1997

Characterization of HF/H₂O vapor phase etching of SiO₂

Bang Bui
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Bui, Bang, "Characterization of HF/H₂O vapor phase etching of SiO₂" (1997). *Master's Theses*. 1555.
DOI: <https://doi.org/10.31979/etd.duc7-ku8q>
https://scholarworks.sjsu.edu/etd_theses/1555

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

**A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600**

CHARACTERIZATION OF HF/H₂O VAPOR PHASE ETCHING OF SiO₂

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Bang Bui

December 1997

UMI Number: 1388173

UMI Microform 1388173
Copyright 1998, by UMI Company. All rights reserved.

**This microform edition is protected against unauthorized
copying under Title 17, United States Code.**

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

© 1997

Bang Bui

ALL RIGHTS RESERVED

APPROVED FOR THE DEPARTMENT OF CHEMICAL ENGINEERING

Dr. Anthony Muscat, Professor, Department of Chemical Engineering

Dr. Art Diaz, Professor, Department of Materials Engineering

Dr. Peter Gwozdz, Professor, Department of Materials Engineering

APPROVED FOR THE UNIVERSITY

ABSTRACT

Characterization of HF/H₂O vapor phase etching of SiO₂

by

Bang Bui

Silicon dioxide etching using gas phase mixtures of HF and water vapor was studied in a stainless steel reactor system at subatmospheric pressure and temperatures between 30 and 50 °C. The results show that SiO₂ etching proceeds in the non-condensed regime as well as in the condensed regime albeit at a slower rate. Response surfaces at 30, 40, and 50°C generated from a Box-Behnken design of experiments to map out the etching rate as a function of the water and HF partial pressure parameter spaces suggest that there are three different regimes where etching can occur: non-condensed or gas/solid, multilayer, and condensed. The multilayer and condensed regimes occur at higher HF and water partial pressures than the thermodynamic vapor/liquid equilibrium curve would suggest due primarily to the need to nucleate the HF/water layer on the moderately hydrophobic silicon oxide surfaces used in this study.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER 1. INTRODUCTION	1
CHAPTER 2. LITERATURE REVIEW	4
CHAPTER 3. HYPOTHESIS & METHODS	15
3.1. Hypothesis	15
3.2. Research Approach	16
CHAPTER 4. EXPERIMENTAL	21
4.1. Description of Apparatus	21
4.2. Experimental Procedure	23
CHAPTER 5. RESULTS	27
5.1. The Process	27
5.1.1. Reactor Characterization	27
5.1.2. Determine the Uniformity on 1cm x 1cm Samples	28
5.1.3. Obtaining the Etching Rate	28
5.1.4. Effect of the Mass Flow Rate on the Etching Rate	29
5.1.5. Effect of Aqueous Cleans on the Etching Rate	30
5.2. Objectives of Study	30
5.2.1. Oxide Etching in the Non-condensed Regime	31

	Page
5.2.2. Langmuir-Hinshelwood Kinetics	31
5.2.3. Box-Behnken Design	32
CHAPTER 6. DISCUSSION	45
6.1. Oxide Etching in the Non-condensed Regime	45
6.2. Langmuir-Hinshelwood Kinetics	47
6.3. Box-Behnken Design	48
CHAPTER 7. CONCLUSIONS	53
REFERENCES	54
APPENDICES	55
Appendix I. Conversion	56
Appendix II. Workable Ranges of HF and H ₂ O	57
Appendix III. Superficial Velocity	58
Appendix IV. Controller's Circuit Diagram	59
Appendix V. H ₂ O Contactor	60
Appendix VI. Box-Behnken Design	61
Appendix VII. Manual of the Apparatus	62

LIST OF TABLES

	Page
Table 2.1. Summary of etch results	13
Table 5.1. Summary of etch results of various aqueous cleans	37
Table 5.2. Summary of etch results at 30 °C	37
Table 5.3. Summary of etch results at 40 and 50 °C	38

LIST OF FIGURES

	Page
Figure 2.1. Schematic diagram of the various steps occurring during the etching of SiO_2 .	11
Figure 2.2. Partial pressure diagram indicating what ranges correspond to a stable condensed phase.	12
Figure 2.3. A proposed model of oxide etching in gas phase HF/vapor mixtures.	13
Figure 2.4. Etching rates at various temperatures	14
Figure 3.1. A partial pressure diagram at 30 °C indicates what ranges correspond to a stable condensed phase of HF and H_2O . 14 runs, which are represented by the dots, were performed.	19
Figure 3.2. A partial pressure diagram at 40 °C indicates what ranges correspond to a stable condensed phase of HF and H_2O . 4 runs, which are represented by the dots, were performed.	19
Figure 3.3. A partial pressure diagram at 50 °C indicates what ranges correspond to a stable condensed phase of HF and H_2O . 4 runs, which are represented by the dots, were performed.	20
Figure 3.4. A Box-Behnken design for three factors.	20
Figure 4.1. A schematic of the experimental apparatus.	25
Figure 4.2. Spots on a sample where the oxide thickness were measured before and after an etch.	26
Figure 5.1. Etching profile of a 4-inch wafer.	35
Figure 5.2. Etching profile of a 1 cm x 1 cm sample.	35
Figure 5.3. Etched oxide thickness is linear with time.	36
Figure 5.4. Influence of the mass flow rate on the etching rate.	36
Figure 5.5. Etching rates in the non-condensed and the condensed regime.	38
Figure 5.6. Natural log of the etching rate as a function of the inverse of temperature.	39

	Page
Figure 5.7. Etching rate results of the Box-Behnken design.	39
Figure 5.8. Test the validity of Equation 8.	40
Figure 5.9. 3-D plot at 30 °C	41
Figure 5.10. 3-D plot at 40 °C	42
Figure 5.11. 3-D plot at 50 °C	43
Figure 5.12. To verify the parabolic dependence of the etching rate on H₂O fractions at 2% Psat of HF.	44
Figure 5.13. To verify the linear dependence of the etching rate on HF fractions At 10% Psat of H₂O.	44

CHAPTER 1. INTRODUCTION

Cleaning the contaminants in the layered films that make up integrated circuit devices is an important part of integrated circuit fabrication for the contaminants can damage the circuit devices over time. Currently, as much as twenty percent of the process flow for device fabrication process is related to cleaning⁽¹⁾, and most of these cleaning steps are done in the liquid phase. For example, organic contaminants are removed with a mixture of sulfuric acid, hydrogen peroxide, and water, commonly called piranha, and silicon oxide is removed with a solution of hydrogen fluoride (HF) and water.

Although aqueous cleaning satisfies the current technological demands, it has a few drawbacks. The shortcomings include the high cost of chemicals, environmental problems, self-contamination, ineffectiveness in cleaning small geometries, and the inability to be incorporated in a vacuum cluster-type system. These factors may make aqueous cleaning difficult to implement in the near future. Hence, a possible alternative to aqueous cleaning is gas phase cleaning because gas phase cleaning which addresses the shortcomings of liquid phase cleans.

One advantage of gas phase cleaning is that a large chemical volume is not required. Typically, a gas phase clean requires less than 1/100 of the volume of an aqueous clean⁽²⁾. Not only will the cost of manufacturing be decreased, but the environmental impact will be reduced as well since some chemicals, such as HF, are quite toxic. This is important because severe contamination problems in the ground water supplies through faulty storage tanks have been cited in Silicon Valley⁽²⁾.

Another benefit to gas phase cleaning is that redeposition of contaminants back onto the wafers is reduced with gas phase cleaning. Aqueous cleaning, on the other hand, has been shown to redeposit contaminants back onto the wafers⁽²⁾. Evidence can be found in the deionized water rinsing and drying steps. Tests showed that self-contamination in gas phase cleaning is minimal⁽²⁾.

In the next decade, the semiconductor industry is planning to sell gigabit chips with the feature size that measures between 0.1 to 0.2 micrometer in length⁽³⁾. As the feature size on a chip is getting smaller and smaller, liquid surface tension may become an issue. However, there are no surface tension effects in gas phase cleaning.

Perhaps the greatest advantage is that gas phase cleaning can be used in a vacuum cluster-type arrangement as suggested by Ma and his colleagues⁽⁴⁾. In typical chip fabrication, after a wafer has been etched, it has to be cleaned prior to going to a deposition process. Currently, the etching and deposition processes are done in vacuum in the vapor phase, and the cleanings are done in aqueous solutions. As a result, a vacuum integrated process can not be used. Besides gas phase cleaning is vacuum compatible; it will process wafers more efficiently in terms of a turnover ratio. In addition, gas phase cleaning will reduce contamination since the wafers will not be exposed to ambient air, which is a source of contamination.

