Non-Perfluorocompound Chemistries for Plasma Etching of Dielectrics

by
Benjamin A. Tao

S.B., Materials Science and Engineering
Massachusetts Institute of Technology, 1993

Submitted to the Department of Materials Science and Engineering
in partial fulfillment of the requirements for the degree of

Master of Science
in Materials Science and Engineering
at the
Massachusetts Institute of Technology
June 1996

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ABSTRACT

Perfluorocompounds commonly used by the microelectronics industry are considered potent global warming gases. These fully fluorinated compounds have global warming potentials thousands to tens of thousands times greater than that of carbon dioxide. Using gases with lower or zero global warming potential as replacements is an option for reducing this environmental threat. This thesis begins the work of determining the viability of using replacement chemistries as an option for controlling perfluorocompound emissions. This work was comprised of three stages. The first stage determined what processes used PFC most heavily and what past work on non-perfluorocompound chemistries was relevant. The second stage was a selection process of potential candidate chemistries. The third stage was a set of etch viability experiments on one of the families of candidate chemistries, namely the hydrofluorocarbons.

By conducting an extensive literature and industry survey, it was determined that perfluorocompound usage is dominated by two processes: wafer patterning and *in-situ* cleaning of PECVD chambers. In addition, the actual materials that are etched in both these processes are dielectrics such as silicon dioxide and silicon nitride. It was further determined that little relevant work on non-perfluorocompound alternatives had been done and that fluorine-based chemistries were the most likely candidate chemistries.

In selecting candidate chemistries, expected performance and environmental, safety, and health consideration were used to screen over one hundred potential candidates. In the end, the following general criteria were used. The candidates had to be fluorine-based. They had to have no or low long term environmental impact. Handling and ease of use was a consideration, but not a barrier to selection. However, no known mutagenic, teratogenic, and/or carcinogenic chemistries were selected. The list of final candidate chemistries fell into three general families: hydrofluorocarbons, iodofluorocarbons, and unsaturated fluorocarbons.

Before starting detailed experiments with the candidate chemistries on the specific applications of wafer patterning and chamber cleaning, it was decided that a screening experimental stage would be done to prioritize the candidates just on their ability to etch silicon dioxide and silicon nitride. This thesis reports on the results of this screening stage for the hydrofluorocarbons. Using an Applied Materials Precision 5000, a magnetically enhanced reactive ion etcher, the average etch rates of thermally grown silicon dioxide and LPCVD silicon nitride films were determined as a function of total pressure (35-150 mTorr), magnetic field strength (0-100 Gauss), and oxygen flow (0-20 sccm) for octafluoropropane (C_3F_8), pentafluoroethane (C_2F_5H), 1H-heptafluoropropane (CF_3-CF_2-CF_3H), and 2H-pentafluoropropane (CF_3-CFH-CF_3). Applied power (600 Watts) and etch gas flow rate (40 sccm) were held constant. A Design of Experiments (DOE) software package called NNAPER (DuPont) was used. Etch rates were measured *in-situ* using a LES Full Wafer Imaging Interferometer system (optical emission interferometry). The etch rates of these hydrofluorocarbons were found to be comparable to those of octafluoropropane. In general, increasing magnetic field increased etch rate. Increasing oxygen flow resulting in a peak in etch rate for silicon dioxide etching, while it lead to a monotonically increasing etch rate for silicon nitride. The effect of pressure was mixed. In addition, the isomers of heptafluoropropane exhibited different oxide etch behaviors at low oxygen flows and magnetic fields; 1H deposited a polymer and 2H etched. Neither was found to polymerize on nitride under these conditions.

A series of one-at-a-time experiments were conducted on three more hydrofluorocarbons: difluoromethane (CF_2H_2), trifluoroethylene (CF_2=CFH), and 1,1,1,2-tetrafluoroethane (CF_3-CFH_2). Low pressure (35 mTorr) experiments were conducted with these gases because they polymerized at higher pressures. Power was 600 Watts, magnetic field was 50 Gauss, etch gas flow was 15 sccm, and oxygen flow ranged from 0-45 sccm. For oxide etching with difluoromethane and trifluoroethylene, the etch rate of both gases increased with the introduction of oxygen flow. At higher flows, the etch rate peaked and then descended. Difluoromethane etched without oxygen while trifluoroethylene deposited a polymer. A similar dependence with increase oxygen flow was observed for nitride etching with tetrafluoroethane and trifluoroethylene. Difluoromethane nitride etch rate monotonically decreased with increasing oxygen flow. Tetrafluoroethane and trifluoroethylene deposited with no oxygen while difluoromethane etched.

Based on these etch viability tests, pentafluoroethane and the isomers of heptafluoropropane should be given priority in subsequent experimental stages. Furthermore, the use of difluoromethane, trifluoroethylene, and 1,1,1,2-tetrafluoroethane for PECVD chamber cleaning is unlikely because of their strong tendency to polymerize. They may be useful for wafer patterning applications, however.

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Acknowledgments

In doing the work that is contained in this thesis, I am indebted to so many people from the Microsystems Technologies Laboratories, from the Institute, and from the Industry. This thesis was really a team effort. It could have not been done without the excellent support and hard work of the people mentioned here.

The person that I would like to thank first is my thesis advisor, Professor Rafael Reif. I think that I am a different person than when I first started graduate school at MIT, and Professor Reif is primarily responsible for the positive changes in me. More important than the specific academics, Professor Reif taught me lessons that extend into real life. By his example, Professor Reif taught me the importance of communication and teamwork and the need to rely on others instead of just myself to get the job done. He has taught me what it means to be an engineer, to take raw knowledge and ideas and shape them in something useful and coherent. I appreciate the support, patients, confidence, and trust that he has shown me. I have enjoyed working for him very much and have the greatest respect for him.

For all of their administrative support and general friendship, I would like to thank Carolyn Zacarria, Erika Satrape, and Diane Hagopian. I would like to thank Carolyn for her tireless efforts and sacrifice in doing the two jobs of taking care of the Office of the Director and the Reif Research Group simultaneously. I appreciate Carolyn's effort in helping me with the bureaucracy of MIT and getting me quick access to Professor Reif whenever I needed it. I would like to thank Erika for continuing Carolyn's work and for helping run the SRC/MIT Technology Transfer Course that we were responsible for. Finally, I would like to thank Diane for keeping the ship running smoothly in the last, hectic month of this spring semester.

I would like to thank the entire staff of MTL for all of their support and help with this project. I would like to thank Sue Peterson and Sam Crooks for their help with all of the financial aspects of my project and for their help with our various proposals. I would like to thank Kurt Broderick and Debroah Hodges-Pabon for their help with various MIT administria. I would also like to thank Deb for our interesting conversations and the occasion cookies and chips. I would like to thank Brian Foley, Joe Walsh, and Bernard Alamariu for their support of the Applied 5000 etcher and the growth of the films that I used. I would like to thank Joe specifically for the tremendous efforts he made (almost on a daily basis) in keeping the Applied running and fixing it when it went down. I would also like to thank Linus Cordes and Vicky Diadiuk for their help with my use of the MTL facilities and the Applied 5000 in particular. Linus also provided some excellent technical and project management advice which I appreciate.

I would like to thank all the member of Reifgroup for their friendship and general support. I would like to thank Weize Chen for his UNIX expertise. I would like to thank Alex Cherkassky for his continual supply of new computers for the group. I would like to thank Rajan Naik for making me realize that there are more careers out there than the ones that involve science and engineering. I would like to thank Simon Karecki, my project partner, for his support and hard work on this project. It was always

fun working with him. I would also like to thank my two former officemates, Andy Tang and Dr. Julie Tsai, for all of the good times that we had together in the office, such as all getting in at 11:00 am and then going straight out to lunch. I would also like to thank Dr. Kenneth Liao for his help and our conversations about airplanes.

I would like to thank in particular my family and friends for their love and support. I would like to thank my mother for her love and understanding. She is always there for me whenever I need her. I would like to thank my father for the example that he gave me; it has shaped me into the person I am today. I would like to thank my sisters Alex, May, and Joyce and my brother Chih-Kuang for their love and help. I would like to thank Anna Lee, my best friend and girlfriend, for all of the love, support, and tenderness that she has given me, especially through the tough times of graduate school. Finally, I would like to thank Tom, the cat, for his warmth and expensive medical bills.

I would like to thank various MIT faculty and staff for their help with this project. I would like to help Professors Herb Sawin and Duane Boning for their occasional technical advice. I would like to thank Professor James Chung for his career advice. I would like to thank my thesis reader, Professor Eugene Fitzgerald, for reading my thesis on such short notice. I would like to thank Mary Pensyl of the Computerize Library Search Service for her excellent technical help with the many literature searches that this project required. I would also like to thank Mr. Paul McQuillan of the Office of Sponsored Programs for his help with the various proposals that funded this project and for his tireless efforts in helping negotiate our contract with SRC.

Finally, I would like to thank all of the member companies of SRC and SEMATECH for their advice and financial support. In particular, I would like to thank Dr. Walter Worth, my Project Manger, for his patience and support of this work. He is an incredibly generous and supportive person. I would like to thank Dr. Phyllis Pei and Dr. Ray Kerby for their support and advice on this project. I would like to thank the support of Dr. Daniel Herr, my project manager at SRC. I would like to thank his assistant Marlene Rosa for all of her help. I would like to thank 3M Specialty Chemicals for their donations of octafluoropropane and TFAA. I would like to thank DuPont for their donations of pentafluoroethane, tetrafluoroethane, the NNAPER software, and the AEDEPT database. I would especially like to thank Dr. Mike Mocella for his tremendous and selfless support and advice. Finally, I would like thank all of the tool vendors, in particular Applied Materials, Lam Research, and Novellus Systems, for all of their assistance.

To my father and mother…
They made me who I am…

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Chapter 1

Introduction

1.1 The Global Warming Phenomenon

In the last several years, global environmental issue and problems due to anthropogenic gas emissions have gathered significant attention. The most notorious example has been appearance of a hole in the ozone layer, apparently caused by the destruction of atmospheric ozone by chlorofluorocarbons (CFCs). The potentially devastating effect of this damage has prompted a world-wide ban on CFCs, with few exemptions. More recently, a different phenomenon know as global warming has gained attention. While the natural presence of carbon dioxide creates a natural global warming effect, the man-made emissions of certain gases have amplified this effect. The relation of specific compounds present in the atmosphere to the phenomenon of global warming can be explained in terms of the concept of radiative forcing. Radiative forcing is defined as the change in the balance between incoming shortwave (visible and ultraviolet) and outgoing longwave (infrared) radiation passing through the Earth's atmosphere [1]. Approximately 30% of the incoming radiation is reflected by the Earth's surface and atmosphere. The remainder is absorbed by the surface. The surface is warmed by this, which results in the release of infrared radiation from the surface. A portion of this outgoing longwave radiation, however, is absorbed by atmospheric constituents. Approximately half of this energy is re-emitted outward into space and half inward towards the surface. This naturally-occurring phenomenon is shown in Figure 1.1.

Positive radiative forcing is brought about when the atmospheric concentration of infrared-absorbing gases is increased, resulting in a rise in the amount of infrared radiation being re-emitted toward the surface. Clearly, the infrared absorbency of a gas is a critical factor in assessing its potential contribution to radiative forcing. An equally important term involved in the calculation of a gas's impact on climate change is the time horizon over which it is present in the atmosphere.

Greenhouse gases are compared using an index called global warming potential (GWP). Global warming potential is defined as the time-integrated warming effect resulting from an instantaneous release of unit mass (1 kg) of a given greenhouse gas in today's atmosphere, relative to that from 1 kg of carbon dioxide [1]. GWP is a function of both the atmospheric lifetime and the radiative forcing effectiveness of a gas, as given by Equation 1.

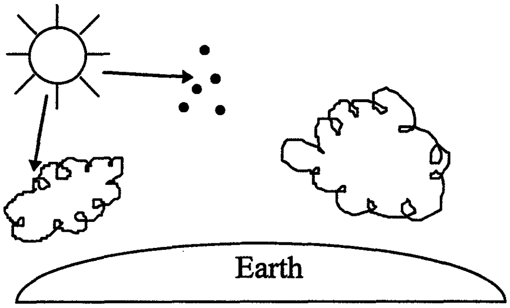


Figure 1.1a: Little of the sun's EM energy is absorbed by the atmosphere. The energy's quanta is too weak to break up air molecules, but too strong to excite vibrations.

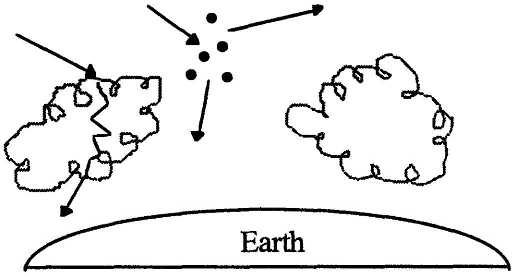


Figure 1.1b: The clouds and earth's surface reflect the light, while the air and particles scatter it. The energy of the reflected light is lost to space.

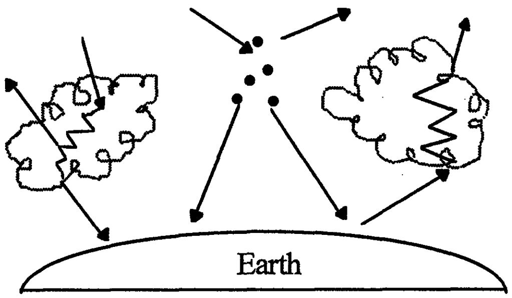


Figure 1.1c: The energy that is not reflected or absorbed by the atmosphere hits the surface where most is absorbed.

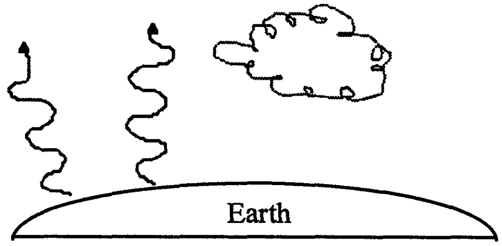


Figure 1.1d: The surface gets warm and radiates EM energy (heat). Without radiation, the earth's temperature would rise continuously.

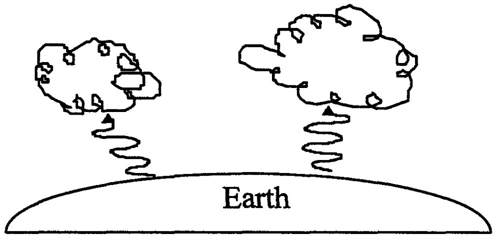


Figure 1.1e: The energy radiate from the earth is absorbed by atmospheric constituents. It has the correct quanta.

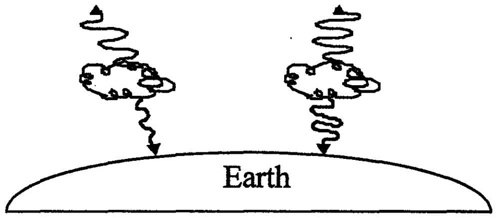


Figure 1.1f: The constituents radiate the energy, half of which goes down to the surface and the other half to space. Thus, the surface gets warmer.

Figure 1.1: The Global Warming Phenomena [2]

$$GWP_T = \frac{\int_0^T a_i c_i dt}{\int_0^T a_{CO_2} c_{CO_2} dt} \qquad (1)$$

where a_i = the instantaneous radiative forcing resulting from a unit increase in atmospheric concentration of trace gas i,
c_i = the concentration of trace gas i, remaining in the atmosphere at time t after the release of unit mass at t = 0, and
t = the number of years over which the calculation is performed [4].

The microelectronics industry is a user of a particularly potent family of suspected global warming gases, the perfluorocompounds (PFCs). Perfluorocompounds (fully-fluorinated compounds) possess both strong infrared absorbancies and long atmospheric lifetimes. Not surprisingly, PFCs have been assigned potentials up to several tens of thousands times that of carbon dioxide, as shown in Table 1.1. PFCs may be particularly insidious because their effect may be nearly permanent, by virtue of the extremely long atmospheric lifetimes. In addition to the five perfluorocompounds listed, the use of trifluoromethane (CHF_3) by the microelectronics industry is considered problematic because of its large GWP and atmospheric lifetime.

Table 1.1: Global Warming Properties of Perfluorocompounds

Gas	Lifetime (years)	Global Warming Potential (100 Yr. Integrated Time Horizon)
C_2F_6	10,000	12,500
CF_4	50,000	6,300
SF_6	3,200	24,900
NF_3	740	8,100
$C3F_8$	6,950	5,600
CHF_3	390	12,100
CO_2	50-200	1

All except NF_3, CO_2, and C_3F_8 from [1]. NF_3 from [3]; CO_2 from [4], C_3F_8 from [5].

Presently, gases such as CO_2, N_2O, and CH_4 account for the bulk of all anthropogenic greenhouse gas emissions [1]. Furthermore, the microelectronics industry's present share of total PFC emissions is small [4]. However, its usage of PFCs is growing steadily to match its needs, while emissions by other industries (most notably the aluminum industry) are already decreasing [6]. It should be pointed out, however, that the aluminum industry's PFC emissions are process by-products and can be substantially reduced through process optimization. In the microelectronics industry, however, PFCs are consumables that are essential to microelectronics fabrication. Over the last several years, several drivers have emerged to push this issue to forefront of the industry's concerns.

1.2 The Drivers for a Solution

Over the last eight years, several major governmental bodies have called for action to address global warming due to anthropogenic emissions. In 1988, the World Meteorological Organization and the United Nations Environment Program established the Intergovernmental Panel on Climate Change (IPCC). In their 1990 report, the IPCC stated that "..emissions resulting from human activities are substantially increasing concentrations of greenhouse gases...These increases will enhance the greenhouse effect, resulting on average in an additional warming to the Earth's surface [7]." The report also predicted that global mean temperatures could increase by 0.3°C per decade during the next century if no changes were made [4]. This might result in an average global mean sea level rise of 6 cm per decade due to the thermal expansion of the water and to the melting of ice [4].

In 1992, the United Nations Conference on Environment and Development (UNCED) was held in Rio de Janeiro, Brazil. The Rio Conference produced five major documents. Two of them, the Convention on Climate Change and Agenda 21, specifically called for actions related to global warming [8]. Agenda 21 (Chapter 35) called for the observation and study of global sources and sinks of greenhouse gases [8]. The Convention on Climate Change made calls to industrialized nations to develop national emission limits and emission inventories. It was without specific targets and dates, but called for reductions to earlier levels by the turn of the century. It also called for "a stabilization of greenhouse-gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system...within a time frame sufficient to allow ecosystems to adapt naturally [9]".

In response to the Rio conference, the Clinton Administration announced the U.S. Climate Change Action Plan on October 19, 1993. This plan called for the reduction of emissions of CO_2 and other greenhouse gases to their 1990 levels by the year 2000. In addition to targeting more common gases such as CO_2, CH_4, and N_2O, the plan called for reductions in high GWP CFC substitutes such as certain perfluorocompounds and hydrofluorocarbons. Specific HFCs and PFCs mentioned include CHF_3 (a byproduct of the refrigerant HCFC-22 production), and carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6). For the PFCs, the specific target for reductions was the aluminum industry. In the Climate Change Action Plan, the aluminum industry agreed that CF_4 and C_2F_6 emissions "may be reduced by 30-60% through management and technological reforms by the aluminum industry [10]." In addition, they agreed "to a target reduction by 2000 [10]."

The most specific and notable driver to reduce the perfluorocompound emissions of the microelectronics industry has come from one of the largest producers of PFCs: E. I. du DuPont de Nemours. In 1994, DuPont announced the following sales policy for Zyron® 116 (C_2F_6):

> "After 12/31/96, DuPont will see Zyron® 116 (C_2F_6) only to those applications that contain, and either recover or destroy this compound subsequent to use. A minimum of 80% 116 emission reduction will be required by this date, assuming commercial technology is available to accomplish such reduction [11]."

This announcement on the restriction on the usage of C_2F_6, the most commonly used PFC, sent the industry into a flurry of activity to determine the best emission control technology, as will be described in the next section.

The two most recent policy events have had mixed effects on the PFC issue. The first was a decision by DuPont to revise its C_2F_6 policy in February of 1996 to be more flexible because of current technological limitations. In the revision of its policy, DuPont stated that it would only sell C_2F_6 to those manufacturers who sought to *minimize* their PFC emissions and had a *philosophy* of zero emissions. It also stated that it would continue to support efforts to develop means of controlling PFC emissions. Finally, DuPont stated that it would phase out C_2F_6 production by the end of 1999 if no solutions were forthcoming by that time [12]. The second development was the agreement on a Memorandum of Understanding (MOU) between the USEPA and the major companies of the US microelectronics industry. There are two main parts of the MOU. First, the industry will report its emissions of PFCs to EPA, using 1995 as the baseline year. Second, the industry will be given a two year window to perform research and development on the best PFC emission control options. The parties will meet in two years to determine what progress has been made. The significance of this MOU is that it is the first formal action by the federal government to address the PFC emissions by the microelectronics industry. It does differ from tradition actions of the EPA in that it is a cooperative effort between the industry and the EPA.

1.3 The Microelectronics Industry's Approach

Since 1994, the U.S. microelectronics industry has moved aggressively to address the potential environmental problem that its PFC emissions may cause. The main coordinating organization behind the industry's efforts is SEMATECH's Global Warming Gas Reduction Program (S69). The mandate of the program is to "...decrease the use and reduce the emissions of potential global warming semiconductor processing materials; specifically the perfluorocompounds (PFCs), such as CF_4, C_2F_6, NF_3, and SF_6 [13]." The S69 program is exploring the viability of four general options: process optimization, especially for *in-situ* chamber cleaning, decomposition/destruction, recycle/recovery, and chemical alternatives. These options are shown in Figure 1.2.

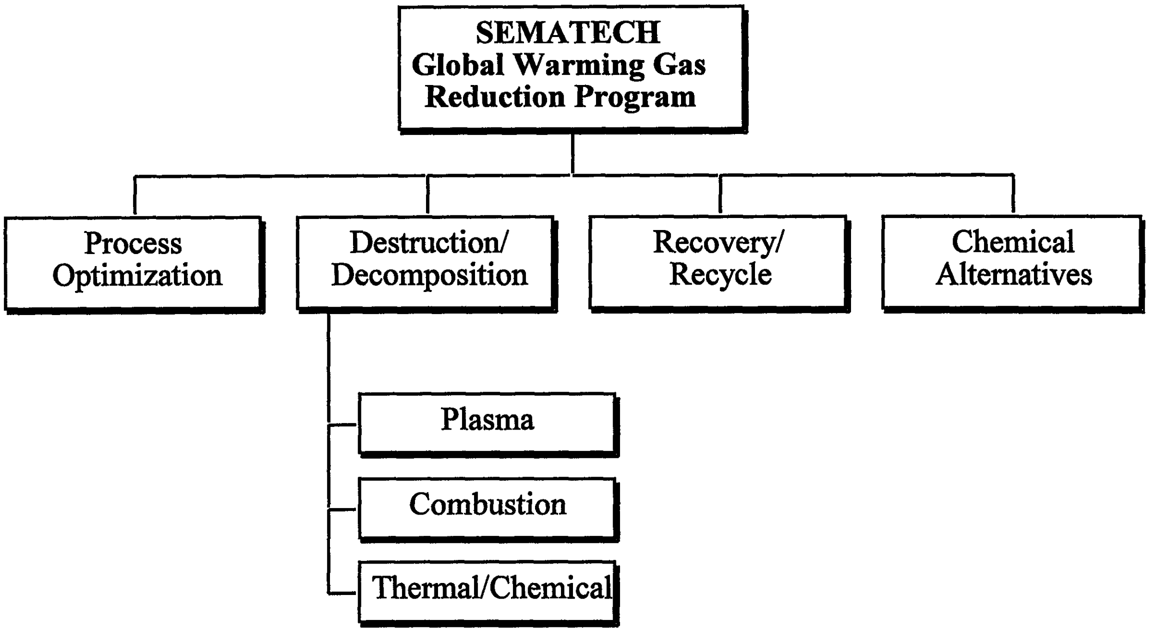


Figure 1.2: Industry Options for Controlling Perfluorocompound Emissions

1.3.1 Process Optimization

The option of process optimization is the one that has received the most attention. It is also the only option that has been implemented in the manufacturing setting. It has been primarily applied to *in-situ* chamber cleaning.

The idea behind process optimization is to use the particular feed gas in the most efficient and effective manner. Greater efficiency leads to lower emissions levels. The work on process optimization has been in four areas: endpoint control, hardware modification, gas selection, and process recipe generation using a Design of Experiments (DOE) methodology. These areas are not mutually exclusive; all overlap.

