxide etch process.

Recently, there has been increased activity in exploring the use of mixing CO gas with fluorocarbon gas to achieve a highly selective oxide etch process. The working hypothesis is that a thin layer of carbon is deposited on both Si and SiO_2 surfaces. However, the process condition is such that the carbon layer is removed faster than it is deposited on the SiO_2 surface. Most of the experiments are carried out using high density plasma (HDP) tools which are more costly than the conventional RIE etchers and still in the development stages. In addition, there are toxicity concerns with using CO gas, thus necessitating safety precautions, such as double containment gas lines.

It is the intent of this thesis to determine the selectivity of oxide etch process using CO_2 gas in conjunction with fluorocarbon gas in a conventional RIE etcher. The motivation is two-fold: 1) The “next generation” high density plasma etchers are very expensive and are not yet fully characterized. The availability of a highly selective oxide etch process using conventional RIE etcher means tremendous savings for companies who have already invested in the current generation of etchers. 2) Although highly selective etching is possible with CO gas, CO is toxic, thus making it unsafe and expensive to use. Using CO_2 in place of CO, is safer, and the results of a preliminary investigation by the author of this thesis has shown that similar etch results may be possible.

3.1 SiO₂ Etch Mechanisms

Reactive ion etching (RIE) is a plasma-based dry etching technique characterized by a combination of physical sputtering with the chemical activity of reactive species.

Physical sputtering results when positive ions bombard the wafers perpendicularly as a result of the dark space electric field. Accelerated ions can remove materials by physical sputtering, locally enhance the surface reaction with reactive neutrals, and suppress the surface polymerization. Chemical etching is the result of reactive neutrals, hitting the wafer surface at random, without any impact directionality. These neutrals serve two purposes: (1) chemically react with the surface material to form volatile compounds, which are removed, (2) produce surface coatings by polymerization, either directly, from the source gas, or indirectly, from the product formed in the reaction with the substrate.^[16]

The etching species for Si and SiO₂ in fluorocarbon plasmas is the fluorine atom produced by the dissociation of the fluorocarbon. The etch rate for SiO₂ etching by fluorine radicals are about 1 to 2 orders of magnitude higher than the etch rate of Si. Ion assistance is the major factor that increases the etch rate of SiO₂. Selectivity in the etching of SiO₂ can be increased by decreasing the fluorine atom concentration or increasing the polymerization.

The formation of HF reduces the fluorine atom concentration in the plasma. HF does not react with Si, but it reacts with SiO₂ and produces SiF₄ and H₂O according to the following reaction.

HF formation can be enhanced by the addition of gases to the flow stream such as H₂ and CO, which will be discussed later in this section.

A fluorine deficiency can also be attained by using other Freon gases which have a lower fluorine to carbon ratio. Gases such as C₂F₆, and C₃F₈ have a lower F/C atom ratio than CF₄ and etching by these gases leads to a higher selectivity in oxide etching. This is shown in Table 1.

Table 1: C to F ratio of fluorocarbon gases w/r/t SiO₂ to Si etch selectivity ^[14]

Gas	Formula Weight	C:F atom ratio	SiO ₂ :Si selectivity
CF ₄	88.01	1:4	1:1
C ₂ F ₆	138.01	1:3	3:1
C ₃ F ₈	188.02	1:2.7	5:1
CHF ₃	70.01	1:2	10:1

Unsaturated fluorocarbon radicals are the precursors to the inhibitor sidewall film that promotes anisotropic etching. Unsaturated fluorocarbon polymers also consume the

fluorine radicals for saturation. Difluorocarbene radicals formed from the fluorocarbon feed gas are the precursors for polymer films. The main reaction in the CHF₃ plasma is:

3.2 SiO₂ Etching by CHF₃ and CF₄

M. Wiling et al. used only CHF₃ and CF₄ gas mixtures to achieve a high SiO₂/polycrystalline silicon (poly) etch ratio in a triode etcher.^[17] It was found that the CHF₃ provided the needed additional hydrogen to have a more selective etch process. By increasing the CHF₃ flow to 65% of total gas mixtures, the polymer coating formation was enhanced. Compared to pure CF₄ process, 65% CHF₃ + 35% CF₄ gas mixtures improved SiO₂/poly etch ratio from 11 to 29. However, the two gas process resulted in contact holes that were sloped due to polymerization. To straighten out the hole profile, the etch process was divided into two steps. First step used a low etch ratio process to remove most of SiO₂. The second step, with high SiO₂/poly etch ratio, was used to remove the remaining oxide plus an overetch to achieve a near 90 degree profile. The intent of this study was to use the existing tool to optimize the gas chemistry to achieve a high SiO₂/poly etch ratio.

Oehrlein et al.^[18] investigated the fluorocarbon deposition and etch rate for CHF₃ and CF₄ plasma in a Electron Cyclotron Resonance (ECR) etcher with variations in pressure, microwave power, and rf bias. The ECR etcher is a high density plasma tool and it is

still considered to be in a research and development stage. Figure 7 is a schematic representation of an experimental ECR etcher. The authors found that with no rf bias voltage, both the CHF_3 and CF_4 plasma produced fluorocarbon deposition, and the CHF_3 plasma yielded higher fluorocarbon deposition rate. As the microwave power was increased from 300W to 1400 W, the fluorocarbon deposition rate increased with both types of plasma, as shown in Figure 8a. Increasing pressure from 1 to 16 mTorr had the opposite effect, as shown in Figure 8b.

Fig. 7: Schematic drawing of the experimental Electron Cyclotron Resonance etcher ^[18]

Fig. 8: Fluorocarbon deposition rate onto a Si substrate as function of (a) microwave power and (b) pressure. ^[18]

The rf bias voltage was applied to overcome the fluorocarbon deposition so that etching can take place. In Figures 9(a) and (b), the increase in rf bias changed the fluorocarbon etch rate from negative to positive, or from deposition to etch. The horizontal line at zero indicate the equilibrium point between deposition and etch mechanism. As the rf bias voltage was increased, the etch rate of fluorocarbon film increased for both CF_4 and CHF_3 plasma.

The increase in the fluorocarbon etch rate for CHF_3 was slower than the CF_4 plasma.

This was due to higher fluorocarbon generation of CHF_3 plasma, as shown in Figure 8 without the rf bias voltage.