Because of the potential economic and environmental benefits as discussed above, a few studies have been done to better understand gas phase cleaning. However, most of the gas phase cleaning processes are still not well understood, in particular oxide cleaning using an HF/H₂O vapor phase mixture as an alternative to a liquid HF/H₂O mixture, which

is currently implemented to remove silicon oxide prior to silicon epitaxy or gate oxide growth.

One study proposed that HF/H₂O vapor phase etching of SiO₂ occurs in a condensed layer⁽⁵⁾. However, this model, which was proposed by Helms and Deal, may make it difficult to incorporate gas phase cleaning into a vacuum cluster-type system due to the condensed layer of water and HF which would require a long pump down time. In 1993, Vermeulen *et al.* found that “etching may take place in a gas phase, multilayer adsorption, or condensation regime”⁽⁶⁾. The study has practical importance because etching of SiO₂ using a HF/H₂O vapor phase mixture can be done in a gas phase regime, where no condensation layer is necessary, making it possible for gas phase cleaning to be integrated into a vacuum cluster-type system. Another study, which was done by Muscat *et al.*, produced results that lend support to a theory that gas phase HF etching can proceed via a gas-solid reaction and follows a Langmuir-Hinshelwood mechanism⁽⁷⁾.

Although various researchers have characterized certain aspects of HF/H₂O vapor phase etching of SiO₂, a detailed understanding of the process is needed to make the process industrially viable. This study was undertaken to characterize HF/H₂O vapor phase etching of SiO₂.

CHAPTER 2. LITERATURE REVIEW

In 1966, Holmes and Snell were the first to report the capability of vapor phase HF/H₂O mixtures to etch SiO₂. Three important results came out of their study. First of all, water is necessary for etching to occur. Secondly, they found that “the rate of attack of the oxide by the vapor close above the etching bath was comparable with that in the bath”⁽⁸⁾. Thirdly, they observed that the etching rates are optimal between 20°C and 30°C and fall rapidly above 40°C, suggesting that surface condensation plays an important role in oxide etching.

As a result of the work, in 1992, Helms and Deal used Holmes’ and Snell’s data to present a model explaining the mechanisms of HF/H₂O vapor phase etching of SiO₂⁽⁵⁾. The basis of their model is the assumption that vapor phase etching only occurs when there is a condensed film of HF and H₂O. Helms and Deal believed that gas phase etching of SiO₂ is a gas-liquid-solid reaction, instead of a gas-solid reaction, which normally would be expected in a typical gas phase reaction. Their proposed model, which is illustrated in Figure 2.1, has an overall reaction as follows:

H₂SiF₆ then decomposes via:

where SiF₄ desorbs from the surface since it has a high vapor pressure.

Figure 2.1 does not show the actual chemistry, but instead shows the major steps occurring during the etching of SiO_2 . According to Helms and Deal, a SiO_2 surface is exposed to a vapor phase $\text{HF}/\text{H}_2\text{O}$ mixture initially, but no etching occurs [Fig. 2.1a]. Etching can only occur if the temperature is sufficiently low to allow a condensed layer of HF and H_2O to form [Fig. 2.1b]. Etching occurs via equation (1), forming H_2SiF_6 and H_2O [Fig. 2.1c]. Some of the H_2SiF_6 decomposes by way of equation (2), where gaseous SiF_4 is formed. Once etching is complete, the liquid $\text{H}_2\text{SiF}_6/\text{HF}/\text{H}_2\text{O}$ can be rinsed off.

Experimental results in the literature agree quite well with Helms' and Deal's model. As mentioned above, Holmes and Snell observed that the etching rate falls to zero above 40°C . The reason, as suggested by Helms and Deal, is that at high temperatures a condensed layer of H_2O and HF can not be sustained, hence etching will not occur. A recent study done by the Hashimoto Chemical Industries/Tohoku University groups⁽⁹⁾ revealed that there is no etching if HF is below a critical concentration, a finding which agrees with the theory of a condensed medium. In other words, because of the low partial pressures of HF and /or H_2O , a condensed layer cannot be sustained, hence no etching will occur.

Helms and Deal constructed a graph, which is shown in Figure 2.2, indicating the ranges where a condensed layer can be obtained. They based the graph on experimental vapor-liquid equilibrium data recorded by Munter *et al.* According to the model, in regions where no condensation can be sustained, which is the region below the line, no etching will occur. Once the partial pressures of HF and H_2O are high enough that a condensation layer is formed, which is the region above the line, vapor phase etching can

occur. However, Helms and Deal did not perform experiments to show that there is no etching in the regions where no condensation layer is formed.

Despite the lack of experimental data, Helms' and Deal's model of vapor phase etching of SiO_2 has been well received. It is thought that gas phase etching starts with the formation of a condensation layer of HF and H_2O , and proceeds in the same manner as that of liquid phase etching. Since Judge⁽¹⁰⁾ and Verhaverbeke *et al.*⁽¹¹⁾ had fully characterized liquid phase etching of SiO_2 , it is then believed that gas phase etching of SiO_2 is characterized as well.

However, in 1993, Vermeulen *et al.* found that HF gas phase etching of SiO_2 can proceed without a condensed layer of HF and H_2O ⁽⁶⁾. Adsorption experiments were performed to understand the characteristics of HF/ H_2O vapor mixtures. Vermeulen *et al.* discovered that there are three different regimes in which gas phase etching can occur, as illustrated in Table 2.1. When the total pressure is less than 50 percent of the saturated pressure of the mixture of HF and H_2O ($P < 0.5P_{\text{sat}}$), oxide etching is done in the gas phase regime, where etching rates are minimal because the adsorption of HF and water is limited. However, etching rates increase when the total pressure is in the enhanced adsorption regime ($P = 0.6P_{\text{sat}}$), where HF and H_2O are adsorbed easily onto the oxide. In the condensation regime ($P = P_{\text{sat}}$), etching rates are comparable, yet are less than those in the enhanced adsorption due to diffusion limitations.

Although Vermeulen *et al.* have distinguished the three different regions that can influence etching rates, their study was not well defined. Vermeulen *et al.* used the saturated pressure of the mixture of HF and H_2O , instead of using the saturated pressures

of HF and H₂O as separate variables. Since only two parameters- the fractions of the saturated pressures of the mixture of HF and H₂O and the etching rate- were used to characterize gas phase etching, Vermeulen *et al.* did not know which variable, HF or H₂O, had a greater effect on the etching rate. Furthermore, the boundaries that separate the three regions have an error of 10 percent, and the reaction kinetics were not characterized. In the final analysis, Vermeulen *et al.* only did a preliminary study. Yet the work was a major step in gas phase cleaning technology, because Vermeulen *et al.* were able to get etching of SiO₂ in a non-condensed regime, making it possible to incorporate gas phase etching into a vacuum cluster-type system.

In 1994, Muscat and his colleagues at MIT independently showed that gas phase etching of SiO₂ can proceed via a gas-solid reaction ⁽⁷⁾. Muscat *et al.* concluded from their experimental measurements of pump down times and film thicknesses that a condensed film is not required for oxide etching. Pump down times from the operating temperature 250 torr to 10⁻⁷ torr were on the order of 5 to 10 minutes, suggesting that there is no condensed layer, because adsorption experiments showed that the pump down time is about 20 minutes when there was water vapor near its saturation vapor pressure. Film thickness measurements using the *in situ* ellipsometer suggested that on the order of a monolayer is present on the surface, indicating that etching can proceed without a condensed layer.

From these observations, they believe that oxide etching can occur via a gas-solid reaction and hypothesized that the reaction follows a Langmuir-Hinshelwood mechanism. According to the model, HF and water molecules first adsorb onto the surface of SiO₂,

then further polarize the Si-O bonds as shown in Figure 2.3. As the polarization of the Si-O bonds increases, the Si-O bonds become weakened, thus making them more susceptible to an attack by an HF molecule. Consequently, etching can proceed by the formation of the Si-F and Si-O-H bonds. The process can be repeated, and eventually, SiF_4 is produced and desorbs. The Si-O-H groups can form Si(OH)F_3 or $\text{Si(OH)}_2\text{F}_2$ which maybe volatile.