The use of endpoint control has been used extensively for plasma etch applications. Typically, the endpoint of a etch recipe is done by monitoring the optical emission of a specific species in the plasma whose concentration either increases or decreases at the end of the etch. For example, a common endpoint species for silicon etch is fluorine Unlike plasma etching, chamber cleans were typically run for a set period of time that was determined to be adequate by the specific tool vendor. The exact length of time that the clean is run is not a critical parameter in chamber cleaning. Thus, chamber cleans might run for times well beyond those that are necessary to clean the chamber. By incorporating endpoint measurements into the chamber cleaning process, it is run only the length of time that is actually needed to clean the chamber. Therefore, unnecessary emissions of PFC can be avoided.

To reduce gas usage during its chamber cleans, Applied Materials has made available a minor hardware modification to its systems. PECVD chambers are typically designed to deliver optimum deposition capabilities. Less emphasis on the cleaning processes of these chambers is placed on their design. For pressure higher than 3.5 Torr, Applied Materials determined that the plasma did not clean the area outside the electrode efficiently because of non-uniform gas flows. The standard pumping plate that was used was a solid plate with clear holes for pumping ports. The flow of gas was high near the holes and low in between the holes. By introducing a plenum plate, Applied Materials was able to reduce the high gas flows that had been previously necessary to fill the dead zones. This drop in gas flow leads to a reduction in gas usage. While the Applied Materials plenum plate represents a successful hardware modification that reduced gas usage, more significant hardware modifications on equipment already on the manufacturing line is unlikely.

In an effort to reduce PFC emissions, several tool vendors have considered gas changes to their chamber cleaning processes. The criteria for changing gases would be a more efficient chemistry (faster etchant) and a higher conversion efficiency. C_2F_6 is by far the most common chamber cleaning gas. In lieu of C_2F_6, tool vendors and gas companies have examined NF_3 and C_3F_8 because of these reasons. Both are more efficient chamber cleaning gases compared to C_2F_6. However, since both are still targeted PFCs, industry interest in converting to these gases from C_2F_6has been limited.

The most popular aspect of process optimization has been the use of Design of Experiments to develop the best clean processes. DOE will be discussed in Chapter 5. Coupled with its plenum plate modification, Applied Materials has claimed a reduction of 50% in C_2F_6 gas usage using its optimized clean recipe [14] while Novellus Systems has claimed 10-20% reductions [15]. While process optimization can lead to reductions in PFC emissions, these reductions are still incremental at best. Clearly, the implementation of other options is necessary.

1.3.2 Destruction/Decomposition

While destruction and decomposition abatement is the least environmentally friendly option, it does have the benefit of being the most technologically advanced. In fact, combustion is currently the only effective means of controlling emissions of most PFCs. The types of destruction and decomposition technologies being considered are combustion-based systems, plasma systems, and thermal/chemical systems.

SEMATECH has evaluated a large number of either commercially available or prototype combustion-based abatement systems. The majority of the systems tested appear to have high destruction removal efficiencies (DRE) for most of the PFCs except for CF_4. CF_4 is the most difficult to destroy because it is very stable (see its atmospheric lifetime in Table 1.1). Despite their efficiencies, these abatement units do have problems. Typically, the fuels used by the commercial units are methane or hydrogen/nitrogen mixtures. It is necessary for these units to run at temperatures on the order of 1000 ^{o}C. However, the existing systems that were modified for PFC abatement were originally not designed to run at such high temperatures. Because of this, the maintenance of these units is high. In addition, they may produce NO_x, CO_x, and SO_x depending on the feed gases. Finally, many require post treatment of the effluents.

Three chemical/thermal systems have been surveyed by SEMATECH. All are still in the development stages. Operating at elevated temperatures, these units use packed beds made of a variety of substances such as inorganic granules and pelletized metal oxide solids to adsorb PFC and chemically break them down. The main problem with these systems is that they can only destroy certain PFCs. In addition, the technology is still underdeveloped, making an evaluation difficult.

Plasma abatement has been investigated by Professor Herb Sawin at MIT. Placed before the mechanical pump, the device uses a microwave plasma source (2.45 Ghz.) to decompose the unreacted effluents. Efficiencies greater than 90% have been achieved for pure flows of PFCs. However, destruction removal efficiency drops when gas mixtures are used. In addition, the byproducts produced by this unit include corrosive acids that must be scrubbed. Finally, there are concerns with "back-talk" between the plasma abatement unit and the plasma processing unit, since the abatement device is placed before the mechanical pump. Further work is progressing on this system.

1.3.3 Recovery/Recycle

From an environmental standpoint, a recovery/recycle system is very desirable. The majority of the systems being demonstrated by vendors are recapture systems. The recycle part may be done at the gas supplier's site. The systems use technologies such as carbon-based adsorption/desorption and cold-traps to recover the PFCs. Vendors claim to have very high efficiencies with their prototype systems. Some problems include the need for most of the systems to be prescrubbed and the potentially high cost of ownership. In addition, the recovery systems are very large. Most systems are remote, to be placed outside of the fab because of their size. The recyclability of the reclaimed gases is also highly questionable because of the extreme purities needed for microelectronics fabrication (99.999% to 99.9999% pure). All of these units are still in the development stage.

1.3.4 Chemical Alternatives

A very limited amount of work with non-PFC alternatives has been done by the industry (see Chapter 3). The idea behind replacement chemistries is to use gases that present no long term environmental threat, while still minimizing any local safety and health threat. Ideally, a new replacement chemistry could be dropped into an existing process or developed with a new tool set. No other modification to the facility or no add-on equipment would be needed. While a simplistic sounding solution, the option of using replacement chemistries represents the most technically challenging problem because of the specialized requirements of the processes that use them (see Chapter 2 and 3). In addition, it must be verified that the effluent of any replacement chemistries does not itself create any environmental, safety, and/or health problems.

In summary, factors such as effectiveness, "greenness", and cost will determine the best combination of solutions. While information on these factors is sparse for chemical alternatives, exploration of its viability is clearly necessary to complete the evaluation of the potential PFC emission control options because none of the other technologies has emerged with a clear-cut advantage, as shown in Table 1.2.

Table 1.2: A Comparison of PFC Emission Control Options

Strategy	Operation	Limitations
Process Optimization	• Optical endpoint control and DOE. • 10-50% reduction reported.	• Only partial reductions in emissions possible
Combustion-Based Destruction	• Many commercial units • C_2F_6 >90% reported	• High CoO ($47K-$125K) • Produces NO_x, SO_x, CO_x. • Low CF_4 DRE efficiencies.
Plasma Destruction	• DRE >90% for most PFCs.* • Low CoO (?)	• Still in experimental stage. • Produces acids.
Thermal/Chemical Destruction	• Packed bed at elevated temperature to convert PFCs to harmless substances.	• Disposal cost of packed beds. • Not effective (yet) for all PFCs.
Recapture/Recycle	• Many use cold traps or activated carbon to capture PFCs (>90%).	• Still in development. • CoO (?) • Captured gas reusability (?) • Most are prescrubbed.
Chemical Alternatives	• Use env. benign replacements. • Phase-in with new equipment.	• Technically most difficult. • Effluent composition (?)

* <80% for PFCs + H_2/NH_3 mixtures

1.4 Organization of Thesis

This thesis begins the work of exploring the viability of using replacement chemistries for perfluorocompounds as a means of controlling the microelectronics industry's emissions of these potent global warming gases. This thesis is the culmination of three major stages of work. The first stage was an extensive survey of both the literature and the industry to answer the following: 1) What applications (both material and process) used perfluorocompounds most heavily?; 2) What chemistries had been used before perfluorocompounds, and what research had been done on non-perfluorocompounds chemistries that could be applied to perfluorocompound processes?;

and 3) Where non-fluorine chemistries viable replacements? This information is contained in Chapter 3 and 4.

Based on the survey results, it was decided that the experimental work would concentrate on wafer patterning and PECVD chamber cleaning for dielectric materials. With these more focused criteria and using the knowledge gained in this first stage, over one hundred candidate chemistries were screened. The selection of three families of initial candidate chemistries was made during the second stage. The selection process and the candidate chemistries are given in Chapter 4.

Before testing the candidate chemistries directly on the two specific processes, it was decided that a screening stage would be helpful. Thus, the third major stage of this thesis was to start screening the candidate chemistries just for their ability to etch dielectric films. This experimental stage will serve to prioritize the candidate chemistries for subsequent experimental work on wafer patterning and PECVD chamber cleaning. The results of this screening stage for the hydrofluorocarbon family of candidate chemistries is given in Chapter 6.

The contents of the other chapters is as follows. An introduction to this PFC - global warming gas emission problem is given along with the drivers for a solution in Chapter 1. In addition, the industry's approach to this problem is reviewed. Chapter 2 reviews some basic concepts and dependencies of plasma etching. Chapter 5 discusses the experimental methods and tools that were used to conduct the screening experiments on the hydrofluorocarbon chemistries. Chapter 7 offers conclusions as to the initial viability of the hydrofluorocarbon chemistries tested. Chapter 8 offers a suggested path for future work on replacements chemistries for perfluorocompounds. Finally, the Appendix provides some more detailed environmental, safety, and health and literature information on the three families of suggested candidate chemistries.

Chapter 2

A Brief Review of Plasma Etching

This chapter is meant to familiarize the reader with some basics of microelectronics fabrication. A brief description of the overall process will be presented to highlight the importance of plasma etching and PECVD applications. A brief description of glow discharges, the type of plasma used for etching, will then be given. Finally, the mechanisms of plasma etching will be discussed, as well as the dependencies of etch rate on various process parameters.

2.1 Microelectronics Fabrication

The fabrication process can be segmented into two stages: front-end-of-the-line (FEOL) processes and back-end-of-the-line (BEOL) processes. FEOL processes are those involved in making the actual devices (*e.g.*, transistors). The BEOL processes are those involved with fabricating the interconnect layers that wire the devices together.

A generic FEOL process is shown in Figure 2.1, as given by Jaeger. FEOL processes usually include several depositions of a blanket film followed by a plasma etch step to pattern the film that has been defined by a photolithography step. For example, a blanket film of silicon nitride is deposited in Figure 2.1a, followed by a plasma etch step in Figure 2.1b. This is repeated with the silicon dioxide film and the aluminum film.

BEOL processes typically are a series of depositions of alternating layers of metal (aluminum) and insulator (silicon dioxide). The metal lines are usually connected by vertical tungsten plugs that fill holes (vias) that are etched through the insulator. A typical interconnect structure with three layers of metal is shown in Figure 2.2. Today's state of the art ICs incorporate three to five levels of metal.

The interlevel dielectric layers (ILD) are typically silicon dioxide films that are deposited using plasma enhanced chemical vapor deposition (PECVD). PECVD is a process by which films are grown from gaseous species that react on a solid surface. These gaseous precursors to the solid films are supplied by a feed gas that is dissociated by a plasma. In addition to being used to deposit the ILD layers, PECVD is used to deposit the final passivation layer that is typically composed of silicon nitride. PECVD is one of the preferred technologies for depositing these layers because it is a low temperature process. The presence of the aluminum lines limits the processing temperatures to below 400 °C.

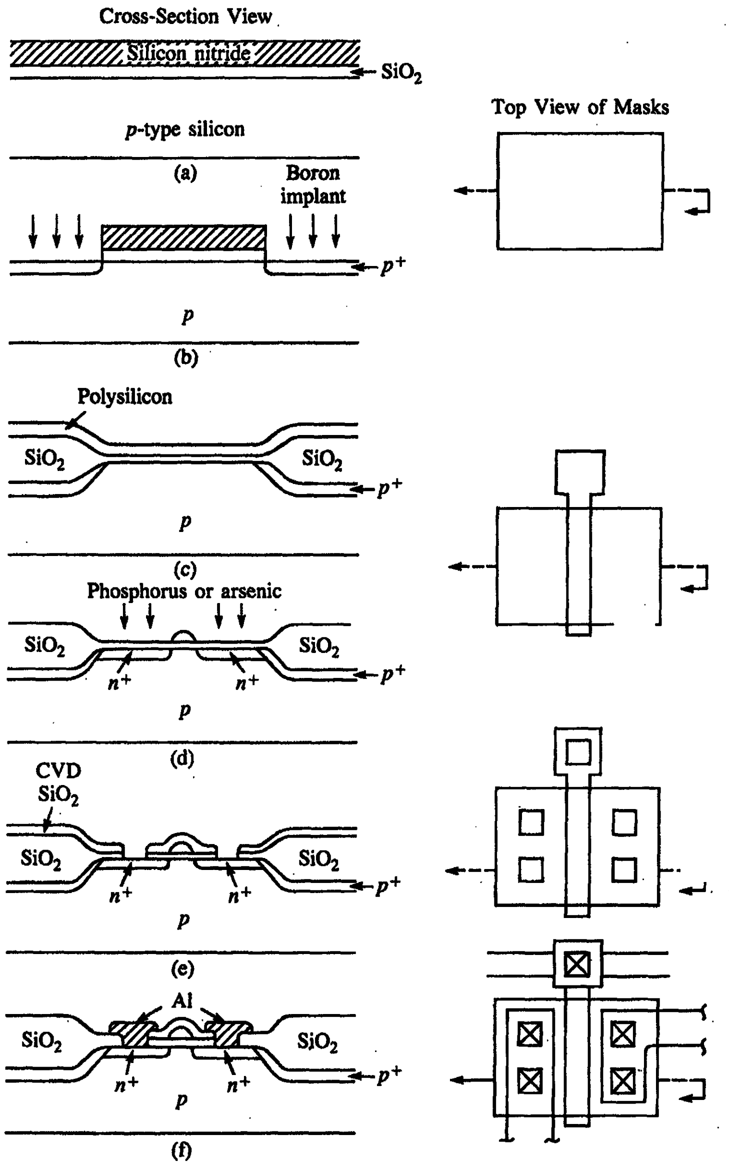


Figure 2.1: Process Sequence for a Semirecessed Oxide NMOS Process. (a) Silicon wafer covered with silicon nitride over a thin padding layer of silicon dioxide; (b) etched wafer after first mask step. A boron implant is used to help control field oxide threshold; (c) structure following nitride removal and polysilicon deposition; (d) wafer after second mask step and etching of polysilicon; (e) the third mask has been used to open contact windows following silicon dioxide deposition; (f) final structure following metal deposition and patterning with fourth mask [16].

In summary, plasma etching is prevalent in both FEOL and BEOL processes, while PECVD is mainly confined to BEOL processes. BEOL processes will begin to dominate the overall percentage of time and effort needed to fabricate ICs as their complexity grows.

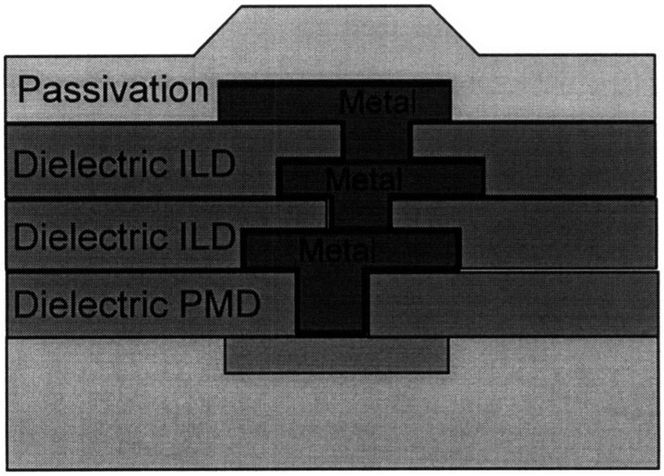


Figure 2.2: A Typical Interconnect Structure

2.2 Glow Discharges

The plasmas used for microelectronics processes are called glow discharges. This name refers to region within which these plasmas exists, as a function plasma density (density of charged particles) and the electron temperature. This region is shown in Figure 2.3.

For microelectronics fabrication, plasmas are created using an ac electric field operating at a frequency of 13.45 MHz. These plasma are called rf plasmas. The choice of 13.45 MHz. is dictated by the fact that that frequency has been put aside by the government for industrial applications. While other plasmas such as microwave high density plasmas use different frequencies (2.45 GHz.), the use of rf plasmas is dominant in the industry.

The application of electric fields that range from 100 to 1000 volts between two electrodes (anode and cathode) leads to a breakdown of the gas and the formation of a plasma, a partially ionized gas consisting of an equal number of negative and positive charges. Plasma etchers operate at pressures ranging from 1 mTorr to 1 Torr; this corresponds to a gas density of 10^{13} to 10^{16}, respectively [1717]. For glow discharges, the degree of ionization is typically on the order of 10^{-4}; thus, the plasma consists mainly of neutrals [17]. The degree of dissociation, however, is much greater, on the order of 10% [17]. In addition to neutrals from the feed gas, the plasma consists of electrons, ions, radicals, and excited ions and neutrals. It is the relaxation of the excited species and the emission of photons that gives plasmas their characteristic glow. These charged and uncharged species are created by collisions within the plasma.

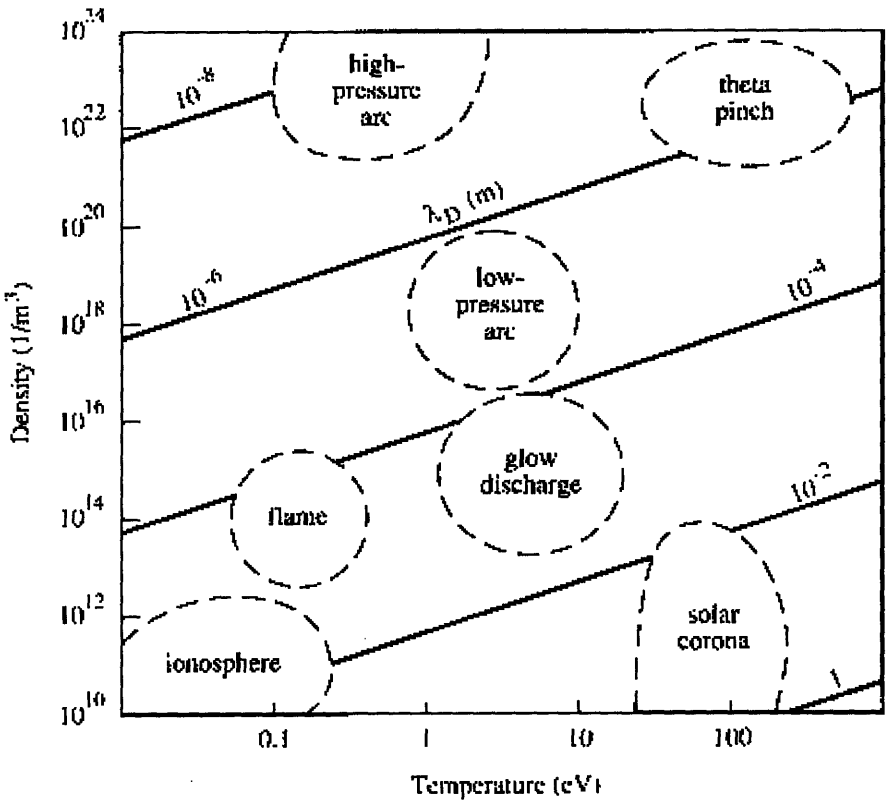


Figure 2.3: Plasma Domains [18]

Glow discharges are non-equilibrium plasmas. The temperature of the electrons are typically 23,200 K (2 eV) while the ions and neutrals are nearly at room temperature (ions, 500 K, 0,04 eV; neutrals, 293 K, 0.025 eV) [17]. Electrons possess greater energy because their mass is much smaller than the mass of neutrals or ions.

Thus, the electrons in the plasma are much more energetic than the neutrals and ions. The overall charge of the plasma, however, remains neutral.

The fact that the electrons have greater mobilities and have large energies leads the plasma to be at a positive potential (V_p), as shown in Figure 2.4. Before the application of the electric field, all of the species in the reactor are neutral. Upon the application of an electric field, free ions and electrons are created by collision processes. Because the electrons have greater mobilities, they can leave the plasma more quickly than the positively charged ions. This starts a negative charging of the chamber wall. For a time, the chamber wall will continue to charge negative. As a result, the electrons are repulsed, and the ions are attracted. At some steady state, the flux of ions and electrons leaving the plasma is balanced. In Figure 2.4, the anode is grounded while a negative potential is applied to the cathode.

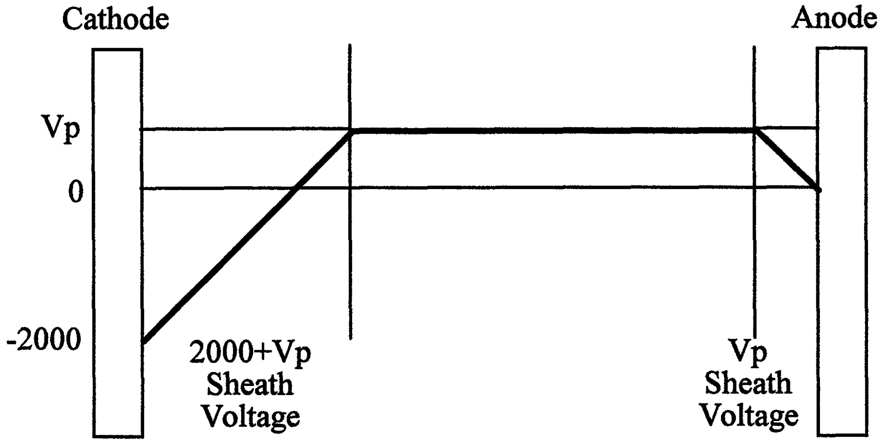


Figure 2.4: Potentials in a Plasma [17]

As can be seen from Figure 2.4, the body of the plasma is at a positive potential but is electric field free. At the edges of the plasma, a region called the sheath is formed. This region can be seen in a plasma by the lack of emission coming from it. This is due to the fact that little excitation occurs in the sheath region. The sheath is created to balance the flux of electrons and ions leaving the plasma, as discussed above. When ions enter the sheath from the body of the plasma, they are accelerated by the electric field. As the ions traverse the sheath, they may collide with neutrals, depending on the process pressure (see Section 2.3.3). Collisions with other ions is unlikely because of coulombic repulsion and low ion concentrations. Collisions in the sheath reduce the bombardment energy and widen the directional distribution of the ions. Upon crossing either sheath, the ions bombard the electrode. Depending on the pressure, this ion bombardment may be in a distribution that is nearly all unidirectional. This unidirectional bombardment aids in directional (anisotropic) etching, as will be discussed in the next section.

2.3 Plasma Etching

Plasma etching is a critical process in IC fabrication. It was developed in the late 1970's and has dominated etching ever since. The two primary advantages of plasma etching over wet etching is that it allows anisotropic etching and that it is a dry process. As IC continue to scale down in size, critical control of features is necessary. Thus, anisotropic etches are highly desirable. By being a dry process, plasma etching can easily be integrated with other dry processes. In addition, dry processes can offer significant environmental, safety, and health benefits over wet processes.

Plasma etching uses a glow discharge to dissociate the feed gas into reactive species. The unenergized feed gas does not etch the film itself. The reactive species diffuse to the surface where they are adsorbed. They react with the film to form volatile products that diffuse away from the surface of the wafer. In this manner material is removed. This process is shown in Figure 2.5. In addition to the chemical attack, the wafer is also bombarded by ions created in the plasma. A synergistic effect between the chemical etch and ion bombardment has been observed, with the magnitude of the etch rate being greater than either component alone. The directionality of the ion bombardment also aids in the anisotropy of the etch.

Plasma etching is the process that can deliver the best anisotropic etch. Wet etches typically etch in all directions at the same rate (*i.e.,* isotropically). As shown in Figure 2.6, lateral undercutting of a pattern can lead to feature sizes that were larger than the original dimensions. Anisotropy is defined as the vertical dimension change (d) divided by the horizontal dimension change (u).

