HF Vapor Etching and Cleaning of Silicon Wafer Surfaces

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Abstract

The objectives of this project are to understand the reaction mechanisms for oxide etching by both HF/H₂O and HF/alcohol processes and to develop a vapor phase HF cleaning process to remove metallic contamination and native oxide on a silicon surface. Although the HF vapor process has been studied intensively for past several decades, the commercial application has not been very successful due to the unknown nature of the process. This study, performed at MIT, has emphasized on finding possible applications to the semiconductor industry as a replacement to the aqueous phase cleaning processes. The ultimate purpose of this project is to demonstrate feasibility of the HF vapor process for a vacuum compatible and clustered cleaning process.

In this study, the etching experiments were carried out in a stainless steel vacuum chamber connected to a vacuum wafer transfer system. Samples were introduced through a load lock chamber and transferred to the HF vapor reaction chamber. The base pressure of the system was maintained under 10⁻⁷ Torr. The system can handle sample sizes between 1 cm square and 10 cm diameter silicon wafers. The etching rates were measured by an in situ ellipsometer installed on the HF vapor reactor.

Ellipsometric measurements suggest that oxide etching can occur without a condensed layer or with a condensed layer on the oxide surface. The etching rates of oxide in the condensed regime were very high (3,000-12,000 Å/min) compared to the gas phase regime (0-300 Å/min). The etching regime in which a condensed layer is formed is a function of not only the partial pressures of HF and H₂O in the feed gas, but also a function of the mass transport of the products from the sample in the gas phase. We have categorized two different etching regimes: the gas phase regime and the condensed phase regime. In the gas phase etching regime, reactant molecules are adsorbed on the oxide surface in sub-monolayer, monolayer, or multilayer films.

In the multilayer adsorption regime, the etching rate is usually low (typically 0~400 Å/min) and is linearly proportional to the partial pressure of HF and H₂O. The etching rate in this regime is greatly affected by the temperature of the substrate. The mass
transfer rate limits the etch rate of oxide in the multilayer adsorption regime. In the sub-monolayer or monolayer adsorption regime the etching rate is described by Langmuir-Hinshelwood kinetics. The etching rate is governed by surface kinetics in this regime. Advantages of this etching regime are: 1) smoother etched surface, 2) low selectivity to TEOS, 3) haze-free etched surface, 4) no metal attack, 5) perfect removal of native oxide, and 6) vacuum compatible process. The HF vapor process in this regime is an ideal process for contact cleaning and polymer removal after metal or via etching.

Electrostatic charge on the wafer surface affects the etching reaction significantly in the non-condensed regimes. A positively charged surface enhanced the etching reaction in the submonolayer and monolayer etching regimes. Direct ionization of HF on the oxide surface is responsible for the enhancement in this regime. A negatively charged surface mainly enhanced the etching in the multilayer regime. A thicker multilayer, induced by the formation of fluorosilicate, is responsible for the etching enhancement in this regime.

We have demonstrated a successful removal of sodium from both oxide and silicon surfaces using HF/H₂O, HF/IPA, and HF/H₂O/SiF₄ processes in reduced pressure operation. All experiments were performed in a vacuum environment and in-situ XPS was used to measure the surface concentration of sodium. The sodium contamination on oxide surface was successfully removed by both HF/H₂O and HF/IPA processes. The HF/H₂O process could not remove all of sodium contamination on a silicon surface. The addition of SiF₄ in the HF/H₂O process greatly enhances the cleaning effect, reducing Na contamination below the detection limit of our XPS, even on a silicon surface.

Based on our study, we have reported a true gas phase and vacuum compatible HF vapor process, operated in the monolayer adsorption regime at elevated temperature. A successful removal of RIE residue was performed with a combined cleaning procedure of HF vapor and ashing process. This combined process is a perfect dry cleaning process for contact cleaning method. This process sequence is ideal for a vacuum cluster configuration in which a single wafer is processed at a time and is not exposed in the ambient.

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Chapter 1 Introduction

1.1 Objective

The objectives of this project are to understand reaction mechanisms for oxide etching by both HF/H₂O and HF/alcohol processes and to develop a vapor phase HF cleaning process to remove metallic contamination and native oxide on a silicon surface. Although the HF vapor process has been studied intensively for the past several decades, a commercial application has not been very successful due to the unknown nature of the process. This study, performed at MIT, has emphasis on possible applications to the semiconductor industry as a replacement of aqueous phase cleaning processes. The ultimate purpose of this project is to provide a feasible HF vapor process for a vacuum compatible clustered cleaning process.

1.2 Cleaning Process in Microelectronic Manufacturing

Wafer cleaning processes have become more important than ever before as the critical size of microelectronic devices shrink. In fact, cleaning technologies have become one of the key technologies in the fabrication of ULSI circuits. In order to maximize the production yield, cleaning processes are required to remove unwanted contamination on the wafer surface without damaging and consuming the substrate. Unwanted contamination is generally introduced from other processes, ambient or human beings in the cleanroom area. In contemporary manufacturing process, approximately one third of the total manufacturing process steps are cleaning steps, consuming a large amount of time and money.
The traditional cleaning processes are based on aqueous phase cleaning processes, which use acids, bases, and mixtures of various chemicals. This aqueous phase cleaning methods have been very effective in manufacturing. However, cleaning of submicron features has become ineffective and the selection of chemicals is limited due to the ever increasing number of metal layers. In addition, environmental impacts and safety concerns became problematic, encouraging the development of vapor phase cleaning methods.

1.2.1 Contamination in Semiconductor Manufacturing

Most contamination on wafer surfaces are particles, organic residue, contaminant films or adsorbed metal ions, most of which are come from the other process steps. Current cleaning methods can remove this contamination very effectively. However, the defect responsible for more than 80% of device failures is submicron sized particle contamination in lithographic processes. These can result in a line-bridge form, an abnormal growth of CVD layer, and a local implantation blocking. Particle contamination usually comes from equipment, processing gases, piping, and handling of wafers by humans. Mechanical movements of processing equipment and wafer containers are a common source of particles.

Metal ion contamination generally degrades electrical performance of devices. This ionic contamination originates from chemicals, de-ionized water, and humans. Acid based cleaning solutions can effectively reduce metal ions adsorbed on the silicon surface to less than the detection limits of most sophisticated analytical tool if it is used properly.
Photoresist residue after resist stripping is another serious form of contamination. If photoresist remains on the surface and undergoes a high temperature process such as oxidation, all the wafers and equipment in that process will become contaminated. In order to achieve perfect removal of photoresist, the industry uses an extreme condition of acid chemicals such as “piranha” (mixture of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$) and “SC1” (mixture of $\text{NaOH}$, $\text{H}_2\text{O}_2$, and DI water) solution.

Contamination control is more important than the cleaning of contamination. If the wafer surface is perfectly clean during all entire processing steps, the necessity for cleaning is reduced. Moreover, the prevention of contamination is generally easier than the cleaning. Therefore, maintaining a contamination free manufacturing environment and obtaining clean processing conditions must be achieved prior to enhancing the cleaning process.

1.2.2 Pre-Diffusion or Oxidation Cleaning

The chemical cleaning of silicon wafers prior to high temperature processes, such as diffusion, oxidation, anneal, and LPCVD, is very important in order to make contamination free films. It is generally performed by a wet chemical cleaning in a dip type processing tool. The most popular wet cleaning methods are based on peroxide solutions mixed with an acid or alkaline solution, known as the RCA cleaning process, developed by Kern. Another widely used cleaning method is the piranha clean, which is a mixture of sulfuric acid and peroxide solution for the removal of organic contamination. A dilute HF solution is also widely used for the removal of native oxide and metallic impurities on the wafer surface. Wet cleaning processes are performed mostly by a
simple immersion technique. A batch of wafers is immersed in the liquid container of a cleaning solution. The cleaning chemicals are immediately washed away by overflow quenching with pure water before the wafers are transferred to a flow rinse system or other cleaning solution.

Pre cleaning is generally achieved by the peroxide based SC1 and SC2 solution at an elevated temperature. SC1 solution is a mixture of NaOH, H₂O₂, and water at 50 – 80 °C, which is designed to clean organic residues and particles on the surface. Particles are removed from the surface by a slow etching of the silicon surface under the particles and the highly penetrating effects of the cleaning solution due to low surface tension. When combined with a sonic wave, the particle removing effect of SC1 solution can be enhanced. Disadvantages of SC1 cleaning include formation of a native oxide on the silicon surface, incomplete removal of metal contamination, and attacking the silicon surface when H₂O₂ is not mixed in the solution. Metal ion contamination is removed by the SC2 solution, which consists of HCl, H₂O₂, and deionized water. The highly acidic solution dissolves metal ions easily into the solution, rather than leaving them on the surface.

Native oxide layers must be removed before any high temperature processes because a thin layer of oxide is always present on a silicon surface and metal contamination is sometimes trapped in this native oxide layer. A dilute HF solution is generally used to remove native oxide in a pre cleaning process. When the HF solution etches the native oxide layer, the contamination is also removed from the surface, resulting in a very clean surface. Therefore, the HF solution must have an extremely high purity to make a pure surface. The bare silicon surface which is cleaned by HF solution is
highly hydrophobic and very susceptible to organic and particle contamination. As soon as the pre cleaning process is finished, one must proceed to the next process immediately to prevent cross contamination and regrowth of a native oxide layer from the ambient air.

### 1.2.3 Photoresist Stripping

Photoresist must be removed from the wafer surface as soon as possible without leaving any contamination and harming the substrate after plasma etching, ion implantation and other processes involving photoresist. This process is generally performed by an acidic stripper, organic stripper, O$_2$ plasma asher or a combination of the previous process.

An O$_2$ plasma is widely used to remove damaged photoresist from plasma etching processes and ion implantation processes, regardless of the kind of substrate. It has some advantages over conventional wet stripping process, including safer operation, cheaper cost, environmentally friendly, and no attack of the underlying substrate. In industry, O$_2$ plasma process is used in combination with wet stripping processes to accomplish complete photoresist removal.

The common acidic solution used in industry for removing photoresist is a mixture of H$_2$SO$_4$ and an oxidizer, such as H$_2$O$_2$, known as a piranha cleaning solution. This is a very powerful solution that can dissolve photoresist instantly. One disadvantage of this process is that it can not be used with metal layers because it will also dissolve the metal layer.

Organic stripper performs photoresist stripping by the solvating effect of an organic solution breaking the bond structure of the photoresist. Since these solvents do not attack the metal layer, organic stripper is used on the layers involving metals.
Drawbacks of an organic stripper are low stripping rates, a need for organic waste disposal and expense. Some organic strippers can still corrode metal surfaces, so care must be taken to select and operate this process.

1.2.4 Particle Removing Process

Particle cleaning is generally performed by a SC1 cleaning solution and brush scrubbing technique. When a sonic wave is applied to a SC1 solution tank at a frequency of approximately 1 MHz, the removal efficiency of the SC1 solution is greatly enhanced, removing more than 99% of particles from the surface. The sonic waves are transferred though the liquid medium in a direction parallel to the immersed wafers, generating pressure waves. These sonic waves are generated from a piezoelectric device usually attached to the bottom or side of the solution tank. Since this doesn’t work with pure water, it is not an effective tool when it applied to metal layers.

The scrubbing process operates by a rotating brush on the spinning wafer while dispensing water or chemicals. It is very effective tool for cleaning particles on a very flat surface. Liquid must be supplied between the brush and the wafer to prevent direct contact of the brush to the wafer, which can cause excessive scratches or damage. This process is now widely used in microelectronic industry to clean particles after CVD, CMP, and metal sputtering processes.
1.3 *Wet chemical Cleaning*

1.3.1 *Wet Cleaning Methods*

Wet benches are the most common method for performing the wet chemical cleaning process by simple immersion technique. Wafers are immersed in a series of baths, which are filled with chemicals or DI water. A cassette of wafers is dipped in a chemical solution for a period of time, followed by a DI water-rinsing step to wash residual chemicals from the wafer and cassette. After the chemical process and rinse steps, wafers are dried in a dryer to complete the whole cleaning process. Figure 1.1 shows a typical wet bench commonly used in semiconductor manufacturing.

![Wet Bench Diagram](image)

Figure 1.1 A typical full automatic wet bench designed to perform RCA cleaning and piranha cleaning process. (Reprinted from the web site of Verteq, Inc.)

Most cleaning chemicals and DI water are generally heated to maximize the cleaning effect. Circulation and filtration are also employed to enhance the agitation effect and maintain low particle levels in the solution. It is believed that more than 90%
of chemical cleaning process are performed in a wet bench type machine. In a fully automatic wet bench, a cassetteless transfer system is widely used to handle large wafers, reducing the bath size, chemical consumption and cross contamination from the cassette.

Spraying chemicals on spinning wafers is another way of achieving wet cleaning process. FSI Corporation first introduced this type of machine. The main advantage of the spraying tool is its compact size. It also uses smaller amounts of chemicals to do the same task. Since the processing chamber is isolated, it is safer than a wet bench. All chemical processes are performed in a single chamber including water rinse and drying. Despite these advantages, this process machine is not as popular as conventional wet benches in critical cleaning processes such as pre-oxidation cleaning due to particle generation from moving parts inside the chamber.

A single wafer cleaning process system has been introduced in industry, which is similar to the spinning processor widely used for photoresist coating and developing. A single wafer is mounted on a rotating chuck and cleaning chemicals, including rinse water, are dispensed from a nozzle located above of wafer. Because single wafer processing reduces the total throughput and increases the waiting time for the first wafer, this system has not been very successful in a manufacturing environment.