Fig. 9: Fluorocarbon deposition and etch rates in (a) CF_4 and (b) CHF_3 as a function of rf voltage for different pressures. ^[18]

Oehrlein et al. ^[19] further examined the effect of the rf bias on etch rates of SiO_2 and Si in an ECR tool. It was demonstrated that both the CHF_3 and CF_4 plasma etched both SiO_2

and Si faster with increasing rf bias, as shown in Figure 10. The CHF_3 plasma had a lower SiO_2 etch rate compared to CF_4 plasma. However, the CHF_3 plasma also had a much lower Si etch rate due to a lower fluorocarbon etch rate. The rf bias was used to control the fluorocarbon formation on both SiO_2 and Si surface. With the rf bias set at 130 volts, CHF_3 plasma achieved SiO_2/Si etch ratio of 15-to-1.

Fig. 10: (a) SiO_2 and Si etch rates in CF_4 and CHF_3 as a function of rf voltage for fixed microwave power (1000W) at 1 mTorr pressure. (b) The SiO_2/Si etch rate ratio corresponding to the data of (a). ^[19]

3.3 Effect of Hydrogen Addition to Fluorocarbon Plasma

Bell et al.^[20] investigated the selective SiO_2 etching in an inductively coupled high-density plasma using CHF_3 , C_2F_4 , C_3F_6 and their mixtures with hydrogen. The source for the high density plasma etcher was dubbed the radio frequency inductive (RFI) discharge and it is shown in Figure 11.

Fig. 11: Schematic drawing of RFI system^[20]

Their work confirmed the findings of Oehrlein et al.^[18,19], where without a radio frequency (rf) bias to the substrate, extensive fluorocarbon deposition takes place. When the hydrogen content was increased in the gas mixture, the fluorocarbon deposition rate increased correspondingly. However, when the rf bias was applied, fluorocarbon deposition was suppressed, and the etch rates for both SiO_2 and Si increased. This is

shown in Figures 12(a) and (b). As the rf bias was further increased, the etch rates for both films also increased. The fluorocarbon layer on both SiO_2 and Si surfaces was etching increasingly faster than it was depositing. Consequently, the Si etch rate increased, resulting in lower SiO_2/Si etch rate ratio. This is shown in Figure 13. Without H_2 in the input gas stream, the etch selectivity was limited to below 16. By using a gas mixture of C_2F_4 with 30% H_2 addition and lower rf bias, SiO_2/Si etch rate ratio up to 45 was achieved.

Fig. 12 SiO_2 (a) and Si (b) etch rates as a function of rf bias power in a CHF_3 , C_2F_4 , and C_3F_6 discharge containing 20% H_2 . The operating pressure was 15 mTorr and the rf top power 1000W. ^[20]

Fig. 13 Comparison of the SiO_2/Si etch rate ratio as a function of rf bias power in a pure CHF_3 , C_2F_4 , or C_3F_6 discharge and with additive H_2 . ^[20]

3.4 Effect of CO Addition to Fluorocarbon Plasma

Gambino et al.^[21] used C_4F_8 +CO mixtures in a magnetron reactive ion etch (MERIE) reactor to achieve a highly selective boro-phosphosilicate glass (BPSG)-to- Si_3N_4 etching. The type of dielectric layer used was typical of self-aligned contact (SAC) etch process, where BPSG (a doped SiO_2) was selectively etched until it reached the underlayer film (Si_3N_4). As the BPSG layer is etched to form contact holes, the underlayer film becomes exposed to the plasma. A thin layer of polymer forms on the Si_3N_4 , but not on the BPSG film, allowing the BPSG film to be completely etched. The author theorized that the C_4F_8 + CO gas mixture maximized the concentration of C-rich species such as $C_2F_4^+$, which provide a high etch rate ratio, and minimized the concentration of F-rich species, such as CF_3^+ . Higher concentration of F-rich species results in low etch ratio and is not desirable. TEM analysis confirmed that there is a thin layer of polymer which remains on the Si_3N_4 surface after the SAC etch process removed the BPSG layer.

Berruyer et al.^[22] studied the effect of CO addition to a C_2F_6 plasma on the etch rates of various doped SiO_2 and Si. The study was done on a commercially available high density, inductively coupled plasma reactor (ICP) from Applied Materials^[23]. This is shown in Figure 14. The concept is similar to the RFI system used by Bell et al.^[20], but the chamber design is very different.

By introducing a low CO gas flow to the C_2F_6 plasma, a high BPSG/Si etch ratio was obtained. When the CO content was increased in the gas mixture, the etch rate ratio

decreased, with higher Si consumption and increased etch rate of photoresist. This was explained by the presence of oxygen in the chemistry. The author was able to achieve a highly selective etch process by increasing the source power and lowering the temperature of the chamber to 260°C. This process demonstrates the feasibility of CO gas addition to the C_2F_6 plasma to etch BPSG film selectively to Si substrate.

Fig. 14: Schematic of high density plasma reactor ^[22]

Lastly, Ueno et al.^[24] studied the effect of CHF_3 , $CHF_3 + CO$, and CF_4 plasma on the etch rate of silicon oxynitride (SiO_xN_y) using a magnetron reactive ion etcher (MERIE). The etch rate of SiO_2 decreased in the order of CF_4 , CHF_3 , and $CHF_3 + CO$ plasma, while SiO_2/SiO_xN_y etch ratio increased in the same order. The etch rates for SiO_2 and SiO_xN_y

were found to correlate to both thickness and elemental composition of the fluorocarbon coating deposited on both surfaces. The carbon-rich CF_x films deposited on SiO_xN_y surface were found to be resistive to plasma etch, thus resulting in low SiO_xN_y etch rate.

Ongoing efforts to achieve a highly selective etch process utilize a high density plasma reactors, such as an ECR, ICP, or MERIE. Both ECR and ICP tools uses rf bias to control the fluorocarbon film deposition. The most important factor in achieving high etch rate ratio is using either H_2 or CO additive with the Freon gas. It was evident that there has to be a fine balance between suppressing polymer formation and using too much additive which reduces the high etch ratio of the etching process.