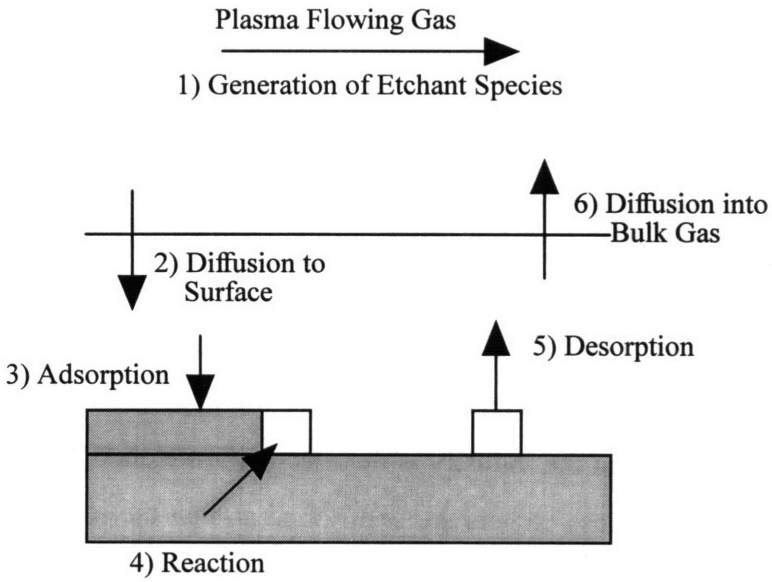


Figure 2.5: Plasma Etching

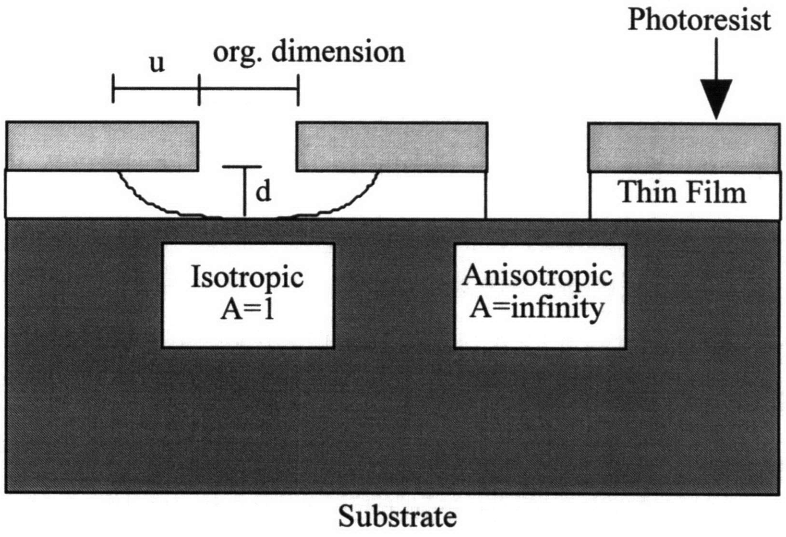


Figure 2.6: Anisotropy vs. Isotropic Etching [19]

In addition to anisotropy, there are several factors that characterize an etch process. The most common ones are etch rate, selectivity, and uniformity. Etch rate is simply the rate of removal of material. This work is primarily interested in this parameter. Selectivity is the ratio of the etch rate of the material being etch and the etch rate of a second material in contact with the plasma. For example, when etching an oxide film that lies on top of silicon, a selective oxide etch with respect to silicon is desired. Once the process has etched completely through the oxide film, it should etch very little or none of the underlying silicon. Finally, uniformity is defined as the maximum differences between etch rates over the wafer normalized by twice the average etch rate. Typical uniformity would be below 5% [19].

A comment is needed on a particular type of plasma etcher. The plasma etcher described in the previous section refers to a generic parallel plate reactor with equal area electrodes. More common in the industry is the reactive ion etcher (RIE); this work was performed with an RIE. These etchers are configured so that the ions attain a very high bombardment energy that significantly enhances etching, in particular anisotropic etching. This is typically done by using electrodes with asymmetric areas in which the wafer is placed on the smaller electrode. Quite often a single electrode design is used with the other electrode being the chamber wall. The pressures at which RIE systems typically operate are one to one hundred mTorr, slightly lower than for plasma etchers [19]. The lower pressure reduces the number of collisions of ions with neutrals in the sheath region as described above. The results is very high energy ions that hit the wafer at near normal directions. While the lower pressure results in increased anisotropy, it may result in lower etch rates (less reactants).

The following sections will discuss the etching of dielectrics and the effects of different process parameters on etch rate. It is important to note that plasma etching is still very much an empirical study. Although it has been used successfully for over a decade by the microelectronics industry, surprisingly little fundamental scientific understanding exists because of the extremely complex nature of the plasma. The mechanisms responsible for etching, selectivity, *et cetera* are still a matter of much debate. The discussion below represents a view that understandingly may not be accepted by all for these reasons.

2.3.1 The Etching of Silicon Dioxide

The discussion of the plasma etching will be broken into two parts. The first part will describe what happens in a macroscopic sense. The second part will describe what happens on the surface of the film. In discussing the first part, I will used the specific example of etching silicon and silicon dioxide with CF_4 alone and in combination with oxygen or hydrogen. A generalization of the observed effects will be then presented within the context of the F to C ratio model. In explaining the second part, I will focus on the specific example of oxide etching. I will end with a discussion of the effect of ion bombardment on plasma etching.

The etching of silicon dioxide has traditionally been done with a fluorocarbon gas. The main reason to use a fluorocarbon gas is that it provides selectivity to silicon, as will shortly be discussed. Silicon or silicon dioxide is not etched in the presence of the fluorocarbon gas alone. A plasma is necessary to dissociate the feed gas into reactive species. For example, fluorine can be created by electron impact dissociation of CF_4, as shown in Equation (2).

$$CF_4 + e^- \Rightarrow CF_3 + F + e^- \qquad (2)$$

These fluorine atoms can then attack the silicon and silicon dioxide surface and form volatile SiF_x (usually SiF_4) species that are then transported away from the surface. Both of these materials can be etched in the presence of pure fluorine, but at relatively slow rates.

The addition of oxygen substantially enhances the etch rate of both materials. The oxygen atoms are believed to increase the concentration of fluorine atoms by converting CF_3 into COF_2 and fluorine atoms [20]. The COF_2 itself can dissociate into CO and F_2 [20]. These reactions are shown in Equation (3).

$$CF_3 + O \Rightarrow COF_2 + F; \;\; COF_2 \Rightarrow CO + F_2 \qquad (3)$$

Measurements of fluorine concentration in a CF_4/O_2 plasma shows that it rises with increasing oxygen content and then peaks. At higher oxygen contents, the fluorine concentration drops as the oxygen begins to dilute the plasma. The etch rate of both materials follows the same behavior as the fluorine concentration with increasing oxygen content.

If hydrogen is added to pure CF_4, the etch rate of silicon drops, reaching zero at 40% hydrogen [20]. Conversely, oxide etch rate remains constant for concentrations up to 40% hydrogen [20]. The drop in silicon etch rate is attributed to the formation of HF by the hydrogen and fluorine; this results in a drop in the free fluorine atom concentration. The hydrogen is said to scavenge the free fluorine. This divergence in etch behavior of the two materials is due to two phenomena. The first is the deposition of a nonvolatile layer, and the second is the role of the oxygen in the silicon dioxide. A fluorine-carbon polymer-like residue (subsequently called polymer) has been found to form on surfaces in a CF_4/H_2 plasma. It also preferentially forms on silicon as opposed to silicon dioxide. Thus, this fluorocarbon film blocks etching of the silicon while it continues for silicon dioxide. This film is formed from CF_x species within the plasma. When they deposit on silicon dioxide, the oxygen in the silicon dioxide reacts with the carbon to form CO and CO_2 while the fluorine is available for attack of the silicon. Thus, less fluorocarbon film forms on the silicon dioxide because the oxide has an internal supply of oxygen. An alternative explanation of this observed selectivity is that the CF_x species preferentially recombine on oxides with fluorine or oxygen from the gas phase. This prevents the accumulation of a thick polymer layer. This recombination does not occur on the silicon surface, which does have a buildup of the polymer layer. That is, the type of material plays an important role in determining the surface recombination kinetics of CF_x species with fluorine or oxygen. Regardless of the actual mechanism, it can be seen that the etching of oxides in a fluorocarbon plasma is a balance between an etching and a deposition reaction. By adjusting the process conditions, it is possible to go from etching to polymer deposition. This can not only occur on silicon, but also on silicon dioxide if conditions are pushed far enough into a deposition regime. A discussion of the fluorine to carbon ratio model will illuminate this boundary between the etch and deposition regimes.

Coburn and Winters developed the fluorine to carbon ratio (F/C) model to explain the observed, competing behavior of fluorocarbon gases to deposit and etch [21]. The F/C model is not specific to a particular gas. Rather, it explains etching in terms of the ratio of all F to C species present in the plasma. F and C are examined because they are considered the active species in this phenomenon. Additives to the plasma may lower or raise the F to C ratio and thus alter the behavior of the plasma. Alternatively, by using feed gases with different F to C ratios (*e.g.*, CF_4, C_2F_6, C_3F_8), similar behaviors can be exhibited. Increasing F/C increases silicon etch rates relative to silicon dioxide, while decreasing F/C decreases silicon etch rates. This corresponds to decreased and increased polymer deposition rates, respectively. This model is shown in Figure 2.7.

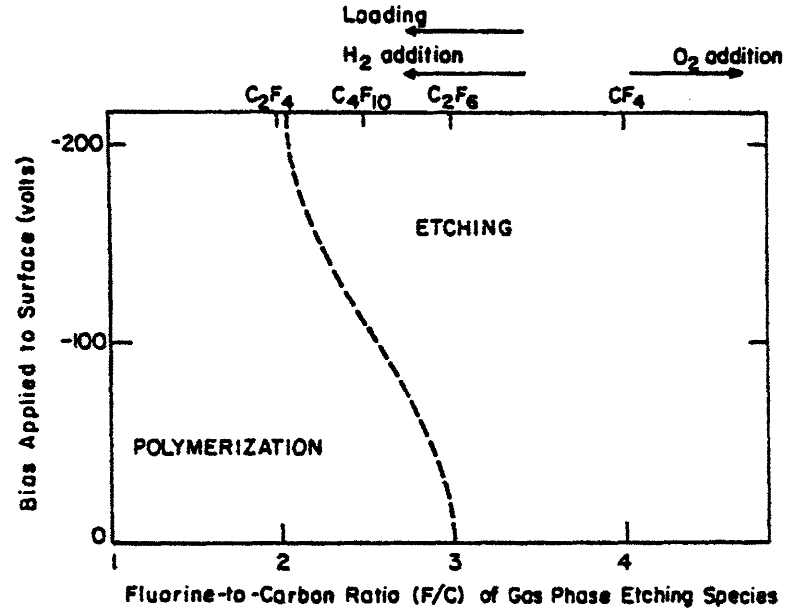


Figure 2.7: F to C Ratio Model [20]

CF_4 again serves as a good example to which to apply the F/C model. The F to C ratio for CF_4 is 4. When CF_4 is used to etch silicon, the F/C drops because the fluorine is being consumed by the silicon. Thus, the silicon etch rate drops. Similarly, adding hydrogen to a CF_4 plasma causes the F/C to drop because of the scavenging effect of the hydrogen. Again, etch rate drops. A similar decrease in etch rate can be attained by using chemistries with a smaller F/C ratio than CF_4. For example, the concentrations of fluorine atoms have shown to decrease while the concentrations of CF_x species increase in order of $CF_4 > C_2F_6 > C_3F_8$; a similar trend of decreasing etch rate is seen for the same order [22].

Oxygen can have to opposite effect. Oxygen boosts the fluorine concentration by reactions like that shown in Equation (3) above and by the effect of oxygen combining with carbon that is deposited on the surface. Thus, with the addition of oxygen, the F/C increases, as does etch rate. The line between the etch regime and the deposition regime is shown in Figure 2.7 as a function of the F to C ratio. Note that going to larger negative biases shifts the line from a F/C of 3 to a F/C of 2. That is, the increased ion bombardment energy appears to extend the etch regime further into the deposition regime. The effect of ion bombardment is discussed below.

A closer examination of the surfaces processes during oxide etching is now warranted. In the discussion above, it appeared that the reactive species adsorb onto the surface, react with the oxide, and then the effluent evaporates away. In addition, the reactant species was given as simple fluorine atoms. Both of these descriptions were simplifications as now will be discussed.

During oxide etching, a fluorocarbon film, roughly 10 Å in thickness, appears to form on the oxide surface, as shown in Figure 2.8 [23].

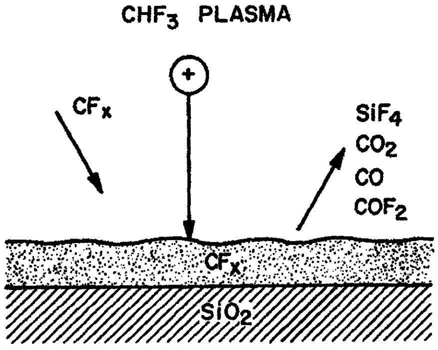


Figure 2.8: Fluorocarbon Film Formation During Oxide Etching [23]

It is CF_x and/or F species within this film that react with the oxide surface and gasify it by forming SiF_x species. The attack by the CF_x or F species of the oxide film is also an ion-enhanced reaction. The ion bombardment produces damage in the form of dangling bonds and radical groups that can be readily attacked by the reactant species in the fluorocarbon film. Potential means of attack of such sites by various reactive species is suggested in Figure 2.9. Without the ion enhanced component, etching would occur at a slower rate. Depending on the F/C ratio, it may even stop without the presence of ion bombardment (see Figure 2.7). Ion bombardment aids other stages of etching as discussed below.

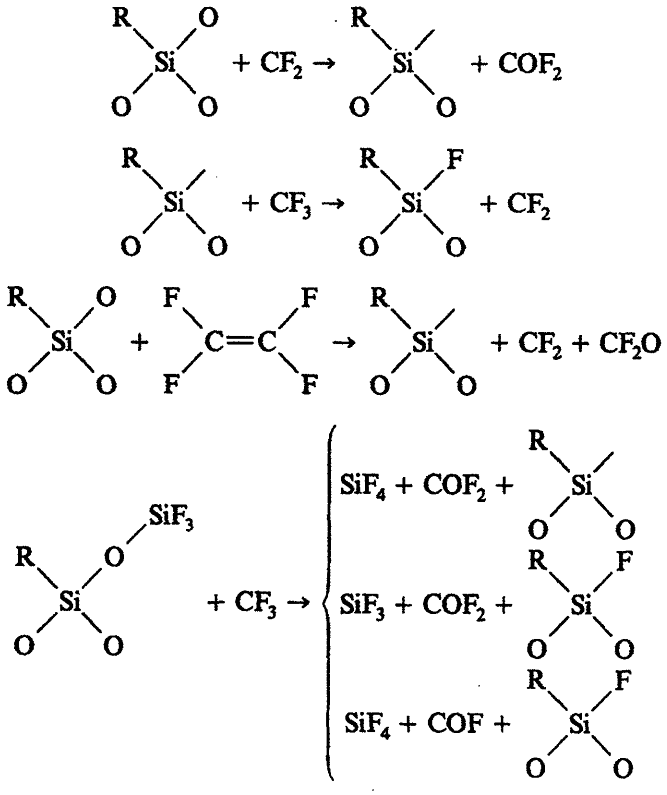


Figure 2.9: Possible Surface Reactions During Oxide Etching [24]

The thickness of the fluorocarbon film depends on the feed gas composition. It can range from being undetectable by Auger analysis up to 20 Å thick [23]. This film is much thicker on silicon (~150 Å or more) because there is no oxygen present in the silicon to gasify the carbon layer [23]. If thick enough, this film will block etching. This is the mechanism that provides selectivity to silicon when performing an oxide etch.

Ion bombardment provides several enhancements to etching. Ion bombardment can damage and amorphize the substrate and allow for easier attack of the film. This damage can extend down several monolayers. Ions can also sputter the adsorbed reaction products. The bombardment can aid in the incorporation of the halide into the film. Finally, ion bombardment can reduce the amount of coverage by the fluorocarbon polymer (the effect seen in Figure 2.7).

2.3.2 The Etching of Silicon Nitride

Silicon nitride is etched using both fluorocarbon plasmas and fluorine-only plasmas (*e.g.*, NF_3 and SF_6). It shows etching characteristics between that of silicon and silicon dioxide. Fluorocarbon films that etch silicon dioxide etch silicon nitride as well. Selectivity to silicon dioxide can be achieved by adding CF_3Br or nitrogen to CF_4 plasmas [23]. It has been suggested that an oxide etch selective to nitride can be achieved by adjusting the feed gas composition so that the CF_x film preferentially thickens on nitride (which has no oxygen to gasify the fluorocarbon) [23]. However, there are indications that nitrogen can combine with carbon to form a volatile CN product [25,26]. Finally, fluorine atoms alone can etch nitride well in the presence of ion bombardment. This is expected since fluorine etches silicon well. None of these mechanisms are not well understood due to the fact that less fundamental work has been done with silicon nitride etching.

2.3.3 The Effect of Pressure on Etch Rate

The effect of pressure on etch rate is inconsistent. However, some general observations can be made. First, the pressure is directly related to the concentration of the reactive species. The reaction kinetics of the chemical component of the etch rate therefore has a first order dependence with pressure. Thus, this mechanism increases etch rate with increasing pressure. While etching, especially of dielectrics, appears to be ion-enhanced, it has been noted that the two mechanisms may be considered in parallel [24]. Pressure also has an effect on the reaction kinetics of polymerization. As can be seen in Equation (4), the polymerization kinetics is generally a second order function of pressure [24].

$$CF_2 + CF_2 \Rightarrow C_2F_4$$

$$r = k_2 N^2_{CF2} \; (\propto P^2) \tag{4}$$

Thus, as pressure increases, the reaction kinetics of etching are overcome by the reaction kinetics of polymerization. Increasing pressure can also lead to a decrease in the electron energy and thus a drop in dissociation rates. Finally, decreasing pressure leads to an decrease in ion scattering and an increase in the sheath voltage. Both of these lead to higher ion bombardment energies which further enhances etching.

2.3.4 The Effect of Flow Rate on Etch Rate

Two competing mechanisms affect the etch rate as a function of total flow. The first is supply rate limited etching. The second is pumping rate limited etching. Both are shown in Figure 2.10.

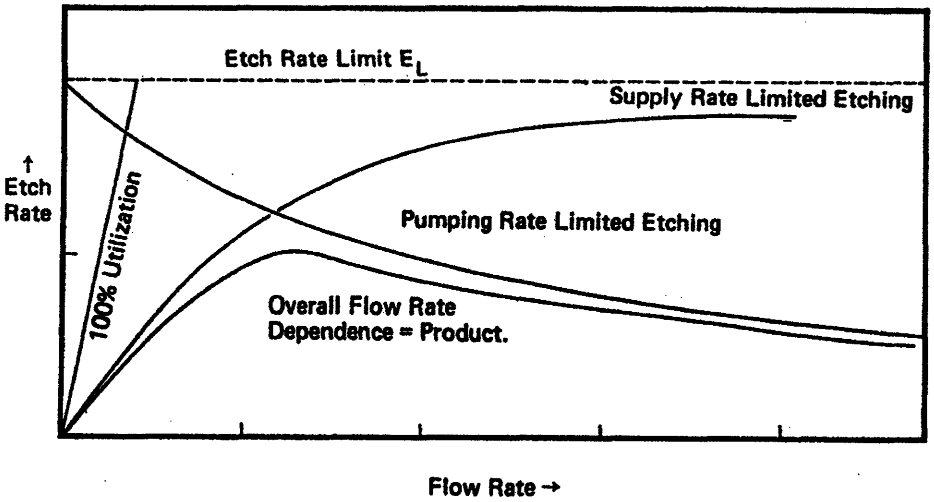


Figure 2.10: Etch Rate Dependence on Flow Rate

In the supply limited regime, increasing flow basically provides a fresh supply of reactants at a faster rate. Thus, etch rate increases. For the pumping rate limited regime (also called residence time limited regime), the reactants are being pumped out of the chamber before they have time to react with the thin film. That is, there exists a minimum reaction time, t, for the etch reaction to occur. Residence time, T, in a reactor is defined by Equation (5).

$$T = PV/Q \tag{5}$$

where P is pressure in Torr, V is volume in liters, and Q is flow rate in sccm. Thus, etch rate begins to be residence time limited when $t \approx T$.

2.3.5 The Effect of Magnetic Field on Etch Rate

Magnets are used on some etchers to confine the plasma. The Applied Materials Precision 5000 used for this project applies a rotating magnetic field perpendicular to the vertically applied electric field and parallel to the cathode (see Chapter 5 for a description of the Applied Materials Precision 5000). The magnetic field has two effects. When ions hit the cathode, secondary electrons are emitted. These secondary electrons are then accelerated across the sheath into the body of the plasma. The electrons experience a Lorentz force (eVxB) that is perpendicular to their direction of motion. As a result, the electrons are forced to travel in a helical motion. The magnetic field effectively increases the distance traveled by these very energetic electrons during which they have more opportunities to collide with species in the plasma. In addition, magnetic confinement reduces the loss of electrons to the walls of the chamber. This results in a glow discharge with higher electron densities [19]. Both these effects result in greater amounts of dissociation and ionization. More radicals are available for etching and the ion flux to the surfaces of the chamber is greater. Thus, etch rate is enhanced. The effect of the magnetic field on the motion of the ions is negligible because of their much larger mass.

The application of a magnetic field also appears to have an effect on the dc self-bias. The dc self-bias has not been previously discussed; it roughly corresponds to the ion bombardment energy. In a CF_4 and CF_4/H_2 plasma, it was observed that the magnitude of the dc self bias dropped as a function of increasing magnetic field [27]. This effect was attributed to a decrease in the electron mobility perpendicular to the magnetic field, while have a lesser effect on the ions. This drop in electron mobility reduced the need for the dc self-bias. Since dc self-bias is smaller, the ion bombardment energies are smaller.

2.3.6 The Effect of Power on Etch Rate

The effect of power on etch rate is more certain than the other parameters discussed above. Etch rate increases with increasing power at low power densities. Increasing power increases the amount of dissociation and therefore increases the radical and ion densities. However, the concentration of charged species saturates at high power. Increasing the applied power also increases the ion bombardment energy. Using excessively high powers, however, will result in surface damage and mask erosion due to substrate heating and excessive ion bombardment.

Chapter 3

The Use of Perfluorocompounds by the Microelectronics Industry

Perfluorocompounds are used by the microelectronics industry for two major plasma processes: wafer patterning of thin films, especially dielectric films, and the *in-situ* cleaning of PECVD chambers. The question of which process uses PFCs most heavily has been debated in the industry. However, a SEMATECH study conducted by the Global Warming Program offers some insight into the answer of this question. Table 3.1 shows the purchases of PFCs by the microelectronics industry in 1993.

Table 3.1: PFC Usage Baseline (U.S. Microelectronics Industry) [28]
1993 Purchases of PFCs (metric tons)

	CF_4	C_2F_6	NF_3	SF_6	Total
Estimated US Total	67	177	18	45	307
% of Total	22	58	6	14	100

If the usage of C_2F_6 and NF_3 is assumed to be for PECVD chamber cleaning, then chamber cleaning usage is approximately 64% of the total. Therefore, while chamber cleaning usage represents a majority, it is not a overwhelming majority, as thought by some in the industry. However, it is expected that PFC usage for chamber cleaning will rise significantly while etch consumption will remain fairly constant [29]. This can be attributed to the increasing levels of metallization in leading edge IC, as mentioned earlier. It appears that PFC usage for both wafer patterning and PECVD chamber cleaning is important, with the balance shifting towards chamber cleaning in the future. Thus, this project is concerned with replacement chemistries for both processes.

In this chapter, the usage of PFCs for wafer patterning and PECVD chamber cleaning applications will be discussed. In addition, work on non-PFC chemistries for applications that currently use PFCs will be reviewed. The bulk of this information was gathered during a six month survey of the literature and industry experts at the beginning of this project. Thus, much of the information presented was by private communication and might be considered the collective knowledge of the industry in this area.

3.1 Perfluorocompound Use

All of the major materials used in microelectronics fabrication are patterned by plasma etching during various stages of the fabrication process. Table 3.2 lists the main materials that are etched by PFCs, in addition to other chemistries.

Table 3.2: Wafer Patterning Applications of Perfluorocompounds[30]

Material Etched	Gases
Silicon	C_2F_6, SF_6, NF_3, CF_4, BCl_3, HBr, Cl_2, HCl.
Silicon Dioxide	C_2F_6, SF_6, CF_4, CHF_3.
Silicon Nitride	CF_4, C_2F_6, SF_6, CHF_3.
Tungsten	SF_6, NF_3, Cl_2.

In the past. silicon etches relied heavily on fluorocarbon or fluorocarbon/chlorofluorocarbon chemistries. These processes have moved towards mixtures of chlorine and bromine chemistries such as HBr/Cl_2. One reason for this change is the reduced amount of etch residue that these newer chemistries produce. As has been discussed, fluorocarbon chemistries often leave fluorocarbon residues behind. In addition, these bromine mixtures are very selective to oxide films. This is particularly crucial for polysilicon etches that define the gate electrode and must stop on gate oxides that have thicknesses of less than 100 Å in leading edge ICs. In addition, some polysilicon etch processes still use SF_6. Aluminum etching is done with chlorine chemistries such as BCl_3/Cl_2 because the aluminum chloride is the only volatile aluminum halide. PFCs are used for tungsten etchbacks, but this etch process is being replaced by chemical-mechanical polishing because it offers better planarization and faster removal rates. As can be seen in Table 3.2, dielectrics (silicon dioxide and silicon nitride) rely exclusive on perfluorocompounds to do their etching. This is the reason why this project is focused on dielectric materials.