1.3.2 Wafer Drying Methods

Wafers cleaned by wet chemical cleaning processes must be dried before proceeding to another process. Spin drying is the most common method in which centrifugal force from spinning wafers at high speed removes large amounts of water from the wafer surface instantly. The pressure drop and high mass transfer rate inside the drying chamber resulting from high speed air flow evaporates the remaining thin layer of
water. In this method, particles can be generated from the mechanical moving parts in the drying chamber. Electrostatic charge build up due to high speed air flow is a serious problem for particle attraction. Water spots are sometimes generated on the wafer after the drying process, due to residue remaining after the drying of the thin water layer in which gaseous contamination is dissolved. A water spot or watermark is a killer defect in industry that can be minimized by using very high rotating speed or supplying purified N\textsubscript{2} instead of using air. Spin drying is the most common drying method in industry because of its simplicity, low cost of operation and easy of maintenance.

Vapor drying is an alternative method for the drying process. Water layers on the wafer are replaced by highly volatile solvents by placing wafers in a chamber in which the solvent vapor is evaporated from the bottom of the chamber by heating. Then, wafers are moved to the ambient where the solvent condensed on the wafer surface is easily evaporated due to its high volatility. Since this process doesn’t involve any mechanical movement, particle generation is minimal compared to the spinning method. This process is not likely to make water spot on the wafer surface either.\textsuperscript{2} The solvent used in vapor dryers is primarily isopropyl alcohol (IPA). There is some concern about carbon residue after the drying and safety issues due to the high flammability of the solvent. Presently, industry is shifting drying processes from the spinning method to vapor drying because of its low particle generations and watermark free surface.

A drying method based on the surface tension and capillary action of water has been developed by industry. In this method, wafers are slowly pulled from the water surface where wafers are initially rinsed. Capillary action of water pulls the water layer from the wafer surface to the water bath. Remaining water on the wafer is evaporated
from the surface because the water involved in this process is generally heated. This drying technique has not been widely accepted to the industry due to the unknown mechanism and its questionable drying performance.

1.4 **Dry Cleaning Method**

1.4.1 **Drawbacks of Wet Chemical Cleaning**

The wet cleaning methods mentioned in the above section are the most commonly used technologies in the semiconductor industry now. They have excellent particle removing abilities, better metal removal efficiency and higher productivity than any other processes. However, the wet cleaning method itself has some inherent drawbacks that may affect to the manufacturing of future generation microelectronic devices.

As the device size is shrinking, it has become more and more difficult to clean submicron or high aspect ratio features with aqueous phase cleaning methods. Drying of the rinse water after the cleaning process is another difficult task on a small-scale device. In order to dry water in a deep trench, it needs to be evaporated from the trench, which is likely to leave dissolved contamination behind the structure, causing serious device problems.

It is anticipated that vacuum clustering will be the next generation manufacturing tool. Process integration is easily accomplished by a vacuum cluster tool without having to expose wafers in the air. This integrated processing method enhances the productivity and reduces the cross contamination level. Since wet cleaning involves aqueous materials, it is impossible to incorporate into a vacuum cluster tool, preventing the
semiconductor industry from introducing a real in-line manufacturing tool. Without a dry cleaning module in a vacuum cluster tool, it is impossible to perform a series of processes in a vacuum environment.

Wet benches are one of the largest machines in a cleanroom, occupying up to 10'×30' in footprint, or 1/3 of the total cleanroom area. Wet benches are also suspected to degrade cleanroom quality by corroding metal parts of the building and other processing equipment. If a dry cleaning process is fully employed, the size of the cleanroom can be reduced, significantly saving the initial investment cost.

Finally, wet cleaning processes use large amounts of high purity chemicals and DI water, which are very expensive. In addition, the disposal cost of such chemicals has become an environmental issue. A typical fabrication line uses huge quantity of chemicals and water, as listed in Table 1.1. It is believed that half of current wet cleaning processes can be replaced by dry cleaning methods that use virtually no liquid phase natural resources.

Table 1.1 Typical chemical and water consumption in a current semiconductor manufacturing facility producing 20000 of 8" wafers per month.

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<thead>
<tr>
<th>Chemical</th>
<th>Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>23,000,000 gal/month</td>
</tr>
<tr>
<td>H2SO4</td>
<td>10,000 gal/month</td>
</tr>
<tr>
<td>NH4OH</td>
<td>3,500 gal/month</td>
</tr>
<tr>
<td>HF</td>
<td>4,000 gal/month</td>
</tr>
<tr>
<td>H2O2</td>
<td>13,000 gal/month</td>
</tr>
</tbody>
</table>
1.4.2 Gas or Vapor Phase Cleaning

HF vapor cleaning is the most common vapor phase cleaning process that has been studied. The purpose of HF vapor treatment is mainly to remove native oxide or etch oxides selectively. A HF vapor process is now used for some specific applications but it is not fully applied to manufacturing process due to certain problems. Most serious problem is the residue remaining on the wafer surface after clean. It is necessary to add a water rinse step after the process, preventing operation in perfectly dry conditions.

A HF vapor cleaning process can be performed in situ using vapor phase HF with \( \text{H}_2\text{O} \), or an alcohol, which could etch oxide films as an aqueous HF does. Little is known about removing metallic contamination by this technique. Although the etching and cleaning mechanism has been studied by numerous groups,\(^6\),\(^7\),\(^8\),\(^9\),\(^10\) how the HF vapor process removes native oxide and cleans hydrocarbon contamination is poorly understood. It has also been demonstrated that HF and alcohol processes operating at a reduced pressure can minimize the surface residue and provide better controllability over a HF/\( \text{H}_2\text{O} \) process, due to the high vapor pressure of alcohol.\(^11\),\(^12\)

1.4.3 UV Excited Cleaning

Photochemically excited dry wafer cleaning is a gas phase cleaning method which enhances the chemical reactivity of gases by photolysis of otherwise less reactive gases. A low-pressure mercury lamp is a common source of UV light, to generate photons to dissociate or excite gas molecules. This process is generally vacuum compatible and does not require any post or pre treatments. Recently, a surface photolysis mechanism has been suggested by Lawing, \textit{et al.}, to clean Cu contamination from the silicon surface.\(^13\) UV/O\(_2\) and UV/Cl\(_2\) have been considered as promising technology to remove
contamination from the wafer surface in the gas phase. UV/O\textsubscript{2} is the most widely used technology now by industries to avoid radiation damage from O\textsubscript{2} plasmas during organic cleans.\textsuperscript{14} However, it is used for removal of photoresist rather than surface cleaning. UV/Cl\textsubscript{2} technology can be considered as a promising technology for removal of metallic contamination even though the mechanism is poorly understood.\textsuperscript{15}

**1.4.4 Other Cleaning Methods**

Remote plasma cleaning can be a good alternative cleaning process for low temperature surface cleans. By generating an active plasma in a region remote from the substrate, active chemical species can diffuse to the substrate, which reduce the ion induced damage on the substrate.\textsuperscript{16, 17} More recently, a high density plasma source such as an ECR(electron cyclotron resonance) can be applied at low pressure, for low temperature cleaning.

Particle cleaning by a CO\textsubscript{2} jet and cryogenic Ar gas are being developed as a dry scrubbing method. High pressure CO\textsubscript{2} is directed toward the substrate to be cleaned forming very small CO\textsubscript{2} particles, which collide with particles on the surface, transferring enough momentum to remove the particle contamination from the surface.\textsuperscript{18, 19} Instead of using CO\textsubscript{2} gas, purified Ar and N\textsubscript{2} mixtures which are cooled and expanded through a nozzle to create the same solid dusts have been developed to achieve gas phase particle cleaning.

Supercritical fluids have excellent physical properties to apply to wafer cleaning.\textsuperscript{20} Supercritical fluids have liquid-like solvating effects and gas-like transfer properties allowing rapid penetration into submicron features. Particles and organic contamination can be easily displaced from small features by cycling the pressure difference of
supercritical fluid. CO₂ is commonly used as a supercritical fluid. It easily becomes a supercritical fluid at relatively low pressure and temperature. It also has low viscosity, high diffusivity and low surface tension, in addition to its low cost and chemical inertness. Bok, et al.²⁰ have reported successful removal of organic contamination, metal ions and particles with more than 98 % of efficiency using supercritical CO₂.

1.4.5 In-Situ Cleaning in a Cluster Tool

An in situ cleaning process is the combination of two or more sequential processes in manufacturing of semiconductor devices in a controlled environment. Thus, the cleanliness of interfaces between processes is preserved by controlling the ambient and surface cleanliness through the multi-process sequence.²¹

The cluster-tool configuration, shown in Figure 1.2, typically consists of a central handling system which transfers wafers from a loading chamber to various process chambers. The wafers are exposed to only a vacuum environment during transport. These cluster-tool type configurations are generally radial or linear. Future device structures may not be fabricated without reducing contamination level significantly and removing of the presence of natural oxide, which can only be achieved by controlling the ambient which wafers are exposed to during fabricating. If we are able to use a dry cleaning process for fabricating devices, a cluster-tool could be the most favorable method for numerous applications such as contact cleaning before metal deposition, pre-oxide cleaning before gate oxidation followed by polysilicon deposition, and pre-epitaxial cleaning. It is certain that fully automated and single wafer processing will be the next generation fabrication method, using cluster-tool type machines.
1.5 Etching Mechanism of HF Vapor Process

The purpose of this study is to understand the mechanism for HF vapor etching of oxide films. Compared to the liquid phase etching process, the HF vapor phase etching of oxide films is a relatively new technology which is being studied intensively. It is understood that the etch rate of oxide films exposed to anhydrous HF is critically dependent on the concentration of $\text{H}_2\text{O}$ in the etch ambient. It is also known that a mixture of HF and $\text{H}_2\text{O}$ or other solvent is required to obtain controlled etch rates.

This etching process can occur in both a gas phase regime and a liquid phase condensation regime. In the gas phase regime, etching is taking place through a gas-solid reaction that is activated by adsorbed water molecules on the surface. In the condensation regime, HF/ $\text{H}_2\text{O}$ vapor is condensed on the surface, forming a liquid film.
and the etching process occurs in a way similar to liquid phase etching. Adsorption and condensation are critical steps in the etching process. 

![Ellipsometric signal change of water adsorption on the oxide surface.](image)

Figure 1.3 Ellipsometric signal change of water adsorption on the oxide surface. Water vapor is supplied into the reactor at the saturated vapor pressure.

As shown in Figure 1.3, we can measure the presence of a condensed film on the oxide surface by in-situ ellipsometry, although it is difficult to measure an exact thickness of the films. It shows us that there are three adsorption regimes which are the sub-monolayer adsorption regime, the monolayer adsorption regime and the condensed layer regime.

Figure 1.4 shows three different adsorption regimes. The etching mechanisms of three adsorption regimes, depending on the partial pressures of HF and \( \text{H}_2\text{O} \), are very distinct. This is also be affected by the kind of solvent used, such as IPA or methanol.

The overall etching reaction of oxide by HF can be written as follows.
\[ \text{SiO}_2 + 6\text{HF} \Leftrightarrow 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6 \]  
\[ \text{SiO}_2 + 4\text{HF} \Leftrightarrow 2\text{H}_2\text{O} + \text{SiF}_4 \]

It is clear that the etching of oxide by HF/H\(_2\)O vapor process is quite complex. It is also very difficult to describe a detail etching mechanism of oxide by HF vapor process from the above equations.

![Figure 1.4 Schematic illustration of various adsorption regimes](image)

Helms and Deal reported the mechanism of HF/H\(_2\)O etching and cleaning of an oxide surface in the condensed regime. They claim that the role of water is to provide a condensed liquid layer on the surface, which is crucial for the process. The etching reaction is performed in the condensed layer like aqueous HF etching and the etch rate is a function of the aqueous concentration of HF in the condensed layer, as written in the following equation.

\[ \text{Etch rate} = [\text{HF}] + 7[\text{HF}_2] + 0.3[\text{HF}]^2 \text{ (Å/ sec)} \]  

C. S. Lee, et al. modeled the mechanism of oxide etched by HF/CH\(_3\)OH and H\(_2\)O in a gas phase etching regime at reduced pressure by assuming that the etching rate is limited by the ionization reaction between the adsorbed HF and H\(_2\)O. They also described
the etch rate based on a gas-solid reaction which is a function of the amounts of adsorbed HF and H$_2$O molecules on the oxide surface. They concluded that the model, described in the following equations, predicts the etch rate and selectivity of oxide precisely.\(^{25}\)

\[
2\text{HF}(\text{ads}) + \text{H}_2\text{O}(\text{ads}) \rightarrow \text{HF}_2^-\text{(ads)} + \text{H}_3\text{O}^+(\text{ads})
\]

(1.4)

\[
\text{Etch rate} = k \theta_{\text{HF}}^2 \theta_{\text{H}_2\text{O}}
\]

(1.5)

Vermeulen, \textit{et al.} recently studied the etching characteristics of oxide etching at three adsorption regimes: gas phase, enhanced adsorption and condensed regimes.\(^{22}\) They reported that low etch rate and high selectivity between thermal oxide and TEOS are achieved in the gas phase regime while high etch rate and low selectivity are obtained in the condensed regime.