The Langmuir-Hinshelwood kinetics can be expressed as follows:

$$(3) \quad \text{etching rate} = k \cdot \Theta_{\text{HF}} \cdot \Theta_{\text{water}}$$

where k is the rate coefficient, Θ_{HF} is the surface coverage of HF, and Θ_{water} is the surface coverage of water. All the variables are temperature dependent.

Muscat *et al.* varied temperatures and the surface coverage of HF and H_2O to study the kinetics of the reaction. To better understand the influence of temperature on the rate constant k , it is necessary to decouple the temperature dependence of Θ_{HF} and Θ_{water} . As a result, instead of using the absolute partial pressures of HF and water as surface coverages, Muscat *et al.* used the percentage of the saturation vapor pressures of HF and water as coverage metrics, and plotted the etching rate as a function of these fractions.

The results are shown in Figure 2.4.

From analyzing the graphs, Muscat *et al.* concluded that the vapor pressure fraction is the correct scaling for the surface coverage because the shape of the curves are similar for the temperature between 26°C to 55°C at a given HF and H_2O fraction. Effectively, Muscat *et al.* was able to study the effect of temperature on the rate constant k without the influence of the surface coverage variables.

Muscat *et al.* obtained results that indicate etching rates are dependent on temperature, indirectly suggesting that gas phase etching can be described by a Langmuir-Hinshelwood mechanism. As the temperature increases, the etching rate increases as well. As shown in Figure 2.4, etching rates are the highest at 55°C, where the maximum etching rate is around 260 Å/s. However, at 40°C, the etching rates are smaller than those at 26°C, which is inconsistent with a Langmuir-Hinshelwood mechanism. Despite the fact that Muscat *et al.* found the correct metric to scale the surface coverage which consequently allowed them to study the kinetics, their theory, which states that HF etching of SiO₂ in the gas phase follows a Langmuir-Hinshelwood, is inconclusive.

In evaluating Muscat's and his colleagues' work, they proposed a model suggesting that oxide etching proceeds via a gas-solid reaction and follows a Langmuir-Hinshelwood mechanism. They were able to produce results to support their theory that oxide etching using a HF/H₂O vapor mixture can proceed in a non-condensed regime using thickness measurements and adsorption experiments. However, there was no data to back up their model suggesting that the mechanism is Langmuir-Hinshelwood.

In summary, Helms and Deal were the first to present a thermodynamic model that suggested that a condensed layer of HF and H₂O is required for gas phase oxide etching. However, Vermeulen *et al.* showed that gas phase etching can proceed without a condensed layer, and distinguished the three different etching regimes as shown in Table 2.1. Although the study was a preliminary one, it was a major step in gas phase technology since it showed that gas phase etching can proceed via a gas-solid reaction.

Muscat *et al.* independently showed that oxide etching in the gas phase proceeds via a gas-solid reaction. Muscat *et al.*'s work was more defined than that of Vermeulen *et al.*'s work because they manipulated the variables to get the correct metric for the surface coverage. Yet Muscat *et al.* were not able to get a conclusive understanding of oxide etching.

Although the works of Muscat *et al.* and Vermeulen *et al.* have clarified some aspects of vapor phase etching, further studies are needed in order to completely understand oxide etching in the vapor phase before it can be implemented in industry.

Figure 2.1. Schematic diagram of the various steps occurring during the etching of SiO_2 .

Figure 2.2. Partial pressure diagram indicating what ranges correspond to a stable condensed phase.

Table 2.1. Summary of etch results.

Etch regime	Etch rate (nm/min)		Selectivity TEOS/TOX	Inhibition TOX (s)	Equivalent TOX etched for FSI-b oxide removal (nm)
	TOX	TEOS			
I. Gas Phase ($P < 0.5 \text{ Pa}$) $\text{H}_2\text{O}/\text{HF} < 1$ $\text{H}_2\text{O}/\text{HF} > 1$ ($P = 0.48 \text{ Pa}$)	0.3	4.3	25	5-60	<1.0
	0.7	30.0	45	<15	>20
II. Enhanced Adsorption ($0.60 \text{ Pa} < P < 0.95 \text{ Pa}$)	22-28	51-64	2.3 - 2.7	<5	<1.0
III. Condensation ($P = \text{Pa}$)	23.9	29.2	1.2	<5	<1.0

Figure 2.3. A proposed model of oxide etching in gas phase HF/vapor mixtures.

26 °C etching rate response surface. The axes on the floor of the plot are scaled using the saturation vapor pressure fractions of HF and water.

40 °C etching rate response surface. The axes on the floor of the plot are scaled using the saturation vapor pressure fractions of HF and water.

55 °C etching rate response surface. The axes on the floor of the plot are scaled using the saturation vapor pressure fractions of HF and water.

Maximum etching rate contour.

..... > 200 Å/s at 26 °C

..... > 160 Å/s at 40 °C

——— > 260 Å/s at 55 °C

Figure 2.4. Etching rates at various temperatures.

CHAPTER 3. HYPOTHESIS & METHODS

3.1. Hypothesis

Helms and Deal constructed a plot based on thermodynamics indicating in which region a condensed layer of HF/H₂O can be formed as shown in Figure 2.2. The graph consists of a curve which separates the non-condensed region, below, from the condensed region, above. According to Helms and Deal, there should be no etching underneath the curve. However, we hypothesize that oxide etching of SiO₂ can occur within the region that is underneath the curve where no condensation of HF and H₂O is possible. Within this regime, we also hypothesize that oxide etching of SiO₂ follows Langmuir-Hinshelwood kinetics as proposed by Muscat *et al.*

In addition to investigating the nature of silicon dioxide etching using a mixture of HF and H₂O in the non-condensed regime, we examined SiO₂ etching in the condensed regime as well. We hypothesize that oxide etching in the gas phase can not be categorized as simply falling in either the non-condensed regime or the condensed regime. We believe that oxide etching starts in the non-condensed regime where the etching rate is low, then increases with the build up of the layer of HF and H₂O, and levels off as the layer of HF and H₂O becomes so thick that mass transport through the condensed layer is rate limiting.

3.2. Research Approach

To test if oxide etching in the gas phase can occur via a gas-solid reaction, or in the non-condensed regime, a partial pressure diagram of HF and H₂O showing when a condensed medium can be formed was calculated for 30 °C and is shown in Figure 3.1. The data that was used to construct the diagram was taken from the paper of Helms and Deal.

The experimental runs, which are represented by points in Figure 3.1, were chosen because they were within the limitation of the apparatus, and were performed to compare the etching rate between the non-condensed and the condensed regime. The HF fractions chosen were 1%, 2%, and 3.2% P_{sat} of HF. Within each HF fraction, H₂O fractions were chosen appropriately to correspond to the two different regimes.

In addition to the 30 °C graph, two graphs at 40 °C and 50 °C, which were made to test the Langmuir-Hinshelwood kinetics, are shown in Figure 3.2 and 3.3, respectively. For both graphs, 2% was chosen as the HF fraction. Again, as above, H₂O fractions were chosen to correspond to the two different regimes.

The Langmuir-Hinshelwood kinetics can be described as follows:

$$(4) \quad \text{etching rate} = k \cdot \Theta_{\text{HF}} \cdot \Theta_{\text{water}}$$

where k is the rate coefficient, and Θ_{HF} and Θ_{water} , as suggested by Muscat *et al.*, are percentages of saturated pressures of HF and H₂O, respectively. The rate coefficient, k , is defined as

$$(5) \quad k = A \exp(-E_A/RT)$$

where A is a pre-exponential coefficient, E_A is the activation energy, R is the gas constant, and T is the temperature. When substituting equation (4) into equation (3), the etching rate can be expressed as follows:

$$(6) \quad \ln(\text{etching rate}) = \ln A + \ln(\Theta_{\text{HF}} * \Theta_{\text{water}}) - E_A/RT$$

A graph of $\ln(\text{etching rate})$ as a function of $(1/T)$ was done. If an analysis of the graph revealed that there is a linear relationship, it would lend support to a Langmuir-Hinshelwood reaction mechanism.

To characterize the non-condensed regime and condensed regime, a Box-Behnken design of experiments was performed. A Box-Behnken design is a three-variable design for fitting response surfaces. The three variables were temperature and the partial pressure fractions of HF and H₂O. An advantage of using a Box-Behnken design of experiments is that the vertices of the cube, representing the extremes, were not tested, which was important in this case because of the physical constraints in the process.