Chamber cleaning is not a process that is used directly for the fabrication of microelectronics. Rather, it is a necessary step that allows the continued manufacture of microelectronics. When using PECVD, a certain amount of the material is deposited on the electrodes and chamber walls in addition to on the wafer. After prolonged periods without cleaning these deposits, they may spaul off and result in elevated levels of particles in the chamber. Elevated particle levels reduce reliability and yield. Thus, periodic cleaning of the chamber is necessary. Since the late 1980's, PECVD chambers have been cleaned *in-situ* using the same gases that were used for dielectric wafer patterning. The process condition, however, are different. A typical clean process would run at several Torrs pressure for several minutes using liters/min. flow rates. These cleans are run at very high powers, usually on the order of KWs. The three gases that are used for cleaning processes are C_2F_6, CF_4, and NF_3, with C_2F_6 being the most common by far. The heavy reliance on C_2F_6 is why the DuPont's restrictive 1994 policy sales announcement motivated the industry to find a means of controlling their PFC emissions.

Because the process condition are different from those of plasma etching, the mechanism of chamber cleaning is most likely a purely chemical one [31]. The walls of the PECVD chamber do experience some ion bombardment, but far below the energies experienced by wafers during RIE. In addition, PECVD chambers can be cleaned with chemistries that are source of only fluorine atoms (*i.e.*, CF_x species are not present). In fact, NF_3, a very rich source of atomic fluorine, is an excellent chamber cleaning gas, as has been demonstrated by Air Products and Chemicals [36]. Thus, the chemical requirements for chamber cleaning are more relaxed than for wafer patterning. The key characteristic of a clean gas is that it is a rich source of fluorine. There is no need for a selectivity mechanism, as with wafer patterning. It is anticipated that a replacement chamber cleaning gas might be more readily found than a wafer patterning replacement.

3.2 Non-Perfluorocompound Use

A review of the literature revealed that PFCs and CFCs have been used almost exclusively by the industry since plasma etching of dielectrics and *in-situ* PECVD chamber cleaning first found widespread use. To date, little detailed non-PFC work that could be applicable to mainstream microelectronics processing has been done by the microelectronics industry or the research community in general.

The most prevalent non-PFC chemistry that industry has recently investigated is the family of hydrofluorocarbons (HFCs). C_2F_5H was investigated by Applied Materials before 1990, during the introduction of *in-situ* chamber cleaning. It was rejected in favor of PFCs because its etch rate was deemed too slow [32]. Recently, both Applied Materials and Novellus reexamined HFCs for chamber cleaning [15,33]. Novellus reported etch rates using C_2F_5H to be 412 Å/min., as compared with etch rates of 9,100 Å/min. using C_2F_6 [15]. Again, the etch rate was found to be too slow for chamber cleaning.

For dielectric wafer patterning, LAM Research and MIT have investigated a combination of HFCs in a high-density (TCP) inductively coupled oxide etch tool. Using a mixture of CHF_3/ C_2F_5H, etch rates of BPSG SiO_2 and of photoresist were found to be about 13,000 and 2,800 Å/min., respectively, with an overetch slightly greater than 100% [34]. No etching of the underlying silicon was reported. Additional experiments using one or both of these HFCs were done with thermal oxide. Average etch rates for SiO_2 and photoresist were reported to be 10,000 Å/min. and 2,200 Å/min., respectively, for an overetch of 60% with a $C_2F_4H_2/CHF_3/Ar$ mixture [34]. Again, no etching of silicon was reported. The use of $C_2F_4H_2$ in high concentrations, however, resulted in the formation of a heavy polymeric coating inside the chamber. This polymer formation was attributed to the greater hydrogen content in $C_2F_4H_2$, as opposed to C_2F_5H. Hydrogen atoms were believed to contribute to the polymerization. In the same study, Mohindra *et. al.* investigated these mixes in an Applied Materials Precision 5000 (MERIE) oxide etcher. Polymeric formation was reported with the use of C_2F_5H and $C_2F_4H_2$. Oxygen was added to counteract this effect. Thermal oxide etch rates of 3,000 Å/min. using C_2F_5H/O_2 and $C_2F_4H_2/O_2$ separately were reported [34]. A mixture of $C_2F_5H/Ar/O_2$ resulted in an increased etch rate of 4,200 Å/min. [34]. Finally, maximum oxide etch rates of C_2F_6/O_2, C_2F_5H/O_2, and $C_2F_4H_2/O_2$ mixtures were reported to be 3,300 Å/min., 2,400 Å/min., and 1,500 Å/min., respectively [34]. The results of the C_2F_6 chemistry served as a point of reference to compare the HFC chemistries to a simulated C_2F_6 chamber clean. From a global warming standpoint, combinations that include CHF_3 might not be acceptable. As shown in Table 1.1, CHF_3 has a long atmospheric lifetime and large GWP.

Cypress Semiconductor has also investigated the use of HFCs for a specific application. A self-aligned contact (SAC) etch was developed for an advanced SRAM process; the process etched oxide and stopped on nitride. In this work, CHF_3 and $C_2F_4H_2$ were flowed in combination in a LAM 384T Triode etching system. Etch rates were reported to range from 2,000 to 2,500 Å/min. [35]. Good selectivity to nitride was reported [35].

Besides HFCs, focused effort has been expended in looking for specific replacements for C_2F_6. Novellus has investigated the use of NF_3 in place of C_2F_6 for PECVD chamber cleans [36]. Nitrogen trifluoride has been reported to have a faster etch rate than C_2F_6 [36]. Thus, its use would result in more efficient cleans. There also is no current restriction on the sale of NF_3, as there is with C_2F_6. However, this solution is a sideways step since NF_3 is considered a global warming gas like C_2F_6. The 3M Company is proposing using higher C_xF_y compounds (e.g., C_3F_8 and C_4F_{10}) in lieu of C_2F_6 for both wafer patterning and PECVD chamber cleaning [37]. These higher C_xF_y compounds, however, are also global warmers [2]. Again, as with NF_3, this approach only circumvents the C_2F_6 sale restriction and does not address the larger problem of global warming gas emissions by the microelectronics industry.

Non-industrial work has also been minimal. The majority of the work on dielectric etching with non-PFC chemistries has been done to understand basic etching mechanisms. A significant amount of it was done without a plasma (*i.e.*, spontaneous etching). Spontaneous etching of silicon and silicon dioxide using xenon difluoride was investigated in the early 1980's at AT&T Bell Laboratories [38]. The silicon was etched, but the oxide was not. This result was attributed to the fact that XeF_2 did not dissociate into xenon and free fluorine before it was transported to the surface. The XeF_2 served rather as an etch precursor that physisorbed onto the surface. Once physisorbed, it underwent diffusion to sites where dissociative chemisorption took place. The fluorine atoms then attacked the silicon. In a plasma, it would be expected that the XeF_2 would dissociate in the gas phase, and free fluorine atoms would then be available for transport and etching of the silicon or silicon dioxide surface. The use of XeF_2 in a 50 keV inert gas ion beam was reported to etch silicon nitride. Enhanced etch rates of 40, 80, and 160 times greater than physical sputtering rates were reported using argon, krypton, and xenon beams, respectively [39]. These studies suggest that XeF_2 might be a viable replacement. However, a significant drawback of XeF_2 is its extreme cost.

Molecular fluorine has also been examined as a means to understand the fundamental mechanism of etching. Early theories suspected that CF_x was responsible for SiO_2 etching, and that fluorine atoms did not spontaneously etch oxides. However, studies done at AT&T Bell Labs reported spontaneous etching of oxides with fluorine atoms using molecular fluorine as a source gas, albeit very slowly. Fluorine, however, is difficult to handle because of its extremely corrosive nature.

Interhalogens such as ClF_3, BrF_3, BrF_5, IF_5, and ClF have been investigated for spontaneous dry etching of silicon. It was reported that all of these interhalogens etched silicon, but not oxide. The reason for this behavior is analogous to that of XeF_2, *i.e.*, these compounds do not dissociate in the gas phase, but physisorb onto the surface of the film [40]. ClF_3 has also been investigated for wafer cleaning. It was observed that the etch rate of a native oxide layer was greatly enhanced by the use of UV irradiation [41]. It was speculated that the UV irradiation generated fluorine atoms by photolysis of the ClF_3. In another study, a mixture of ClF_3 and CHF_3 was used in a plasma for contact hole etching [42]. Particle generation was significantly lower than with a process that used a CHF_3/CF_4 mixture. In addition, no polymer deposition was reported. Thus, interhalogens might be a viable alternative for dielectric etching. Interhalogens, however, are extremely strong oxidizers and thus difficult to handle.

The use of anhydrous hydrogen fluoride has been investigated in wafer cleaning experiments similar to those in which ClF_3 was used [43,44,45]. Anhydrous HF had been combined with water vapor at atmospheric pressure to generate isotropic oxide etch rates of 900 to 24,000 Å/min. [44]. A Japanese patent has reported the use of anhydrous HF to perform a PECVD chamber clean using a plasma [46]. Again, there are handling difficulties resulting from HF's corrosive nature.

The use of sulfur monofluoride has been reported for the etching of silicon, silicon dioxide, and silicon nitride in various Japanese patents. The sulfur is believed to provide sidewall passivation that will allow an anisotropic etch. In addition, it has been theorized that the S-F bond in S_2F_2 is weaker than the N-F bond in NF_3 [47]. As has been mentioned above, NF_3 is a commonly used etch gas whose N-F bond is fairly easily broken. Thus, it is expected that S_2F_2 could potentially be an even richer source of fluorine than NF_3 is. Residual sulfur has been reported, but it can be easily sublimated by heating the wafer [48].

Of all of the chemistries reviewed above, only the two HFCs mentioned are not considered problematic from an ESH standpoint. Most of the chemistries have extreme handling problems associated with them, while a supplier for one (S_2F_2) has not been identified. The specific concerns are summarized in Table 3.3. Thus, the experimental work reported in the literature does not appear to be a good source from which to draw potential replacements for current PFCs, as was the initial assumption.

Table 3.3: Concerns Associated With Chemistries That Have Been Experimentally Examined

Chemistry	Concern(s)
Pentafluoroethane (C_2F_5H)	slow etch rate, but promising.
Tetrafluoroethane ($C_2F_4H_2$)	slow etch rate, but promising.
Nitrogen trifluoride (NF_3)	still a PFC; lifetime: 740 years, GWP: 8,100.
Xenon difluoride (XeF_2)	strong oxidizer; low vapor pressure, very expensive.
Fluorine (F_2)	extremely strong oxidizer, very corrosive.
Interhalogens (ClF_3, BrF_3, BrF_5, IF_5, ClF)	very strong oxidizers; corrosive.
Anhydrous HF	corrosive.
Sulfur monofluoride (S_2F_2)	supplier unknown.

Chapter 4

Potential Candidate Chemistries

The selection of initial candidate chemistries was the second major stage of this work. In this Chapter, the general selection criteria used will be discussed. Using these criteria, three major families of chemistries were selected for experimentation: hydrofluorocarbons, iodofluorocarbons, and unsaturated fluorocarbons. The advantages and disadvantages of each family will be reviewed along with any experimental work done with them.

4.1 General Selection Criteria

The selection criteria can be loosely divided into two parts: technical criteria and environmental, safety, and health (ESH) criteria. The main technical criteria was to pick candidate chemistries that had an anticipated etch rate that was fast. The selection process was confined to halogen chemistries, as those are the only that had been used for conventional plasma etching. As can be seen from Chapter 2 and 3, dielectric etch processes are performed solely with fluorine-bearing species, as opposed to other halogens. Chlorine chemistries can etch silicon dioxide films slowly [49], but would not be acceptable replacements for current dielectric etch chemistries because the current hardware consists partially of unanodized aluminum. Chlorine chemistries are used to etch aluminum films. Attack of the chamber by chlorine would occur and would result in unacceptable hardware damage. Bromine chemistries are typically used to etch silicon because they are selective to silicon dioxide (*i.e.*, bromine does not etch silicon dioxide) [20]. Thus, bromine chemistries would not be a suitable starting point. Iodine species have been the subject of some limited studies. These studies have investigated the etching of silicon only. They have indicated that etching of silicon is possible, but at lower rates than those experienced with chlorine or fluorine chemistries and again with selectivity to oxides [50]. This might be expected given the lower reactivity of iodine as compared with the other halogens. Thus, fluorine-bearing chemistries were decided upon, in particular because of the extensive work done with fluorine chemistries for the etching of dielectrics and because no other halogen species appeared promising in the literature.

In eliminating chemistries based on ESH consideration, a trade-off between environmental concerns and health and safety concerns was necessary. PFCs are considered low safety and health impact chemicals because of their great stability. However, this extreme stability is also one of the root causes of their environmental threat. Thus, to minimize any long term environmental impact such as global warming or ozone depletion, any replacement chemistries must have little or no atmospheric stability. Such chemicals, however, inevitable have higher safety and/or health impacts. An optimum point on the environmental, safety, and health curve had to be chosen. The point that was chosen for the selection of the candidate chemistries was one of low environmental impact and acceptable health and safety impact. As stated, low environmental impact meant selecting candidate chemistries that had, in particular, low atmospheric lifetimes. In addition to the technical reasons, bromine and chlorine chemistries were eliminated because of their potential for ozone depletion. Ozone depletion is not a concern for fluorine chemistries. Handling and ease of use was a consideration from an safety and health standpoint, but it was not a high barrier. However, mutagens, teratogens, and carcinogens were specifically ruled out, as per the suggestions of the SEMATECH S69 PTAB.

Using these general criteria, chemistries from the hydrofluorocarbon, iodofluorocarbon, and other fluorine-bearing chemistries were selected from over one hundred initial candidates. The specifics chemistries will now be discussed. Detailed information on ESH factors (primarily from MSDSs) and past work with these chemistries is given in the Appendix. Finally, because no quantitative atmospheric lifetime data for most of the IFCs and unsaturated fluorocarbons was found, discussions with MIT Professor Mario Molina were held to get his opinion on these classes of chemistries. Qualitatively, he felt that these two families of chemistries did not pose a global warming risk because of their inherent instability.

4.2 Hydrofluorocarbons

As discussed in Chapter 3, some members of the hydrofluorocarbon (HFC) family have been used for plasma etching in the past. This made the selection of HFCs as potential candidate chemistries a fairly safe one. Because HFCs are very similar to perfluorocarbons, their handling and usage does not involve any substantial unknowns. In addition, no hardware compatibility issues were expected. Past work has indicated that HFCs might be acceptable from a performance standpoint, but the HFC family also has the most serious environmental concerns associated with them compared to the other two families. The HFCs still possess significant GWPs; however, they are smaller than those of PFCs and CHF_3. In addition, their atmospheric lifetimes are short, well under a hundred years. Thus, their effect is not permanent, as with PFCs.

The use of difluoromethane has been examined in combination with other HFCs and PFCs for its ability to promote polymer deposition during the etching of silicon dioxide (*i.e.*, for selectivity reasons). Both low and high (electron) density systems were used. High density systems are a new type of etcher that use inductive coupling or electron cyclotron resonance to produce high electron density plasmas. Finally, difluoromethane is flammable; health effects appear to be minimal except in large quantities.

Research using pentafluoroethane and 1,1,1,2-tetrafluoroethane has been discussed in Chapter 3. Pentafluoroethane and 1,1,1,2-tetrafluoroethane were originally developed as alternative refrigerants to CFCs. Their health effects are minimal, except in very large quantities. DuPont has determined that pentafluoroethane's and 1,1,1,2-tetrafluoroethane's toxicity is very low. Neither is flammable.

The use of either isomer of heptafluoropropane has not been reported in the literature. Both gases are stable and nonflammable. Unfortunately, little health data exists for either isomer.

Trifluoroethylene is the only unsaturated HFC examined. No reports of its use are present in the literature. Because it is unsaturated, trifluoroethylene is flammable. Hazardous polymerization will occur. Little health data has been reported.

The characteristics of these HFCs are summarized in Table 4.1.

Table 4.1: Hydrofluorocarbons

Chemical Name	Chemical Formula	Flamm.	Toxicity	GWP$_{100}$	Atm. Lifetime	Etch Matrix
Difluoromethane	CF_2H_2	Y	high	580	6 yrs.	N
Pentafluoroethane	CF_3-CF_2H	N	slight	3,200	36 yrs.	Y
1,1,1,2-Tetrafluoroethane	CF_3-CFH_2	N	slight	1,300	14 yrs.	N
1H-Pentafluoropropane 2H-Pentafluoropropane	CF_2H-CF_2-CF_3 CF_3-CFH-CF_3	N	slight	? 3,300	? 41 yrs.	Y Y
Trifluoroethylene	CF_2=CFH	Y	N/A	?	?	N

4.3 Iodofluorocarbons

From an etching standpoint, the IFCs represent an unknown quantity. Little work has been reported in the literature on the usage of IFCs. The only know use is of CF_3I in combination with SF_6 for a trench etch of silicon in a low pressure, batch diode system. One expected technical advantage of the IFCs over the HFCs is that they are not expected to polymerize as heavily as the HFCs because they do not possess hydrogen. They may be particularly useful for chamber cleaning processes.

In general, all the chemicals in the IFC family give off iodine readily by photolysis since the C-I bond is easy to break. This tends to make them unstable in the atmosphere and thus desirable from a global warming/ozone depletion standpoint. The liberation of iodine may lead to pump oil degradation in wet pumps, albeit very slowly. Except for 1,2-diiodotetrafluoroethane and 1-iodoheptafluoropropane, no toxicity data is available from the MSDS's. Other sources, however, have collectively describe IFCs as irritants to the eyes, mucous membranes, and respiratory tract, though not acutely toxic (except for 1,2-diiodotetrafluoroethane). None are flammable. Indeed, some IFCs are being considered as halons. It should be noted that, unlike F, and like Br and Cl, atomic iodine is an effective ozone-destroying agent. However, IFCs are believed to be so short-lived in the atmosphere, that their ozone depleting capacity is negligible. For example, the expected ODP for CF_3I is less than 0.008 while its lifetime is about 1 day [51]. It should also be pointed out that there exist very large natural sources of iodocarbons.

"These sources are so large that it would be difficult for human activities to approach them, in sharp contrast to chloro- and bromocarbons [51]."

As the larger members of this family have high boiling points and low vapor pressures, the installation of heated lines for their use may be necessary to avoid condensation and/or mass flow controller damage. Personnel at Applied Materials believe that no serious hazards should arise from the use of iodine-bearing compounds in a process tool such as the one described in this thesis. The characteristics of the IFCs are summarized in Table 4.2.

Table 4.2: Iodofluorocarbons

Chemical Name	Chemical Formula	Flamm.	Toxicity	Vapor Pres. @ 20°C	Boiling Point
Iodotrifluoromethane	CF_3I	N	irritant	85 psi	-22.5 °C
Iodopentafluoroethane	$CF_3\text{-}CF_2I$	N	irritant	35 psi	12-13 °C
1,2-Diiodotetrafluoroethane	$CF_2I\text{-}CF_2I$	N	irritant	N/A	112-113 °C
1-Iodoheptafluoropropane	$CF_2I\text{-}CF_2\text{-}CF_3$	N	N/A	N/A	40 °C
2-Iodoheptafluoropropane	$CF_3\text{-}CFI\text{-}CF_3$	N	N/A	7.1 psi	38 °C
Iodotrifluoroethylene	$CF_2{=}CFI$	N	irritant	N/A	30 °C

4.4 Unsaturated Fluorocarbons

Because of the similarities of unsaturated fluorocarbons to HFCs and PFCs, unusual handling and usage situations are not expected. In addition, no hardware compatibility issues are expected. No environmental information on these compounds exists. However, since these compounds are unsaturated, they are expected to have negligible atmospheric lifetimes. The presence of double or triple carbon-carbon bonds also make it unlikely that these compounds possess any atmospheric stability.

Tetrafluoroethylene has been examined in combination with HFCs and other unsaturated fluorocarbons for selective etching of silicon dioxide in high density plasmas. It was also examined in combination with CF_4 for its ability to promote polymer deposition during the etching of silicon and silicon dioxide. It is flammable, but does not appear to have any substantial toxicity. Hazardous polymerization may occur.

Hexafluoropropylene has been examined in combinations with HFCs and other fluorocarbons is both low and high density etchers for selective etching of silicon dioxide. It is flammable. Inhalation may affect the nervous system. Other health effects may occur.

Hexafluoro-1,3-butadiene has not been used for etching applications. It is not flammable. Little health data exists on it. Hexafluoro-2-butyne has also not been used for etching applications. It is flammable and highly toxic. Finally, hexafluorocyclobutene has been examined for silicon etching in a low density system. It is not flammable but is highly toxic.

The C_4F_8 family has been used for etching. It was unclear whether octafluoro-2-butene was used in some of these studies (There are two other isomers of C_4F_8.). Octafluoro-2-butene is not flammable and little health data exists for it. The unsaturated fluorocarbon family is summarize in Table 4.3.

Table 4.3: Unsaturated Fluorocarbons

Chemical Name	Chemical Formula	Flammability	Toxicity
Tetrafluoroethylene	$CF_2{=}CF_2$	Y	none
Hexafluoropropylene	$CF_3\text{-}CF{=}CF_2$	Y	moderate
Hexafluoro-2-butyne	$CF_3\text{-}C{\equiv}C\text{-}CF_3$	Y	high
Hexafluoro-1,3-butadiene	$CF_2{=}CF\text{-}CF{=}CF_2$	N	slight
Hexafluorocyclobutene	$CF_2\text{-}CF_2\text{-}CF{=}CF\text{-}$	N	high
Octafluoro-2-butene	$CF_3\text{-}CF{=}CF\text{-}CF_3$	N	slight

Chapter 5

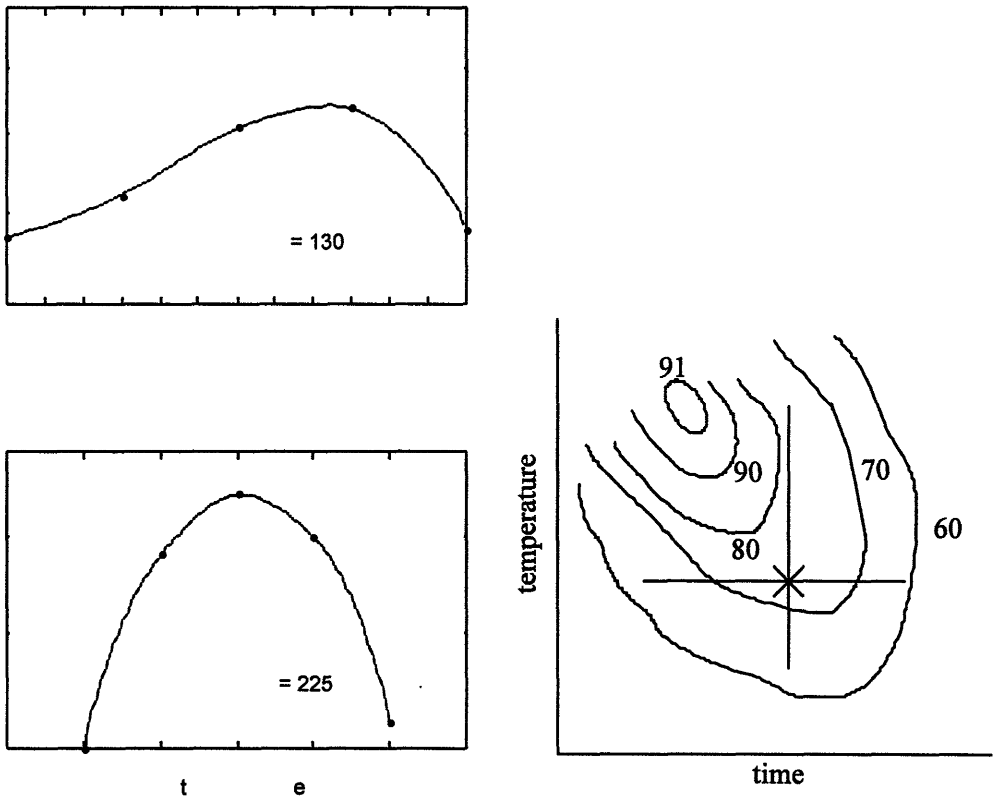
Experimental Method

This chapter will discuss the experimental method used for the etch viability experiments on the hydrofluorocarbon candidate chemistry family. A Design of Experiments (DOE) method was used to plan the experiments. The basic advantages of DOE will be outlined. In addition, a description of the DOE software NNAPER used to plan the experiments and model the results will be given. The experiment condition under which the NNAPER matrices were run will be outlined, as well as the conditions of the low pressure experiments. Finally, a description of the Precision 5000 etcher and the *in-situ* etch rate measurement tool will be given.