The reactivity of HF molecules on the oxide surface is catalyzed by hydroxyl groups or water molecules on the surface. This mechanism is proposed graphically in Figure 1.5, from Muscat.\(^8\) Since the water is liberated, the reaction can be considered as an autocatalytic reaction. Muscat, \textit{et al.} recently showed the presence of autocatalytic reaction in the gas phase regime, where the reaction product on the oxide surface enhances the etching reaction.
Figure 1.5 Proposed reaction mechanism of oxide etching for HF/H₂O.

1.6 Primary Goals of the Study

The study of the oxide etching mechanism by the HF/H₂O vapor process is the primary goal of this study for different adsorption regimes. Different characteristics of various etching regimes have also been investigated in this experimental study. The second goal of this study is to develop a processing condition for in situ HF vapor contact cleaning as a post RIE treatments. Finally, the metal removal by HF vapor process is also covered by this study.

HF vapor etching of oxide in the condensed regime is discussed primarily in Chapter 3. Etching characteristics in the non-condensed regime is described in Chapter 4. The surface state dependencies of the etching reaction in the monolayer adsorption regime are discussed in Chapter 5. In Chapter 6, sodium removal from the wafer surface is described in detail.
From these experimental studies, an in situ HF vapor process for contact cleaning, via contact cleaning and polymer removal after metal etching processes is suggested in Chapter 7.

1.7 References


Chapter 2 Experimental

2.1 Integrated Processing Apparatus

In our laboratory, a large in situ vacuum cluster tool illustrated in Figure 2.1 was constructed. The cluster system consists of 11 individual processing chambers, including the HF vapor processing chamber. Most chambers can process both small samples and 4” wafers. These samples can be transferred to the system through the load lock chamber by a cart that runs in the center transfer tube. The wafers are transferred to any chamber through the transfer tube without exposure to ambient air. Center transfer tube is maintained under a high vacuum environment of $10^{-8} - 10^{-9}$ Torr by two cryogenic pumps. All chambers have an individual gas supply system and electronic controllers, which allows independent operations while other processing chambers are working. All gas lines and processing chambers are pumped by a mechanical pump connected to the individual chambers by a conduit.

Figure 2.1 Schematic diagram of the Integrated Processing Apparatus.
In this work, we have used the HF vapor chamber, XPS chamber, Plasma etching chamber, Sputter deposition and UV/Cl\textsubscript{2} chamber. Each chamber will be described in detail in the following sections.

2.2 HF/Vapor Chamber

In this study, the etching experiments were carried out in a stainless steel vacuum chamber connected to the vacuum wafer transfer system. Samples were introduced through a load lock chamber and transferred to the HF vapor reaction chamber. The base pressure of the HF vapor was maintained under $10^{-7}$ Torr. The system can handle sample sizes between 1 cm square and 10 cm diameter silicon wafers. Figure 2.2 shows a schematic of the HF reactor and gas handling system. The process gases were introduced through a specially designed gas handling system in which water vapor is supplied directly from the water tank via a mass flow controller without using a carrier gas. Anhydrous HF and N\textsubscript{2} were supplied to the reactor through parallelly connected mass flow controllers. All mass flow controllers were calibrated by measuring the rate of pressure rise of the reaction chamber. The entire gas handling system, including mass flow controllers was maintained at 55 to 120 °C to prevent condensation within the system. The pressure of the reaction chamber was controlled by a throttle valve and measured by a capacitance manometer.

The etching rate of oxide was measured using \textit{in situ} spectroscopic ellipsometry (J. J. Woollam M44) to monitor the oxide thickness in real time. Thermally grown oxide films on 10 cm wafers were used for the experiments. The samples for these experiments were 2.54 cm square samples or full 10 cm wafers. Each sample was subjected to an SC1
clean and followed by 100:1 dilute HF cleaning in a spin processor. Before each run, dry nitrogen was introduced into the reaction chamber to stabilize the pressure. The change in film thickness as a function of time was measured by in situ ellipsometry at 44 different wavelengths.

Figure 2.2 Schematic of the HF vapor etching chamber and gas handling system. All gases are metered with mass flow controllers. The lines and mass flow controllers are heated so as to prevent condensation in the gas delivery system. The sample is mounted on a temperature-controlled surface that is cooler than the feed gas or chamber walls. Ellipsometry is used to monitor the etching rate and formation of films on the surface during etching.

HF and water partial pressures were varied to study both the gas phase and condensed phase etching regimes. The etching rate has also been measured at different total pressures and flow rates to investigate the effects of mass transport of reactant and product gases. The diameter of the gas showerhead was also varied to study the mass
transport effects. Temperature of the sample was held constant during processing using a water cooled sample holder at a temperature lower than the chamber wall, thereby preventing condensation on the chamber walls.

We have used two showerheads. A small one is 2” in diameter and a bigger one is 4” in diameter. The reactant gases are supplied from the outside of the chamber through a \( \frac{1}{4} \)" stainless steel tube and distributed by a stainless steel screen attached on the showerhead in order to obtain evenly distributed flow over the 4” wafer. A stainless steel baffle located inside the showerhead blocks a possible jet stream from the stainless steel tube.

An order of magnitude calculation of pressure drop for both inside showerhead and the stainless steel screen can give some valuable information about the flow uniformity across the showerhead. The pressure drop inside the showerhead was calculated by the following equation provided by Goodlin.\(^1\)

\[
\Delta P_{\text{max}} = \frac{3\eta Q}{4\pi H} \ln \frac{R_2}{R_1},
\]

where \( \Delta P_{\text{max}} \) is the maximum pressure drop between the center and the edge of inside showerhead, \( \eta \) is viscosity of the gas, \( Q \) is the flow rate, \( H \) is the gap height, and \( R_2, R_1 \) are the radii of the showerhead and the gas tube, respectively. For our processing condition, the maximum pressure drop inside the showerhead is approximately 0.1 Pa compared to the operating pressure on the order of \( 10^4 \) Pa. In order to calculate the pressure drop across the small hole in the stainless steel screen, we assumed that the gas flow is in a viscous flow regime due to the high operating pressure. The pressure drop is given by the following equation.
where $D$ is the diameter of hole, $l$ is the length of hole, and $P$ is the pressure in the showerhead. The calculated pressure drop for these holes is about 10 Pa. Since the pressure drop through the screen hole is at least two orders magnitude higher than that inside the showerhead. It is thus concluded that almost the flow resistance is in the showerhead screen and not in the showerhead. Therefore, gas flow is uniformly distributed across the screen over the 4” wafer for our processing conditions.

Figure 2.3 Cross section of the showerhead used in this experiment. A stainless steel screen is used to distribute the gas stream uniformly over the sample surface. The perforated stainless steel screen has 9% open area, 0.008” thickness with 0.007” diameter holes, and a 0.022” hole pitch with 60° orientation.
2.3 *Detailed Experimental Procedure*

The HF vapor reactor can etch an entire 4” wafer or a 1”x1” small sample which is diced using diamond scribe pencil from 4” wafers. For the etch rate measurement, 5500Å of thermal oxide grown on 4” silicon wafers is used.

Samples are cleaned by a CO$_2$ ice jet. The sample is placed on a vacuum holder to prevent movement when the high pressure CO$_2$ is applied to the sample. Then, the high-pressure gun held in one hand and aimed away from sample and people. The ice stream is then formed and stabilized before the sample is cleaned. The typical cleaning procedure involves manually positioning the nozzle over one end of the sample and then moving the stream from side to side across the entire surface area. The left to right motion is performed as the nozzle is advanced toward the far side of the sample. The incident angle is generally between 30 and 45 degree from normal to the surface and the distance between the nozzle and the sample is maintained at about 1-1.5” during cleaning. The cleaning time is 1-2 min for a 1”x1” sample and 3-4 min for a 4” wafer.

For transfer a 4” sample cleaned by the CO$_2$ jet is placed on the specially designed sample holder for our system. A small sample is placed on a 4” stainless steel wafer, which goes on the sample holder. The sample is transferred from the load lock chamber to the transfer tube in the vacuum clustered system at less than 1x10$^{-8}$ Torr. The load lock chamber is pumped down below 1x10$^{-7}$ Torr before transferring to the tube. Then, the sample is placed on the sample holder in the HF vapor chamber where wafer temperature is controlled by circulating water.

When the sample is placed in the HF vapor chamber, the oxide thickness is measured by an in situ ellipsometer. N$_2$ is supplied to bring the chamber up to the
operating pressure while the pressure controller is on. Next water vapor is supplied to the chamber, and immediately HF vapor is supplied to the chamber while measuring oxide thickness with respect to time in order to calculate the etching rate. When HF gas is supplied, the flow rate is increased from 0 to the target flow rate slowly to prevent an overshoot of the flow rate, which takes about 5-10 sec. The process is then continued for 5-10 min, depending on the etch rate of the oxide for etch rate measurements. For surface cleaning, the process is generally performed for less than 2 min. Usually, the etch rate is calculated using data taken from 2 min for 4-5 min to minimize an initial effect due to different concentration of reactants near the sample in the beginning. When the process is complete, the chamber is immediately pumped down through the mechanical pump and the MFCs are closed. When the pressure reaches to the base pressure of the mechanical pump, the gate valve for the mechanical pump is closed and the gate valve to the turbo pump is opened. When the pressure of the chamber is below $5 \times 10^{-6}$ Torr, the sample can be transferred to the transfer tube and moved to an other chamber for further analysis or removed from the clustered system.

### 2.4 XPS Analytical Chamber

X-ray photoelectron spectroscopy (XPS) is used to analyze surface atomic composition of the cleaned sample. The rotation of the sample holder in the XPS chamber allows for angle resolved surface analysis in this system. Angle resolved XPS data enhances the surface sensitivity of atomic compositions. The angle between the sample and the analyzer can be adjusted by rotating the sample holder. The angle
between the X-ray source and the electron analyzer is fixed at 67°. The take off angle of secondary electrons is adjusted 90° to a glancing angle of 20°.

![Schematic diagram of the analytical chamber.](image)

Figure 2.4 Schematic diagram of the analytical chamber.

A photon of sufficiently high energy can ionize an atom and eject free electrons from the solid surface. The kinetic energy of ejected electrons, \( KE \), depends on the photon energy and the binding energy of the electrons, which is expressed by the following equation:

\[
KE = h\nu - BE
\]  

(2.3)

where \( BE \) is the binding energy of the ejected electrons to the atom, and \( h\nu \) is the known photon energy of the X-ray source. The binding energy can be determined by measuring the kinetic energy of ejected electrons with an electron energy analyzer. This method can detect all elements except hydrogen and helium and is very surface sensitive. The
detection limit of this technique is approximately 0.01 – 0.3 % of surface composition, depending on the equipment used.

2.5 CO₂ Jet Cleaning

CO₂ cleaning is a surface cleaning method using a high velocity stream of carbon dioxide. The CO₂ cleaning is performed by creating a stream of small dry ice droplets from the expansion of liquid or gaseous carbon dioxide via a small orifice. Adiabatic expansion of high pressure carbon dioxide gas generate a large temperature drop within the nozzle resulting in nucleation of small dry ice particles.

The cleaning mechanism of the CO₂ jet is primarily a momentum transfer between ice particles and contaminants. In removing submicron particles, the adhesion force is so large that the simple drag force of a moving fluid can not clean the particles effectively. Small dry ice particles from the jet cleaning method can overcome the adhesion force and set free the particles from the surface by the momentum transfer process. When the particle contamination is released from the surface, the particles are swept away by the CO₂ gas stream. Condensed liquid phase CO₂ on the surface has a great solvating effect to hydrocarbon contamination. Surface hydrocarbon contamination is absorbed by the liquid CO₂ and cleaned by the dry ice jet.

Figure 2.5 shows the simple CO₂ jet cleaning apparatus used in this study. A specially designed nozzle is connected to a high purity CO₂ cylinder. CO₂ comes out from the nozzle as either a liquid or a gas. A dip tube allows withdrawal of CO₂ directly from the liquid inside the cylinder. Wafer samples are placed on an aluminum sample holder and held by vacuum suction to enhance thermal contact and prevent motion under
the high pressure cleaning process. In order to prevent water condensation on the sample due to excessive cooling by the CO₂ jet, the aluminum sample holder is heated by a heating block.

![Figure 2.5 Schematic illustration of CO₂ jet cleaning](image)

**2.6 Ellipsometer**

Variable angle spectral ellipsometry is a very powerful technique for measuring a thin film thickness with a polarized light source. Ellipsometry is generally more accurate than a simple reflection measurement. The combination of variable angle of incidence, and spectroscopic measurements can handle a broad range of materials and characterize
complex film structure, which cannot be achieved by a single angle or single wavelength ellipsometer.

Ellipsometry measures the change in polarization information of light reflected from the sample surface. The measured values are expressed as $\psi$ and $\Delta$. The ratio of Fresnel reflection coefficients $R_p$ and $R_s$ for $p$ and $s$ polarized lights, $\rho$, is a function of $\psi$ and $\Delta$ as shown following equation.

$$\rho = \frac{R_p}{R_s} = \tan(\psi)e^{i\Delta} \tag{2.4}$$

The ratio is a complex number containing the phase information, which makes ellipsometry a very accurate measurement tool for thin films.