3.5 Justification for the Current Work

The hypothesis of this research project is that a CO_2 / Freon gas mixture will selectively etch SiO_2 to Si. There are numerous reports describing the use of CO and Freon gas mixtures to achieve high SiO_2/Si etch ratio. Therefore, it is hypothesized that there exists a process regime using CO_2 with Freon gas where SiO_2 can be etched with high selectivity to silicon. This argument is supported by comparing the thermodynamic properties of CO and CO_2 , as shown in Table 2. Note that there is very little difference in both ionization potential and the heat of formation (ΔH_f) of ions between the two gases. It is also hypothesized that the highest etch selectivity can be realized by using $\text{CO}_2 + \text{CHF}_3$. This is based on previous work^[17,18,19,20] which has consistently shown that

the CHF₃ plasma produced more fluorocarbon film, thus increasing the SiO₂/Si etch rate ratio. The results obtained from our experiment confirmed the hypothesis.

Table 2: Selected values of chemical thermodynamic properties of CO₂ and CO^[25]

Gas	Formula weight	ΔH_f° @ 0 K (Kcal/mole)	ΔH_f° @ 298 K (Kcal/mole)	Ionization Potential (eV)	ΔH_f of Ion (Kcal/mole)
CO ₂	44.01	-93.963	-94.051	13.769	232
CO	28.01	-27.199	-26.416	14.013	297

4. EXPERIMENTAL PROCEDURE

The approach of this study was to coat oxidized silicon wafers with photoresist (resists or PR), pattern it, etch them with different mixtures of CHF_3 and CO_2 gas, and measure the response variables. The RIE etcher used to carry out plasma etching is the Applied Materials AME-8110 system. Silicon wafers were thermally oxidized and were patterned using contact photolithography. A CO_2 gas cylinder was installed onto the etcher. There were many input variables which needed to be characterized for their contribution to the overall SiO_2/Si and SiO_2/PR etch rate ratio. In order to conduct the experiment in an efficient manner, design of experiment was used to come up with an initial screening matrix. Additional screening matrices were performed to eliminate the factors that were not significant and focus on those that affect the responses. The responses were etch rates, etch uniformity, and etch rate ratios.

4.1 Wafer Preparation

4.1.1 Thermal Oxidation of Si Wafers

Single crystal silicon wafers (100mm in diameter, [100] orientation, p-type 6 - 20 ohm-cm) were prepared by growing silicon dioxide. A thin layer of SiO_2 film was grown thermally to a thickness of 5000 to 6000 Å in a horizontal furnace at one atmosphere and 1100°C. The wafers were held vertically in slotted quartz boats and were loaded into the furnace. The setpoint temperature was reached by ramping up slowly to prevent wafer warpage. Once the temperature stabilized, oxygen was introduced at a pre-determined

flow rate for 36 hours. The O₂ gas was then shut off, the temperature of the furnace was ramped down slowly, and the thermally oxidized silicon wafers were removed and stored for later use.

4.1.2 Photolithographic Process

In addition to thermally grown wafers, plain silicon wafers were also patterned using contact photolithography sequence. The wafer was coated with positive photoresist S1400-27 by Shipley in the spinner at about 5000 RPM for 30 seconds for even coverage across the wafer surface. The coated wafers were then put into a soft-bake oven at 90°C for 30 minutes to drive out any solvents and moistures. After cooling, a photomask, a thin transparent sheet with the pattern shown in Figure 15 was placed on top of the wafers.

The wafers were individually exposed under a UV light for one minute, upon which the area of photoresist exposed to UV light become soluble in a solvent solution. To develop the pattern on the wafers, the exposed wafers were immersed in the developer, AZ400K, for one minute. The pattern was delineated when the exposed resist dissolved in the developer, leaving a pattern of the unexposed resist on the wafer. The developer was washed away from the wafer using DI water rinse and blown dry with air jet. A schematic drawing of the patterned thermally grown oxide wafer is shown in Figure 16.

Fig. 15: Pattern used to define holes and spaces. The nine holes were used to measure the film thickness using the Surface Reflectometer [actual size].

Fig. 16: Schematic representation of patterned wafer

4.2 Preparation of Plasma Etcher

The plasma etcher used was the Applied Materials AME-8110 hexode RIE system and is schematically shown in Figure 17. The system is capable of handling up to five separate gas types, to which three gases were already connected: CHF_3 , CF_4 , and O_2 , each equipped with its own MFC (mass flow controller) to control the amount of gas introduced into the etch chamber. An additional gas line was installed onto the system to accommodate the CO_2 gas.

The etcher is a batch type reactor, able to accommodate a total of 24 four-inch wafers at each pass. The process chamber consists of a stainless steel bell jar that can be raised and lowered by a mechanical hoist assembly and a vertical, hexagonal RF cathode or hexode. The hexode is mounted on an aluminum base plate. When the bell jar is lowered, it seals to the base plate and encloses the hexode to form the process chamber. During processing, power is supplied by a radio frequency (RF) power supply at a frequency of 13.45 MHz and “tuned” through a matching network to minimize reflected power. The grounded base plate and bell jar together form the anode. The anode to cathode ratio is about 2.5 - to - 1. This asymmetrical electrode configuration leads to a high ion energy towards the substrate surface and low anode sputtering. The gas mixture is introduced into the process chamber uniformly by means of the six stainless steel tubes installed on the inside wall of the bell jar. A combination of cryogenic and turbo pump systems is used to evacuate the chamber. The mass flow controllers are used to

separately regulate the flow of each gas. The pressure in the process chamber is monitored by a combination of thermocouple vacuum gauge, ion gauge and capacitance manometer, regulated by a feedback loop to a gate valve. All the system functions are controlled by a microprocessor.

Fig. 17: Schematic diagram of Applied Materials 8110.

The wafers are held in place by wafer platens, which can accommodate up to four wafers per platen. Each platen is held in place at each face of the hexode column such that backside of the wafer is in contact with the hexode. The temperature of the wafer is controlled by water channels going from the water chiller to the inside of the hexode column, and back out, thus maintaining the set temperature constant at 25°C.

The power can be controlled either by setting a desired wattage and monitor the resulting dc bias, or by setting the dc bias and monitor the wattage. All plasma etching was

performed with constant power, and monitoring the bias to note the stability of the plasma. The plasma stabilizes within the first ten seconds, and any fluctuations in the plasma during the remaining process time was monitored by changes in the dc bias voltage readings.