5.1 Design of Experiments

For the experimental work described in this thesis, a Design of Experiments (DOE) methodology was used. DOE is well established statistical technique that is used heavily by industry for process development [52,53,54,55]. The particular advantage of this statistical method is that it can "lead, in a relatively few experimental runs, to precise estimates of the effects of these factors on the response [56]." This section will briefly describe DOE and compares it to traditional one-at-a-time experiments.

With traditional "one-at-a-time" experiments, one particular experimental factor is varied while the others are held constant. The response to the variation of this one variable is then mapped. The process is then repeated with all of the variables of interest. In examining the responses gathered by this method, two assumptions are being made. First, it is assumed that the variables act additively. Second, there is no measurement of any interactions among factors. If these assumptions are wrong, then the optimum point will not be found. As an example, let us assume that an engineer is attempting to determine the optimum yield for a manufacturing process as a function of time and temperature. He might conduct the following experiments, as shown in Figure 5.1a. First, he would vary time to determine the response of the yield at a fixed pressure. After determining the time that produced the highest yield (130 s), he would run a second set of experiments that look at yield as a function of temperature while setting time constant to 130 s. He would then determine that a temperature of 225 degrees produced a maximum in yield. Finally, he would conclude the optimum yield would be about 75%, as defined by t = 130 s and T = 225 degrees. In actuality, the optimum yield might lie at a different set of conditions and be on the order of 91+% as shown in the contour map shown in Figure 5.1b. By not taking into account that the factors might be interactive, the optimum yield was not found. Figure 5.2 shows that interaction effects can range from non-existent to very strong.



(a) One-at-a-time Experiments

(b) Actual Optimum Point

Figure 5.1: Traditional Experiments

Of course, the engineer could attempt to map the entire surface shown in Figure 5.1b with one-at-a-time experiments, but this would be costly and time consuming. When using DOE, a full exploration of the experimental space can be done and interaction effects can be measured in a efficient manner.

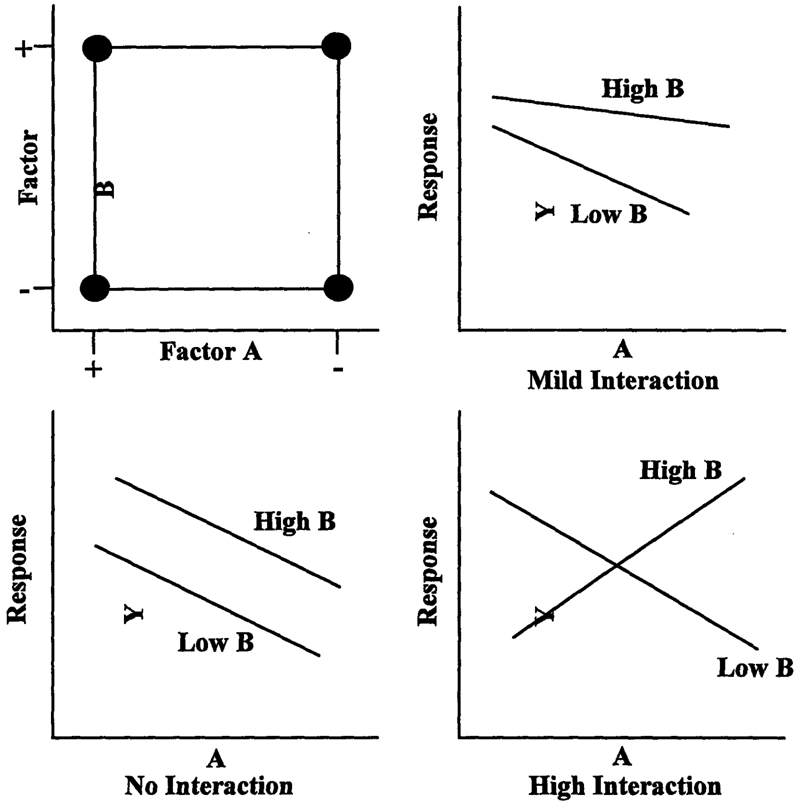


Figure 5.2: Interaction Effects

DOE consists of three parts. The first part is the selection of the parameters to vary. Selection of the appropriate variables is key. For example, selecting variables that do not affect the output greatly will not yield very informative results. The second part is design the experiment. DOE experiments are full or partial factorial experiments, depending on the design technique chosen. For a full factorial experiment, the number of experiments run is given by m^k, where k is the number of factors and m is the number of levels per factor [20]. A complete "one-at-a-time" design would require (K+1)/2 times more experiments[20]. Many types of experiment designs can be used. The third step is to use regression to determine the primary effects and interaction effects and model the response(s). For example, to develop a response surface model like the contour map in Figure 5.1b, a central composite design can be used. This design is shown in Figure 5.3. By using non-linear regression of the data points from the central composite design a response surface can be derived.

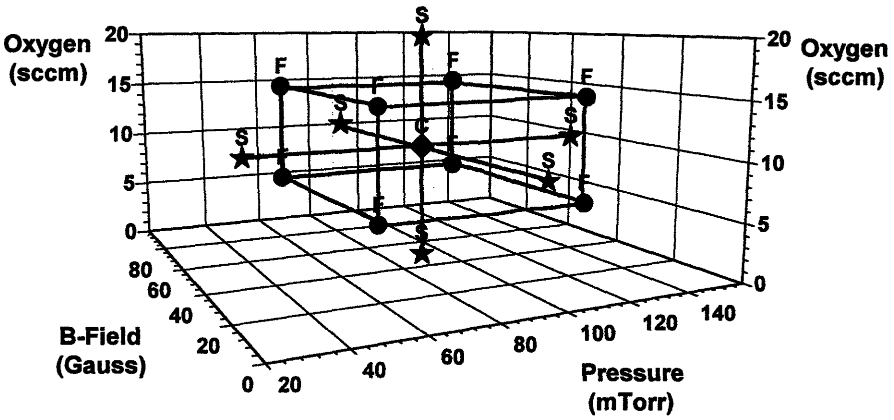


Figure 5.3: Central Composite Experimental Design

By using DOE, the actual responses (negative or positive dependence) to input variables can be determined with fewer experiments. A much more complete description of DOE is found in [20,56,57].

For this work, DuPont's Neural Network Analyzer for Process Evaluation Responses (NNAPER) software was used to design the experiments and generate the model using a neural network. A brief description of NNAPER will now be given.

5.2 NNAPER

NNAPER is a neural network-based process analysis software. The use of a this software has been demonstrated to be effective in industry [58]. The description of the neural network approach was given in [58] and is summarized here.

In a traditional DOE experiment, a direct mathematical transformation is made between the input and the outputs of the experiment. A polynomial that describes the relationship between the output and input variables is chosen, and coefficients are selected that provide the best fit. In this representation, the response of what happens to the process (etch rate, selectivity, etc.) is directly related to what "dials" (power, pressure, *etc.*) are changed.

From a more sophisticated standpoint, more levels of interaction are occurring. In reality, the dials are affecting factors in the plasma (plasma density, ion bombardment energy, *etc.*) that, in turn, affect the measured responses. Thus, a two stage transformation may be more appropriate than a traditional one-stage transformation.

NNAPER uses a back propagation neural network. The structure of a three input variable, two hidden nodes, 3 output responses network is shown in Figure 5.4.

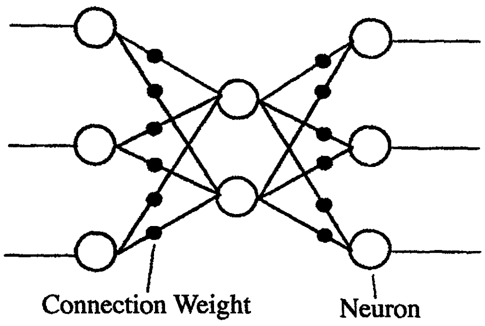


Figure 5.4: A Three-Layer Neural Network (3-2-3) [59]

The hidden nodes might be though of as the fundamental properties of the plasma (plasma density, ion bombardment energy, *etc.*). In actuality, they are simply mathematical constructs.

A neural network consists of two parts. The primary part is called the neuron (output response). The neuron is a non-linear structure that sums the strengths of all its input signals and passes the sum through a "squashing function" such as $y(x)=1/(1+e^{-ax})$ [59]. The second part of the network is the weights that interconnect the neurons to each other. These weights are called synapses. The neural learning is contained within the weights. This process is shown in Figure 5.5.

The neural network is simply a powerful tool that aids in the selection of a particular non-linear function that fits the data. In non-linear regression, parameters are optimized to make a selected function fit the data the best. Using NNAPER, the neural network is trained so that it can find the values for the weights that will reduce the root-mean-squared function between the neural network function and the actual experimental values.

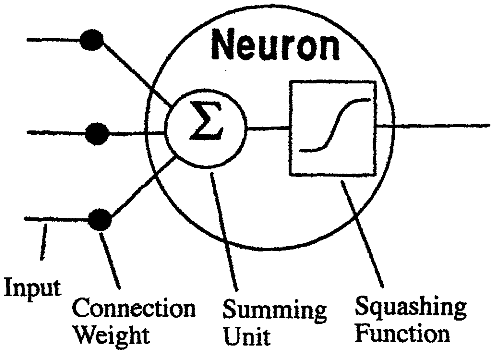


Figure 5.5: Neural Network Model Generation Method [59]

NNAPER uses a central composite design for the experimental design. This design is shown in Figure 5.3. NNAPER incorporates test, center, and training points in the experimental matrix. The center points are used to determine process drift. The neural network is trained using the training data. The initial model is then used to predict the test data to determine the goodness of the model. The data is then combined to form an overall model. The user has the option of varying the number of hidden node in order to produce the model with the best fit.

The NNAPER software shields the user from the complexities described above. It consists of three main parts. The first part designs the experiment for the user, based on the number of factors and ranges desired. After the experimental data is inputted, the neural network is training automatically. The user can select the number of hidden nodes to produce the best fit. After the training has been completed, the model is now available for output (graphs, etc.).

5.3 Etch Viability Studies

Two sets of experiments were run. The first set was a matrix of experiments (referred to as matrix experiments) designed by the NNAPER software. The second set of experiments were one-at-a-time, low pressure experiments. Both sets of experiments used an Applied Materials Precision 5000 Magnetically Enhanced Reactive Ion Etcher (MERIE) located in the Integrated Circuits Laboratory (ICL) at the Microsystems

Technology Laboratories. The Applied 5000 is a workhorse tool commonly found in the industry. A more specific description is given in Section 5.4.

Four inch, p-type (2.5-12 ohm-cm) silicon substrates were used. Two types of dielectric films were etched: thermally grown silicon dioxide and LPCVD silicon nitride. The silicon dioxide films were grown in Tube B5 in ICL using a water vapor mixture (Recipe 223; Step 7, 10 minutes; Step 8, 2 hours). All of the films used were approximately 10,500 Å thick, as determined by Nanospec. The silicon nitride films were grown in Tube A5 in ICL using a silane and ammonia mixture (Recipe 460; Step 8, 3 hours). All of the films used ranged from 4,000 to 5,500 Å in thickness, again determined by Nanospec. The range of thickness was due to variances in the growth conditions of the tube. The films were etched in an unpatterned state. Etch rate was measured *in-situ* using a Low Entropy Systems Full Wafer Imaging Interferometer system described in Section 5.5 below. Using the light of the plasma, the LES system employs a CCD camera to measure etch rates by optical emission interferometry. Average etch rates as determined by the LES system were used as responses in the NNAPER model.

In preparation for a series of experimental runs with each chemistry, the following procedure was adopted. The etch chamber was cleaned using an oxygen flow of 80 sccm and a CF_4 flow of 5 sccm. Power was set to 700 Watts, pressure to 200 mTorr, and no magnetic field was applied. Cleans were done for fifteen minutes. Subsequent to the clean, the chamber was seasoned by running the center point condition of 600 Watts power, 40 sccm of etch gas, 10 sccm of oxygen, 93 mTorr pressure, and 50 Gauss magnetic field for fifteen minutes using a bare silicon wafer. Both the clean and season steps were as suggested by Applied Materials.

5.3.1 Matrix Experiments

The primary purpose of this stage was to determine the etch viability of the candidate chemistries. It was meant to serve as a prioritization stage for subsequent experiment work described in Chapter 8. To this end, the primary parameter of interest was the etch rate of the dielectric films. At the same time, however, some information on the etch behavior of the candidate chemistries under various conditions was desired.

Thus, the selection of variables was a balance between gathering interesting information on etch behavior while keeping the number of experiments per chemistry to a manageable size so as not to consume more time than was necessary to satisfy the main goal of this stage. It was decided that a three parameter study which corresponding to 24 etch experiments per chemistry per dielectric was the best balance (1 boat of wafers). The three chosen parameters were total pressure, magnetic field, and oxygen flow. Total pressure was chosen as a parameter because of its anticipated effect on the polymerization rate of the hydrofluorocarbon gases (See Chapter 2). Magnetic field was chosen because its effects on etch rate were not well documented in the literature. Finally, oxygen flow was chosen because oxygen was know to counteract the polymerizing effect of the hydrogen present in the HFCs. Power was held constant at 600 W. Its effect on etch rate was already well know; etch rate monotonically increases with etch rate. Thus, a study of its relationship to etch rate for these gases would have not been very illuminating. Finally, etch gas flow rate was also held constant. Table 5.1 summarizes the parameters used for these experiments. The selected ranges for the variables represented the range of normal operation for the Applied 5000. Table 5.2 gives the experimental matrix derived by NNAPER that was used for all of the matrix experiments.

Table 5.1: Experimental Conditions for Matrix Experiments

Parameter	Range
Power	600 Watts
Etch Gas Flow	40 sccm
Total Pressure	35-150 mTorr
Magnetic Field	0-100 Gauss
Oxygen Flow	0-20 sccm

For this set of experiments, the 1H and 2H-heptafluoropropane used were from PCR Specialty Chemicals. The octafluoropropane was supplied by 3M Specialty Chemicals. The pentafluoroethane was supplied by DuPont. All of the gases were 99+% pure.

Table 5.2: NNAPER Experimental Matrix

Run #	Type of Point	Pressure (mTorr)	Magnetic Field (Gauss)	Oxygen Flow (sccm)
1	C	93	50	10
2	C	93	50	10
3	C	93	50	10
4	S	35	50	10
5	S	93	0	10
6	S	150	50	10
7	S	93	50	0
8	S	93	100	10
9	S	93	50	20
10	T	97	82	6
11	C	93	50	10
12	F	60	21	15
13	F	60	79	15
14	T	150	8	18
15	F	126	21	15
16	F	60	21	6
17	C	93	50	10
18	T	57	63	11
19	F	60	79	6
20	F	126	79	15
21	F	126	79	6
22	T	86	46	6
23	C	93	50	10
24	F	126	21	6

5.3.2 Low Pressure Experiments

For three of the HFCs tested (difluoromethane, 1,1,1,2-tetrafluoroethane, and trifluoroethylene), heavily polymerization occurred at the center point conditions. Because of this, it was decided that much of the experimental matrix would not be useful. In a effort to determine at least some conditions under which these chemistries would etch the two dielectrics, a series of one-at-a-time experiments were run. Pressure was set to 35 mTorr, the lowest, stable setting on the Applied 5000. As discussed in Chapter 3, polymerization kinetics are a 2nd order function of pressure. Thus, reducing pressure was expected to alleviate somewhat the polymer deposition. Etch gas flow was set constant at 15 sccm, while power and magnetic field were set constant at 600 Watts and 50 Gauss, respectively. Etch rate was determined as a function of oxygen flow rate ranging from 0 to 45 sccm. The LES system was used to measure deposition rates as well as etch rates. The difluoromethane and trifluoroethylene were supplied by PCR. The 1,1,1,2-tetrafluoroethane was supplied by DuPont. Again, all gases were 99+% pure.

5.4 A Description of the Applied Materials Precision 5000

The Applied Materials Precision 5000 is a multi-chamber processing tool equipped with a load-lock and a dual wafer cassette loader. The Precision 5000 platform can support up to four etch or (PE)CVD chambers. The mainframe and the arrangement of the chambers, load-lock, and wafer cassette holders are shown in Figure 5.6. Currently the Applied 5000 in the MTL ICL is equipped with two etch chambers, one for oxide etch (Chamber A) and one for polysilicon etch (Chamber B). The system is configured for four inch wafers. An etch chamber is shown in Figure 5.7. The oxide chamber was used for this work.

The Applied 5000 uses magnetically enhanced reactive ion etch chambers. As is typical for RIE, the cathode forms the bottom electrode upon which the wafer sits. The walls of the chamber are the anode, giving the chamber its asymmetric area electrodes. The chamber is surrounded by four magnets that provide the magnetic confinement. The magnets are arranged so that the magnetic field is perpendicular to the direction of the vertical electric field and parallel to the cathode. The magnetic field typically rotates at a frequency of approximately 0.5 Hertz. A modification to the lid of the chamber has been made. To provide the LES system with a view that overlooks the entire surface of the wafer, a viewport was machined in the center of the lid. The LES CCD camera sits on top of the lid when in operation.

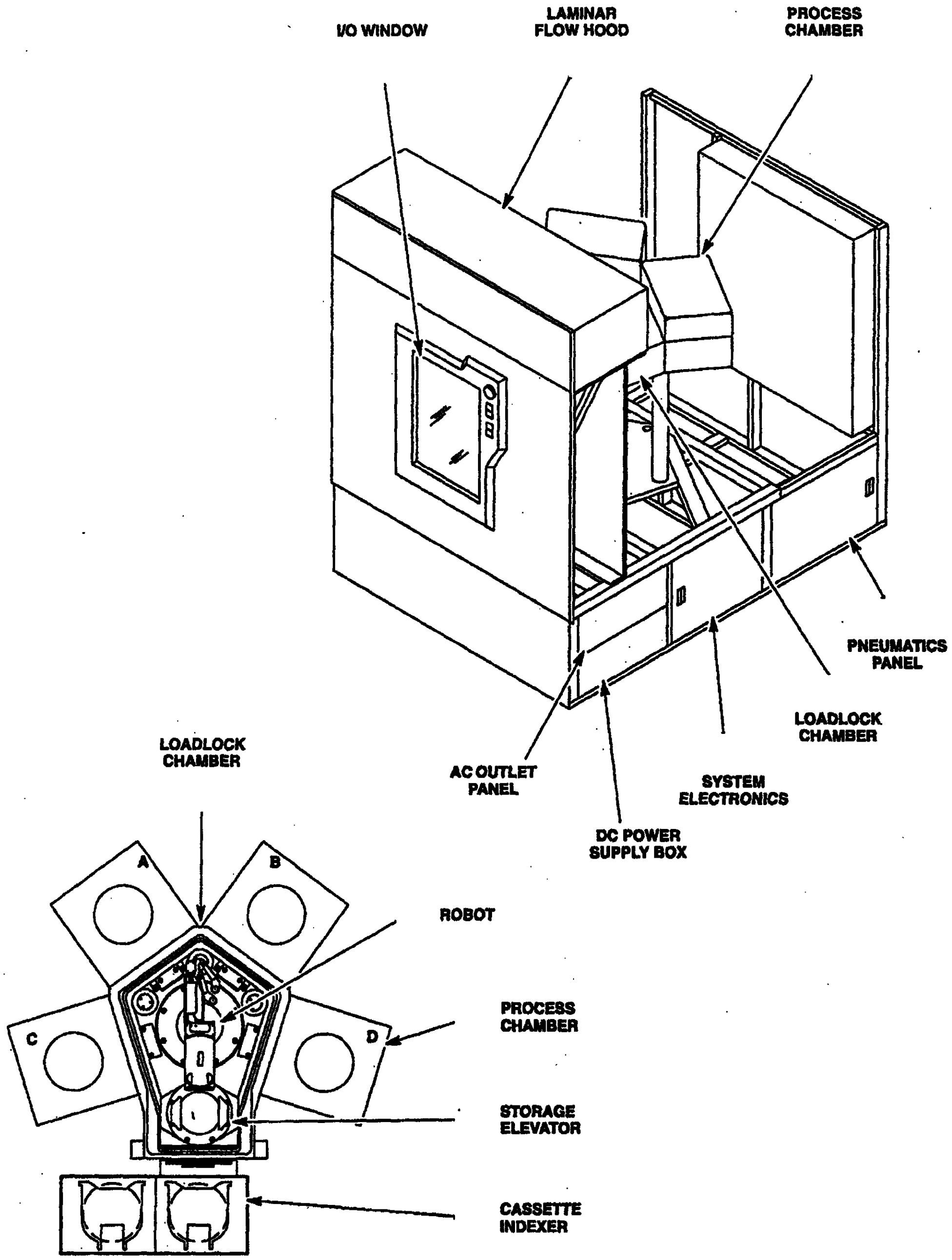


Figure 5.6: Applied Materials Precision 5000 Mainframe [60]

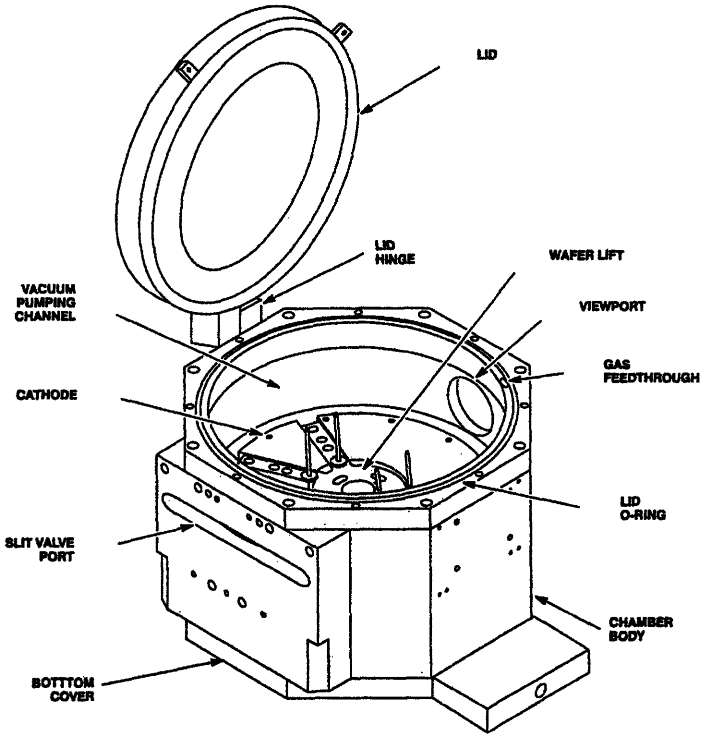


Figure 5.7: Applied Materials Precision 5000 Etch Chamber [60]

5.5 A Description of Full Wafer Interferometry

A Low Entropy Systems (LES) 1000-IS Full Wafer Imaging Interferometer system was used to measure etch rate *in-situ*. Its use has been successfully demonstrated in a manufacturing setting [61]. Using the light of the plasma, the LES system employs a CCD camera to measure etch rate by optical emission interferometry. Interferometry is the use of the phases differences between coherent waves to measure the difference in path lengths that the two waves have traveled. The difference in path length is constantly changing as material is etched or deposited. The reflected light waves go through maxima and minima due to interference between the waves. The etch rate is determined by Equation (6).

$$\text{Etch Rate} = \lambda/(2n_2\cos(\Theta_2) * 1/T \qquad (6)$$

where λ is the wavelength of the light, n_2 is the index of refraction of the thin film, Θ is the angle of the light from the normal direction, and T is the signal modulation period [62]. For the experiments detailed in this thesis, Θ was zero (*i.e.*, the camera sat directly overhead of the wafer).

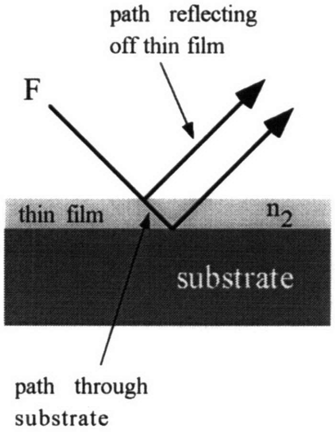


Figure 5.8: Thin Film Interferometry

A filter is used to select the wavelength that the CCD camera sees. The 486 nm wavelength was chosen for this work because fluorine has a strong emission line there. The pixel array on the CCD has 753 by 244 (HxV) pixels. The user of the LES system defines a grid of regions (a region has a minimum size of 2 pixels) on the wafer that are measured for etch rate. The pixel array then can resolve the interference pattern of each region that make up the grid. In this manner, the entire area of the wafer can be imaged, and the etch rate for each region determined. The average etch rate of a circular grid of regions (10 regions to a circle and 5 equicenter circles) was used for the NNAPER model input. A more complete description of full wafer interferometry is given elsewhere [61,63].