In this study, we have used the multi-wavelength ellipsometer, mode 44 provided from J. A. Woollam Co., Inc. This system uses 44 wavelengths from the light source. Data analysis is performed with WVASE32 software, which is running under Windows® 95 on a Pentium® PC. The ellipsometer can be operated in both ex situ and in situ configurations. Schematics of the in situ ellipsometer attached to the HF vapor chamber is shown in Figure 2.6.
2.7 Plasma Etching Chamber

An inductively coupled plasma (ICP) etching chamber was used for this work. In this chamber, a high density plasma is generated by an inductive coil which is located on the top of quartz window. Main plasma power is supplied from the top coil and inductively coupled to the plasma through the quartz, generating a high density plasma. A bottom power source biases and provides an RIE effect on the wafer. The top and bottom powers are operated at different frequencies to minimize interference between the two power sources. The bottom electrode is cooled or heated by a refrigerated or heated circulating bath.

The heat transfer between the wafer and the electrode is enhanced by helium backside cooling, which is widely accepted in the semiconductor industry for plasma etchers. Since the pressure of plasma chamber is on the order of 10 mTorr, the wafer is
very difficult to cool without using any He flow between the gap. When He is flowing to the backside of the wafer, the wafer should be clamped to the electrode in order to maximize the heat transfer rate and not to shift its position in the plasma chamber. In this chamber, the wafer is clamped electrostatically by supplying a high DC voltage to the electrode. The electrode is insulated by Kapton tape, which also acts as a dielectric material when the plasma is on. The metal electrode and the wafer act like a large capacitor in which the build up of charge generates an attracting electrostatic force between the electrode and the wafer. 4, 5, 6

For this study, the plasma chamber is used as an initial surface cleaning method to clean the oxide surface prior to the vapor etching. The surface charge on the oxide sample makes a huge difference in the vapor etching process in the sub-monolayer or monolayer adsorption regime. In this study, the surface charge on the oxide wafer has been created by the plasma chamber by varying electrostatic clamping voltages. The polarity of the charge is also changed by switching the polarity of the high voltage power source. The process condition for initial cleaning was 30 mTorr of the total pressure, 10 sccm of O₂ gas flow, 150 W of the top power, and ±1000 V of the clamping voltage. Ar gas was used for generating the surface charges on the oxide wafer. The plasma was applied to the sample for less than 1 min.

2.1 UV/Cl₂ Chamber

The UV/Cl₂ chamber for this experiment is illustrated in Figure 2.7. The sample wafer is placed on an anodized aluminum plate, the temperature of which is controlled by an electrical heater located inside the aluminum block. UV light is illuminated from an outside UV source through a quartz window placed top of the reactor. Cl₂ gas is supplied
from an outside gas source by a mass flow controller. The pressure of the reactor is controlled by a throttle valve connected to a vacuum pump. A 1000W high pressure Hg-Xe arc lamp is used as the UV source. The UV source provides a power density of 1 W/cm² in the wavelength range of 235-400 nm. The illuminating area on the sample is about 1 inch in diameter, centered on the sample surface, providing enough area for further analysis.

This chamber is primarily used for cleaning and generating electrostatic charge on the surface. Since the work function of silicon dioxide is about 5 eV, the UV source can provide enough energy to excite surface electron on the sample. The UV source has intense short wavelength components, less than 250 nm, corresponding to a photon energy greater than 5 eV. This chamber also serves as a hot plate in a vacuum environment because the temperature of the sample plate can be controlled in the range of 20 – 150 °C.

![Figure 2.7 Schematic illustration of UV/Cl₂ process.](image)

Figure 2.7 Schematic illustration of UV/Cl₂ process.
2.8 Sputtering Chamber

The primary use of this chamber is for aluminum deposition on the wafer. A DC magnetron aluminum sputtering target is located on the top of chamber facing toward the sample location. RF power is also supplied to the sample providing negative bias to attract ions from the plasma. In this study, the chamber is used for providing a thin layer of aluminum and charging the oxide surface from the bottom RF power source. We believe that the RF treatment in this chamber provides negative charges on the oxide surface.
2.9 References


Chapter 3 Condensed Etching Regime

3.1 Condensation of the Reactants

Ellipsometric measurements suggest that oxide etching can occur without a condensed layer or with a condensed layer on the oxide surface under certain conditions. At lower temperatures and higher vapor pressures, a condensed layer was formed. Figure 3.1 shows that two distinct etching mechanisms are associated with the etching reaction. As we increased the partial pressure of HF with respect to time, the etching reaction started at a low rate and the ellipsometric signal change became much faster than the previous etching state. The condensed layer of the reactants started to form when the partial pressure of HF reached the vapor-liquid equilibrium state at a fixed water vapor pressure. At a surface temperature of 40°C and a partial pressure of water of 5.4 torr, condensation occurs when the partial pressure of HF is greater than 33 torr, according to the graph.

The spectroscopic ellipsometric signals in the first part, the non-condensed regime, are well fit between measured values and calculated values in 44 wavelengths. Incoming light from the ellipsometer is not interfered with by the surface of the condensed layer or adsorbed molecules in this regime. However, the spectroscopic signal in the condensed regime is different from calculated values due to interference from the thin non-uniform condensed layer shown in Figure 3.1. It is also very difficult to estimate the oxide thickness by ellipsometry in the condensed regime.
Figure 3.1 Typical ellipsometric signal showing both non-condensed and condensed regimes. Well fit ellipsometric signals for multiple wavelength are observed in the non-condensed regime while there is a lack of fit for film thickness in the condensed regime.
Figure 3.2 Typical spectroscopic signals and in situ measurements of the etching rate by ellipsometry. (a) A spectroscopic signal of $\psi$ for different thicknesses of oxide. (b) In situ measurements of $\psi$ at 4502 Å in the condensed regime. $\psi$ started to decrease and became constant when the etching process completed (5500 Å of thermal oxide etched) in 0.65 min. (c) In situ measurements of $\psi$ in the non-condensed regime. $\psi$ started to increase and took 3 min to etch 300 Å of oxide.
Figure 3.2 shows typical spectroscopic signals of $\psi$ for the thermal oxides from the in situ ellipsometer. At a wavelength of 4502 Å and an initial thickness of 5500 Å, $\psi$ increases as the thickness of oxide decreases or decreases when the oxide thickness increases or the condensed layer forms on the top of the oxide. The decrease in $\psi$ is always observed at 4502 Å when etching occurs in the condensed regime due to the formation of a condensed layer on the oxide. Since there is no condensed layer in the non-condensed regime, the $\psi$ signal increases, indicating that the oxide layer is being etched and no condensed layer is formed on the surface.

The etch rates of oxide are calculated from the spectroscopic signals in the non-condensed regime. Since a spectroscopic signal can be obtained at any time, the etch rate is calculated by the difference in thickness for a certain time interval during the process. However, in the condensed regime, the etching process must be performed until the whole oxide is etched because it is impossible to calculate the oxide thickness from spectroscopic signals.

3.2 Vapor-Liquid Equilibrium of HF/H$_2$O Binary System

The partial pressures of the reactants condensing on the oxide surface are obtained at a sample temperature of 40°C by performing the above mentioned experiments at various partial pressures of HF and water. Figure 3.3 shows the regions in which condensation was observed during etching at 40 °C as a function of HF and H$_2$O partial pressures in the feed gas. The vapor-liquid equilibrium data obtained by Munter and Brosheer is also plotted on the graph. The data indicate that condensation occurred at
lower partial pressures of reactant gases than predicted by the HF-H₂O vapor equilibrium measurements of Munter. Ellipsometric observation of water condensation was also carried out to confirm the temperature and pressure control of the reaction chamber. The data generated in this experiment was in agreement with the steam tables. This depression of the condensation point indicates that the oxide etching product forms a ternary mixture of HF/SiF₄/H₂O thereby decreasing the vapor pressure and causing condensation. The reduction in vapor pressure by the ternary mixture HF/SiF₄/H₂O was measured by Munter et al. The etching rates of oxide in the condensed regime were very high (3,000-12,000 Å/min) when compared to those of the gas phase regime (0-300 Å/min). The region in which a condensed layer is formed is therefore a function of not only the partial pressures of HF and H₂O in the feed gas, but also a function of the mass transport of the reactants to and the products from the sample.

We have categorized two different etching regimes: the gas phase regime and the condensed phase regime. In the gas phase etching regime, reactant molecules are adsorbed on the oxide surface in sub-monolayer, monolayer, or multilayer films. In the condensed phase regime, a condensed film is formed that is very non-uniform in thickness. The thickness and non-uniformity of the condensate film gives rise to measurable ellipsometric signals during oxide etching. The etching reaction in the condensate film is thought to occur in a manner that is very similar to that in wet HF etching. For both gas-phase and condensed phase etching, the products must desorb and diffuse from the surface. Since the effective kinetics are a function of both the partial pressure of the reactants and the transport to and from the surface, both surface kinetics and transport must be considered to correctly model the etching process.
Figure 3.3 Vapor-Liquid Equilibrium and Condensate Phase Diagram for HF-H$_2$O at 40 °C. The solid line indicates HF-H$_2$O phase equilibrium data from Munter et al. Formation of condensate films during oxide etching for these partial pressures are obtained at a total pressure of 250 Torr and total flow rate of 500 sccm.
3.3 Etching Reaction in the Condensed Regime

Etching rates of more than 3000 Å/min have been achieved in the condensed regime. We have identified condensation experimentally in this regime through the observation of an apparent increase in the oxide thickness (measured ellipsometrically) at the onset of etching. The presence of liquid phase condensation is confirmed indirectly by the increased pumping time needed to reach base pressure after the etching process. The reaction products dissolved in the condensed phase must desorb into the gas phase or be cleaned by a water rinse after the etching process otherwise the remaining reaction products produce "particulate" contamination on the wafer surface after etching. From the observation that condensation is present at a lower pressure than predicted by the vapor-liquid equilibrium data from Munter et al., it is concluded that the product concentration in the condensed phase is high enough to reduce the vapor pressure of the liquid phase. High concentrations of the products in the condensed phase can lead to residues on the surface, which is one of the basic problems in the HF vapor etching process. It has been reported in the literature that H₂SiF₆ in the aqueous phase evaporates to form SiF₄ at low pH's, but at higher pH's forms SiFₓ(OH)ₙ which precipitates to form a solid deposit on the surface. To avoid this problem, HF vapor processing equipment must use a water rinse step after processing to remove particulates, or incorporate wafer heating while processing to desorb excess product more efficiently.

The etching rate increases as the partial pressure of HF increases, as is shown in Figure 3.4. The effect of HF partial pressure decreases under conditions that lead to poorer mass transport to the sample; i.e. higher pressure, lower flow rates, and a larger showerhead. The smaller showerhead produces a higher etching rate than the larger
showerhead at the same flow rate. In this regime the etching rate is not controlled by adsorption on the surface but is governed by the mass transfer rate of reactant from the gas phase to the condensed phase or the transfer of products built up in the condensed phase to the gas phase.

![Graph](Image)

Figure 3.4 Etch rate as a function of $P_{HF}$ in the condensed regime. $P_{H2O}=27$ Torr, $T=40$ °C, and Flow Rate = 500 sccm. The variation with pressure and showerhead size is consistent with mass transport effects reducing the etching rate.
The etching rates of the condensed regime are proportional to $P_{HF}^{0.32}$ as shown in Figure 3.5. This figure is reconstructed in a log-log scale graph from Figure 3.4 and clearly shows linear trends with the same slopes for the three different conditions. The partial pressure of HF is varied from 3 torr to 100 torr, giving an etch rate from 3000 to 12000 Å/min. From the spectroscopic ellipsometer measurements, we confirmed that all etching occurred in the condensed regime. Since the etching reaction occurs in the condensed phase, the etching rate is governed by the concentration of HF in the liquid phase, and not the gas phase pressure. The partial pressure of HF in the gas phase only affects the liquid phase HF concentration. The previous work done by Helms modeled the condensed regimes by calculating the liquid phase HF concentration from the gas phase information.

Aqueous phase HF etching has been studied by numerous people. Kline and Fogler reported that the dissolution rate of silicate is described by a Langmuir-Hinshelwood rate law for the aqueous phase. Judge suggested a first order dependency on the etch rate of oxide shown in the following equation.


where A, B, an C are constants. Generally, most of the previous studies show that the etch rate of oxide is linearly dependent with the concentration of HF in the aqueous phase. It is implied from Figure 3.5 that the concentration of HF in the condensed phase is proportional to $P_{HF}^{0.32}$.

The temperature dependence of the etching rate in the condensed regime is shown in an Arrhenius plot in Figure 3.6. A greatly reduced temperature dependence relative to
the gas phase regime is observed. The etching reaction in the condensed phase is thought to be similar to that of wet chemical etching in aqueous HF solution, where the etching rate increases with increasing temperature. Spierings reported an activation energy for wet HF etching of 4 – 8 Kcal/mol. Therefore, an increase of etching rate between 28-56 % would be expected with an increase in temperature from 30 to 40°C. At the higher etching rates in this regime, the mass transport of reactants to the surface may begin to affect the observed etching rate as well. To avoid these effects, HF vapor processing equipment should be designed to exhibit a high mass transfer rate through the use of high gas flow rates and/or reduced operating pressure.
Figure 3.5 Etch rate plotted on a log-log scale as a function of $P_{HF}$ in the condensed regime. $P_{H2O}=27$ Torr, $T=40 \degree C$, and Flow Rate = 500 sccm. The plot indicates that the etch rate is proportional to $P_{HF}^{0.32}$. 
Figure 3.6. Etch rate as a function of Temperature in the condensed regime. The lack of variation in the etching rate differs from that observed in the gas phase regime (next chapter) at the same temperatures. The temperature dependence in this regime is consistent with that of aqueous oxide etching in which a small increase in etching rate is observed with increasing temperature.
3.4 Mass Transfer Effect on the Etching Rate

Figure 3.7 shows that mass transport in the gas phase affects the oxide etch rate. A detailed description of the reaction mechanism and transport is beyond the scope of this work. The data given in this plot show that the observed etch rate varied with total process pressure even though the reaction temperature and partial pressure of the reactants was held constant. The data can be interpreted correctly when plotted versus \((QD/Lp)^{1/2}\), the scaling factor for a mass transfer controlled process. The mass transport rate should be proportional to the concentration gradient by a mass transfer coefficient. The mass transfer coefficient in the gas phase is the diffusivity divided by a boundary layer thickness of gas phase. For laminar flow at low Reynolds numbers in a stagnation configuration, the mass boundary layer thickness is independent of the radial position.