4.3 Measurement of SiO₂ Etch Rate

The etch rates of SiO₂ were determined by measuring the film thickness before (t_o) and after (t_f) each run, using the Nanospec™ Surface Reflectometer. The reflectometer calculates the film thickness by measuring the refractive index of the film through a range of wavelengths to derive what's known as an "optical" thickness. The thickness of the SiO₂ layer was the average of nine measurement sites shown as open circles in Figure 15. The etch rate in angstroms per minute was calculated by dividing the difference between oxide thickness ($t_o - t_f$), by the etch time (5 minutes). The etch uniformity was calculated by taking the difference between the maximum and the minimum values in the data set, and dividing it by twice the average of the data set. The minimum film thickness that can be accurately measured using the NanoSpec is 100 Å.

4.4 Measurement of Si Etch Rate

The etch rates of silicon were calculated by using both the surface profilometer and a scanning electron microscope (SEM).

4.4.1 Using Profilometer to Calculate Si Etch Rate

Patterned silicon wafers were etched for 30 minutes and the resist was stripped away by immersing for 3 minutes in a stripper bath of 10% p-toluene sulfonic acid by weight in DMSO which was maintained at 75°C. This was followed by a water rinse and air jet drying of the wafer. Moisture was removed by baking the wafers in a oven for 30 minutes at 100°C. A surface profilometer, equipped with a sensitive stylus, was then used to physically measure the step height of the silicon wafer surface. The Si etch rate was calculated by simply dividing the step measurement by total etch time, in this case 30 minutes.

4.4.2 Using SEM to Calculate Si Etch Rate

The patterned oxide wafers were etched for 30 minutes. This is enough time for the SiO₂ layer to be completely removed and overetch to occur into the silicon underlayer. A portion of the etched wafer was cleaved using diamond tipped scribe and the sample was dipped into a buffered HF bath to “decorate” or highlight the surface of the cross section. The sample was sputtered with gold and inserted into the SEM. The amount of Si loss was measured at 90,000x magnification. Equation 4 was used to calculate the etch time remaining (t_r) after SiO₂ has cleared.

$$t_r = \frac{t_i \left(\overset{\circ}{\text{\AA}} \right)}{ER_{ox} \left(\overset{\circ}{\text{\AA}}/\text{min} \right)} \quad \text{Equation (4)}$$

In this equation, t_i is the initial SiO_2 thickness and ER_{ox} is the SiO_2 etch rate. The Si etch rate was calculated by dividing the amount of Si loss (measured from SEM analysis) by t_r . There was very good agreement between the calculated Si etch rates using the surface profilometer and SEM techniques.

4.5 Measurement of Photoresist Etch Rate

The same sample used for measuring Si loss was also used to calculate the etch rate of photoresist. Since the photoresist was not stripped off before preparing the sample for the SEM analysis, it was used to measure the photoresist thickness after etch. The initial resist thickness was also measured with SEM to establish a good correlation to optical thickness, measured with the reflectometer. There were differences in final photoresist thickness obtained by two different methods. Detailed discussions on final photoresist thickness differences and how it was resolved is given in Appendix A.

4.6 Experimentation

There are process parameters, such as power, pressure, temperature and gas mixture ratios, which effect the etching process. However, the etching results vary depending upon the type of etcher and gases used. The combined effects of all the process parameters can be very complex. It is impossible to predict the etch rates when all the variables are changed simultaneously. Therefore, to conduct the experiment in an efficient manner, design of experiment was used to establish an initial screening matrix.

The purpose of the screening matrix was to characterize the main effects of each input variable. Whether CHF₃ and CO₂ gas mixtures alone was sufficient to prevent over-polymerization during etching process needed to be established. Thus, three types of gas mixtures were examined: (a) CHF₃ + CO₂ + O₂, (b) CHF₃ + CO₂ and (c) CHF₃ + O₂. The CHF₃+O₂ is the standard gas mixture of choice for the etcher and it was used to establish and monitor the performance of the tool throughout the experimentation.

The initial ranges for the process variables were chosen within the limits of the etcher capabilities from the literature reports on related processes^[26], and are listed in Table 3. The temperature of the hexode was kept constant at 25°C.

Table 3: Initial Screening Matrix Variables and their Ranges

Process Variables	Range
Pressure	30 - 90 mTorr
Power	1000 - 1600 Watts
CHF ₃ Flow Rate	50 - 100 sccm
CO ₂ Flow Rate	5 - 25 sccm
O ₂ Flow Rate	0 - 15 sccm

The results from the initial screening matrix were used to select the range settings for the first order experiment. These settings are listed in Table 4. A Half fraction, 2⁴⁻¹ screening design was used to generate the 9 experimental conditions. The temperature of

the hexode was again set constant at 25°C and the power was set at 1300 watts throughout this experiment.

Table 4: First Order Experiment Variables and their Initial Ranges

Process Variables	Range
Pressure	30 - 70 mTorr
CHF ₃ Flow Rate	50 - 100 sccm
CO ₂ Flow Rate	5 - 25 sccm
O ₂ Flow Rate	0 - 15 sccm

From the data analysis of first order experiment, a full factorial design was used to choose the range settings for the second order experiment. These setting are listed in Table 5. The constant process parameters were 25°C, 1300 watts power and 30 mTorr.

Table 5: Second Order Experiment Variables and their Initial Ranges

Process Variables	Range
CHF ₃ Flow Rate	50 - 100 sccm
CO ₂ Flow Rate	5 - 25 sccm

The closeness of fit obtained from both the first and second order experiment was very good, as discussed later in Sections 5.1 and 5.2, respectively. The design of experiments, chronology of data collection, and data analysis are discussed in detail in Appendix B.

5. RESULTS

The etch rates, uniformity and etch rate ratios of SiO₂/Si and SiO₂/resist were analyzed using a statistical analysis program STATGRAPHICS.^[27] The R-squared term was used to estimate the closeness of the fit, derived by performing an analysis of variance. Higher R-squared term indicate goodness of fit for the response variables.

5.1 First Order Experiment

The data obtained from the initial screening matrix (Table B2 in Appendix B) was used to generate the half-fractional design for the first order experiment described in Table 4. The process variables and the response variable for each run are listed in Table 6. The highest etch ratios of SiO₂/Si and SiO₂/PR obtained were 9.4 and 3.0, respectively.