Chapter 6

Results and Discussion

6.1 Matrix Experiments

6.1.2 Octafluoropropane (C_3F_8)

Previous work in the literature on plasma etching with octafluoropropane is scarce. Some work has reported on its polymerization behavior relative to carbon tetrafluoride (CF_4) and hexafluoroethane (C_2F_6) with and without hydrogen [64,65]. Chen and Lee compared fluorine atom and CF_2 concentrations of octafluoropropane, carbon tetrafluoride, and hexafluoroethane [66]. However, the authors' interest in octafluoropropane was prompted by the work done by Novellus Systems, Inc. This work has demonstrated that octafluoropropane was a more efficient *in-situ* PECVD chamber cleaning gas than hexafluoroethane [67]. Indeed, before the Memorandum of Understanding (MOU) to reduce PFC emissions was finalized between the EPA and the major microelectronics companies, octafluoropropane was touted as a more environmentally friendly alternative to hexafluoroethane. Its use would result in lower PFC emissions due to greater process efficiency. Thus, while little work has appeared in the literature on etching with octafluoropropane, I believe that it serves as a good reference gas because of the recent industrial interest in its use.

The silicon dioxide etch rate of octafluoropropane varied strongly with magnetic field, total pressure, and oxygen flow rate. The oxide etch rate reached a maximum as a function of pressure for all ranges of oxygen flows and magnetic fields. Figure 6.1 shows this maximum occurring between 86 and 92 mTorr for no oxygen flow and a magnetic field of 50 Gauss. In addition, the location of this maximum etch rate moves to higher pressures with increases oxygen flow. For 20 sccm of oxygen, it occurs at 131 mTorr. The initial increase in etch rate with pressure is due to an increase in the concentration of reactants. The decrease in etch rate with pressure may be due to the expected effects of increasing pressure. As discussed in Chapter 2, some of these include increased ion scattering and thus lower ion bombardment energies, a decrease in electron energy, and the increasing effect of polymerization, whose reaction kinetics are usually a second order effect with pressure [24]. The effect observed with the increasing oxygen flow may be due to the ability of oxygen to oxidize further the polymerizing CF_x species and liberate free fluorine (*e.g.*, $CF_3 + O \Rightarrow COF_2 + F$; $CF_2 + 0 \Rightarrow COF + F$).

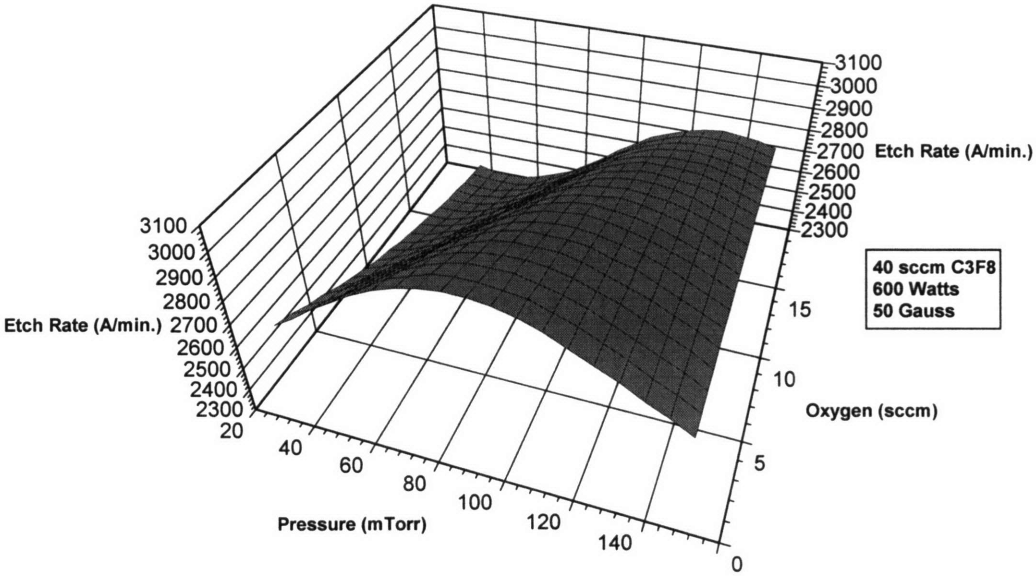


Figure 6.1: Silicon Dioxide Etch Rate of C_3F_8

With increasing magnetic field strength, the location of the maximum etch rate moves to lower pressures, as shown in Figure 6.2. For 0 Gauss, it occurs between 124 to 137 mTorr; for 50 Gauss, it occurs between 86 to 92 mTorr; for 100 Gauss, it occurs at 80 mTorr. This behavior may be attributed to the decrease in dc self bias with increasing magnetic field observed by Yeom [27]. A drop in the dc self bias results in lower ion bombardment energies. Thus, this effect may contribute to the effect that increasing pressure has in reducing the ion bombardment energy. In general, etch rate increases with increasing magnetic field at constant pressure and oxygen flow as can be seen in Figure 6.2.

Increasing oxygen flow appears to have a negative effect on oxide etch rate at low pressures. Figure 6.3 represents the same conditions as in Figure 6.1 but is rotated to show this dependence. At 35 mTorr, etch rate drops from 2,750 Å/min at 0 sccm of oxygen to 2,320 Å/min. at 20 sccm oxygen. However, at higher pressures, this dependence flattens. This effect might be due to residence time limited etching if the process conditions are within that flow rate regime [17]. Dilution of the plasma may be another possibility.

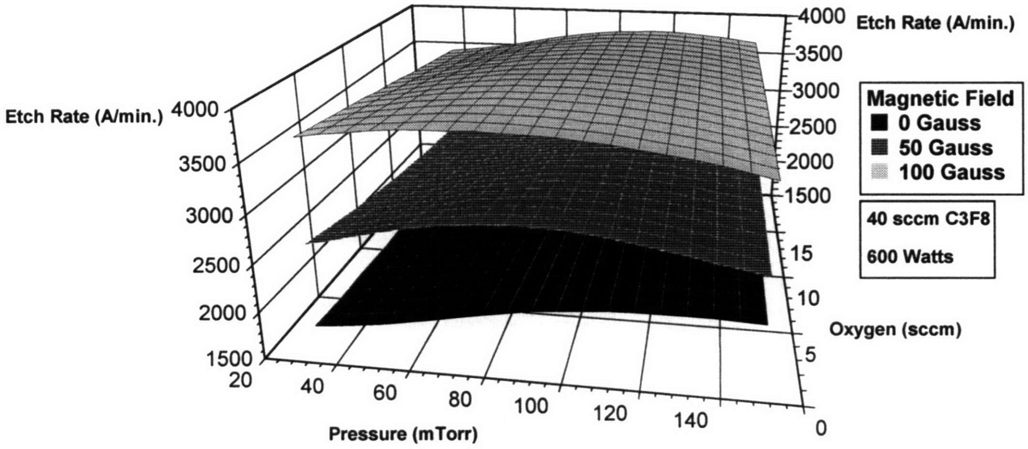


Figure 6.2: Effect of Magnetic Field on C_3F_8 Silicon Dioxide Etch Rate

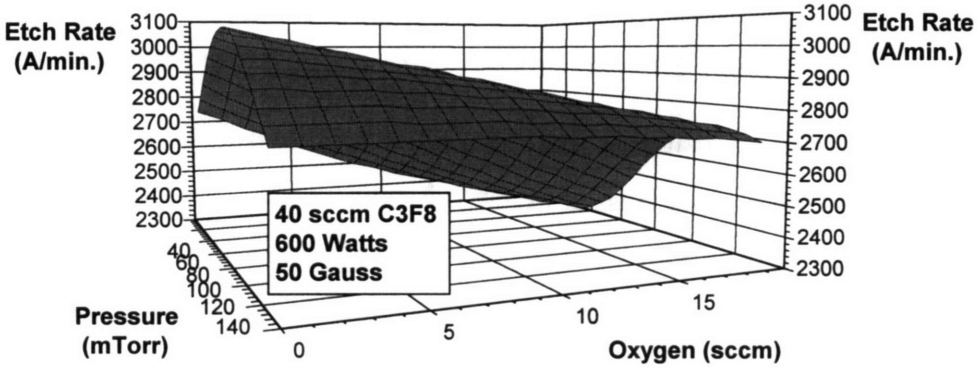


Figure 6.3: Effect of Oxygen Flow in C_3F_8 Silicon Dioxide Etch Rate

The silicon nitride etch rate of octafluoropropane increases with increasing oxygen flow and magnetic field, as shown in Figure 6.4. The etch rate generally has a weaker positive dependence on pressure. However, at high oxygen flows and increasing magnetic field, this pressure dependence flattens. In the low pressure, low oxygen flow, and low magnetic field regions, etch rate descends into a low etch rate trough (~1,000 Å/min.). Increasing any of the variables raises this trough. In Figure 6.4, the effect of increasing magnetic field from 0 Gauss to 100 Gauss shows this trend.

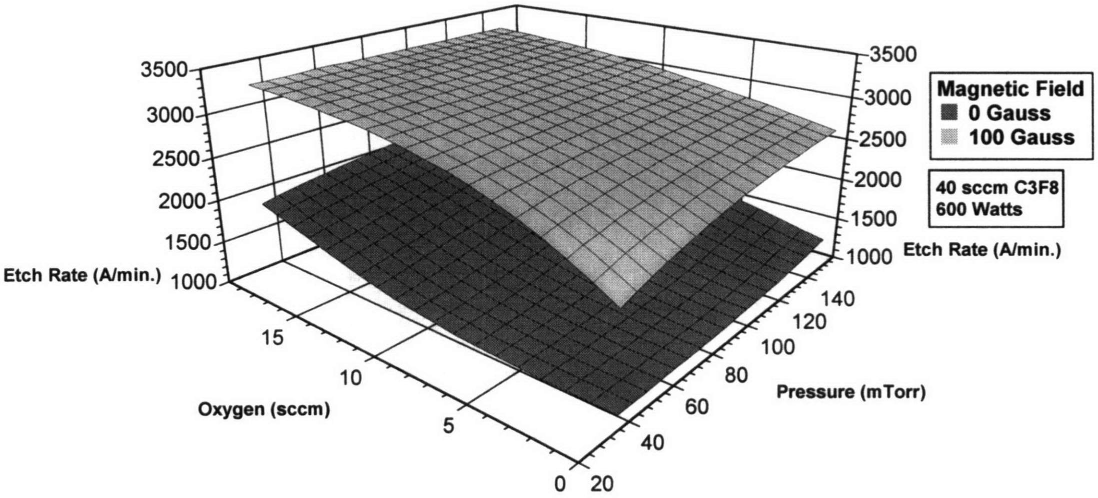


Figure 6.4: Silicon Nitride Etch Rate of C_3F_8

6.1.2 Pentafluoroethane (C_2F_5H)

The variable that most strongly affects the silicon dioxide etch rate of pentafluoroethane is oxygen flow. The etch rate increases rapidly with the initial introduction of oxygen flow. It is likely that the addition of oxygen aids in the removal of a fluorocarbon film that inhibits etching, the formation of which is particularly evident in hydrogen-containing fluorocarbon plasmas [68,69]. It is also likely that oxygen atoms react with CF_x to boost the free fluorine concentration and counteract the scavenging effect of the hydrogen [69,70] and reduce the concentration of polymerizing CF_x species. However, at higher flow rates, this effect saturates and then reverses. In Figure 6.5, this peak occurs between 6 and 7 sccm oxygen at 35 mTorr and 50 Gauss.

This effect roughly corresponds to results from Mohindra *et. al.* At 750 Watts, 100 mT pressure, no magnetic field, and in the same tool, the oxide etch rate of 50 sccm of pentafluoroethane increased for oxygen flows up to 10 sccm [34]. At flows higher than 10 sccm, the oxide etch rate began to decrease. The magnitudes of the etch rates reported by Mohindra *et. al.* also correspond to the these results [34].

With increasing magnetic field, the location of the maximum etch rate descends to lower oxygen flows, as shown in Figure 6.6. At 35 mTorr, the peaks occurs between 9 and 10 sccm oxygen for 0 Gauss, 6 to 7 sccm oxygen for 50 Gauss, and at 5 sccm for 100 Gauss.

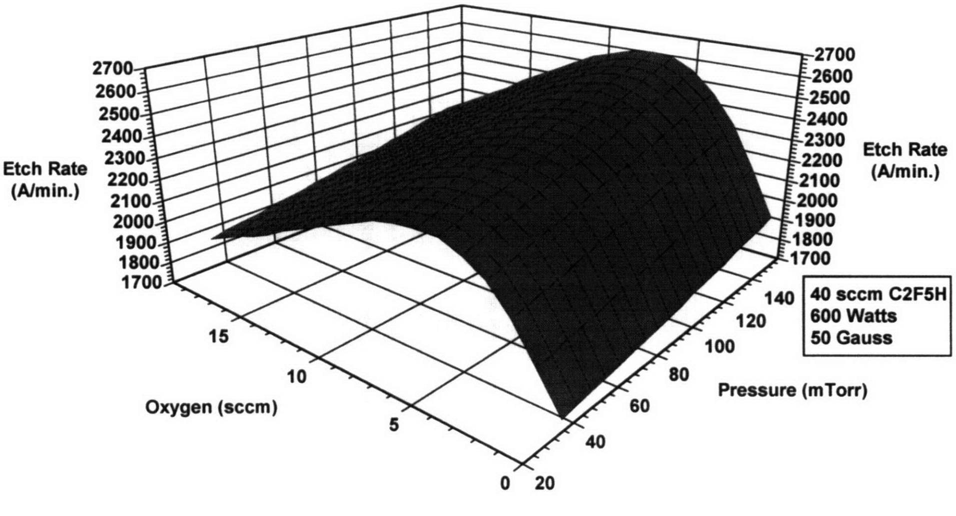


Figure 6.5: Silicon Dioxide Etch Rate of C_2F_5H

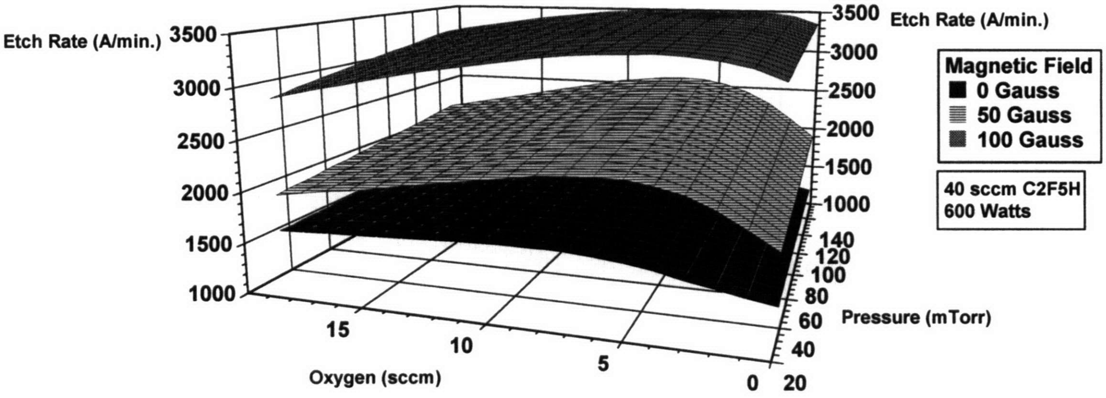


Figure 6.6: Effect of Magnetic Field on Silicon Dioxide Etch Rate of C_2F_5H

In general, etch rate increases strongly with increasing magnetic field, while pressure is observed to have a slightly positive effect on etch rate.

The silicon nitride etch rate of pentafluoroethane increases with oxygen flow and magnetic field. At high magnetic fields, the etch rate approaches saturation with increasing oxygen flow. In addition, increasing oxygen or magnetic field causes the shape of etch rate curve to move from concave to convex. This effect on the pressure-oxygen curve is shown in Figure 6.7 with increasing magnetic field. It appears the etch rate is approaching a region of saturation with increasing oxygen flow for high magnetic fields. Oxygen has a similar effect on the pressure-magnetic field curve. Finally, virtually no dependence on pressure is observed.

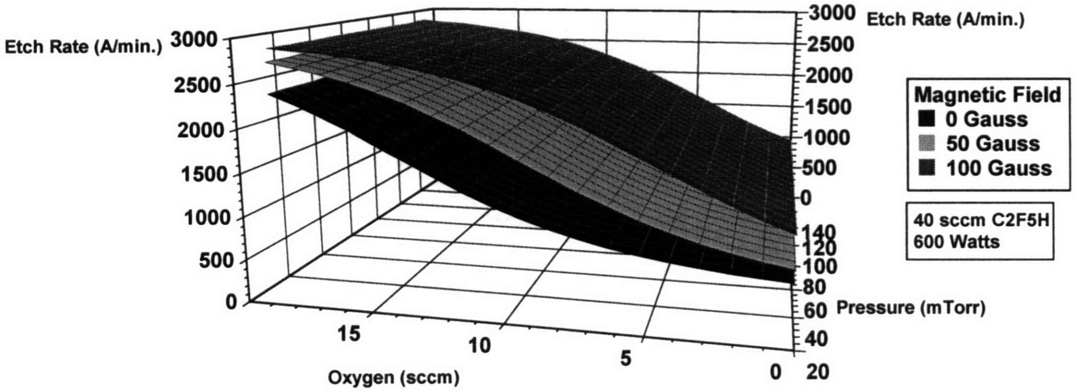


Figure 6.7: Silicon Nitride Etch Rate of C_2F_5H

6.1.3 Heptafluoropropane (C_3F_7H)

The silicon dioxide etching behaviors of 1H-heptafluoropropane and 2H-heptafluoropropane are generally similar. As with pentafluoroethane, the etch rates of both 1H and 2H increase dramatically with the introduction of oxygen. However, with increasing oxygen flow, the oxide etch rate for both isomers saturates. Furthermore, the location at which this saturation occurs appears to move to lower oxygen flows with increasing magnetic field for both gases. This is similar to what is observed for pentafluoroethane. Figure 6.8 shows this saturation and migration to lower oxygen flows with increasing magnetic field for 2H-heptafluoropropane. For 35 mTorr, this saturation point occurs between 12 and16 sccm oxygen at 0 Gauss, between 9 and 10 sccm oxygen at 50 Gauss, and at 7 sccm oxygen for 100 Gauss. For 1H-heptafluoropropane, the effect is virtually identical, happening at the same oxygen flows for the same levels of magnetic field.

A small negative dependence of etch rate on pressure is observed at low flows of oxygen. At high oxygen flows, this effect is slightly positive. Both of these pressure effects become more pronounced with increasing magnetic field (see Figure 6.8). Finally, the location of the etch rate saturation also moves to higher oxygen flows for increasing pressure. This effect is more visible in Figure 6.9.

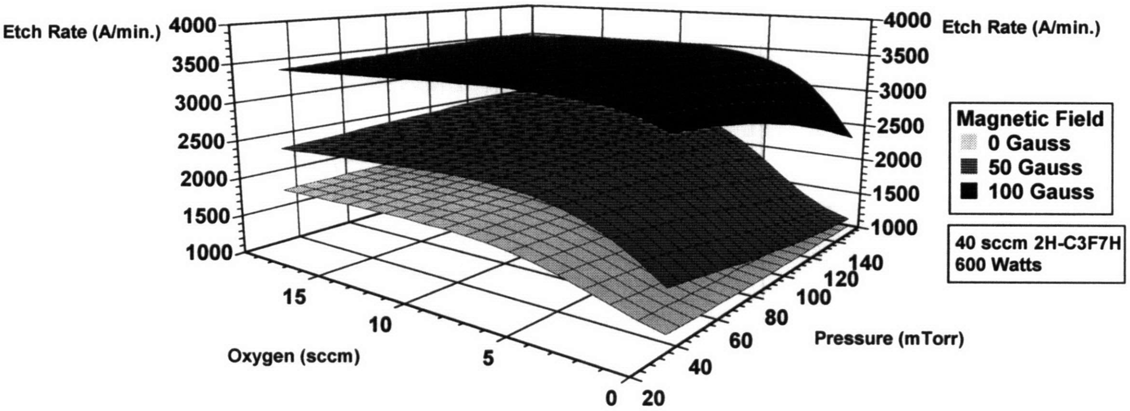


Figure 6.8: Effect of Magnetic Field on Silicon Dioxide Etch Rate of 2H-C_3F_7H

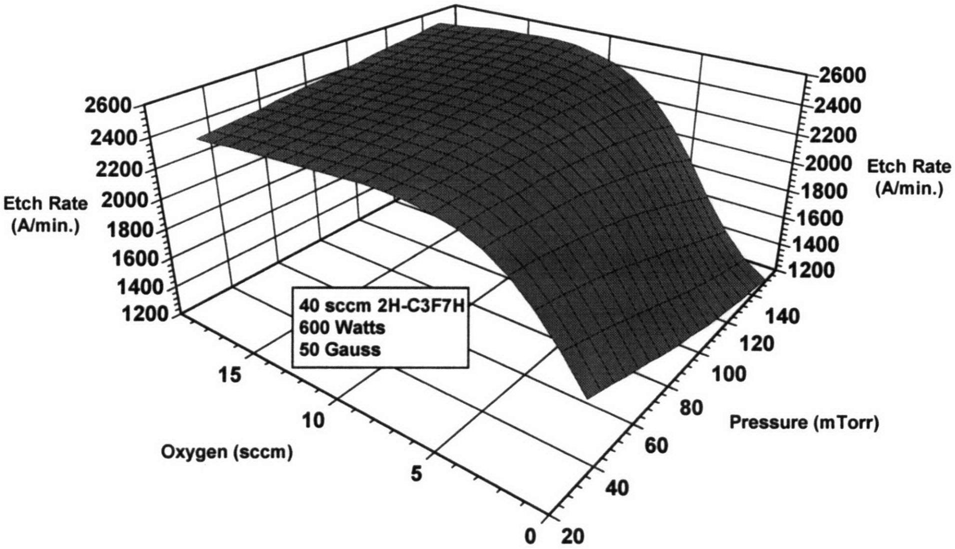


Figure 6.9: Effect of Pressure on Oxide Etch Rate Saturation Point of 2H-C_3F_7H

As with oxide etching, the silicon nitride etch rate dependencies for 1H and 2H are generally similar. In addition, the dependencies of heptafluoropropane are also similar to those of pentafluoroethane. As shown in Figure 6.10, increasing magnetic field results in a similar migration from a concave to convex curve for 1H-heptafluoropropane (see Figure 6.8 for comparison). The behavior of 2H-heptafluoropropane is similar. The nitride etch rate increases with increasing oxygen and magnetic field for both 1H and 2H. The effect of pressure is negligible for 1H-heptafluoropropane, while it is mixed for 2H-heptafluoropropane.

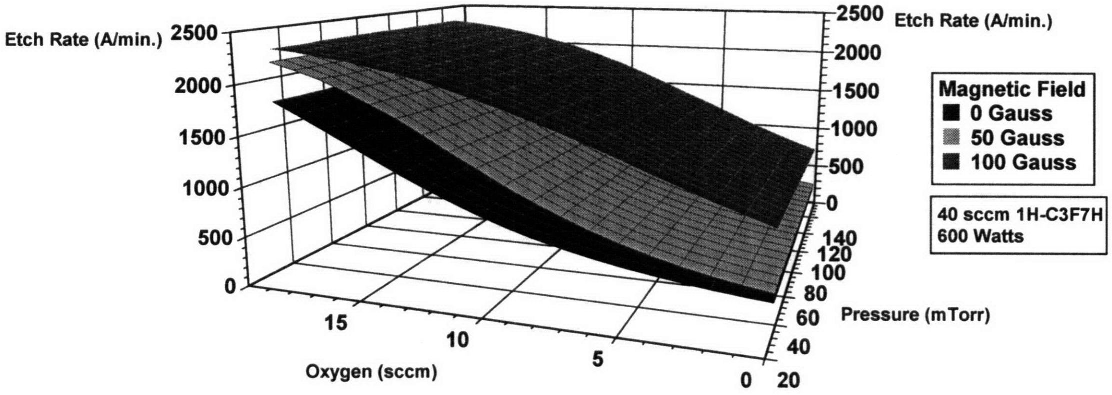


Figure 6.10: Silicon Nitride Etch Rate of 1H-C_3F_7H

While the structural difference between the two isomers of heptafluoropropane does not appear to result in differences in general etch behavior, a range of conditions do exists where their oxide etching behavior appears to diverge. In Figure 6.14 in Section 6.1.4, the model shows this divergence at low flows of oxygen. The etch rate of 1H drops sharply below 4 sccm of oxygen (9%) as compared to 2H. Figure 6.11 shows the predicted behavior of both gases as a function of magnetic field without the addition of oxygen. While both gases exhibit the same behavior, 1H is predicted to deposit at magnetic fields below 28 Gauss. For all magnetic fields, 2H continues to etch. A similar difference is evident when the pressure is varied, as in Figure 6.12. As would be expected with chemistries that polymerize, etch rate for both isomers drops with increasing pressure. Again, 1H is predicted to deposit at pressures higher than 110 mTorr while 2H etches for all pressures. Qualitatively, this difference was noticed when the experimental matrix for these gases was conducted. Oxide etching for 2H proceeded smoothly at reasonable rates, while 1H etching proceeded very slowly for the low oxygen flow points.