A three-variable Box-Behnken design was made and is shown in Figure 3.4. The temperature ranges were chosen between 30°C to 50°C, because the mass flow controllers did not work with temperatures above 50°C. Due to the physical constraints of the process, namely the mass flow controllers, HF and H₂O pressure fractions were chosen in the range of 2 to 12% and 6 to 40%, respectively (Appendix II). A Box-Behnken design required a total of 15 runs and the central point in the cube to be tested three times for reproducibility. In addition, each point was repeated at least one time to estimate the random errors. Once the data was obtained, a surface response method was used to graph

three dimensional contour plots of the etching rate versus the partial pressure fractions of HF and H₂O which are similar to Figure 2.4.

Figure 3.1. A partial pressure diagram at 30 °C indicates what ranges correspond to a stable condensed phase of HF and H₂O. 14 runs, which are represented by the dots, were performed.

Figure 3.2. A partial pressure diagram at 40 °C indicates what ranges correspond to a stable condensed phase of HF and H₂O. 4 runs, which are represented by the dots, were performed.

Figure 3.3. A partial pressure diagram at 50 °C indicates what ranges correspond to a stable condensed phase of HF and H₂O. 4 runs, which are represented by the dots, were performed.

Figure 3.4. A Box-Behnken design for three factors.

CHAPTER 4. EXPERIMENTAL

4.1. Description of Apparatus

The etching experiments were carried out in a round stainless steel reactor which had a dimension of 12 inches by 2 inches. The reactor consisted of two circular plates that were held and secured by four Allen screws. The working space of the reactor had a diameter of 4 inches and a height of 0.25 inches. Two ¼ -inch tubes were welded on the top plate to allow gases to enter and exist the reactor as shown in Figure 4.1.

The reactor was equipped with a stainless steel gas handling system that was capable of delivering four different gases into the reactor. The gas handling system consisted of stainless steel tubing, Unit MFC's, Nupro valves, two gas contactors, and an HF bottle. All components were mounted to a 3 by 5 ft aluminum board.

Two gas contactors were used to produce water and IPA vapors. The vapors were carried into the reactor by nitrogen. The amounts of liquid H₂O and IPA needed to put in each contactor reservoir was calculated to be 40 ml (Appendix V). Unit thermal mass flow controllers (MFC) were employed to meter the amount of gases into the reactor. HF, H₂O, and IPA streams need special MFC's, because HF is corrosive, and H₂O and IPA vapors may condense in the lines. Hence, UFC-1660 MFC's, which have metal seals and are resistant to corrosion, were used. UTS-1100 MFC was used for the nitrogen stream. HF, H₂O, and IPA streams were equipped with purge lines to sweep unwanted gases at the end of the day.

The apparatus up to the gas trap was heated by heating tapes and pads which were controlled by two temperature controllers and two voltage variacs. The heating elements can heat the apparatus from room temperature up to 60 °C. As shown in Figure 4.1, three K-type thermocouples T1, T2, and T3 were placed on the H₂O contactor, near the entrance of the reactor, in the reactor, respectively. Steel tubing and MFC's were wrapped with heating tapes and aluminum foil, and were monitored by two CN7700 Omega temperature controllers that used T1 and T2 as setpoints. The controllers controlled within 1% of the setpoint. The circuit diagram for the temperature controller is shown in Appendix IV. The reactor temperature was monitored by T3 which was used as the process temperature. Two heating pads were placed on the back of the gas handling system and were controlled by a voltage variac. Another heating pad was put on the reactor and driven by a voltage variac.

Pressure control was achieved by using a 628 MKS capacitance manometer, which was capable reading up to 1000 Torr and was mounted on top of the reactor, for pressure readout, and a 248A MKS control valve, which was placed downstream. Both were controlled by a Type 250 MKS controller which controlled within 0.1% of the setpoint. The gain was set at 75% and the phase lead was set at 3 seconds.

A gas trap was installed before the exhaust line was fed to a mechanical pump to remove condensables, in particular HF vapors. Since the boiling point of HF is - 40 °C at 100 milliTorr, the condition at which the gas trap was exposed to, it will liquefy in the gas trap if it was placed in a liquid nitrogen dewar. However, liquid nitrogen source could not be obtained, the gas trap was placed in an ice-water bath. The gas trap prevented HF

from going to the pump where HF can destroy the pump's casing. To remove HF vapor from the apparatus, the ice-water bath was removed and an air venting line was opened to sweep the HF from the trap to the hood.

Chapter 4.2. Experimental Procedure

Eight-inch p-type <100> silicon wafers with approximately 20,000 Å of silicon dioxide were etched using a mixture of HF and H₂O. The wafers were cut into 1 cm x 1 cm samples. The samples were not treated with any aqueous clean because results showed that aqueous cleans, including APM and piranha, do not effect the etching rate. The results section contains further details.

Once a run condition was chosen, an Excel worksheet (Appendix I), titled "Conversion," was used to determine the valve position of the MFC's. A desired temperature was set at least one day before to ensure a steady state temperature. Before a sample was etched, the oxide thickness was measured in three places as shown in Figure 4.2 using a MEAS 4 Nanospec. The median reading was used as the pre-etch thickness.

A sample was introduced into the reactor by unscrewing the four Allen screws and separating the two halves of the reactor. The sample was placed in the center on the backplate, and once it was placed, the four Allen screws were tightened. The reactor was allowed to pump down to 0.5 torr, which normally took 5 minutes, to get rid of contaminants and moisture, as a result of opening the reactor.

After the reactor was pumped down, dry nitrogen with less than 0.001 ppm of H₂O and a nitrogen/water mixture were introduced into the reactor for 10 minutes to saturate

the reactor with water vapor at the partial pressure to be used in the succeeding run. Once pressure was set and was stable, HF was introduced into the reactor for 30 - 120 seconds, depending on the run. To quench the reaction, the by-pass valve was opened immediately and all flows were stopped. The sample was taken out and its oxide thickness was measured in the same three places as mentioned above with a Nanospec. The random error was about ± 2 nm from the spot. Because uniformity on the sample was not achieved (see the results section for details), the 3rd spot from the left was used as the post-etch thickness. To obtain the etching rate, the etched thickness was divided by the time because etching was linear with time. The results section contains more details. The complete experimental procedure, which was written by Ming Le, is in the Appendix VII.

Figure 4.1. A schematic of the experimental apparatus

Figure 4.2. Spots on a 10 cm x 10 cm sample where the oxide thickness was measured before and after an etch.

CHAPTER 5. RESULTS

5.1. Process Characterization

Before experimental runs were performed to test the hypotheses, a series of experiments were done to better understand the process. The experiments included characterizing the reactor, determining the uniformity, obtaining the etching rate, determining in which region, diffusion limited or kinetics limited, the experiments were performed, and understanding the effect of various aqueous cleans on the etching rate.

5.1.1. Reactor Characterization

A 30-second experiment using a 4-inch p-type $\langle 111 \rangle$ wafer with a silicon dioxide thickness of 10,320 Å was performed to examine the etching profile within the reactor. The conditions were 10% P_{sat} of HF and H_2O , 250 Torr, 100 sccm, and 22 °C. A schematic of the etching profile is shown in Figure 5.1 where the post-etch thickness is in Angstroms across the wafer. The 4-inch wafer spanned the distance between the entrance and exit tubes through which the reactive gas mixture flowed.

As illustrated in Figure 5.1, the etching pattern consisted of many different bands representing different etching rates. Etching was highest at the entrance and decreased slowly across the wafer. The etching rate near the entrance was 225 Å/sec and the etching rate near the exit was 164 Å/sec. The reactor exhibited plug flow characteristics which was expected because the superficial velocity was quite slow, approximately 0.11 inch per second. Since the entrance and the exit streams were approximately 2 inches apart, the gas mixture moved across the wafer in approximately 18 seconds. As a result,

the etching rate near the exit was low because etching did not occur near the exit until approximately 18 seconds after the HF was first introduced. Consequently the lag time caused the discrepancy among the etching rates across the wafer. Accounting for the lag time, the etching rates near the entrance and the exit were approximately the same, 225 Å/sec and 227 Å/sec (Appendix III).

5.1.2. Uniformity on 1 cm x 1 cm Samples

All experiments, except to characterize the reactor, were performed on 1 cm x 1 cm samples diamond cut from an 8-inch wafer. One generalization can be made from all of the samples. Uniformity was not achieved because the reactor was in plug flow as discussed above. A sample of the uniformity of a typical run is shown in Figure 5.2 where the etching rates were high at the front of the sample and low at the end of the sample. For each sample, the three spots as shown in Figure 4.2 were measured to obtain the etching rates. On average, the three etching rates varied from each other by up to 35%. The etching rate of the 3rd spot as shown in Figure 4.2 (or the spot as shown in Figure 5.2) was used consistently to evaluate the etching rates on all samples.