Table 6: Etch Rates, Uniformity, and Etch Ratios for the First Order Experiment

RUN	Process Variables				Response Variables					
	Press (mTorr)	CHF ₃ (sccm)	CO ₂ (sccm)	O ₂ (sccm)	SiO ₂		Photoresist		Etch Ratio	
					Etch Rate (Å/min)	Etch Unif (± %)	Etch Rate (Å/min)	Etch Unif (± %)	SiO ₂ to Si	SiO ₂ to PR
1	70	50	5	15	473	2.3	158	3.4	4.3	3.0
2*	70	100	5	0	247	11.6	89	28.4	7.1	2.8
3	30	100	5	15	459	2.1	142	9.9	6.6	3.2
4	30	50	5	0	468	1.2	134	4.5	7.8	3.5
5	50	75	15	7.5	477	1.7	174	9.4	5.6	2.7
6	30	100	25	0	469	1.9	180	1.1	9.4	2.6
7	70	100	25	15	450	2.3	209	1.8	4.5	2.2
8	30	50	25	15	453	2.1	248	5.4	6.0	1.8
9	70	50	25	0	474	2.0	209	2.1	5.9	2.3

* Unstable plasma condition

The R-squared values were calculated using analysis of variance, and are listed in Table

7. The fit for the response variables were all above 96%.

Table 7: Analysis of Variance for First Order Experiment

Response Variable	Variation, R-Squared
SiO ₂ Etch Rate	96.63%
SiO ₂ Etch Uniformity	97.58%
Resist Etch Rate	99.95%
Resist Etch Uniformity	99.17%
SiO ₂ /Si Etch Ratio	96.87%
SiO ₂ /PR Etch Ratio	99.97%

5.2 Second Order Experiment

The second order experiment focused on varying CHF₃ and CO₂ gas flows only, and the resulting response variables are listed in Table 8. Run 2 produced the highest SiO₂/Si and SiO₂/PR etch ratios of 18 and 4, respectively.

Table 8: Etch Rates, Uniformity, and Etch Ratios for the Second Order Experiment

RUN	Input Variables		Response Variables					
	CHF ₃ (sccm)	CO ₂ (sccm)	SiO ₂		Photoresist		Etch Ratios	
			Etch Rate (Å/min)	Etch Unif (± %)	Etch Rate (Å/min)	Etch Unif (± %)	SiO ₂ to Si	SiO ₂ to PR
1	100	25	477	1.94	175	0.5	9.2	2.7
2	100	5	449	1.10	113	4.2	18.0	4.0
3	75	15	468	1.90	154	3.3	12.6	3.0
4	50	5	472	1.70	151	8.1	18.9	3.1
5	50	25	465	2.06	200	3.6	8.5	2.3

The closeness of fit for the resulting response variables were very good, as shown in Table 9. With the exception of the SiO₂ etch uniformity, the R-square values for the remaining response variables were above 98%.

Table 9: Analysis of Variance for Second Order Experiment

Response Variable	Variation, R-Squared
SiO ₂ Etch Rate	99.10%
SiO ₂ Etch Uniformity	94.47%
Resist Etch Rate	99.36%
Resist Etch Uniformity	98.28%
SiO ₂ /Si Etch Ratio	99.03%
SiO ₂ /Resist Etch Ratio	99.97%

5.3 Summary

The results from the first and second order experiments clearly indicated that CHF₃/CO₂ gas stream can successfully achieve high etch ratios of SiO₂/Si and SiO₂/PR. In fact, the etching trends for CO₂ addition was similar to CHF₃ + O₂ chemistry. The overall trends in etch rates and etch ratios are summarized in Section 6.4.

6. DISCUSSION

The main effects and surface response plots were generated by regression fit to show the effects of process variables. A main effects plot shows the effects of individual process variables on the response variable. A surface response plot considers the interaction of two input variables and predicts the effect on the response variable. From the analysis of the plots, the “optimum” process condition is determined by considering both SiO_2/Si and SiO_2/PR etch ratios. If an etch process exhibits high SiO_2/Si ratio, but low SiO_2/PR ratio, it is possible that the protective resist layer will be removed. Consequently, unwanted oxide etching will take place below the areas where resist is removed. Conversely, if the process has high SiO_2/PR ratio but low SiO_2/Si ratio, excessive Si loss would occur.

6.1 Etch Rate Ratio of SiO_2/Si

As previously mentioned in Section 5.3, adding CO_2 to CHF_3 was sufficient to achieve an etch process with relatively high SiO_2/Si etch rate ratio. The effect of CO_2 gas on the etch rates of SiO_2 and Si and the resulting etch ratio is shown in Table 10. A decrease in the CO_2 flow rate from 25 to 5 sccm resulted in 5.8% decrease in SiO_2 etch rate (see runs 1 and 2). However, the decrease of Si etch rate by 52% was more significant, and resulted in SiO_2/Si etch ratio of 18 (run 2).

Table 10: Effect of CO₂ addition on Response Variables

RUN	CHF₃ (sccm)	CO₂ (sccm)	SiO₂ Etch Rate (Å/min)	Si Etch Rate (Å/min)	SiO₂ to Si Etch Ratio
1	100	25	477	52	9.2
3	75	15	468	37	12.6
2	100	5	449	25	18.0

The effects of the CHF₃ and CO₂ flow rates are shown in the main effects plot Figure 18(a), generated from the second order experiment. The significant impact of CO₂ flow on SiO₂/Si etch ratio is shown by the steep line. As the CO₂ gas flow increases from left to right, SiO₂/Si etch ratio decreases from 18 to 8. The effect of CHF₃ flow is much less. As the CHF₃ flow rate increases, thus increasing the F concentration, the change in SiO₂/Si etch ratio is almost negligible.

The surface response plot, in Figure 18(b), shows the combined effects of CHF₃ and CO₂ on SiO₂/Si etch ratio. As CO₂ flow increases from 5 to 25 sccm, the etch ratio decreases. As the CHF₃ gas flow increases from 50 to 100 sccm, the etch ratio decreases slightly at low CO₂ flow regime, and increases at high CO₂ flow regime. Although CHF₃ flow of 50 sccm results in the highest etch ratio > 19, it is not the optimum process. The argument against choosing a low CHF₃ flow process is presented in Section 6.2.

Fig. 18: (a) Main effects plot and (b) Surface response plot of SiO₂/Si etch rate ratio w/r/t CHF₃ and CO₂ flow [from second order experiment].