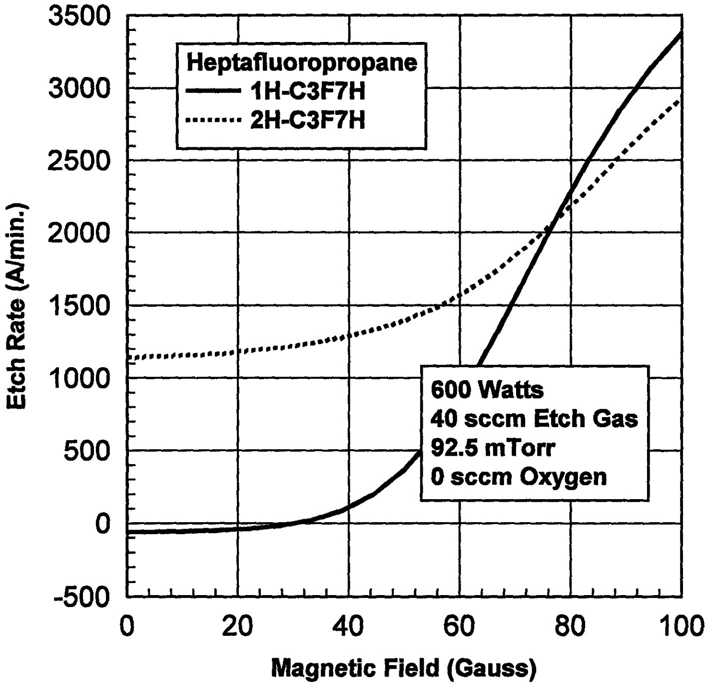


Figure 6.11: 1H and 2H Oxide Etch Dependence on Magnetic Field (no oxygen)

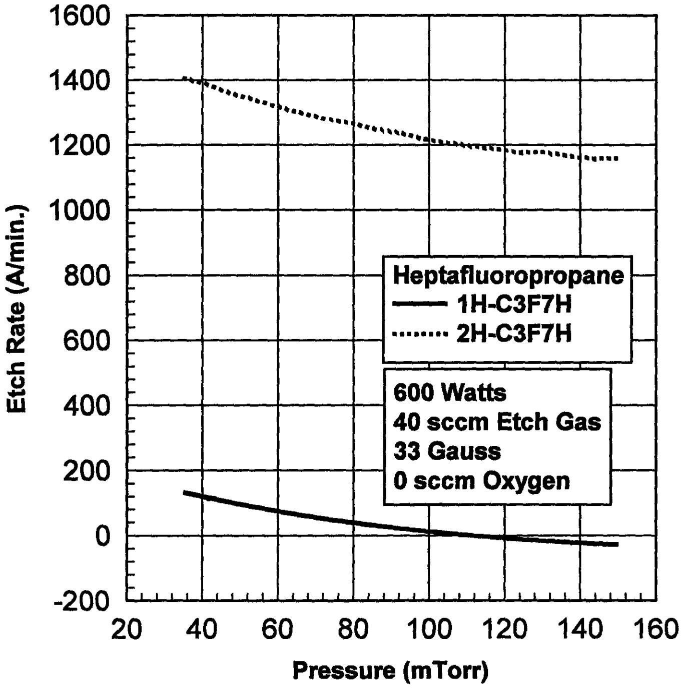


Figure 6.12: 1H and 2H Oxide Etch Dependence on Pressure (no oxygen)

Contrary to the oxide etch behavior, the nitride etching of these two films exhibited a similar behavior in the low oxygen - low magnetic field regimes. Figure 6.13 shows that for increasing magnetic field and no oxygen, both chemistries etch.

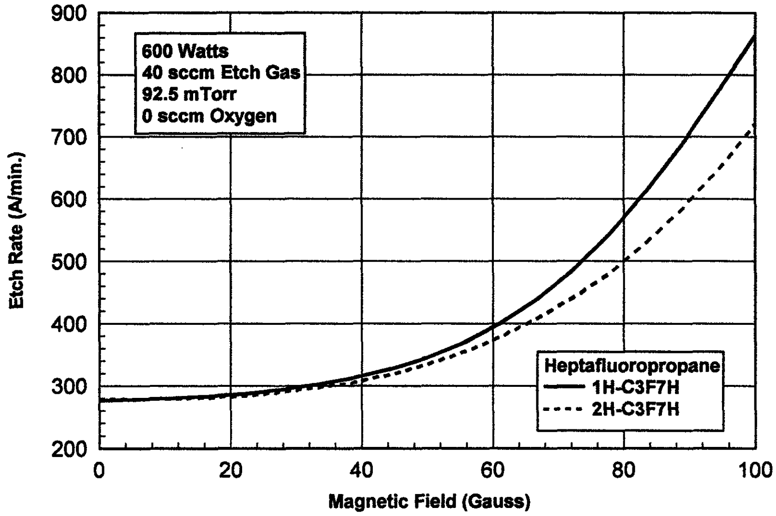


Figure 6.13: 1H and 2H Nitride Etch Dependence on Magnetic Field (no oxygen)

6.1.4 Silicon Dioxide Etching vs. Silicon Nitride Etching

Empirically derived models of the silicon dioxide etch rates for all four gases are given as a function of oxygen flow in Figure 6.14. Pressure and magnetic field are shown constant at 80 mTorr and 50 Gauss, respectively. The etch rates all appear comparable, especially at high oxygen flows. While the etch rate of octafluoropropane drops with increasing oxygen, the etch rates of three hydrofluorocarbons rise dramatically with the introduction of oxygen. The effect seen for octafluoropropane is similar to that observed by Mohindra *et. al.* with hexafluoroethane (for same conditions given above for pentafluoroethane) [34]. As has been noted, the HFCs' etch rates either peak or saturate with increasing oxygen flow.

The modeled silicon nitride etch rates for all four gases are given as a function of oxygen flow in Figure 6.15. The etch rates of the gases rise with increasing oxygen flow. The etch rate of pentafluoroethane actually exceeds that of octafluoropropane at high oxygen flows. In contrast to Figure 6.14, the etch behaviors of the two isomers of heptafluoropropane appear to be similar, with 2H-heptafluoropropane having a slightly larger etch rate.

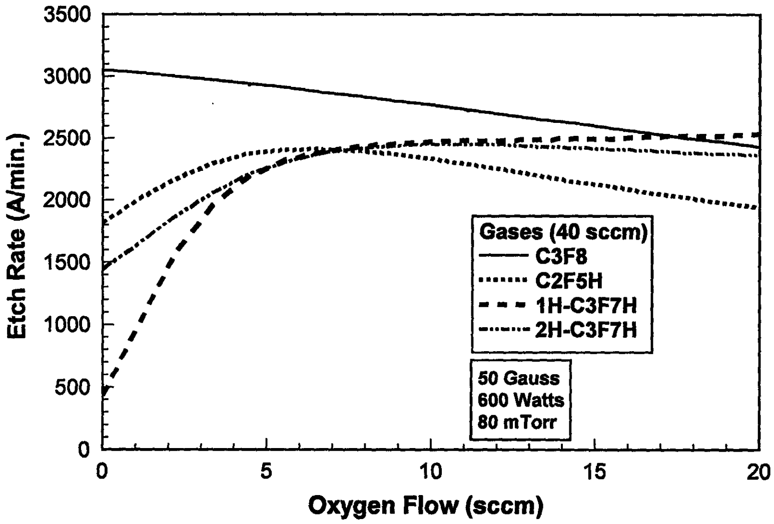


Figure 6.14: Silicon Dioxide Etch Rates

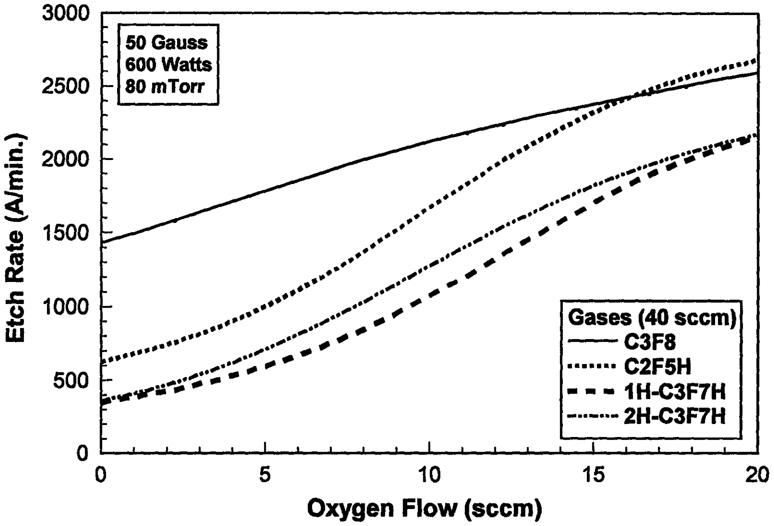


Figure 6.15: Silicon Nitride Etch Rates

Figures 6.14 and 6.15 show that oxygen appears to have different effects on silicon nitride and silicon dioxide etching. For oxide etching, while oxygen has an initial beneficial effect (that offsets the effect of the hydrogen present in HFCs), this effect saturates for heptafluoropropane and becomes negative for octafluoropropane and pentafluoroethane at higher oxygen flows. As discussed earlier, this may be due to dilution or reduced residence time effects. In contrast to this is the positive effect of oxygen for nitride etching by all gases. Differing views in the literature could explain this effect. It has been observed that fluorine atoms and CF_2 are important species for the etching of PECVD silicon nitride films [71,72]. The addition of oxygen could aid in the release of free fluorine atoms from reactions between atomic oxygen and CF_x species, and thus enhance etch rate. In addition, oxygen may play a significant role in removing nitrogen [71]. A second explanation could be the suppression of polymerization on the nitride film by the oxygen [72]. However, experiments by Loewenstein indicated that preferential deposition of a fluorocarbon film seems to occur on silicon and silicon dioxide as opposed to silicon nitride for CF_4+H_2 etches [73]. Either of these may explain the positive effect observed for nitride etching with octafluoropropane and the HFCs. However, further work is clearly necessary before a mechanism for this effect can be given.

6.2 Low Pressure Studies

In running the center point of the experimental matrix for 1,1,1,2-tetrafluoroethane, net deposition was observed on both the seasoning silicon wafer and the first center point oxide wafer. Nanospec confirmed an increase in thickness (*i.e.*, deposition). Auger electron spectroscopy was performed on both wafers. Both a surface analysis and an analysis performed after a five minute sputter indicated a carbon-rich fluorocarbon film with approximately the same F to C ratio. Both films appeared to be thick because of the charging they induced. The AES spectrum for the oxide wafer is shown in Figure 6.16.

Because of polymerization occurred at the center point, it was anticipated that deposition would occur for many of the matrix points, resulting in an incomplete model. Thus, one-at-a-time experiments, as described in Chapter 5, were conducted for the three HFCs with high hydrogen content.

The silicon dioxide etch rates for difluoromethane and trifluoroethylene are given as a function of oxygen flow in Figure 6.17. No 1,1,1,2-tetrafluoroethane data appears because the Precision 5000 went down for extensive repairs before that data could be collected. Virtually all of the oxygen flows result in etching, as opposed to deposition. For difluoromethane, it appears that even at no oxygen flow, the reduced pressure was enough to prevent net polymer deposition. Trifluoroethylene did polymerize heavily without the benefit of oxygen. Interestingly, after the initial introduction of oxygen, the etch rates appear to drop with increasing oxygen flow, similar to the behavior observed with pentafluoroethane. This may be a residence time limited

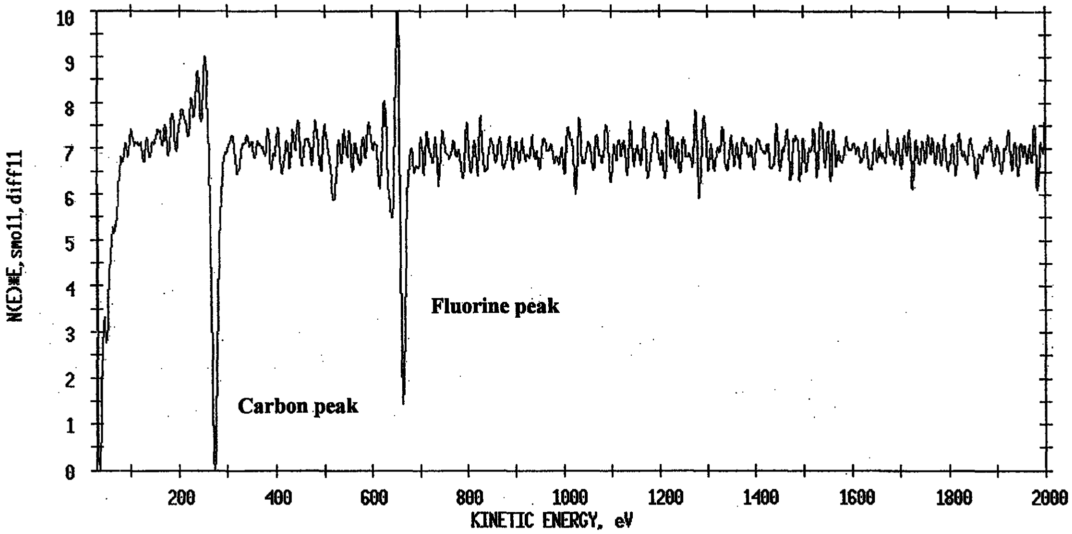


Figure 6.16: AES of the Fluorocarbon Polymer Film Deposited by Tetrafluoroethane

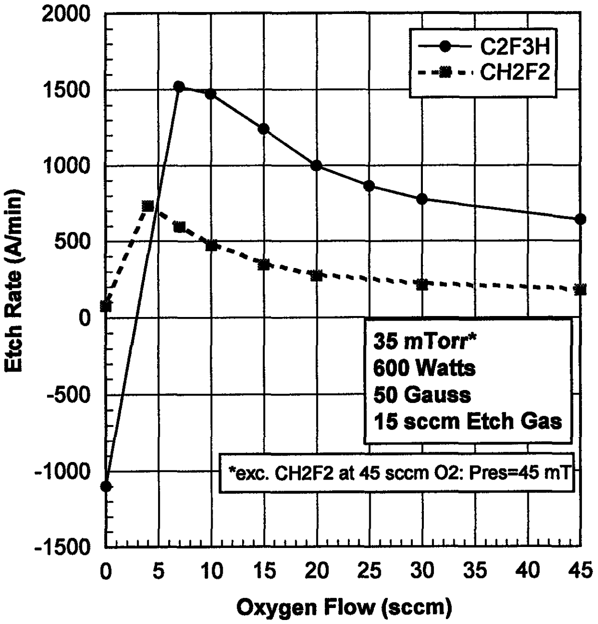


Figure 6.17: Silicon Dioxide Etch Rates Under Low Pressure Conditions

etching effect which would become prevalent at high flows because of the low pressure operating conditions. It also may be due to dilution. Finally, the etch for trifluoroethylene at 6 sccm oxygen is actually quite high for such a heavily polymerizing gas, on the order of 1,500 Å/min. The silicon nitride etch rates as a function of oxygen flow for difluoromethane, trifluoroethylene, and 1,1,1,2-tetrafluoroethane are presented in Figure 6.18. Trifluoroethylene and tetrafluoroethane have a similar behavior to that exhibited by the low pressure oxide etching. Again, both gases deposit without the addition of oxygen, even at this low pressure. The etch rate of both gases peak and then descend with increasing oxygen flow. This tends to support the idea that the etch rate is either residence time limited or reduced because of dilution. That is, the behavior does not appear to be a function of chemistries or material etched. The behavior of difluoromethane is curious in that the addition of oxygen has a negative effect on etch rate. The fact that it does not polymerize on nitride under these conditions is consistent with its oxide etching behavior. The drop in etch with increasing oxygen flow may again be due to residence time limited etching or dilution.

In summary, it appears that for both materials, etching at reduced pressures has helped alleviate the polymerization problem with these multiple hydrogen HFCs. In addition, the addition of oxygen appears to be generally beneficial.

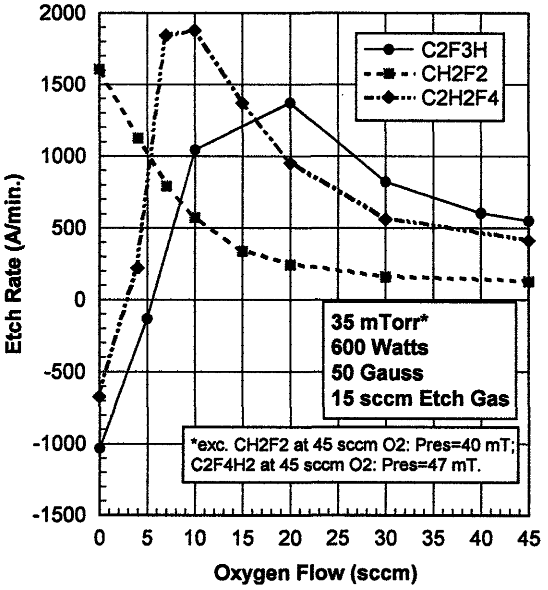


Figure 6.18: Silicon Nitride Etch Rates Under Low Pressure Conditions

Chapter 7

Conclusions

Three sets of conclusions that are segmented by the major parts of this thesis can be made. The first set of conclusions comes from the results of the literature and industry survey. Clearly, the emissions of perfluorocompounds from both wafer patterning applications and *in-situ* PECVD chamber cleaning must be addressed. For both applications, the exploration of the viability of replacement chemistries is applicable. The type of materials that uses perfluorocompounds most heavily is dielectrics, including both silicon dioxide and silicon nitride. As far as the potential for solutions to emerge from previous work is concerned, little has been done to look at non-perfluorocompound chemistries for applications that currently use perfluorocompounds. Finally, it appears that investigations of fluorine-bearing and fluorocarbon chemistries offer the best chance of success. Other halogen chemistries either have environmental constraints that would make their use undesirable or have been demonstrated in the literature to not be the most promising areas of exploration for the etching of dielectrics.

The selection stage of this thesis was concerned with what fluorine-bearing or fluorocarbon chemistries were the most appropriate. In examining potential candidate chemistries, it become clear that a real tradeoff between long-term environmental concerns and safety and health concerns existed. Most current perfluorocompound chemistries are considered benign and easy to handle (*i.e.*, low safety and health concerns). This is primarily due to their great stability. Yet, this stability is precisely one of the causes of environmental concern. Thus, to reduce this concern, candidate chemistries must be unstable. Some of these unstable chemistries, however, have serious safety and handling concerns. It was decided to balance low/no environmental impact with acceptable safety and health risks. However, no chemistries known to be mutagenic, teratogenic, and/or carcinogenic chemistries were selected. Three major families of chemistries of fluorocarbons were deemed to meet this criteria. Hydrofluorocarbons, iodofluorocarbons, and unsaturated fluorocarbons represent potentially viable replacement chemistries for perfluorocompounds.

The experimental etch viability stage in this thesis screened the hydrofluorocarbon chemistries just for their ability to etch. In general, it appears that there exists condition where the etch rates of some of the hydrofluorocarbons are comparable to that of octafluoropropane. As was expected from the hydrogen content, the hydrofluorocarbons appear to polymerize, which has favorable selectivity implications. The multiple hydrogen hydrofluorocarbons difluoromethane, trifluoroethylene, and 1,1,1,2-tetrafluoroethane appear to require either low process pressures or an oxygen additive to etch dielectrics films because they polymerize easily. To use this chemistries as successful wafer patterning chemistries, it may be necessary to operate at low pressures or at high power/magnetic fields. This behavior also suggests that these three hydrofluorocarbons might not be suitable chemistries for chamber cleaning processes, which typically occur at high pressures on the order of Torrs. This is not necessarily the case of pentafluoroethane and the two isomers of heptafluoropropane, which appear to etch dielectrics well. Thus, pentafluoroethane and the isomers of heptafluoropropane should received priority over difluoromethane, trifluoroethylene, and 1,1,1,2-tetrafluoroethane. Finally, there appears to be an oxide etch dependence on the chemical structure of hydrofluorocarbons. Such a dependence was observed in the modeled behavior of 1H and 2H heptafluoropropane at low oxygen flows. For similar conditions, 1H deposited a polymer and 2H etched.

Chapter 8

Suggestions for Future Work

A suggested path of future work is given in Figure 8.1 Clearly, the etch viability experiments should continue with the iodofluorocarbon and unsaturated fluorocarbon families of chemistries. After that experimental stage is complete and a prioritization of the candidate chemistries based on those results is made, two parallel efforts should be made to look at the two applications that use perfluorocompounds with these candidate chemistries.

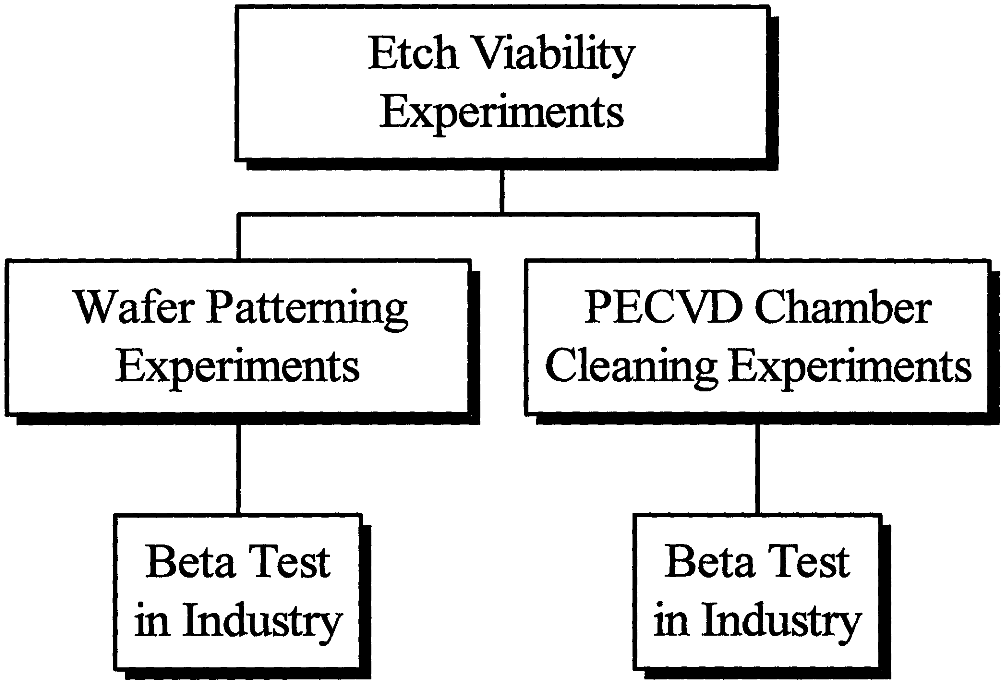


Figure 8.1: Suggested Future Work

For the wafer patterning stage, patterned films with generic structures such as long bars, squares, circles, and gratings should be used. Both thermal silicon dioxide and LPCVD silicon nitride films should be examined. A Design of Experiments method should continue to be used. Work should continue in the Applied Materials Precision 5000 in the ICL at MTL to build on the work done during the etch viability experiments. Measurements of the dielectric, silicon, and photoresist etch rates should be made to determine the particular process's selectivity. Anisotropy should be also determined using SEM. To gain a better understanding of the plasma chemistry, optical emission spectroscopy (OES) should be performed during each experimental run. Relative measurements of fluorine and CF_x concentrations should be made with OES. Polymer residues should be identified using either Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS). Finally, process effluents must be identified to determine if the replacement processes produce any new environmental, safety, and/or health problems. Quadrupole mass spectroscopy (QMS) or FTIR should be used for this.

For the PECVD chamber cleaning experiments, many of the same procedures from the wafer patterning stage should be used. In addition, the methodologies that have been utilized in the industry for the perfluorocompound process optimization of chamber cleans should be applied. Again, designed experimentation should be used. A Novellus Concept One PECVD tool is to be installed at the ICL at MTL and should be utilized for this study. OES again should be used to study the plasma composition. Etch residue should be characterized by AES or XPS. Effluent identification and process efficiency should be determined using QMS or FTIR. In addition, dielectric films grown after an alternative clean should have their electronic and compositional characteristics determined and compared to films grown after a conventional clean. This comparison can serve as an measure of any indirect effects that the alternative clean may have on the PECVD process.