The mass transfer coefficient for laminar stagnation flow in the lubrication regime can be shown to be proportional to the square root of \((\text{volumetric flow rate per showerhead area})(\text{diffusivity})/(\text{spacing between the showerhead and the sample})\). Since the volumetric flow rate and diffusivity are both inversely proportional to the pressure for an ideal gas, the transfer coefficient changes inversely with the process pressure. The transport coefficient (which can also be thought of as the reciprocal of resistance for mass transport) for a given showerhead scales in proportion to \((QD/Lp)^{1/2}\) where \(Q\) is the feed gas molar flow rate, \(D\) is the diffusivity in the gas, \(L\) is the showerhead-sample spacing, and \(p\) is the process pressure. This implies that the HF vapor process should be operated at a high flow rate and low pressure to ensure operation in the surface reaction limited regime. The surface reaction limited regime is probably more reproducible than
the mass transfer limited regime unless careful reactor design has been made to assure uniform mass transport to the wafer.

The etching rates are linearly dependent to the scaling factor, \((QD/Lp)^{1/2}\), regardless of the process condition as shown in Figure 3.7. These results indicate that the mass transfer rate of the product is limiting the whole reaction rate in the condensed etching regime for HF vapor etching process.

![Figure 3.7 Mass transfer effects on the etch rate in the condensed regime. The etch rates are plotted against \((QD/Lp)^{1/2}\) which is a scaling factor for a mass transfer controlled etching process in a 1-D lubrication flow system and is equivalent to the mass transfer coefficient.](image-url)
3.5 References


Chapter 4 Non-Condensed Regime

4.1 Various Etching Regimes of HF vapor Process

Gas or vapor adsorption on a solid surface is usually described by an empirical adsorption function, measured experimentally. The adsorption isotherm is generally determined by expressing the amount of adsorbed molecule as a function of vapor pressure or temperature. Water adsorption on silica or silicate has been studied intensively by numerous research groups.\(^1\),\(^2\) Figure 4.1 shows a basic concept of physical adsorption of the reactant molecules in the HF vapor process. As the pressure approaches the saturation point, the amount of HF adsorbed increases rapidly and finally reaches the condensation point where the reactant molecules start to form a liquid layer on the surface. When the pressure is low, the fraction of adsorbed sites is less than 1, indicating that there is an equilibrium relationship between the pressure and the fraction of adsorbed sites. This is described by Langmuir adsorption isotherm expressed in the following equation.

\[
\theta = \frac{KP}{1 + KP} \tag{4.1}
\]

where \(\theta\) denotes the ratio of adsorbed sites and total available adsorption sites, \(K\) is an equilibrium constant and \(P\) is the vapor pressure.

More realistically, the adsorption isotherm with multilayer adsorption is described by the BET equation suggested by Brunauer, Emmett, and Teller, and is a derived from a form of the Langmuir equation.\(^3\) This BET equation can be written as following.

\[
\frac{\theta}{\theta_m} = \frac{cx}{(1-x)(1+(c-1)x)} \tag{4.2}
\]
where $x = P/P^o$ and $c$ is a constant exponentially related to the heat of adsorption on the surface and the heat of condensation.

The oxide etching reaction of the HF vapor process in the non-condensed regime involves the adsorption of gas phase molecules on the surface before reacting with the oxide. Direct measurement of the adsorption state of reactant molecule is very difficult because the etching reaction is involved on the surface. However, the etch rate measurements at various temperatures or vapor pressures give us some information about the adsorption state of the reactant molecules. Figure 4.2 shows the etching rate of oxide with changing temperature at fixed partial pressures of the reactants, indicating that various adsorption states are associated with this graph. This plot explains the detailed

Figure 4.1 Schematic illustration of adsorption of HF and water on silicon oxide surface.
adsorption states ranging from sub-monolayer adsorption to the condensed phase, and even gives some kinetic information.

![Arrhenius Plot](image)

Figure 4.2 Various etching characteristics of HF vapor etching of oxide shown in an Arrhenius Plot.

In Figure 4.2, both the condensed and non-condensed etching regimes are plotted in the same graph. From 0 °C to 25 °C, the etching rate decreases as the temperature decreases, which is consistent with the aqueous phase etching results in region 1. The etch rate does not change with respect to the temperature in region 2 suggesting that the surface kinetics are no longer limiting the etching rate. As we discussed in the previous chapter, the mass transfer rate of the product in the gas phase becomes a rate limiting
step. The etching rates in this range are much higher than the other regimes by one or two orders of magnitude.

In region 3 of the above graph, the apparent activation energy is about -25 Kcal/mol. For a regular chemical reaction, this value should have a positive value and the reaction rate should increase as the temperature increases. A thick multilayer formation on the oxide surface is formed in this regime, implying that the apparent activation energy includes the adsorption energy in addition to the kinetic term. Region 4 is a transition region between the thick multilayer adsorption regime and the monolayer adsorption regime, i.e., a thin multilayer regime.

In region 5, the oxide etching rate increases as the temperature increases, indicating that the oxide surface is saturated with reactant molecules in the monolayer adsorption state. In this regime, the amount of adsorbed molecule does not change very much for small temperature changes. As we further increase the temperature, the slope of increasing etching rate decreases, and the apparent activation energy becomes smaller. This regime is believed to be a sub-monolayer adsorption state in which the number of adsorbed sites are decreasing with increasing temperature.

As shown in Figure 4.2, the etching rate in the submonolayer or monolayer regimes is much slower than that of the condensed regime, in the range of 10 – 100 Å/min. This is a desirable rate for the purpose of native oxide cleaning. Because the surface kinetics are limiting the reaction in these regimes, the etching uniformity on the wafer will be much better than that of other etching regimes.
4.2 Multilayer Adsorption Regime

Without the formation of a condensed layer, the etching reaction must involve three steps: adsorption, reaction, and desorption.\(^4\) The etching rate in this regime is usually low (typically 0-400 Å/min) relative to the condensed regime.

Figure 4.4 shows the etching rate as a function of partial pressure of HF. The etch rate is generally proportional to the partial pressure of HF up to 35 torr. A sudden increase in etching rate above 35 torr is caused by a transition between the multilayer regime and the condensed regime on the surface. The etch rate of oxide is also linearly proportional to the partial pressure of H\(_2\)O as shown in Figure 4.3. The HF and water concentrations or the amount of adsorbed reactants on the surface are linearly dependent on the partial pressures of gases. However, in the condensed regime, etch rate was proportional to \(P_{HF}^{0.32}\) implying that the concentration of HF in the condensed layer is not proportional to \(P_{HF}\) in the gas phase.

If we assume that the etching rate is proportional to the adsorbed reactants on the oxide surface,

\[
E.R = k_r v_{HF} v_{H2O}.
\]

where \(v_{HF}\) and \(v_{H2O}\) are the amount of adsorbed HF and H\(_2\)O on the oxide surface in the multilayer adsorption regime, respectively. \(v_{HF}\) and \(v_{H2O}\) could be associated with compositions on top of the monolayer. Since \(v_{HF}\) and \(v_{H2O}\) increase with increasing partial pressures of the reactants in this state, it is reasonable to assume first order dependence with respect to the partial pressures. Therefore, they can be represented that

\[
v_{HF} = K_{HF} P_{HF},
\]
and \[ \nu_{\text{H}_2\text{O}} = K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \] \hspace{1cm} (4.4)

where \( K_{\text{HF}} \) and \( K_{\text{H}_2\text{O}} \) are equilibrium constants for the adsorption of HF and \( \text{H}_2\text{O} \). We have used the same equilibrium constants as used in the monolayer. The etching rate finally can be written as a function of HF and \( \text{H}_2\text{O} \) pressures.

\[ \text{E.R} = k_r K_{\text{HF}} K_{\text{H}_2\text{O}} P_{\text{HF}} P_{\text{H}_2\text{O}} \] \hspace{1cm} (4.5)

From Figure 4.2, the apparent activation energy for the thin multilayer adsorption state, region 4, is approximately -8 Kcal/mol. The negative sign of the activation energy means a increasing etching rate with decreasing temperature. The overall activation energy can be derived from equation 4.6.

\[ E_{\text{app}} = E_r + \Delta H_{\text{HF}} + \Delta H_{\text{H}_2\text{O}} \] \hspace{1cm} (4.6)

where \( E_{\text{app}} \) is the apparent activation energy, \( E_r \) is the activation energy for the chemical reaction, \( \Delta H_{\text{HF}} \) is the heat of vaporization of HF, and \( \Delta H_{\text{H}_2\text{O}} \) is the heat of vaporization of water. The values for \( E_r, \Delta H_{\text{HF}} \) and \( \Delta H_{\text{H}_2\text{O}} \) were determined as follows: \( E_r = 15.5 \) Kcal/mol, \( \Delta H_{\text{HF}} = -13 \) Kcal/mol, and \( \Delta H_{\text{H}_2\text{O}} = -10.5 \) Kcal/mol, as will be discussed later. Therefore, \( E_{\text{app}} = (15.5)+(-13)+(-10.5)=-8 \) Kcal/mol. From this calculation, it is concluded that the etching rate in the thin multilayer regime is limited by the surface reaction rate with an apparent activation energy of -8 Kcal/mol.
Figure 4.3 Etch rate of thermal oxide as a function of H$_2$O partial pressure for low HF partial pressure, 7 Torr.

Figure 4.4 Etching rate of thermal oxide as a function of P$_{HF}$.
In the thick multilayer regime for region 3 in Figure 4.2, the apparent activation energy is much higher than that of the thin multilayer implying that another resistance is playing a major role in the etching reaction. The apparent activation energy is between -25 and -40 Kcal/mol in this region. As the adsorbed layer becomes thicker, the adsorbed HF molecules can be hydrated by the adjacent adsorbed water molecule to form an ionic species that can etch oxide at a much faster rate. We believe that the mass transfer rate in the gas phase is responsible for control of the etching rate in the thick multilayer adsorption regime. The mass transfer limited etching reaction with steady state desorption/adsorption can be written by the following relationships.

\[
\text{Desorption : } \quad \text{E.R.} = k_d u_{SiF_4} - k_a P_{SiF_4} \quad (4.7)
\]

\[
\text{Mass transfer : } \quad E.R. = k_L P_{SiF_4} \quad (4.8)
\]

Combining equation (4.8) and (4.9) leads to

\[
E.R. = \frac{k_L}{K_{SiF_4}} u_{SiF_4} \cdot (4.9)
\]

where \( k_L \) is a mass transfer coefficient for SiF\(_4\) from the oxide surface to the gas phase and \( K_{SiF_4} \) is a equilibrium constant for the adsorption of SiF\(_4\). If we assume that the adsorbed SiF\(_4\) is in equilibrium with the adsorbed HF and H\(_2\)O (i.e. surface reaction is at equilibrium), then

\[
\theta_{SiF_4} = K_{EQ} u_{HF} u_{H_2O}. \quad (4.10)
\]

Thus, the overall etching rate is
From the equation (4.12), the apparent activation energy for the thick multilayer adsorption regime is the summation of \(-\Delta H_{\text{rxn}}, \Delta H_{\text{HF}}, \Delta H_{\text{H}_2\text{O}}, \text{ and } -\Delta H_{\text{SiF}_4}\). If we use the values from the gas phase reaction data, \(\Delta H_{\text{rxn}}\) is approximately \(-17\) Kcal/mol. Assuming that \(\Delta H_{\text{SiF}_4}\) is \(10\) Kcal/mol, which is very common for an adsorption of gas molecules on a solid surface, the overall activation energy is calculated to \(-30\) Kcal/mol. This value is consistent with the experimental value obtained from Figure 4.2. Therefore, the large apparent activation energy is explained well by the assumption of a mass transfer limited etching reaction.

4.3 Mass Transfer Effect

4.3.1 Mass Transfer of Reaction Product

The etching reaction usually involves four steps: adsorption, reaction, desorption and mass transfer.\(^5\) Figure 4.5 shows the etching rate as a function of partial pressure of HF, indicating a linear dependency. A sudden increase in etching rate above 35 Torr is due to the formation of a condensed layer on the oxide surface. Both the partial pressures of the reactants in the feed gas and the transport of product away from the surface control the onset of condensation. In Figure 4.5, the etch rates obtained at the total pressure 250 torr tend to saturate at earlier partial pressures of HF than those at 125 torr and have a lower etch rate at 15 – 30 torr of HF. The transition to the condensed regime at 250 torr total pressure also occurs at a lower HF partial pressure than at 125 torr. Since the partial pressures of reactants in the feed gases for both data sets are the same, the variation in observed etching rates are attributed to mass transport limitations. Therefore, in the
partial pressure range of 15 to 30 torr, the mass transfer rate greatly affects the etch rate as well as the transition point to the condensed regime.