The main effects plot of pressure and gas flows on SiO₂/Si etch ratio is shown in Figure 19(a), generated from the first order experiment. Both pressure and O₂ flow had the biggest impact on SiO₂/Si ratio. As pressure and O₂ flow increased, the etch ratio dropped from 7.4 to 5.3. It is evident that O₂ had a greater effect on etch ratio than CO₂, which is consistent with the findings by Shanfield and Hendricks.^[8] Their study found even greater sensitivity of etch ratio to percentage O₂ as compared to CO₂.

A surface response plot between CHF₃ and O₂ was generated from the first order experiment, which contains confounded effects for interactions between pairs of process variables. This is shown in Figure 19(b). With the increase of O₂ from 0 to 15 sccm, the SiO₂/Si etch ratio drops from 7.8 to as low as 4.8, depending on the CHF₃ flow. As the

CHF_3 gas flow increases from 50 to 100 sccm, the etch ratio increases both at low and high O_2 flow regime.

Fig. 19: (a) Main effects plot and (b) Surface response plot of SiO_2/Si etch rate ratio w/r/t CHF_3 and CO_2 gas flows [from first order experiment].

6.2 Etch Rate Ratio of $\text{SiO}_2/\text{Photoresist}$

As discussed in the beginning of this chapter, deciding on an “optimum” process should consider both the SiO_2/Si and SiO_2/PR etch ratios. The main effects of CHF_3 and CO_2 gas flows on SiO_2/PR etch ratio is shown in Figure 20(a). The corresponding surface response plot is shown in Figure 20(b). It can be seen that as the CO_2 gas flow increases, the SiO_2/PR etch ratio decreases from 3.2 to 2.2. The effect of CHF_3 , however is the opposite, as the flow rate increases, SiO_2/PR etch ratio increases slightly. Therefore, the

desired etch process for high etch ratio is to use high CHF_3 and low CO_2 gas mixture of 100 and 5 sccm, respectively.

Fig. 20: (a) Main Effects Plot for SiO_2/PR etch ratio [from first order experiment] (b) Surface response plot of SiO_2/PR etch ratio with changes in CHF_3 and CO_2 [from second order experiment].

The main effects plot for pressure gas flows on SiO_2/PR etch ratio is shown in Figure 21(a), generated from the first order experiment. The effect of CO_2 gas flow is the most significant factor on the etch ratio, similar to the finding from the second order experiment. As the CO_2 flow increases, the SiO_2/PR etch selectivity decreases from 3.2 to 2.2. The remaining response variables are secondary effects.. The surface response plots for CHF_3 and O_2 and their effects on SiO_2/PR etch ratio are shown in Figure 21(b).

The O_2 flow has a similar effect as the CO_2 flow; the etch ratio of SiO_2 /PR decreases with increasing O_2 flow. The etch ratio is slightly improved when the CHF_3 flow increases.

Fig. 21: (a) Main effects and (b) Surface response plots for SiO_2 /PR etch ratio [from the first order experiment].

6.3 SiO_2 , Si, and Photoresist Etch Rates

Since the etch ratio calculations of SiO_2 /Si and SiO_2 /PR involve etch rates of three different films, closer examination of the etch rates of each film are presented.

6.3.1 SiO_2 Etch Rate

The first order experiment shown in Figure 22(a) reveals that all four process variables contribute to the changes in the SiO_2 etch rate. When pressure and CHF_3 increase, the oxide etch rate decreases, whereas when CO_2 and O_2 flow rates increase, the oxide etch

rate increases. When the effects of pressure and O₂ gas flow are eliminated (second order experiment), a similar trend is shown in Figure 22(b) where CO₂ gas flow has more significant effect on the SiO₂ etch rate.

Fig. 22: Main effects plots from (a) first order and (b) second order experiment for SiO₂ etch rate.

The data used in Figure 22(a) is again plotted as surface response plots to show the effects of pressure with either CHF₃, CO₂, or O₂ on the oxide etch rate. These plots are shown in Figures 23(a), (b), and (c), respectively. For all three plots, the increase in pressure had the same effect – increased oxide etch rate. Higher CHF₃ flow rate resulted in lower SiO₂ etch rate due to increased polymer deposition rate. When either CO₂ and O₂ flow rates are increased, the SiO₂ etch rate is increased due to the increased oxygen ions which aid in removing the deposited fluorocarbon layer on SiO₂ surface.

(a)

(b)

(c)

Fig. 23: Surface response plots for SiO₂ etch rate: Pressure versus (a) CHF₃, (b) CO₂ and (b) O₂

6.3.2 Si Etch Rates

The main effects plot from the first order experiment, shown in Figure 24(a), reveals that the most significant variable effecting Si etch rate is the O_2 flow. When compared to the trend observed for SiO_2 etch rate, the effects of CO_2 and O_2 flow are similar. As oxygen concentration increases, the rate of polymer removal from the Si surface increases, leading to increased Si etch rate. The effect of CHF_3 flow on Si etch rate is also similar to SiO_2 etch rate trend—higher CHF_3 flow resulted in lower Si etch rate. The effect of pressure, however is the opposite—higher pressure resulted in higher Si etch rate.

When the effects of pressure and O_2 flow are eliminated (second order experiment), the CO_2 flow has the most significant effect on the Si etch rate. This plot is shown in Figure 24(b).

Fig. 24: Main effects plot for Si etch rate from (a) first order and (b) second order experiment.

6.3.3 Photoresist Etch Rates

The main effects plots of process variables on the photoresist etch rate are shown in Figure 25. In both the first (25a) and second (25b) order experiments, the CO_2 flow had the most significant effect on the photoresist etch rate. While small amount of oxygen atoms, (from the decomposition of CO_2), promote F atom formation, thereby enhancing SiO_2 etch rates, further increase in O atoms are expected to simultaneously promote resist erosion rate.^[8]

Fig. 25: Main effects plot for photoresist etch rate from (a) first order and (b) second order experiment.

6.4 Influence of Process Variables

The effects of input variables on the etch rates and selectivity are summarized in Table

11. This table was generated from the trends observed in the main effects and surface response plots (Figures 18 to 25).

The effect of pressure is quite complex. Free radical concentrations decrease and the number of bombarding ions increases with pressure at a constant rf power (see Section 2.3.1 for details). With an increase in pressure, there will be a decrease not only in the fluorine atom concentration but also in the thickness of the in-situ fluorocarbon polymer film. These effects lead to an increase in oxide etch rates (Figure 23) and a steady increase in silicon etch rates (Figure 24a) under the experimental ranges studied.

Table 11: Influence of Process Variables on the Response variables.