5.1.3. Obtaining the Etching Rate

Another set of experiments was done to obtain the relationship between the oxide etched thickness and the reaction time. The experimental conditions were 10% Psat of HF and H₂O, 400 Torr, and 22 °C. Using 1 cm x 1 cm samples, 10 experiments were performed at different times, between 5 to 90 seconds with an increment of 10 seconds.

A graph of the oxide thickness that was etched as a function of time was done and is shown in Figure 5.3. A linear regression fit was performed, and the R^2 value was 0.9919, which indicated that thickness was linear with time. As a result, a comparison of the etching rate with different runs was valid even if the etched time was not constant among the runs. In other words, to obtain an etching rate the amount of oxide etched was divided by the running time.

5.1.4. Effect of the Mass Flow Rate on the Etching Rate

Five experimental runs were performed using 1 cm x 1 cm samples to determine the effect of the total mass flow rate on the etching rate. The conditions were 25% Psat of H_2O , 2% Psat of HF, 600 Torr, 40 °C, and 90 seconds. The ranges for the mass flow rates were 50 sccm to 250 sccm. A graph of the mass flow rate as a function of the etching rate was done and is shown in Figure 5.4. Initially, as the mass flow rate increased the etching increased linearly as well. However, the etching rate started to level off at 250 sccm.

One possible explanation for the observed trend is that within the tested mass flow rate range the diffusion of the reactants was rate limiting. In other words, within the diffusion limited regime, the kinetic rate was high enough that it depleted the supply of reactants as fast as it diffused to the surface. In theory, to study the kinetics of a reaction, it is preferred that experiments should be run in the reaction limited regime, rather than the diffusion limited regime. The reason is that when working within the diffusion limited regime not only kinetic phenomena but also diffusion phenomena would be

included. The true kinetic data, such as E_A , the activation energy, consequently would not be obtained. As a result, when testing the Langmuir-Hinshelwood kinetics, the mass flow rate was set at 300 sccm, which should be out of the diffusion limited regime. However, most of the experiments were performed in the diffusion limited regime because it minimized the use HF.

5.1.5. Effect of Aqueous Cleans on the Etching Rate

Using 1 cm x 1 cm samples, 6 experiments were run to observe whether the etching rate was influenced by pre-etch treatments with various aqueous cleanings. The conditions were 32% Psat of H_2O , 4% Psat of HF, 600 Torr, 30 °C, and 110 seconds. Two samples were dipped in APM ($NH_4OH:H_2O_2:H_2O$) with a ratio of 1:1:5 for 2 minutes, another two samples were dipped in piranha ($H_2SO_4:H_2O_2$) with a ratio of 4:1 for 2 minutes, and the last two samples were not treated. Once the samples were treated, they were blown dry and etched immediately. The etching rates of the various cleans are shown in Table 5.1. The results show that pre-treating samples with the aqueous cleans shown did not affect the etching rates. As a result, samples were not pretreated with any aqueous clean before etching.

5.2. Objectives of Study

Experiments were performed to determine whether silicon dioxide etching using a gas phase mixture of HF and H_2O vapor occurs in the non-condensed regime and follows Langmuir-Hinshelwood reaction kinetics. Also the boundary between the non-condensed

and the condensed regimes was characterized by implementing a Box-Behnken design of experiments at 600 Torr and temperatures from 30 to 50°C.

5.2.1. Oxide Etching in the Non-condensed Regime

A set of 14 experiments was performed using 1 cm x 1 cm samples to test if oxide etching occurs within the non-condensed regime. The conditions were 600 Torr, 300 sccm, and 30 °C. 1%, 2%, and 3.2% were the HF fractions tested. Within each HF fraction, at least 4 H₂O fractions were chosen across the curves as shown in Figure 4.1 which accounted for a total of 14 runs. To ensure reproducibility all of the runs were repeated. The average etching rate and its standard error for each run are shown in Table 5.2. A graph of H₂O and HF fractions as a function of the etching rate was made and is shown in Figure 5.5. At 1% Psat of HF, the etching rates were minimal, ranging from 0.22 to 2 Å/sec in the non-condensed regime and increased up to 67 Å/sec in the condensed regime. A similar trend was observed at 2% Psat of HF. The etching rates ranged from 24 to 55 Å/sec in the non-condensed regime, and increased to a plateau at a maximum etching rate of 112 Å/sec in the condensed regime. However, at 3.2% Psat of HF, the order of magnitude of the etching rates in the non-condensed and the condensed regime was approximately the same, ranging from 135 to 161 Å/sec.

5.2.2. Langmuir-Hinshelwood Kinetics

Another set of experiments was performed at 40 and 50 °C to test if the reaction followed Langmuir-Hinshelwood kinetics. The run conditions for both temperatures

were 300 sccm and 600 Torr. The % Psat of HF and H₂O are shown in Figure 3.2 and Figure 3.3. At 40 °C, each experiment was run twice, and at 50 °C, each experiment was run once. The results for 40 °C and 50 °C experiments are shown in Table 5.3. At 40 °C, the etching rates were minimal, about 2 Å/sec, in the non-condensed regime, and increased up to a maximum to 28 Å/sec in the condensed regime. However, at 50 °C, the etching rates in the non-condensed regime and the condensed regime were the same, ranging from 2 Å/sec to 6 Å/sec. A graph of ln (etching rate) as a function of the inverse of temperature was done for 2% Psat of HF and 5% Psat of H₂O and is shown in Figure 5.6. From 30 to 40 °C, an inverse Arrhenius trend was observed. In contrast, an Arrhenius trend was seen from 40 to 50 °C, but the difference in the two data points is not big enough to substantiate whether the reaction followed Langmuir-Hinshelwood kinetics.

5.2.3. Box-Behnken Design

A Box-Behnken design of experiments study was implemented to understand the influence of temperature, %Psat of HF, and %Psat of H₂O on the etching rate. Only a few random points were run twice to test reproducibility. The results of the etching rates and the standard errors for the Box-Behnken design are shown in Figure 5.7. The data of the box was fitted with a 2nd order fit that had the following form.

$$(7) \quad \text{Rate} = a[\text{HF}] + b[\text{HOH}] + cT + d[\text{HF}]^2 + e[\text{HOH}]^2 + fT^2 + g[\text{HOH}][\text{HF}] + h[\text{HOH}]T + i[\text{HF}]T + j$$

where a, b, c, d, e, f, g, h, i and j are constants, and Rate, [HF], [HOH], and T are the etching rate, %Psat of HF, %Psat of HOH, and temperature, respectively. A nonlinear regression was done using Excel, and the fit had an R^2 value 0.90 (Appendix VI). The following equation was obtained from the regression analysis.

$$(8) \text{ Rate} = 7[\text{HF}] + 13[\text{HOH}] + 35T + .22[\text{HF}]^2 - .26[\text{HOH}]^2 - .56T^2 - .73[\text{HOH}][\text{HF}] + .9[\text{HOH}]T + .73[\text{HF}]T - 635$$

To test the validity of Equation 8, a graph of the predicted etching rates as a function of actual etching rates was done and is shown in Figure 5.8. A linear regression was done and R^2 value is 0.90. The predicted values agree adequately with the experimentally measured values.

Using equation 8, 3D graphs of the etching rate as a function of %Psat of HF and %Psat of H₂O were done for 30, 40, and 50 °C, which are shown in Figure 5.9, 5.10, and 5.11, respectively. A few generalizations can be made from the three plots.

One generalization is that the maximum etching rates at 30, 40, and 50 °C, which occurred at the highest HF fraction (12%) and the lowest H₂O (6%), were 300 Å/sec, 340 Å/sec, and 275 Å/sec, respectively. Another generalization is that at a constant HF fraction the etching rate has a parabolic dependence on the H₂O fractions. The results also show that the etching rate has a linear dependence on the HF fractions at a constant H₂O fraction.

Even though the fit had an R^2 value 0.90, two sets of experiments were done to verify the parabolic and linear trends that were observed. The conditions were the same as above. The actual and the predicted etching rates as a function of H₂O and HF

fractions were graphed and are shown in Figure 5.12 and 5.13, respectively. Figures 5.12 and 5.13 show a good agreement between the actual and the predicted etching rates.

Figure 5.1. Etching profile of a 4-inch wafer.

Figure 5.2. Etching profile of a 1 cm x 1 cm sample.