Figure 4.5 Etching rate of thermal oxide as a function of PHF. Since the partial pressures of reactants in the feed gases of both data sets are the same, the deviations in the observed etching rates are attributed to mass transport limitations. Non-monotonic trends with temperature indicate complex surface kinetics. Repeat experiments at 25 torr indicate an experimental error of ±10 Å/min. The difference between the two curves is 5 times more than the experimental error.

The mass transfer effect has been investigated at 25 torr of HF by obtaining the etching rates at various mass transfer rates. Figure 4.6 shows that mass transport of the product diffusing from the oxide surface in the gas phase affects the etch rate in the multilayer adsorption regime. The data given in this plot show that the observed etch rate varied with total pressure even though the reaction temperature and partial pressure of the feed gas were held constant.
Figure 4.6 Etch rate as a function of \((QD/Lp)^{1/2}\), the scaling for a mass transfer controlled etching process. The approximate linear response indicates that the mass transfer is dominant in that regime, however, the scattering in the data suggests a complex surface mechanism in which the products affect the etching kinetics. Spacing of 1.3, 2.0 and 2.6 cm were used.

As we discussed in the previous chapter, the scaling factor is based on a stagnation flow for one-dimensional lubrication flow, which is equivalent to a mass transfer coefficient; \(h\). \(h\) is \(D/\delta\) by definition. From boundary layer theory, the mass transfer coefficient, \(h\) can be expressed as follows.\(^6\)

\[
h = C \left( \frac{U_0}{vL} \right)^{1/2} D \cdot Sc^{1/3}
\]  
\[\text{(4.12)}\]
where $C$ is a constant, $U_0$ is the gas velocity, $v$ is a viscosity of gas, $D$ is diffusivity, $L$ is the spacing between the showerhead and the substrate, and $Sc$ is Schmidt number of gas. For convenience, we have introduced a scaling factor, $(QD/Lp)^{1/2}$ where $Q$ is the feed gas molar flow rate and $p$ is the process pressure. This scaling factor is the same quantity as the above mass transfer coefficient, $h$. This implies that the HF vapor process should be operated at a high flow rate and low pressure to ensure operation in the surface reaction limited regime.

The dependence of the oxide etching reaction on mass transport is explicitly shown in Figure 4.6. At low mass transfer rate, the etching rate increases as the mass transfer rate increases. Then, it begins to saturate at mass transfer coefficients around 2 – 3 cm/sec to an etch rate of 150 Å/min. This indicates that the maximum etching rate at this condition is approximately 150 Å/min and is reduced due to mass transfer resistance. From Figure 4.6, variation from this correlation is due primarily to the assumption of lubrication flow. This data also indicates that the HF vapor process is a highly non-linear system, not completely described with a simple mathematical model. Simultaneous modeling of the fluid mechanics, mass transfer, and surface kinetics would be needed to accurately describe the HF vapor process.

4.3.2 SiF$_4$ Addition Effects on Etch Rate

The effects of SiF$_4$ addition in the gas feed have been investigated to confirm that SiF$_4$ transport from the oxide surface causes the mass transfer effects noted in the previous section. SiF$_4$ is believed to be the volatile product leaving the oxide surface following the etching reaction. As shown in Figure 4.7, a suppression of the etching rate with a partial pressure of 1.06 Torr SiF$_4$ has been observed. This partial pressure is equal
to that expected by transport away from the surface at an etching rate of approximately 1000 Å/min. The addition of SiF₄ lowers the etch rate at low partial pressures of HF. However, at higher HF partial pressures, the SiF₄ addition induces a thicker formation of adsorbed layer or a condensed layer on the surface, accelerating the etching rate. The transition region between the multilayer and condensed regime is shifted to a lower HF pressure when SiF₄ is intentionally added to the feed gas. The amount of etch rate reduction for low HF pressure is a function of the amount of SiF₄ in the gas phase. The higher partial pressure of SiF₄ suppresses the etching rates further. The enhancement of the transition state is also increased as the SiF₄ pressure is increased as shown in Figure 4.8. This result implies that the condensed layer is more likely to form at high partial pressure of SiF₄ in the vicinity of the oxide surface, which is usually achieved by a high etching rate of oxide.

The suppression of the etching rate with SiF₄ addition in the multilayer and condensed regime is thought to be associated with SiF₄ partial pressures in equilibrium with lower energy products formed by hydrolysis/solvating reactions in the condensed or multilayer adsorbed phases. Thermodynamic analysis of HF+SiO₂ ↔SiF₄+H₂O at the partial pressures and temperatures used in this study predicts equilibrium partial pressures of SiF₄ greater than several atmospheres.⁷ The presence of SiF₄ in the gas phase greatly reduces the equilibrium vapor pressure of HF and water in the condensed phase ternary mixture.⁸ It has been noted that the ternary mixture precipitates Si(OH)ₓFᵧ on the surface at lower HF concentrations or evaporates by forming SiF₄ at higher HF concentrations.⁹
Figure 4.7 Suppression of oxide etching rate by SiF$_4$ addition in the multilayer regime. The addition of product (SiF$_4$) at a partial pressure roughly equal to that expected by the transport away from the surface under the experimental conditions shows a suppression of the etching rate at low HF partial pressures. At higher partial pressures, the etching rate is accelerated by the formation of a condensed layer or thicker multilayer film.
4.4 Sub-Monolayer and Monolayer Etching Regime

The etching rate in the monolayer and sub-monolayer regimes is roughly proportional to HF and H$_2$O partial pressures at low reactant partial pressures or high temperatures. However, the saturation of the etching rate has been observed when monolayer coverage is obtained. Figure 4.9 is an Arrhenius plot of etching in the sub-monolayer, monolayer and multilayer states for identical HF and H$_2$O pressure ratios. The etch rate saturates at high temperatures as monolayer coverage is attained, even though the partial pressures of the reactants increases by a factor of two. This graph also shows that the activation energy in the monolayer etching state is roughly 16 Kcal/mol.
The condition located to the left side of the dashed line in Figure 4.9 is believed to be sub-monolayer coverage while the right side is at multilayer coverage of the reactants.

In the sub-monolayer adsorption regime, the etch rate is a function of the partial pressures of HF and H$_2$O. However, in the monolayer regime, the etching rate is dependent on the ratio of HF and H$_2$O partial pressures. The etching rate in the monolayer regime is also affected by the presence of SiF$_4$ in the gas phase. Addition of 1 torr of SiF$_4$ in the gas feed reduced the etch rate in the monolayer regime by 50%, which indicates that SiF$_4$ also adsorbs to the oxide surface and blocks reactive sites.

The thick multilayer adsorption state located to the right side of the dashed line has the apparent activation energy of -30 Kcal/mol. The transition region between monolayer and thick multilayer has the apparent activation energy of -8 Kcal/mol. As we discussed in the previous section, both regions are in the multilayer adsorption regimes with different kinetic limiting steps.
Figure 4.9 Temperature dependence on etch rate for various conditions. This graph shows both monolayer adsorption etching and multilayer adsorption etching. Process conditions are 125 torr (10/4, 15/6 for HF/H₂O), 62.5 torr (5/2), and 31.8(2.5/1) torr and 500 sccm total flow rate. Thermal oxides (5500 Å thick) were etched for 6 min. to measure the etch rates.
4.4.1 Langmuir-hinshelwood Kinetic Expression

The Langmuir-hinshelwood mechanism expresses the dependence of the reaction rate in terms of a single rate coefficient and the concentration of surface adsorbed sites. The etching rate of the oxide film can be described by Langmuir-Hinshelwood kinetics, which are proportional to the fraction of the adsorbed HF and H$_2$O.\textsuperscript{10,11}

\[ E.R. = k_r \theta_{HF} \theta_{H_2O} \quad (4.13) \]

where $\theta_{HF}$ and $\theta_{H_2O}$ are the fraction of the adsorbed HF and H$_2$O, respectively. It has been observed that the adsorptions of HF and H$_2$O are competitive with each other.

\[
\theta_{HF} = \frac{K_{HF} P_{HF}}{1 + K_{HF} P_{HF} + K_{H_2O} P_{H_2O}} \quad (4.14)
\]

\[
\theta_{H_2O} = \frac{K_{H_2O} P_{H_2O}}{1 + K_{HF} P_{HF} + K_{H_2O} P_{H_2O}} \quad (4.15)
\]

Finally, the etching rate is expressed as a function of temperature and the partial pressures of HF and H$_2$O.

\[
E.R. = k_r^0 e^{-E_r/RT} \frac{K_{HF}^0 e^{-\Delta H_{HF}/RT} P_{HF} K_{H_2O}^0 e^{-\Delta H_{H_2O}/RT} P_{H_2O}}{(1 + K_{HF}^0 e^{-\Delta H_{HF}/RT} P_{HF} + K_{H_2O}^0 e^{-\Delta H_{H_2O}/RT} P_{H_2O})^2} \quad (4.16)
\]

where $k_r = k_r^0 e^{-E_r/RT}$. In this expression $K_{HF}$ and $K_{H_2O}$ are the HF and water adsorption-desorption equilibrium constants, which can be written in simplified forms as follows.

\[ K_{HF} = K_{HF}^0 e^{-\Delta H_{HF}/RT} \text{ and } K_{H_2O} = K_{H_2O}^0 e^{-\Delta H_{H_2O}/RT} \quad (4.17) \]
At high temperatures in Figure 4.9 the etching rate increases with temperature with an
activation energy of 15.5 Kcal/mol. As the temperature is increased further, the etching
rate begins to saturate with an apparent activation energy of 0 Kcal/mol. From linear
regression of experimental data, we have obtained all pre-exponential factors and the heat
of vaporization for HF. $\Delta H_{HF}$ calculated from the experimental data is -13 Kcal/mol. The
pre-exponential factors, $k^0_r$, $K^0_{HF}$ and $K^0_{H2O}$ are $1.059 \times 10^{12}$, $1.790 \times 10^9$ and $9.107 \times 10^{-8}$,
respectively. It is assumed that the heat of vaporization for water is -10.5 Kcal/mol. Therefore, the oxide etching rate in the sub-monolayer or monolayer regimes is
formulated as the following equation.

$$E.R. = \frac{1.059 \times 10^{12} e^{-15500 / RT} \times 1.79 \times 10^{-9} e^{13000 / RT} P_{HF} \times 9.107 \times 10^{-8} e^{10500 / RT} P_{H2O}}{(1 + 1.79 \times 10^{-9} e^{13000 / RT} P_{HF} + 9.107 \times 10^{-8} e^{10500 / RT} P_{H2O})^2}$$  (4.18)

In this expression all activation energies are in Kcal/mol. E. R. and the pre-exponential
factors are in Å/min, and the partial pressures are in torr. Figure 4.10 shows both
calculated values from Langmuir-Hinshelwood kinetics and experimental values plotted
in an Arrhenius form indicating that the calculated values are consistent with the
experimental values throughout all process conditions.

We have also investigated the reactant ratio dependencies on the etching rate in
the saturated monolayer regime. Figure 4.11 shows the etching rate of oxide at 90 °C
varying the partial pressures of HF and H$_2$O but keeping the sum of HF and H$_2$O
pressures constant. Under these experimental conditions, the process is believed to be in
the fully saturated monolayer adsorption state. The calculated values from equation 4.18
are plotted on the graph to compare with the experimental values. As shown in Figure
4.11, the calculated values are fairly consistent with the experimental values, having a parabolic shape indicating a maximum etching rate at an optimal reactant ratio.

Figure 4.10 The etching rates of oxide in the sub-monolayer and monolayer regimes. Dots are the experimental values. Lines and dashed lines are the calculated values from Langmuir-Hinshelwood kinetic equation. Process condition: $P_{\text{tot}}=125$ torr (for $P_{\text{HF}}/P_{\text{H}_2\text{O}}=20/8$, 10/4, and 15/6 torr), 62.5 torr (for $P_{\text{HF}}/P_{\text{H}_2\text{O}}=5/2$), and 31.8 torr (for $P_{\text{HF}}/P_{\text{H}_2\text{O}}=2.5/1$). Total flow rate=500 sccm.
Figure 4.11 The reactant ratio dependency on the etching rate in the monolayer regime. Process condition: \( T=90^\circ\text{C}, \) Total pressure=125 torr, Total flow rate=500 sccm, \( P_{\text{HF}}+P_{\text{H}_2\text{O}}=14 \) torr.