Increase in the Process variables below:	Results in the Following Trends				
	SiO ₂ Etch Rate	Si Etch Rate	PR Etch Rate	SiO ₂ /Si Etch Ratio	SiO ₂ /PR Etch Ratio
Pressure ↑	↓	↑	↓	↓	↓
CHF ₃ ↑	↓	↓	↓	↑	↑
CO ₂ ↑	↑	↑↑*	↑↑	↓↓*	↓↓
O ₂ ↑	↑	↑↑#	↑	↓↓#	↓

↑ or ↓ indicates minor change; ↑ or ↓ indicates significant change.

↑↑ or ↓↓ indicates that the effect of the input variable on the response variable is dominant.

* Trend observed in second order fit experiment.

Trend observed in first order fit experiment.

Both the fluorine atom and CF_x radical concentrations will increase with an increase in CHF_3 flow rate. Initially, the etch rates of SiO_2 and Si increase with increased CHF_3 flow rate.^[28] As the CHF_3 flow rate is further increased, the etch rates decrease due to increased polymerization (Figures 22a and 24b). The percent decrease in SiO_2 and Si etch rate as CHF_3 flow increases are -18% and -27%, respectively. Since the decrease in the etch rate of SiO_2 is less than Si, the net effect of increased CHF_3 flow rate results in increased SiO_2/Si etch rate ratio.

The combined effects of increased pressure and CHF_3 flow rate results in lower oxide etch rate (Figure 23a). At constant CHF_3 flow rate, as the pressure is increased, the oxide etch rate is decreased. Similar results were obtained from a literature report by Choe et al.^[7] and is reproduced in Figure 26.

Fig. 26: The effects of CHF_3 flow and pressure on SiO_2 etch rate. [ref. 7]

The effects of decreased pressure and increased CO₂ flow rate results in higher oxide etch rate (Figure 23b). Similar results were again reported by Choe et al.^[7] and is reproduced in Figure 27. They explored the narrow region of CO₂ flow (6 to 9 sccm) and used operating pressures between 40 to 60 mTorr. There is a maximum oxide etch rate at 7.5 sccm, beyond which the etch rate starts to decrease. However, their work did not show whether this downward trend continued with increased CO₂ gas flow.

Our experiment explored a much wider range of CO₂ gas flow (5 to 25 sccm) with larger increments of gas flow change. Thus, the maximum in the oxide etch rate observed in Figure 27 could not be confirmed, indicated by solid circles and squares. However, our study found that beyond 10 sccm of CO₂ flow, at a higher flow region, the oxide etch rate continued to increase.

Fig. 27: The effects of CO₂ flow and pressure on SiO₂ etch rate. [ref. 7]

Carbon dioxide addition increases the etch rates of all three films (Figures 22, 24b, and 25). The increase in the etch rate of Si compared to SiO₂ is significantly greater as CO₂ flow rate is increased. The percent increase in SiO₂ and Si etch rates as CO₂ flow is increased are +2.3% and +118%, respectively. Consequently, SiO₂/Si etch ratio will decrease significantly. Similar result was reported by Shanfield and Hendricks^[8] for SiO₂ to polysilicon etch ratio, reproduced in Figure 28.

Fig. 28: The effect of %CO₂ flow on SiO₂ to Polysilicon etch ratio. [ref. 8]

The highest value of SiO₂/Si and SiO₂/PR etch ratios obtained from the available data correspond to 1300 Watt of rf power, 30 mTorr pressure, 100 and 5 sccm of CHF₃ and CO₂ respectively. Under these conditions, the etch rates of SiO₂, Si, and photoresist were 449, 25, and 130 Å/min, respectively. The etch ratios of SiO₂/Si and SiO₂/PR were 18

and 3.45, respectively. As seen in the previous discussions, CHF_3 flow rate has a small effect on selectivity (less than 2 units for a variation of 50 sccm). The effect of CO_2 was much greater. The decrease in etch ratios occur quickly with small increase in CO_2 flow rate. A minimum of about 5 sccm of CO_2 is required in order to minimize the adverse effects of polymerization, and deliver an etch process with high etch ratios.

6.5 Summary

The overall trends obtained for the etch ratios and etch rates correspond to the expectations discussed in Section 3. The regression analysis obtained from STATGRAPHICS are used in the generation of plots presented in this Chapter. The etching process involves a combination of several mechanisms. While oxygen atoms, (from decomposition of CO_2) promote F atom formation, thereby enhancing SiO_2 etch rates, further increase in O atoms compromise the etch selectivity to Si and photoresist. By considering the interaction of all variables, the observed trends were combined with the physical significance of the data to predict the optimum etch condition.

7. CONCLUSION

Regression analysis was used to obtain etch rate trends for silicon dioxide, silicon and photoresist. The observed trends agreed quite well with the expectations based on the known mechanism. The addition of CO_2 to CHF_3 feed gas mixture led to increase in both oxide and silicon etch rates. Using low CO_2 flow, high oxide etch rate was maintained, while silicon etch rate was kept to a minimum. The maximum SiO_2/Si and SiO_2/PR etch ratios obtained was 18 and 3.2, respectively.

8. APPENDIX A

Nanospec, a surface reflectometer, was used to measure the thickness of photoresist layer before and after the etch to calculate the etch rate. Depending on the gas mixtures of CHF_3 , CO_2 , and O_2 used, the post-etch thickness measurements varied significantly. In some cases, the measurement indicated that there was more photoresist after the etch than the initial thickness. To confirm this data, the same wafer was cleaved to perform scanning electron microscopy (SEM) analysis. The measurements from SEM pictures contradicted the data obtained by Nanospec. Similar analysis was done for all runs from first and second order experiment.

In Table A1, the thickness readings obtained from the reflectometer and SEM analysis are shown. From the first order experiment, the thickness of photoresist for run 2 after etch using the nanospec is higher than the initial thickness. This implies that instead of etching, deposition has occurred on photoresist surface. The photoresist thickness measured from SEM picture is actually less. The differences can be explained by the fact that the nanospec calculates the film thickness by measuring the refractive index of the material over a range of light wavelength. When measuring the photoresist thickness after etch, the assumption is that the refractive index of the film is not changed from the pre-etch condition. However, it is obvious that the refractive index did change after the etch, thus resulting in varying degree of deviation from the thickness values obtained by SEM analysis. For the sake of simplicity, thickness measured with nanospec will be

referred to as “optical” thickness, and “physical” for the thickness obtained for SEM analysis.