For both experimental stages, close coordination with members of industry should continue. When processes are deemed ready, they should be beta tested at industrial sites to determine any side effects that they may have over large wafer runs.

Appendix

Hydrofluorocarbons

Difluoromethane CF_2H_2

CAS # 75-10-5

Etch Performance: Has been examined in combination with other HFCs and PFCs for its ability to promote polymer deposition during etching of silicon dioxide. Used in both low and high density plasma source systems.

Source(s):
ARAI, TSUJIMOTO, and TACH, "DEPOSITION IN DRY-ETCHING GAS PLASMAS," JAP. J. APPL. PHYS., 31, 2011 (1992).

GOTOH, and KURE, "ANALYSIS OF POLYMER FORMATION DURING SIO(2) MICROWAVE PLASMA ETCHING," JPN. J. APPL. PHYS., 34, 2132 (1995).

KADOMURA, "ETCHING GAS AND METHOD," JPN. KOKAI TOKKYO KOHO JP 61,142,744(1986) (TO SONY), and CHEM. ABSTR., 105, 217533 (1986).

LAMM, and CARRASCO, "HYDROFLUOROCARBON PLASMA SUBMICRON SILICON DIOXIDE ETCH IN AN AXISYMMETRIC STATIC MAGNETRON," VACUUM, 45, 555 (1994).

MARKS, WONG, KESWICK, and YANG, "OXIDE ETCHING FROM INTEGRATED CIRCUIT WITH HIGH SELECTIVITY," JPN. KOKAI TOKKYO KOHO JP 06 29, 256 (1994) (TO APPLIED MATERIALS) and CHEM. ABSTR., 121, 193405 (1994).

NABESHIMA, and TAMAKI, "METHOD OF DRY ETCHING," U.S. PATENT 5, 296, 095 (1994) (TO MATSUSHITA ELECTRIC).

SHIN, "PROCESS FOR DRY ETCHING A SILICON NITRIDE LAYER," U.S. PATENT 5,180,466 (1993) (TO FUJITSU)).

TATEIWA, and TSUJI, "ETCHING CHARACTERISTICS OF PLASMA CVD POLYMERS," PROC. 1988 DRY PROCESS SYMP., 74 (1988).

Global Warming Potential: 580 (100 year ITH)

Lifetime: 6 years

Safety: Stable. Flammable; flash point not determined. Incompatible with strong oxidizers (alkali metals). Hazardous decomposition products are HF, CO, and CO(2). No hazardous polymerization.

Health: May cause skin, eye, and respiratory irritation. Narcotic effect. Large exposure can cause damage to heart. 8 Hour TWA:10000 PPM. Not listed as carcinogen by IARC, NTP, or OSHA.

Pentafluoroethane CF_3-CF_2H

CAS # 354-33-6

Etch Performance: Has been examined alone for the etching of patterned silicon dioxide films in both low density and high density etching systems. Has also been examined in combination with CF(4) to improve selectivity during silicon dioxide etching in a high density etcher. Has been examined for PECVD chamber cleaning applications, but etch rate deemed to slow.

Source(s) in Literature:
LAMM, and CARRASCO, "HYDROFLUOROCARBON PLASMA SUBMICRON SILICON DIOXIDE ETCH IN AN AXISYMMETRIC STATIC MAGNETRON," VACUUM, 45, 555 (1994).

MOCELLA, "MATURE AND EMERGING ENVIRONMENTAL ISSUES IN PLASMA PROCESSING: CFC'S AND PFC'S," PROC. 19TH TEGAL PLASMA SEMINAR, 11 (1993).

MOHINDRA, SAWIN, MOCELLA, COOK, FLANNER, and TURMEL, "ALTERNATIVES TO PERFLUOROCOMPOUNDS AS PLASMA PROCESSING GASES: SIO(2) ETCHING USING C(2)F(5)H AND C(2)F(4)H(2)," PROC. ELECTROCHEM. SOC., 94-20, 300 (1994).

OLEWINE, "ALTERNATIVE ETCH CHEMISTRIES AND OPTIMIZATION STUDIES FOR DIELECTRIC REACTOR CLEANING," PROC. SIA/SSA/SEMATECH GLOBAL WARMING SYMPOSIUM, ALTERNATIVES/OPTIMIZATION/RECOVERY SECTION, PAPER #3 (1994).

Global Warming Potential: 3,200 (100 year ITH)

Lifetime: 36 years

Safety: Stable. Not flammable. Incompatible with alkali or alkaline earth metals. Hazardous decomposition (by flame) products are HF and possibly carbonyl fluoride. No hazardous polymerization.

Health: Gross exposure may cause dizziness, confusion, uncoordination, drowsiness, or unconsciousness. May cause irregular heat beat. Systemic toxicity through skin contact appears unlikely. Increased susceptibility to persons with pre-existing disease of the cardiovascular system. Not tested for eye or skin irritation. Has very low toxicity (acts like anesthetic). PEL(OSHA):none established, TLV(ACGIH):none established, AEL(DuPont):1000 ppm, 8 and 12 hr. TWA, WEEL (AIHA):1000 ppm, 4900 mg/m3, 8hr. TWA. Inhalation: 4 hour, ALC, rat: > 709,000 ppm. Not listed as carcinogen by IARC, NTP, OSHA, or ACIGH.

Tetrafluoroethane CF_3-CFH_2

CAS # 811-97-2

Etch Performance: Has been examined alone for the etching of patterned silicon dioxide films in both low density and high density etching systems. Has also been examined in combination with CF(4) to improve selectivity during silicon dioxide etching in a high density etcher.

Source(s):
LAMM, and CARRASCO, "HYDROFLUOROCARBON PLASMA SUBMICRON SILICON DIOXIDE ETCH IN AN AXISYMMETRIC STATIC MAGNETRON," VACUUM, 45, 555 (1994).

MOCELLA, "MATURE AND EMERGING ENVIRONMENTAL ISSUES IN PLASMA PROCESSING: CFC'S AND PFC'S," PROC. 19TH TEGAL PLASMA SEMINAR, 11 (1993).

MOHINDRA, SAWIN, MOCELLA, COOK, FLANNER, and TURMEL, "ALTERNATIVES TO PERFLUOROCOMPOUNDS AS PLASMA PROCESSING GASES: SIO(2) ETCHING USING C(2)F(5)H AND C(2)F(4)H(2)," PROC. ELECTROCHEM. SOC., 94-20, 300 (1994).

O'NEILL and SINGH, "ULTRAVIOLET ABSORPTION SPECTROSCOPY FOR THE DETECTION OF CF2 IN HIGH-DENSITY PLASMAS," J. APPL. PHYS., 76, 5967 (1994).

Global Warming Potential: 1,300 (100 year ITH)

Lifetime: 14 years

Safety: Stable. Not flammable. Incompatible with alkali and alkaline earth metals. Hazardous decomposition (open flame) products are HF and possible carbonyl fluoride. No hazardous polymerization.

Health: Gross exposure may cause dizziness, confusion, uncoordination, drowsiness, or unconsciousness. May cause irregular heartbeat. Increased susceptibility to persons with pre-existing disease of the cardiovascular and nervous systems. May be slight eye and skin irritant. Has very low toxicity (acts like anesthetic). PEL(OSHA):none established, TLV(ACGIH):none established, AEL(DuPont):1000 ppm, 8 and 12 hr. TWA, WEEL (AIHA):1000 ppm, 4900 mg/m3, 8hr. TWA. Inhalation: 4 hour, ALC, rate: 567,000 ppm. Not listed as carcinogen by IARC, NTP, OSAH, or ACIGH. According to a DuPont MSDS, for a two year study, a concentration of 50,000 ppm produced an increase in late-occurring benign testicular tumors, testicular hyperplasia, and testicular weight. The no-effect-level for this study was 10,000 ppm. Slight fetotoxicity observed, but only at levels that produced other toxic effects in adults. No change in reproductive performance in male rats. No genetic damage observed in bacterial or mammalian cell cultures, or in animals.

2H-Heptafluoropropane CF_3-CFH-CF_3

CAS # 431-89-0

Etch Performance: No etching use reported.

Global Warming Potential: 3,300 (100 year ITH)

Lifetime: 41 years

Safety: Stable. Not flammable. Incompatible with molten alkali metals and strong oxidizers. Hazardous decomposition products are HF, CO, and CO(2). Thermal decomposition products may include PFIB. No hazardous polymerization.

Health: Little health data. Toxicity not determined. PEL(OSHA): not established, TLV(ACGIH): not established. Not listed as carcinogen by NTP, IARC, or OSHA.

1H-Heptafluoropropane CF_2H-CF_2-CF_3

CAS # 2252-84-8

Etch Performance: No etching use reported.

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Not flammable. Hazardous decomposition products are HF, CO, and CO(2). Thermal decomposition products may include PFIB. No hazardous polymerization.

Health: Little health data. Toxicity not determined. PEL(OSHA):not determined, TLV(ACGIH):not determined. Not listed as carcinogen by NTP, IARC, or OSHA.

Trifluoroethylene CF_2=CFH

CAS # 359-11-5

Etch Performance: No etching use reported.

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Flammable (flash limits not determined). Inhibited with dipentene (<1%). May react explosively with oxygen. Incompatible with peroxides, radical forming conditions, halogens, and halogen halides. Hazardous decomposition products are carbonyl fluoride, HF, CO, CO(2), and perfluoroisobutylene. Hazardous polymerization occurs.

Health: Little health data. Toxicity not determined. May be harmful if inhaled, ingested, or by skin absorption. PEL(OSHA):not established, TLV(ACGIH):not established. Not listed as carcinogen by NTP, IARC, or OSHA.

Iodofluorocarbons

Iodotrifluoromethane CF_3I

CAS # 2314-97-8

Etch Performance: Has been examined in combination with SF(6) for trench etching of silicon in a low pressure, batch diode system.

Source(s):
BLIZNETSOV, GUTSHIN, and YACHMENEV, "REACTIVE ION ETCHING OF DEEP TRENCHES IN SILICON," PROC. SPIE, 1783, 584 (1992).

Global Warming Potential: < 5 (20 year ITH)

Lifetime: 0.0026 years (about 1 day)

Ozone Depleting Potential: < 0.008 (conservatively), probably < 0.0001

Safety: Stable. Not flammable. May be incompatible with strong oxidizing agents, alkali metals. Hazardous decomposition products may include CO, CO(2), HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. May cause cardiac arrhythmia. Irritant to the skin, eyes, mucous membranes, and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: -22.5 C. Vapor Pressure: 85 psia @ 20 C.

Iodopentafluoroethane CF_3-CF_2I

CAS # 354-64-3

Etch Performance: No etching use reported.

Global Warming Potential: not determined, expected to be negligible.

Lifetime: not determined

Ozone Depleting Potential: not determined

Safety: Stable. Not flammable. May be incompatible with strong oxidizing agents, possibly aluminum. Hazardous decomposition products may include CO, CO(2), Iodine, Perfluorobutane, HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. Irritant to the skin, eyes, mucous membranes, and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: 12-13 C. Vapor pressure: 35 psia @ 20 C, 738.9 mmHg @ 10 C.

Iodotrifluoroethylene CF_2=CFI

CAS # 359-37-5

Etch Performance: No etching use reported.

Global Warming Potential: not determined, expected to be negligible

Lifetime: not determined

Ozone Depleting Potential: not determined

Safety: Stable. Not flammable. May be incompatible with acids, active metals. Hazardous decomposition products may include CO, CO(2), possibly COF(2), HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. Irritant to the skin, eyes, mucous membranes, and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: 30 C (liquid at room temperature). Vapor pressure: not determined.

1-Iodoheptafluoropropane $CF_2I-CF_2-CF_3$

CAS # 754-34-7

Etch Performance: No etching use reported.

Global Warming Potential: not determined, expected to be negligible

Lifetime: not determined

Ozone Depleting Potential: not determined

Safety: Stable. Not flammable. May be incompatible with strong oxidizing agents. Hazardous decomposition products may include CO, CO(2), HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Little health data. Toxicity: ihl-mouse LC50: 404 g/m3 / 2 H. May be harmful if inhaled, ingested or by skin absorption. Irritant to the skin, eyes, mucous membranes, and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: 40 C (liquid at room temperature). Vapor pressure: not determined.

2-Iodoheptafluoropropane $CF_3-CFI-CF_3$

CAS # 677-69-0

Etch Performance: No etching use reported.

Global Warming Potential: not determined, expected to be negligible

Lifetime: not determined

Ozone Depleting Potential: not determined

Safety: Stable. Not flammable. May be incompatible with strong oxidizing agents. Hazardous decomposition products may include CO, CO(2), HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. Irritant to the skin, eyes, mucous membranes, and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: 38 to 40 C (liquid at room temperature). Vapor pressure: 7.12 psi @ 20 C, 23.29 psi @ 55 C.

1,2-Diiodotetrafluoroethane $CF_2I\text{-}CF_2I$

CAS # 354-65-4

Etch Performance: No etching use reported.

Global Warming Potential: not determined, expected to be negligible

Lifetime: not determined

Ozone Depleting Potential: not determined

Safety: Stable. Not flammable. May be incompatible with strong oxidizing agents. Hazardous decomposition products may include CO, CO(2), iodine, HI, and HF. No hazardous polymerization. May generate iodine upon exposure to light.

Health: Toxic by inhalation in rats: ihl-rat: 33 ppm (acute lethal concentration); produces skin necrosis in rabbits in 48 hours; irritant to eyes in test animals: observation of test animals at 24 hrs showed severe redness, moderate iritis and mild corneal opacity. Severe irritant to the skin, eyes, and possibly mucous membranes and respiratory tract. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Other: B.P.: 112-113 C (liquid at room temperature). Vapor pressure: not determined.

Unsaturated Fluorocarbons

Tetrafluoroethylene $CF_2=CF_2$

CAS # 116-14-3

Etch Performance: Has been examined in combination with HFCs and other unsaturated FCs for the selective etching of silicon dioxide films in high density etchers. Also examined in combination with CF(4) for its ability to promote polymer deposition in low density plasma systems during etching of silicon and silicon dioxide.

Source(s):
BELL, JOUBERT, OEHRLEIN, ZHANG, and VENDER, "INVESTIGATION OF SELECTIVE SIO(2)-TO-SI ETCHING IN AN INDUCTIVELY COUPLED HIGH-DENSITY PLASMA USING FLUOROCARBON GASES," J. VAC. SCI. TECHNOL. A, 12, 3095 (1994).

COBURN and KAY, "SOME CHEMICAL ASPECTS OF THE FLUOROCARBON PLASMA ETCHING OF SILICON AND ITS COMPOUNDS," SOLID STATE TECHNOL.,22 (4), 117 (APRIL,1989) and IBM J. RES. DEVELOP., 23, 33 (1979).

D'AGOSTINO, CRAMAROSSA, COLAPRICO, and D'ETTOLE, "MECHANISMS OF ETCHING AND POLYMERIZATION IN RADIOFREQUENCY DISCHARGES OF CF(4)-H(2), CF(4)-C(2)F(4), C(2)F(6)-H(2), C(3)F(8)-H(2)," J. APPL. PHYS., 54, 1284 (1983).

D'AGOSTINO, CRAMAROSSA, and DEBENEDICTIS, "DIAGNOSTICS AND DECOMPOSITION MECHANISM IN RADIO-FRE QUENCY DISCHARGES OF FLUOROCARBONS UTILIZED FOR PLASMA ETCHING OR POLYMERIZATION," PLASMA CHEM. PLASMA PROCESS., 2, 213 (1982).

LAMM, and CARRASCO, "HYDROFLUOROCARBON PLASMA SUBMICRON SILICON DIOXIDE ETCH IN AN AXISYMMETRIC STATIC MAGNETRON," VACUUM, 45, 555 (1994).

OEHRLEIN, ZHANG, JOUBERT, VENDER, HAVERLAG, BELL, and KIRMSE, "HIGH-DENSITY PLASMA ETCHING OF SILICON DIOXIDE AND SILICON USING FLUOROCARBON," GASES, PROC. 19TH TEGAL PLASMA SEMINAR, 1 (1993).

SCHLEMM and MATTHES, "MAGNETIC FIELD ENHANCED PLASMA ETCHING AND GLOW POLYMERIZATION AT A LOW-FREQUENCY DISCHARGE," WISS. Z.-TECH. HOCHSCH. KARL-MARX-STADT, 28, 219 (1986) and CHEM. ABSTR., 106, 42452 (1987).

SIMKO and OEHRLEIN, "REACTIVE ION ETCHING OF SILICON AND SILICON DIOXIDE IN CF(4) PLASMAS CONTAINING H(2) OR C(2)F(4) ADDITIVES," J. ELECTROCHEM. SOC., 138, 2748 (1991).

Global Warming Potential: not determined

Lifetime: not determined

Safety: Unstable. Flammable limits in air: 14-43% by volume; auto-ignition temperature: 620 C. Incompatibilities: reacts violently with air and oxidizing agents. Hazardous decomposition/oxidation products may include COF(2) and HF. Hazardous polymerization may occur. Very reactive and is capable of polymerization with explosive violence, especially in the presence of a catalyst such as oxygen. May explode in contact with exothermally reactive materials. Will explode at pressures above 2.7 psia if not stabilized. Stabilized with alpha-terpinene or alpha-pinene.

Health: Does not appear to have any substantial toxicity. PEL (OSHA):none established, TLV (ACGIH): none established. No carcinogenicity data.

Hexafluoropropylene CF_3-CF=CF_2

CAS # 116-15-4

Etch Performance: Has been examined in combination with HFCs and other unsaturated FCs for selective silicon dioxide etching in low and high density plasma systems.

Sources:
BELL, JOUBERT, OEHRLEIN, ZHANG, and VENDER, "INVESTIGATION OF SELECTIVE SIO(2)-TO-SI ETCHING IN AN INDUCTIVELY COUPLED HIGH-DENSITY PLASMA USING FLUOROCARBON GASES," J. VAC. SCI. TECHNOL. A, 12, 3095 (1994).

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HICHIN, NAKAYAMA, and TANNO, "DRY ETCHING OF A SILICON FILM ON A SEMICONDUCTOR SUBSTRATE," JPN. KOKAI TOKKYO KOHO JP 61,133,630 (1986) (TO MATSUSHITA ELECTRIC) and CHEM. ABSTR., 105, 236904 (1986).

OEHRLEIN, ZHANG, JOUBERT, VENDER, HAVERLAG, BELL, and KIRMSE,

"HIGH-DENSITY PLASMA ETCHING OF SILICON DIOXIDE AND SILICON USING FLUOROCARBON GASES," PROC. 19TH TEGAL PLASMA SEMINAR, 1 (1993).

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Flammable limits: LEL: 2.6, UEL: 21.7. Matheson describes C(3)F(6) as nonflammable at RT and AP. Incompatibilities: active metals. Hazardous decomposition products may include CO(2), CO, COF(2) and HF. No hazardous polymerization. Reacts with C2F4 + air to form explosive peroxides. Anhydrous C(3)F(6) is not corrosive to most common metals of construction; moist C(3)F(6) hydrolyzes slowly and creates corrosive conditions.

Health: Inhalation can cause central nervous system depression. Symptoms of exposure may include dizziness, cardiac arrhythmia, uncoordination. Inhalation of large quantities of this material may also cause liver and kidney damage.

LC50: 750 ppm 4 hours (mouse)
LC50: 20,000 mg/m3 2 hours (rat)
LC50: 2800 ppm 4 hours (rat)
LC50: 11,200 mg/m3 4 hours (rat)
PEL (OSHA):none established, TLV (ACGIH): none established.
OEL (Russia): STEL 5 mg/m3 (Jan 93)

Not listed as carcinogen by IARC, NTP, or OSHA.

Hexafluoro-1,3-butadiene CF_2=CF-CF=CF_2

CAS # 685-63-2

Etch Performance: No etching use reported.

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Not flammable. Incompatibilities: strong oxidizers, acids, possibly air, oxygen. Hazardous decomposition products may include CO(2), CO, COF(2) and HF. No hazardous polymerization.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Hexafluoro-2-butyne CF_3-C≡C-CF_3

CAS # 692-50-2

Etch Performance: No etching use reported.

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Flammable. Incompatibilities: strong oxidizers, active metals. Hazardous decomposition products may include CO(2), CO, COF(2) and HF. No hazardous polymerization. Forms explosive mixtures in air.

Health: Highly toxic by inhalation. May cause severe irritation to nose and upper respiratory system. May cause skin and eye irritation. "In a DuPont study, six rats exposed to 220 ppm of this material during nose-only exposures died. 5 of 6 rats exposed to 55 ppm died either during or immediately after exposure. All six rats survived a 4 hour exposure to 20 ppm." (PCR MSDS) Symptoms of exposure may include difficulty breathing, headache, chest pain, cardiac arrhythmia, and unconsciousness. May aggravate existing heart conditions. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

Hexafluorocyclobutene CF_2-CF_2-CF=CF-

CAS # 697-11-0

Etch Performance : Has been examined alone for the etching of silicon dioxide in a low density plasma system.

Source(s):
YANAGIDA, "DRY ETCHING METHOD," U.S. PATENT 5,338,399 (1994) (TO SONY CORP.).

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Not flammable. Incompatibilities: strong oxidizers, acids, air, oxygen. Hazardous decomposition products may include CO(2), CO, COF(2), perfluoroisobutene, and HF. No hazardous polymerization.

Health: Highly toxic by inhalation. Inhalation may cause unconsciousness, dizziness, nausea, and vomiting.

LCLo: 50,000 ppm (inhalation mouse)
LC50: 50 ppm (unknown test animal)
PEL (OSHA):none established, TLV (ACGIH): none established.

Not listed as carcinogen by IARC, NTP, or OSHA.

Octafluoro-2-butene CF_3-CF=CF-CF_3

CAS # 360-89-4

Etch Performance: The literature search reports the use of C(4)F(8). No indication of which C4F8 isomer was used is given. Some of the sources are listed below.

Source(s):
AKIMOTO, FURUOYA, HARASHIMA, and IKAWA, "ANALYSIS OF FLUOROCARBON FILM DEPOSITED BY C4F8/CO GAS PLASMA," PROC. ELECTROCHEM. SOC., 94-20, 311 (1994).

FUKASAWA, NAKAMURA, SHINDO, and HORIIKE, "HIGH RATE AND HIGH SELECTIVITY SIO(2) ETCHING EMPLOYING INDUCTIVELY COUPLED PLASMA," PROC. 15TH DRY PROCESS SYMP., 103 (1993).

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HISADA, NAKAMURA, and HOSOKI, "HIGHLY SELECTIVE ETCHING OF AN SIO(2) FILM TO A METAL LAYER," PROC. ELECTROCHEM. SOC., 94-20, 320 (1994).

NOJIRI and IGUCHI, "ELECTRON CYCLOTRON RESONANCE PLASMA ETCHING OF SILICON DIOXIDE FOR DEEP-SUBMICRON ULTRALARGE SCALE INTEGRATIONS," J. VAC. SCI. TECHNOL. B, 13, 1451 (1995).

NOJIRI, IGUCHI, KAWAMURA, and KADOTA, "MICROWAVE PLASMA ETCHING OF SILICON DIOXIDE FOR HALF-MICRON ULSI'S," EXT. ABSTR. CONF. SOLID STATE DEV. MATER., 21, 153 (1989).

(NO AUTHOR DISCLOSED), "GAS PLASMA ETCHING METHOD," JPN. KOKAI TOKKYO KOHO JP 80 61,027(1980) (TO CHO LSI GIJUTSU KINKYU KUMIAI) and CHEM. ABSTR., 93, 141980 (1980).

Global Warming Potential: not determined

Lifetime: not determined

Safety: Stable. Not flammable. Incompatibilities: powdered metals, alkali or alkaline earth metals. Hazardous decomposition products may include CO(2), CO, possibly COF(2) and HF. No hazardous polymerization. Anhydrous octafluoro-2-butene is not corrosive to common metals of construction. In contact with water, it is hydrolyzed slowly and will create corrosive conditions.

Health: Little health data. Toxicity has not been determined. May be harmful if inhaled, ingested or by skin absorption. LCLo: 6100 ppm / 4 hours (rat). Exposure to 6100 ppm for 4 hrs causes mild irritation in rats; higher concentrations produce CNS signs (decrease in activity and convulsions). Symptoms of exposure may include light-headedness, giddiness, shortness of breath, possible narcosis, possible cardiac arrhythmia at high concentrations. PEL (OSHA):none established, TLV (ACGIH): none established. Not listed as carcinogen by IARC, NTP, or OSHA.

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