Although the predicted values and the experiments agree very well each other, the model predictions from the equation 4.19 does not explain a sudden etching rate change around the reactant ratio of 0.5. Since the Langmuir-Hinshelwood expression is based on the assumption of 1st order kinetics and a continuous model, it is difficult to describe possible multiple binding states and lateral interactions between adsorbed HF and water which are the probable causes of the discontinuity observed in the experiment.\(^{12}\)
4.4.2 Surface Morphology and Etching Uniformity

The surface morphology of partially etched oxide has been studied to investigate the etching characteristics in the monolayer regime. A hazy surface has been observed on the oxide samples etched in the multilayer regime or in the transition between the multilayer and monolayer regime after 200 Å of partial etching. Atomic Force Microscopy (AFM) was used to measure the surface morphology of the partially etched oxide samples. Figure 4.12 shows a hazy oxide sample etched in the multilayer regime. It exhibits pitting of the surface, causing the hazy surface. The elevated feature to the right side of pitting is an AFM artifact. It should be noted that the size of the pitting is approximately 10,000 Å in diameter and 100-200 Å in depth, indicating that it is not really a deep trench but is a large recessed area due to a high local etching rate. Therefore, it is hard to explain it by a capillary condensation in a narrow space shifting the multilayer to the condensed regime. The pitting in this regime is believed to be a result of localized formation of thicker multilayer films accelerating the local etching rate from the apparent autocatalytic effect discussed in section 4.2.1. A positive feedback mechanism in which increased etching and product buildup leads to increased condensation and etching could cause the pitting.

Figure 4.13 shows the surface morphology by AFM of a sample etched in the monolayer regime. No haze or pitting is observed in this regime. Uniform etching across the whole wafer is also observed in this regime. On the other hand, non-uniform etching occurs in the multilayer regime because the etching is governed primarily by mass transport. In order to achieve uniform etching in the multilayer regime, uniform mass transfer across the entire wafer should be achieved. Since uniform etching was observed
in the monolayer regime regardless of the flow uniformity, surface kinetics are primarily limiting the etching rate. This result also supports the surface kinetic limited etching process, modeled by Langmuir-Hinshelwood kinetics in the previous section.

In commercial HF vapor processing equipment, a water rinse step is sometimes employed to remove excessive precipitates and reduce the formation of pits on the oxide surface. This redundant water rinse step could be removed if the HF vapor process is performed in the monolayer regime. Wafer rotation is often used to enhance mass transfer rate and to provide uniform mass transfer rate. This process involves a mechanical movement in the processing chamber generating possible particle contamination, which could be eliminated by applying the monolayer etching regime.

Figure 4.12 Typical AFM surface scan of a thermal oxide partially etched in the multilayer adsorption regime. Process condition: 40 °C, 125 torr, 500 sccm, PHF=10 torr and PH2O=4 torr. X and Y scales are 10 μm in total length. Z scale is 25 nm per division. RMS(Ra)=0.874 nm.
Native Oxide Removal

Native oxide removal has been studied using the HF/H$_2$O vapor process in the monolayer adsorption regime. Successful native oxide removal for pre cleaning has already been reported. In this study, we have used XPS and contact angle measurements as analytical tools. XPS is an adequate technique to analyze a very thin layer of oxide or sub-monolayer remnants after the etching process. This technique also allows for chemical and quantitative analysis of the Si/SiO$_2$ interface.
Figure 4.14 Silicon 2p, Oxygen 1s, Carbon 1s and Fluorine 1s XPS spectra after HF vapor processing. CO₂ jet cleaning was performed in the ambient air to pre-clean a surface intentionally contaminated by a fingerprint. The HF vapor process was performed in vacuum after CO₂ cleaning. HF vapor process conditions: P_{HF}/P_{H₂O}=10/4 torr, 125 Torr, 500 sccm and 90°C.
Table 4.1 Contact angle measurements after native oxide removal.

<table>
<thead>
<tr>
<th>Process</th>
<th>center(degree)</th>
<th>edge(degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare wafer from the box (native oxide)</td>
<td>15</td>
<td>21.5</td>
</tr>
<tr>
<td>after CO₂ treatment</td>
<td>21</td>
<td>20.5</td>
</tr>
<tr>
<td>after HF vapor (in the monolayer adsorption regime)</td>
<td>84</td>
<td>83.5</td>
</tr>
<tr>
<td>after liquid HF cleaning</td>
<td>73</td>
<td>72</td>
</tr>
</tbody>
</table>

The etching of native oxide was performed for 2 min using HF and water vapor in the monolayer regime. Since the sample was transferred to the analytical chamber through the vacuum chamber, there is negligible oxide regrowth from ambient oxygen. As shown in the silicon 1s spectra from Figure 4.14, the small peak located to the left side of Si metal peak, corresponding to Si-O has disappeared after the HF vapor process. From the oxygen 1s spectra, more than 95% of the oxygen is removed. The small amount of oxygen left may be due to the background level of the vacuum system or oxygen remaining in bulk silicon as impurities. The fluorine level was not increased on the silicon surface after the HF vapor process from observation of the fluorine 1s peak before and after the process, suggesting that the HF vapor process is a very clean process for removing native oxide. Carbon contamination is not removed by the HF vapor process. A carbon removal study was also performed and will be discussed in the following section.
Figure 4.15 XPS scans for silicon 2p, oxygen 1s, carbon 1s, and fluorine 1s after HF vapor processes in multilayer and monolayer regime and liquid phase HF cleaning of native oxide.
Native oxide removal by the HF vapor process is compared to the aqueous phase HF cleaning in Figure 4.15. XPS measurements were used to compare the oxygen remaining on the surface after processing. Since the aqueous phase process is not vacuum compatible, the liquid phase HF etching was performed ex situ. A 10:1 dilute HF solution was used for 1 min followed by a water rinse step and spin drying in a spinner. Hydrophobicity was observed visually on the silicon surface after liquid phase etching. As shown in Figure 4.15, the HF vapor is superior to aqueous phase cleaning in native oxide removal for both multilayer and monolayer regimes. After the liquid HF clean, more oxygen was still detected relative to the HF vapor processes. This could be imperfect removal of native oxide or regrowth in the air. The Si-O peak was still observable after liquid HF cleaning, but was not detected after HF vapor etching. It should also be noted that the remaining fluorine after liquid etching is much larger than from HF vapor etching. Carbon contamination was also observed in aqueous phase cleaning at a higher binding state (295 eV from the figure) indicating that the liquid HF leaves fluorocarbon contamination on the surface. The absolute amount of carbon was reduced after both the HF vapor and liquid HF processes as shown in Figure 4.15. The same result was obtained from other studies. 15, 16

This superior result of HF vapor process has been also confirmed by contact angle measurements on silicon surfaces, as listed in Table 4.1. Water droplets were used to measure contact angles. A higher contact angle means a higher hydrophobicity and less oxygen on the silicon surface. Both vapor phase and liquid phase processes have high contact angles but the vapor process has a higher value than the liquid phase process, indicating that the surface is more oxygen free.
The processing time of the HF vapor process to remove native oxide was measured by the in situ ellipsometer. Although the processing time was 2 min for this study, Figure 4.16 shows that the etching is completed in 25 sec for removing 12-15 Å of native oxide. This result suggests that the native oxide removal process can be performed in less than a minute of processing time, which is within the time required for an in-line wafer manufacturing tool in a cluster system. A similar result was also obtained for the multilayer adsorption regime.

![Etching graph](image)

Figure 4.16 Ellipsometric signal of native oxide etching in the monolayer regime. \( \psi \) is shown at \( \lambda=4502 \) Å. Native oxide is removed for 25 sec in the monolayer regime at 90 °C. Process condition: \( P_{HF}=20 \) torr, \( PH_2O=8 \) torr, Total pressure=125 torr, and Flow rate=500 sccm.

### 4.4.4 Carbon Contamination Removal

Carbon contamination cleaning has been studied using a combined cleaning procedure of the HF vapor process and \( CO_2 \) jet cleaning. XPS was used to measure carbon concentration on the wafer surfaces before and after the cleaning process. The wafer was intentionally contaminated with a fingerprint as a carbon source. \( CO_2 \) jet
cleaning can effectively remove fingerprints from the silicon wafer surface. No evidence of residues or chemical reaction from the CO$_2$ was found on the clean surface. Since the detailed study of CO$_2$ cleaning is beyond our scope, the carbon removal of this study is limited to clean residual carbons after the CO$_2$ cleaning.

The HF vapor cleaning process does not clean the carbon contamination on a silicon surface as shown in Figure 4.17. The carbon contamination level of a fingerprint (not shown in this figure) is generally 3 times greater than the carbon on a clean wafer. The carbon level was back to normal after the CO$_2$ cleaning process. The residual carbon contamination after CO$_2$ cleaning was subjected to the HF vapor cleaning process.

![Figure 4.17 Carbon 1s spectra after HF vapor processing in the monolayer regime. The CO$_2$ cleaning process cleaned carbon back to the level of control wafer. Residual carbon was not cleaned by the HF vapor process on silicon surface.](image)

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This residual carbon was not removed by vapor process. However, on an oxide wafer, the residual carbon was removed by the HF vapor process in the monolayer regime, as shown in Figure 4.18. The HF vapor process was performed for 2 min for both regimes, which is equivalent to ~200 Å of oxide etching. The carbon cleaning in the monolayer regime is more effective than in the multilayer regime. The carbon peak position is shifted 5 eV to 290 eV from 285 eV because of the charging effect of XPS. The carbon cleaning on an oxide surface can be explained by a lifting off mechanism or a formation of a volatile species, e.g., SiFx-R(Alkyl group). Higher temperature is the main reason why the monolayer regime is more effective for carbon removal by enhancing the evaporation of carbon contamination.

Carbon is always present on process wafers in the semiconductor industry due to the IPA vapor drying process after every wet cleaning step. This carbon can be removed by a HF vapor process performed as a pre-cleaning method before CVD or metallization, reducing carbon levels at the point of electrical contact, thereby enhancing the electrical performance of microdevices. We also believe that the HF vapor process can effectively remove polymeric residue after a RIE (Reactive Ion Etching) process whose main constituents are carbon and silicon oxide.
Figure 4.18 Carbon 1s spectra after HF vapor processing in the monolayer regime on an oxide surface. The CO$_2$ cleaning process cleaned carbon back to the level of a control wafer. Residual carbon was not cleaned by HF vapor process on an oxide surface.

Process condition of HF vapor process: $P_{HF}=10$ torr, $P_{H2O}=4$ torr, Total pressure=125 torr, Flow rate=500 sccm, and $T=40^\circ C, 90^\circ C$.

4.5 HF Vapor Etching of TEOS

HF vapor etching of TEOS (tetraethylorthosilicate) has been investigated in the non-condensed regime. TEOS has been used as an interlayer dielectric material between metal lines. It is deposited at a relatively low temperature, reducing the thermal budget of the device. In this study, the etch rates of TEOS are obtained at various temperatures and pressures in the non-condensed regime, and are plotted in an Arrhenius form to investigate detailed etching regimes.
The Arrhenius plot for TEOS shows a similar dependence to that in Figure 4.9, but etching of the undensified TEOS thin film deposited by PECVD is faster than thermally grown oxide layers by a factor of 2-3 at the same process conditions. The relative rate with relative partial pressures is shown for TEOS thin film etching in Figure 4.20, similar to Figure 4.11 for thermal oxide. The TEOS etching exhibits a weaker dependence on the partial pressure ratio. The apparent activation energies in the multilayer and the monolayer regime for TEOS are approximately the same as for the thermal oxide. It is clearly seen in Figure 4.19 that the ratio of the reactant also affects the etch rate of TEOS in the monolayer regime.

![Arrhenius plot for TEOS etching](image)

**Figure 4.19** Temperature dependencies on the etch rate of TEOS oxide for various conditions. This graph shows the similar behavior to thermal oxide but with etching rates higher by a factor of 2-3.
Figure 4.20 Etch Rate of TEOS samples as a function of the ratio of reactants in the monolayer adsorbed etching state.

We have obtained a selectivity of 2-3 to 1 between thermal oxide and TEOS in the monolayer regime. In the multilayer regime the selectivity increases to 10 to 1. Choosing the etching regime for the HF vapor process allows us to control the selectivity of TEOS against thermal oxide depending on the application. Low selectivity is generally needed to clean contacts but high selectivity is often required for a selective removal process. TEOS samples used in this study were deposited by PECVD and no annealing process was performed. If TEOS is densified by heat treatment, we could obtain a lower selectivity in the monolayer regime. It is implied in Figure 4.20 that the etching of TEOS is not affected by water adsorption on the surface in the monolayer regime.
4.6 Aluminum Attack by HF Vapor Process

Aluminum corrosion or attack has been investigated to explore the applicability of HF vapor process to metal involving layers. A contact cleaning process often involves metal layers. Polymer residue after plasma etching processes is a serious problem in microelectronics fabrication. It has been known as a killer defect and has to be removed before subsequent processing. 19,20 Liquid phase diluted HF is known for its excellent capability to clean polymers after plasma etching. However, liquid phase HF solution dissolves the aluminum layer instantly, preventing HF liquid cleaning from being applied to via contact cleaning or polymeric residue removal on a metal layer after the plasma etching process.

In this study, to measure a small amount of etching or corrosion of the aluminum layer by in situ ellipsometry, a very thin layer of aluminum was deposited by DC magnetron sputtering. The thickness of aluminum used in this experiment was less than 20 Å so that it is transparent to the ellipsometer. The HF vapor process was performed for the monolayer, multilayer and condensed layer regimes. Figure 4.21 shows in-situ ellipsometric signals for the three regimes. \( \psi \) was measured with respect to time. The amount of change corresponds to the amount of oxide etched by HF vapor. As indicated in Figure 4.21, the signal change in \( \psi \) in the monolayer regime is less than 0.2 degree for 6 min processing, which suggests that aluminum and the underlying oxide was not etched or damaged during the HF vapor process. The small change in \( \psi \) is probably due to changes in the reflectivity the aluminum surface by fluorination of the aluminum surface. However, in the condensed regime the underlying oxide was etched instantly at a rate of 10000 Å/min indicating that the aluminum layer was dissolved in the condensed layer as
soon as HF was introduced in the reactor. A long inhibition time was observed in the multilayer regime and after that the oxide layer started to etch slowly. This suggests that the thin aluminum layer is not etched rapidly but the adsorbed HF molecule can penetrate the aluminum layer resulting in slow etching of oxide.