A correction factor was calculated by dividing the “physical” thickness by the “optical” thickness. This correction factor was then applied to subsequent photoresist thickness measurements. In Figure A1, the correction factor is plotted against the gas flow ratio of CHF₃ and CO₂ (from the second order experiment). Higher gas flow ratio results in less photoresist erosion due to increased polymerization on photoresist. Therefore, the correction factor is adjusted higher in order to better estimate the photoresist thickness after etch. The plot shows good agreement of correction factors with increasing CHF₃/CO₂ gas flow ratio.

**Table A1: Photoresist thickness using Nanospec and SEM analysis
[Data from First Order Fit Experiment]**

	RUN	Press	CHF ₃	CO ₂	O ₂	Initial Thickness	Nanospec reading “Optical”	SEM analysis “Physical”
1st Order Expt	1	70	50	5	15	11351	8817	6613
	2	70	100	5	0	11938	14278	9281
	3	30	100	5	15	13353	12124	9093
	4	30	50	5	0	12195	10913	8185
	5	50	75	15	7.5	13543	11883	8318
	6	30	100	25	0	12623	11105	7218
	7	70	100	25	15	13814	11599	7539
	8	30	50	25	15	13270	8963	5826
	9	70	50	25	0	12476	9561	6214

Figure A1: Correction Factor versus CHF_3/CO_2 gas flow ratio

9. APPENDIX B

Design of experiment (DOE) was used to come up with the initial screening matrix. The purpose of this screening matrix was to first characterize the etch process using CHF_3 , CO_2 and O_2 gas, with power and pressure set within the machine capability. The ranges of process variables are shown in Table B1. It was decided from the start that the temperature of the hexode will be set constant at 25°C . The response variables were SiO_2 etch rate, uniformity and DC bias. The screening matrix used a 2^{5-1} factorial design with half replicates of 5 process variables in 17 experiment runs including one centerpoint, as shown in Table B2. The 2^{5-1} design of resolution V does not confound main effects with two factor interactions with each other, but does confound two-factor interactions with three-factor interactions, and so on.^[29] As long as the resolution is above III, the confidence level of the data obtained from the experiment are well above 95%.

Initial Screening Matrix

While running the initial screening matrix DOE, the runs which were set at 90 mTorr pressure and 1600 Watts of rf power had plasma instability issue. This was evident by looking through the observation window located at the side of the bell jar. There would be sparks between the wafer carriers, and also intermittent plasma flickering. Quantitatively, the unstable plasma was confirmed by monitoring the changes in the dc

bias. Whenever the plasma was unstable, there were huge fluctuations in the dc bias readings. The instability only occurred at high rf power. Therefore, it was decided that rf power would be set constant at 1300 Watts for all other proceeding experiments.

Table B1: Process Variables and Ranges used in Initial Screening Matrix

Process Variables	Range of Variable	Centerpoint
Pressure	30 ~ 90 mTorr	60 mTorr
Power	1000 ~ 1600 Watts	1300 Watts
CHF ₃	50 ~ 100 sccm	75 sccm
CO ₂	5 ~ 25 sccm	15 sccm
O ₂	0 ~ 15 sccm	7 sccm

Table B2: Initial Screening Matrix using 2⁵⁻¹ fraction DOE

DOE #1 Constant Variable = Temp (20C)

RUN	Press (mT)	Power (W)	CHF ₃ (sccm)	CO ₂ (sccm)	O ₂ (sccm)	Etch Rate (Å/min)	Unif (±%)	DC Bias (V)	Comments
1	30	1000	50	25	0	354	2.12	-568	Plasma Flickering CENTER POINT Plasma Flickering Constant Plasma Flickering Constant Plasma Flickering
2	30	1600	50	5	0	521	2.21	-770	
3	90	1000	50	25	15	265	1.94	-368	
4	30	1600	100	5	15	582	2.27	-753	
5	30	1000	50	5	15	355	2.5	-585	
6	30	1600	100	25	0	577	2.18	-717	
7	90	1600	100	5	0	356	2.54	-515	
8	90	1000	100	25	0	159	2.81	-348	
9	60	1300	75	15	7	461	1.8	-558	
10	30	1600	50	25	15	529	2.33	-726	
11	30	1000	100	5	0	264	2.67	-573	
12	30	1000	100	25	15	357	2.34	-562	
13	90	1000	50	5	0	194	2.8	-390	
14	90	1000	100	5	15	125	5.85	-348	
15	90	1600	50	25	0	395	1.9	-508	
16	90	1600	50	5	15	415	2.32	-522	
17	90	1600	100	25	15	414	2.07	-493	

First Order Experiment

With power set constant at 1300 Watts, the number of process variables were down to four. A 2^{4-1} half factorial design with resolution of IV was used to conduct the first order experiment. A design of resolution IV does not confound main effects and two-factor interactions but does confound two-factor interactions with other two-factor interactions. The process variables were power and gas flows of CHF_3 , CO_2 , and O_2 . The measured responses were etch rates, etch uniformity, and etch ratio of SiO_2/Si and $\text{SiO}_2/\text{photoresist}$.

The purpose of this experiment was to see if CO_2 addition to CHF_3 will be able to etch with high SiO_2/Si and SiO_2/PR etch ratios. During the experiment, no plasma instability was observed. The results from this experiment were very convincing— CHF_3/CO_2 gas mixture can achieve high etch ratios. The data analysis showed that the increase in pressure resulted in slowing down the oxide etch rate. However, the effect of pressure on Si and photoresist etch rates were not significant. Therefore, it was decided that on the next experiment, the pressure would be set constant at 30 mTorr. Besides, at lower pressure, the oxide etch rate was fairly high with excellent etch uniformity.

Second Order Experiment

With pressure set constant at 30 mTorr, the process variables were down to two; CHF_3 and CO_2 gas flow. A windowing of the CHF_3/CO_2 process was performed with a 2^{2-1} half factorial design with resolution of IV was used to conduct the second order experiment.

It was conclusive that from this experiment, CHF_3/CO_2 etch process was able to achieve the maximum SiO_2/Si and SiO_2/PR etch ratios of 18 and 3.2, respectively. Additional runs were done to verify and check for repeatability of this process. The results from the verification runs confirmed the findings from the second order experiment.

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