Figure 5.3. Etched oxide thickness is linear with time.

Figure 5.4. Influence of the mass flow rate on the etching rate.

Table 5.1. Summary of etch results of various aqueous cleans.

Types of Aqueous Cleans	Etching Rate (A/sec)
APM	145 ± 3
PIRANHA	149 ± 4
NONE	145 ± 14

Table 5.2. Summary of etch results at 30 °C.

Regime	%Psat of HF	%Psat of H ₂ O	Etching rate (A/sec)
Non-condensed	1	5	0.22
Non-condensed	1	8	2.5 ± 2
Condensation	1	22	67 ± 1
Condensation	1	45	62
Non-condensed	2	5	24 ± 9
Non-condensed	2	8	51 ± 14
Condensation	2	16	112 ± 6
Condensation	2	29	96 ± 18
Condensation	2	45	97 ± 7
Non-condensed	3.2	3	161 ± 5
Non-condensed	3.2	5	163 ± 1
Condensation	3.2	8	160 ± 4
Condensation	3.2	16	151 ± 1
Condensation	3.2	45	135 ± 1

Figure 5.5. Etching rates in the non-condensed and the condensed regime.

Table 5.3. Summary of etch results at 40 and 50 °C.

Regime	%Psat of HF	%Psat of H ₂ O	Etching rate (A/sec)
Non-condensed	2	5	1.55 ± 0.35
Non-condensed	2	8	1.45 ± 0.49
Condensation	2	16	9.1 ± 9.4
Condensation	2	45	27.5 ± 7.8
Non-condensed	2	5	2.5
Non-condensed	2	8	3.4
Condensation	2	16	5.9
Condensation	2	29	2.8

Figure 5.6. Natural log of the etching rate as a function of the inverse of temperature.

Figure 5.7. Etching rate results for the Box-Behnken Design

Figure 5.8. Test the validity of Equation 8.

Figure 5.9. 3-D plot at 30 °C.

Figure 5.10. 3-D plot at 40 °C.

Figure 5.11. 3-D plot at 50 °C.

Figure 5.12. To verify the parabolic dependence of the etching rate on H_2O fractions at 2% Psat of HF.

Figure 5.13. To verify the linear dependence of the etching rate on HF fractions at 10% Psat of H_2O .

PLEASE NOTE

**Page(s) not included with original material
and unavailable from author or university.
Filmed as received.**

UMI

supply of H_2O is abundant when a thick, condensed layer is present on the surface so the etching rate is higher.

As shown in Table 5.2, all the etching rates in the non-condensed regime were much smaller than those in the condensed regime except at 3.2% P_{sat} of HF, where the etching rates were approximately the same as those in the condensed regime, which was not expected. One possible reason is that the VLE curve at the high HF fractions and the low H_2O fractions is unreliable. Helms and Deal used VLE data from Munter⁽¹²⁾ and fitted them to an equation, which in turn was used to create the partial pressure diagrams. Munter had very little data at the high HF fractions and the low H_2O fractions since the H_2O concentration at high HF fractions was difficult to measure accurately using their technique. From analyzing Helms' and Deal's fitted line and Munter's data, the error in that range was about 3 Torr. As seen in Figure 3.1, the experimental points in the non-condensed regime were approximately 2 Torr beneath the curve. As a result, the supposed "non-condensed" experimental points could be in the condensed regime. The etching rate results imply that those points were in the condensed regime because the etching rates were the same order of magnitude as those in the condensed regime. Due to the uncertainty in the VLE curve the data at 3.2% P_{sat} of HF was not reliable.

Although the etching rates are small in the gas solid regime, or the non-condensed regime, they are still considered high by industry standards, which typically requires approximately 100 Å of silicon dioxide to be removed in a cleaning process or an etching rate of only 2 to 4 Å/sec. This has an important practical implication. Oxide etching using a mixture of HF and H_2O is preferred in the non-condensed regime because it can be

incorporated into a vacuum clustered-type system as discussed before. The reason is that the pump down time in the non-condensed regime is about 4 times less than in the condensation regime. In addition, the pumping requirement, such as the size of the pump, is less stringent in the non-condensed regime. The problem with running the oxide etching reaction in the gas/solid regime is uniformity.

6.2. Langmuir-Hinshelwood Kinetics

Within the non-condensed regime, we hypothesize that oxide etching follows Langmuir-Hinshelwood kinetics. A graph of the natural log of etching rate as a function of inverse temperature was plotted in Figure 5.6 to determine whether the mechanism in the non-condensed regime follows Langmuir-Hinshelwood kinetics. If an Arrhenius trend were found, it would lend support to our hypothesis. As shown in Figure 5.6, an inverse Arrhenius trend was observed from 30 to 40 °C. In contrast, an Arrhenius trend was seen from 40 to 50 °C, but the difference in the two data points is not big enough to substantiate whether the reaction followed Langmuir-Hinshelwood kinetics. In other words, the data is inconclusive. One possible reason is that the apparatus might not have worked properly at temperatures above 30 °C when performing this set of experiments.

All the experiments were carried out in three months. This set of experiments was done after the apparatus had been used for over 200 runs (3rd month). The apparatus experienced some problems in the 3rd month. One was that at high temperatures, 40 and 50 °C, a white film was deposited on the samples. The nature of the white film could not be determined unequivocally since it could not be removed with acetone, water, alcohol,

or HF. The film hindered etching or caused error readings in the oxide film thickness measurements using the Nanospec. As a result, the data was not a reflection of the kinetics.

6.3. Box-Behnken Design

A Box-Behnken design was implemented to investigate the influence of temperature, %Psat of HF, and %Psat of H₂O on the etching rate. An analysis reveals that the influence of the explored temperatures on the etching rate is inconclusive. For an example, a comparison of the maximum etching rates, which occurred at 12% Psat of HF and 6% Psat of H₂O, for the three temperatures shows that the maximum etching rate increased from 300 Å/sec at 30 °C to 340 Å/sec at 40 °C, and decreased to 275 Å/sec at 50 °C. This trend of up and down in the etching rates was observed at other HF and H₂O fractions as well. However, because of the small range of temperatures, the difference in the etching rates was too small that it was hard to know if the difference in the etching rates was due to the influence of temperature or the error in Equation 8. Equation 8, which was used to obtain the etching rates, was estimated to have an error approximately 10%. Consequently, the influence of temperature on the etching rate is not known because the range of the temperatures was too small.

Unlike temperature, the explored range of the fractions of HF and H₂O was wide enough that both the non-condensed and the condensation regime were included. Lines were drawn in for Figures 5.9, 5.10, and 5.11 to show the transition from the non-condensed to the condensation regime, according to Helms' and Deal's curve.

As discussed above, etching occurred in the non-condensed regime, but it was much lower compared to etching in the condensed regime. A similar trend was seen in Figures 5.9, 5.10, and 5.11. There was a sharp increase in the etching rate but no abrupt transition in the vicinity of the VLE curve, which signals the beginning of the condensed regime.

Within the condensed regime, the etching rate should be constant with increasing H_2O fractions. The reason is that in a condensed layer, adding more H_2O to a liquid medium should not change the H_2O fraction. In other words, the H_2O fraction is essentially the same throughout the condensed regime. As a result, etching should be fairly constant throughout the condensed regime.

However, the results show that at a constant HF fraction the etching rate was not constant, but went through a maximum point with increasing H_2O fractions. The maximum trend can be explained. H_2O is a reactant and more H_2O supply means that it promotes the reaction. However, too much H_2O poisons the reaction as well, which indicates that transport is limited. In other words, the layer of H_2O was too thick that diffusion of HF onto the surface of the wafer was hindered. As a result, the etching rate decreased.

The water fraction at which the parabolic dependence in the etching rate was maximized decreased as the HF fraction increased as shown in Figures 5.10, 5.11, and 5.12. Lines were drawn through the maximum points for the three plots. As shown in Figures 5.10, 5.11, and 5.12, the lines are almost parallel to the VLE curves, suggesting the beginning of another regime, maybe the true condensation regime.

One interpretation for the new proposed lines is that condensation of HF and H₂O occurred at much higher HF and H₂O fractions than predicted by the VLE curves. A possible reason for the shift in the lines is nucleation which is not accounted for in the VLE curves which describe the behavior of a vapor and liquid phase already at equilibrium.

Nucleation is the initial process for the formation of a new phase. Since small nuclei of the new phase have higher vapor pressures, or chemical potentials than those of a bulk, they are only stable in a supersaturated mother or vapor phase. In addition, nucleation sites on a surface must be available for nucleation to occur. As a result, nucleation of a condensed layer is heavily influenced by the character of the surface. Due to the hydrophilic nature of HF and H₂O, a hydrophilic surface offers nucleation sites that facilitate the nucleation of a condensed layer. On the other hand, a hydrophobic surface hinders the adsorption of HF and H₂O. As a result, onset of nucleation of a condensed layer can be delayed.

A H₂O test and an Auger spectrum were done to determine the nature of the surface of the samples used. A H₂O droplet was placed on the surface of an untreated sample. If the droplet beads up, the surface is hydrophobic. On the other hand, if the droplet expands out, the surface is hydrophilic. The results show that our surface was moderately hydrophobic because the H₂O droplet beaded up predominantly. An Auger spectrum was done that revealed the presence of carbon on the surface, which was another indication that the surface had some hydrophobic character. Consequently, the

formation of a condensed layer might have been delayed to higher HF and H₂O fractions because of the moderately hydrophobic nature of the surface.

The results imply that the VLE curves of Helms and Deal do not necessarily mark the transition from the gas/solid to the condensed regime for oxide etching since the liquid phase must be nucleated on the surface. In addition, the results show that near the vicinity of the VLE curves of Helms and Deal a steep increase in rate but no abrupt transition suggesting a transition to a new regime, which can be thought as the multilayer regime.

The multilayer regime had the highest etching rate. The reason is that there was a sufficient amount of H₂O to enhance etching, but not enough that diffusion through the film layer of H₂O was an issue. As mentioned above, oxide etching using a mixture of HF and H₂O is preferred in the gas solid, or the non-condensed regime. The multilayer region is still considered as the non-condensed regime since the pump down time is comparable to the gas-solid regime. As a result, the multilayer regime is favored over the gas-solid from the processing standpoint because of the high etching rate and better process control.

Our results, which imply that there are three distinct regimes that control oxide etching within the explored fractions of HF and H₂O, are consistent to a past study done by Vermeulen and his colleagues ⁽⁶⁾. They found that there are three distinct regimes, and characterized them as gas-solid, multilayer, and condensation. However, their parameters were differed from our study. Their study was limited to one HF and H₂O mixture.

In summary, even though the influence of temperature on the etching rate is inconclusive, we have mapped out three distinct regimes as a function of HF and H₂O fractions. The first region is the gas-solid regime where the etching rate is low. The

second regime, which starts with the VLE curve, is multilayer where etching is the highest. Finally, the third region, which starts after the maximum point, is the condensed regime where the etching rate is comparable to that of the multilayer region. The multilayer region may be the most viable regime from a processing standpoint because it offers high etching rates and the opportunity for good process control since mass transport effects are minimized with relatively modest pumping requirements.

CHAPTER 7. CONCLUSIONS

Helms and Deal suggested that the etching of SiO_2 using an $\text{HF}/\text{H}_2\text{O}$ vapor phase could only occur in the condensation regime. However, experiments, which were carried out in a stainless steel reactor equipped with a gas handling system, showed that oxide etching in the gas phase using a mixture of HF and H_2O proceed in the non-condensed regime where etching was lower than that in the condensation regime. Within the non-condensed regime, we hypothesize that oxide etching follows a Langmuir-Hinshelwood mechanism, however, the present results do not support this conclusion.

The results from a Box-Behnken design of experiments show that there are three different regimes where etching occurs. They are the gas/solid regime, where etching was low, the multilayer, where etching was highest, and the condensation regime, where etching was comparable to that in the multilayer. The multilayer region is the most viable regime from a processing standpoint because of the high etching rate and better process control with relatively modest pumping requirements.

Although we have tentatively mapped out the three possible regimes, more work is needed to confirm or to better understand the nature of oxide etching in the gas phase. Future work should focus on defining the surface chemistry better, which should include understanding how hydrophilic or hydrophobic surfaces affect the transition among the different regimes. In addition, FTIR studies, which can measure and identify functional bonding groups in real time, should be done in the three different regimes. Understanding the bonding nature in each regime can reveal the kinetic mechanisms that control etching in the three regimes.

REFERENCES

- 1) Bowling, R. A., S. C. O'Brien, L. M. Loewenstein, M. H. Bennett, and B. K. Bohannon, "MMST wafer cleaning", *Solid State Technology*, pp. 61 (Jan 1994).
- 2) Kern, W., Ed, Handbook of Semiconductor Wafer Cleaning Technology, Park Ridge, New Jersey, Noyes Publications, pp. 275 (1990).
- 3) Stix, G., "Toward Point One", *Scientific American*, pp. 90 (Feb 1995).
- 4) Ma, Y, M. L. Green, L. C. Feldman, J. Sapjeta, K. J. Hanson, and T. W. Weidman, *Journal of Vacuum Science and Technology B*, vol. 13, pp.1460 (1995).
- 5) Helms C. R. and B. E. Deal, "Mechanisms of the HF/H₂O vapor phase etching of SiO₂", *Journal of Vacuum Science and Technology A*, vol.13, pp. 806 (July 1992).
- 6) Vermeulen, W. J. C., L. F. Tz. Kwakman, C. J. werkhoven, E. H. A. Granneman, S. Verhaverbeke, and M. Heyns, "A HF Vapour Etch Process for Integration in Cluster-Tool Processes: Characteristics and Applications", Proceedings of the 3rd International Symposium on Cleaning Technology in Semiconductor Device Manufacturing, New Orleans, vol. 94-7, pp. 241 (Oct 1993).
- 7) Muscat A. J, A. S. Lawing, H. H. Sawin, J. Butterbaugh, D. Syverson, and F. Hiatt, "Characterization of silicon oxide etching in gas phase HF/vapor mixtures", Proceedings of the 4th International Symposium on Cleaning Technology in Semiconductor Device Manufacturing, Chicago, IL, October 8-13, pp. 342 (1995).
- 8) Holmes P. J. and J. E. Snell, Microelectronics and Reliability, (Pergamon, NewYork 1966), vol. 5, pp. 337.
- 9) Miki, N., H. Kikuhama, I. Kawanabe, M. Miyashita, and T. Ohmi, *IEEE Transaction of Electronic Devices*, ED 37, pp. 107 (1990).
- 10) Judge, J. S, "A Study of the Dissolution of SiO₂ in Acidic Fluoride Solutions", *Journal of the Electrochemical Society*, vol. 118, pp. 1772 (Nov 1971).
- 11) Verhaverbeke, S., I. Teerlinck, C. Vinckier, G. Stevens, R. Cartuyvels, and M. Heyns, "The Etching Mechanisms of SiO₂ in Hydrofluoric Acid", *Journal of Electrochemical Society*, vol. 141, no. 10, pp. 2852 (Oct 1994).
- 12) Munter P. A., T. A. Otto, and R. A. Kossatz, "Partial Pressure Measurements on the System Hydrogen Fluoride-Water", *Industrial & Engineering Chemistry*, vol. 41, no. 7, pp. 1504 (July 1949).

APPENDICES

	Page
1. Appendix I. Conversion	56
2. Appendix II. Workable Ranges of HF and H ₂ O	57
3. Appendix III. Superficial Velocity	58
4. Appendix IV. Controller's Circuit Diagram	59
5. Appendix V. H ₂ O Contactor	60
6. Appendix VI. Box-Behnken Design	61
7. Appendix VII. Manual of the Apparatus	62

Appendix I. Conversion

This calculation was done to convert % Psat of HF, H₂O, and HF to % valve position on the MFC's. (This was used to make the Excel sheet titled "Conversion")

CONDITIONS:

2.5% Psat HF	Pressure = 250 Torr
12.5% Psat H₂O	Temperature = 23 C
	Flow rate = 100 sccm

Partial Pressures:

Psat of HF @ 23 C = 859 Torr, Psat of H₂O @ 23 C = 21 Torr

$$\mathbf{HF} = (\%P_{\text{sat HF}}) * (P_{\text{sat HF}}) = (.025) * (859) = \mathbf{21.50 \text{ Torr}}$$

$$\text{H}_2\text{O} = (\% \text{ Psat H}_2\text{O}) * (\text{Psat H}_2\text{O}) = (.125) * (21) = 2.63 \text{ Torr}$$

Mass Flow Rates:

$$\mathbf{HF} = (21.50 \text{ Torr} / 250 \text{ Torr}) * (100 \text{ sccm}) = \mathbf{8.6 \text{ sccm}}$$

$$\text{H}_2\text{O} = (2.63 \text{ Torr}/250\text{Torr}) * (100 \text{ sccm}) = 1.05 \text{ sccm}$$

Fraction of H₂O in the contactor:

Total pressure in the contactor = Amount of nitrogen in the contactor

$$P_{\text{tot}} = 760 \text{ torr (atmospheric)} + 2 \text{ psi} / 14.7 \text{ psi} = 863.4 \text{ Torr}$$

Fraction of H₂O = Psat of H₂O @ 23 C/ Ptotal = (23/863.4) = .027

Amount of H₂O/N₂ line needed to be to deliver 1.05 sccm of H₂O:

$$\text{N}_2 + \text{H}_2\text{O} = 1.05 \text{ sccm} / .027 = 38.9 \text{ sccm}$$

Amount of N₂ needed in the line:

$$\mathbf{N_2 = Total\ flow\ rate - H_2O - HF = 100sccm - 38.9\ sccm - 8.6\ sccm = 52.5\ sccm}$$

% Valve position on the MFC's:

HF MFC: $(8.6 \text{ sccm} / 100 \text{ sccm max from MFC}) * (100) = 8.6 \%$

N₂/H₂O MFC: (38.9 sccm / 200 sccm max from MFC)*(100) = 19.5 %

N₂ MFC: (52.5 sccm / 300 sccm max from MFC)*(100) = 17.5 %

Appendix II. Workable Ranges of HF and H₂O

This calculation was done to find the ranges of % Psat of HF and H₂O that are in the working ranges of the MFC's. (Used the Excel worksheet titled "conversion" to calculate the % valve position)

CONDITIONS: Pressure = 600 Torr
Temperatures: 30 C – 50 C
Flow rate = 200 sccm

Maximum % Psat is:

40 % Psat of H₂O = 57.6 % Valve position
12 % Psat of HF = 82.3 % Valve position
N₂ = 0% Valve position

If the amount of HF or H₂O increased, the N₂ valve position would be negative since the total flow rate is 200 sccm.

Minimum % Psat is:

6 % Psat of H₂O = 8.6 %
2 % Psat of HF = 7.3 %

If the amount of HF or H₂O decreased, its valve position would be smaller than 5 %, which is not reliable.

Appendix III. Superficial Velocity

This calculation was done to find the superficial velocity of the gas in the reactor to determine the time that is needed for the gas to travel from the entrance to the exit.

This calculation was done for the following conditions:

Mass flow rate = 100 sccm

Pressure = 600 Torr

10 % Psat of H₂O

10 % Psat of HF

Cross section of reactor = 0.25 inch x 4 inches = 1 inches²

$$Velocity \cong \frac{100cm^3}{min} \times \frac{min}{60sec} \left(\frac{12inch}{30.48cm} \right)^3 \frac{1}{0.25inch \times 4inch} \times \frac{600torr}{760torr} = \frac{0.08inch}{sec}$$

Distance between entrance and exit = 2 inches

Time to take to travel from entrance to exit = 2 inches/(0.08inches/sec) = 25 seconds.

Etched thickness at entrance = 20320 A – 112 A = 20208 A

Etched thickness at exit = 20320 A – 5430 A = 14778 A

Process Time = 90 seconds.

Etching Rate at entrance = 20208 A/90 sec = 225 A/sec

Etching Rate at exit = 14779 A/90 sec = 164 A/sec

However, the true etching rate at exit must account the time delay. Hence,
Etching Rate at exit = 14779 A/(90seconds – 25seconds) = 227 A/sec

Appendix IV. Controller's Circuit Diagram

DC controlled solid state relay (SSR) used with temperature controller with voltage SSR Driver Output.

Appendix V: H₂O Contactor

This calculation was done to see how much H₂O is needed for the contactor.

Length of contactor = 6 inches

Diameter of contactor = 1 inch

$$Volume = 3.14 \times .5inch^2 \times 6inch \left(\frac{ft}{12inch}\right)^3 \times \frac{2.832 \times 10^4 ml}{ft^3} = 77ml$$

We want half of it.

Hence, the volume of H₂O in the contactor is about 40 ml.

Appendix VI: Box-Behnken Design

The statistical results from a multi-regression using Excel.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.95
R Square	0.90
Adjusted R Square	0.73
Standard Error	59.20
Observations	15

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	9	161341.52	17926.84	5.11	0.04
Residual	5	17525.42	3505.08		
Total	14	178866.93			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>
Intercept	-639.536	549.756	-1.163	0.297	-2052.727
X Variable 1	34.561	25.400	1.361	0.232	-30.731
X Variable 2	7.118	30.663	0.232	0.826	-71.702
X Variable 3	13.191	8.946	1.475	0.200	-9.805
X Variable 4	0.725	0.592	1.225	0.275	-0.797
X Variable 5	0.093	0.174	0.532	0.617	-0.355
X Variable 6	-0.729	0.348	-2.094	0.090	-1.625
X Variable 7	-0.563	0.308	-1.828	0.127	-1.355
X Variable 8	0.217	1.232	0.176	0.867	-2.951
X Variable 9	-0.258	0.107	-2.421	0.060	-0.532

Appendix VII: Manual of the Apparatus

This manual was written by Ming Le.

A. Operation Procedure:

- Set HF flow by turning knob 2 on MFC controller.
- OPEN v16 to vacuum the reactor and wait for pressure inside reactor to reach 0.5.
- OPEN v15, v3, v7, and v12 for 5 minutes.
- CLOSE v.15, v7, and v12.

Turn on HF:

- OPEN HF bottle for 20 minutes.
- CLOSE HF bottle.
- *(Note: make sure you close it all the way down.)*

Set the pressure inside the reactor:

- Set pressure inside the reactor by turning the knob on Pressure Controller 1.
- Turn the switch on the Pressure Controller 1 from CLOSE to AUTO position.
- CLOSE bypass valve v17.

Turn on Nitrogen (N₂) gas:

- Set N₂ flow by turning knob 4 on MFC controller.
- OPEN v10, v14, and v15 to let N₂ feed in to reactor.
- Wait until the pressure indicator on Pressure Controller 1 is the same as the pressure at which you want to operate, then follow the next steps.

Turn on H₂O+N₂:

- Set H₂O+N₂ flow by turning the knob 1 on MFC controller.
- OPEN v1, v5, and v11 to let H₂O/HF feed in to the reactor.

After turning on N₂ gas and H₂O+N₂ gas mixture, you must wait for 10 minutes before introducing HF into the reactor.

Introducing HF to the reactor:

- Set HF flow by turning the knob 2 on MFC controller.
- OPEN v7 and wait for 3 seconds before performing next step.
- OPEN v12 and start timing immediately.

B. Shut-down procedure:

- OPEN by-pass v17, and stop timing at once.
- Turn-off HF by CLOSE v12, v7.
- Then turn-off H₂O/HF mixture by CLOSE v1, v5, and v4.
- Wait for 4 minutes to make sure all unused H₂O/HF gas mixture has been purged out of the reactor.
- CLOSE v10, and v14 to stop N₂ gas flow to reactor.
- CLOSE v16 to isolate the reactor.
- OPEN v10, and v14 to pressurize the reactor back to atmospheric pressure.
- CLOSE v15, v10, and v14 when the pressure inside reactor reaches atmospheric pressure.
- OPEN reactor and take sample out.

Purging procedure:

- CLOSE the reactor by tightening 4 Allen screws
- OPEN v16 to let mechanical pump down the reactor.
- OPEN v10, v14 and v15 to let N₂ feed in to reactor.
- Wait for 2 minutes then OPEN v7 and v12 of HF line for 2 minutes.
- Then CLOSE v10, and v14 of N₂ line.
- OPEN v6 to allow N₂ sweep all unwanted remaining HF and H₂O vapor in the line for 5 minutes.
- OPEN v6, v4, and v11 to make sure all the remaining gases are pumped down for 5 minutes.
- CLOSE v6 and v4 to vacuum the whole line again, wait for 5 minutes.
- OPEN v6 and v4 again for 5 minutes.

- CLOSE **v4** and **v11** for water line.
- CLOSE **v3**, **v6**, **v7**, and **v12** to close all HF/H₂O line.
 - *(Note: Make sure to CLOSE HF bottle carefully.)*
- Bring the pressure inside the reactor to 650 Torr by CLOSE **v16** and OPEN **v10**, **v14** to feed in N₂ to the reactor.
- When the pressure inside reactor reaches to 650 Torr, then CLOSE **v15**, **v14**, and **v10**.