We have concluded that the HF vapor process in the monolayer regime can be applied to metal layers without damaging or corroding metal layers. Polymer residue after plasma etching of via contacts and metal layers often contain not only organic materials from the etchant and resist, but also metallic and inorganic compounds from re-sputtered materials. They are very difficult to remove by conventional cleaning methods, but we believe can be easily removed by the HF vapor process in the monolayer regime. The HF vapor process can also provide a protective layer on the metal surface by fluorinating it. This process does not involve any water rinse process so that it is vacuum compatible for clustering tool application, and reduces further chances of corrosion by water.
Figure 4.21 Ellipsometric signals for aluminum etching processes for three regimes. Process condition for monolayer regime: $P_{HF}/P_{H_2O}=10/4$ torr, 90°C, 125 torr, and 500 sccm. For multilayer regime: $P_{HF}/P_{H_2O}=10/4$ torr, 40°C, 125 torr, and 500 sccm. For condensed regime: $P_{HF}/P_{H_2O}=40/10$ torr, 40°C, 125 torr, and 500 sccm. 5500 Å of underlayer oxide was etched within 40 sec in the condensed regime. No aluminum attack or etching of oxide was observed in the monolayer regime. In the multilayer regime, after a long inhibition period (2 min), the oxide layer started to etch at a rate of 10 Å/min.
4.7 BPSG Etching by HF vapor process

HF vapor etching of BPSG (Boron-Phosphor-silica-Glass) has been studied in the monolayer regime. 5000 Å of undensified BPSG was used. The process conditions used are 10 torr of HF, 4 Torr of water at 90°C. The thermal oxide etching rate at this condition was 60 Å/min. The etching rate of BPSG was more than 8000 Å/min and etched in the condensed regime determined from the spectroscopic ellisomeric signal. The selectivity to thermally grown oxide in this condition exceeds more than 100:1. Although the higher etching rate was expected due to the nature of doped oxide \textsuperscript{21}, this huge difference must be associated with the different etching regimes.\textsuperscript{18}

When BPSG is etched, $\text{H}_3\text{PO}_4$ is formed as a by-product on the oxide surface that is involatile at this temperature generating a thin layer of liquid. This liquid layer further reduces the vapor pressure of HF and water, which leads to the formation of a high concentration of aqueous HF on the surface, shifting the monolayer to the condensed phase etching regime. Utilizing this principle, a selective etching process of BPSG without using any water vapor has been developed.\textsuperscript{18}
4.8 HF/Alcohol Vapor Process.

We have investigated HF/alcohol vapor etching of thermal oxide in the non-condensed regime in which water vapor is replaced with methanol or isopropyl alcohol (IPA) vapor. The substitution of alcohol for water vapor in vapor phase HF etching has been studied for possible advantages over HF/H$_2$O process. It has been suggested that the HF/alcohol vapor process, especially HF/CH$_3$OH is superior to HF/H$_2$O process due to the high volatility nature of alcohol. This high volatility of alcohol minimizes the residue on the surface after vapor etching and increases controllability by minimizing possible condensed layers. In this study, the HF/alcohol vapor process was extensively studied in the multilayer and monolayer adsorption regimes.

4.8.1 HF/IPA Vapor Process

In this study, the etching rate of thermal oxide was obtained using the same partial pressures used in the HF/water study for directly comparison. The etching rates are plotted in an Arrhenius plot as function of the partial pressure of the reactants and temperature. As shown in Figure 4.22, it is very difficult to distinguish between the monolayer and multilayer adsorption regimes. The etching rates generally decrease as the temperature increases. However, at low temperatures for 20/8 Torr of $P_{HF}/P_{IPA}$, the apparent activation energy becomes 0. It is easily estimated that the etching rate will decrease if we decrease the temperature further. The strong inverse Arrhenius behavior seen in the HF/H$_2$O process was not observed in the HF/IPA process, indicating that the mass transfer rate does not limit the etching rate here. It is noted that the etching rate of the HF/IPA process is generally higher than that of HF/H$_2$O process by a factor of 2-5.
for comparable process conditions. Muscat proposed a mechanism of forming more volatile products for the HF/IPA etching process, explaining the higher etching rate of HF/IPA process. 23

\[
\text{SiO}_2 + HF + CH_3CH_2CH-OH \rightarrow \text{SiF}_3 - O - CH(CH_3)_2 + H_2O
\] (4.19)

The insertion of HF and the reaction of IPA to form alkoxy groups are believed to produce alkoxyfluorosilanes which are volatile. Since the production of the alkoxyfluorosilane requires fewer HF insertions, the oxide etches more rapidly than HF/H_2O process.

Figure 4.22 Temperature dependence of the HF/IPA process in the non-condensed regime. Process condition: P_{tot}=125 Torr (for P_{HF}/P_{IPA}=20/8, 10/4, and 5/2 torr), 500 sccm. HF/IPA process doesn’t show a strong inverse Arrhenius behavior.
The partially etched oxide surface doesn’t exhibit any haziness on the surface and etched very uniformly across 4” wafers even in the multilayer regime. The product is immediately desorbed from the surface once it is formed due to the high volatility.

However, after a long period of HF/IPA processing, a white powder, believed to be a polymeric material, is formed inside the HF vapor reactor and the showerhead screen. The following reaction might be responsible for the formation of this white powder. Addition of a proton from the hydrogen fluoride may cause a subsequent reaction of organic compounds and polymerization.

\[
(\text{CH}_3)_2\text{HCOH} + \text{HF} \rightarrow (\text{CH}_3)_2\text{HC}^+ + \text{F}^- + \text{H}_2\text{O}
\]

\[
n(\text{CH}_3)_2\text{HC}^+ \rightarrow (-\text{CH}(\text{CH}_3)-\text{CH}_2-)_n
\]

It is also found that HF/IPA vapor process leaves residues or small particles after native oxide removal and oxide etching, which is confirmed by AFM measurements. We believe that the small dust formation on the wafer is due to polymerization of IPA in the presence of HF gas. If the HF/IPA vapor process is operated at high temperature, this powder formation on the wafer surface could be avoided due to low surface coverage, which may reduce the chances of polymerization. Care must be taken if using IPA as a solvent for HF vapor etching.

### 4.8.2 HF/CH₃OH Vapor Process

HF/CH₃OH process has been studied intensively for the past ten years and is now commercialized. It is known that HF/CH₃OH is superior to the HF/H₂O process due to
the higher vapor pressure of methanol, which minimizes the formation of a condensed layer on the oxide surface. 5

A strong inverse Arrhenius behavior was observed in the multilayer regime for HF/CH$_3$OH process from our experimental results shown in Figure 4.23, indicating that mass transport is a rate limiting step. A hazy oxide surface was also obtained after partial etching of the oxide layer in this regime. The etching rates of the non-condensed regime are comparable to the HF/H$_2$O process for corresponding temperatures. The etching reaction also occurred in the monolayer etching regime, where the sample did not exhibit haziness. Unlike the HF/IPA process, HF/CH$_3$OH does not form more volatile species such as the alkoxyfluorosilane and the etching reaction is probably performed in the same manner as in HF/H$_2$O. It is also found that the condensing temperature for liquid layer formation is less than that of the HF/H$_2$O process. This is probably because of the high vapor pressure of CH$_3$OH or lack of the ternary mixture observed SiF$_4$-HF-H$_2$O system.
4.9 Summary

In this chapter, we have reported that HF/H$_2$O vapor etching can be performed in the non-condensed regime, and works especially well in the monolayer regime. This regime is obtained by operating at high temperatures and low partial pressures of the reactants, where the formation of a multilayer or condensed layer of HF-H$_2$O-SiF$_4$ does
not occur. This parameter space is different from that used in industry and from what has been reported in the literature by others. It has been found that the monolayer etching regime potentially has some advantages over current HF vapor process:

1) The etching rates are on the order of 50 – 100 Å/min, which allows easy control of the etching process.

2) The selectivity of undensified TEOS oxide and thermal oxide etching is approximately 2-3 to 1, which is required to clean sandwich structures without excessive undercutting of TEOS films.

3) The oxide surface after etching does not exhibit haziness. The surface is believed to be smoother or pitting free.

4) Since the etching is performed in a kinetically limited regime, topographical effects are not important. The etching can be very uniform across a wafer without great attention to mass transport of reactants or products. Significant transport effects have been observed in the multilayer and condensed regime.

5) The formation of particulates from the products of the etching process is avoided as the products are immediately evaporated, rather than building up on the surface, as can occur in a multilayer or condensed regime.

6) The high temperature process conditions that are well above condensation temperatures allow rapid pumping of the reactor making it compatible with vacuum clustered processing.
4.10 References


Chapter 5  Etching Characteristics in the Monolayer Adsorption Regime

5.1 Effect of the Surface Preparation on the Etch Rate

5.1.1 Irreproducible Etching Rate in the Monolayer Regime.

When the oxide sample is being etched in the monolayer regime, two different etching rates are observed, depending on the sample and reactor conditions, independent of the process conditions. The etch rates can differ by a factor of 5. Although the monolayer regime has many advantages, as mentioned in the previous chapter, it has been observed that the etching rate in the monolayer does not show a reproducible result and is highly dependent on sample preparation, condition, and surface state. For example, the etching rate varies from 10 – 60 Å/min at the process condition of 90 °C, 10 torr of HF, 4 Torr of H₂O, and 125 Torr of total pressure. Two different etching states are observed in the monolayer regime while the etching rate in the multilayer regime is not changed.

Figure 5.1 shows two different etching behaviors in the monolayer regime at the same process conditions. Dots represent the experimental data etched at a relatively high etch rate, which is called the “High etching state” or “activated etching state”. Circles in Figure 5.1 show data points etched at a lower etching rate, described as the “low etching state” or “non-activated state”. This result implies that the etching rate is affected by a surface state or condition of the oxide, especially in the monolayer regime due to the kinetic limited process. However, this etching rate difference is not observed in the multilayer regime as shown in Figure 5.1 because it is not a surface sensitive process.
It has been observed that surface electrostatic charge on the oxide affects the etching rate significantly. The amount and polarity of electrostatic charge are greatly affected by the cleaning method of the oxide sample, sample history, and HF vapor processing conditions. Details will be discussed in following sections.

![Graph showing etch rate vs. 1/T(K) with data points for different 1/T(K) values.

Figure 5.1 Two different etching characteristics in the monolayer regime. Process condition: P_{HF}/P_{H2O}=10/4 torr, Total pressure=125 torr, Total flow rate=500 sccm. In the multilayer adsorption regime no difference was observed. Different etching rates are observed in both thin multilayer and monolayer regimes.

5.1.2 Surface Treatments of Oxide Sample

The oxide sample cleaned by a water rinse before HF vapor etching always etched in the non-activated state. Static charge on the oxide wafer is released by electrically conductive water contact. Therefore, it is believed that a charge free oxide surface is usually etched in the non-activated monolayer etching regime.
CO$_2$ jet cleaning also makes the oxide sample etch in the non-activated state. The CO$_2$ jet cools the oxide surface resulting in a condensation of water from the ambient air, which probably releases the surface electrostatic charge. On the other hand, if CO$_2$ cleaning is performed on a heated sample to prevent condensation, the oxide is probably etched in the activated etching state due to the charging of oxide.\(^1\)

In order to understand the non-activated etching state, the etching rate dependence on the reactant ratio was obtained. Figure 5.2 shows this dependence in the non-activated state, indicating that the etching rate is not affected by the reactant ratio. It should be noted that the etching rate is a strong function of the reactant ratio in the activated state, as shown in the previous chapter. As we will discuss later, the etching rate is a function of the adsorbed HF only in the unactivated regime.

![Figure 5.2 Etch rate dependence on the ratio of reactants in the non-activated etching state. Process condition: Temperature=90 °C, Pressure=125 torr, Flow rate=500 sccm, and PHF+PH$_2$O=28 torr.](image)

\(^1\)
An oxide sample left in ambient air for 24 hr was etched in the activated etching state. The etching rate was 60 Å/min at 90°C, as compared to the non-activated etching rate of 10 Å/min. An oxide sample contaminated with hydrocarbons from boiling vacuum pump oil was also etched in the activated etching state. Wiping the surface of an oxide wafer with Kimwipes®, a laboratory grade cleaning tissue, made the oxide sample etch in the activated state. One might consider that carbon contamination induces a catalytic effect. However, a large carbon contamination was not observed by in situ XPS on the above samples except the one directly contaminated with boiling oil. An oxide sample wiped with a regular tissue was not etched in the activated state even though it had a small amount of carbon on it. Therefore, the electrostatic charge build up on the oxide surface is responsible for the activated etching state. We believe that wiping with Kimwipes®, which have anti-static coating, generates a positive charge on the oxide surface.

The activated etching state was also observed for alcohol solvents on the monolayer HF vapor process. The difference in the etching rate between the activated and non-activated state for water was the largest among the three solvents including methanol and IPA, as shown in Figure 5.3. In the non-activated state, HF/IPA process has the highest etching rate while HF/H₂O process was the highest in the activated etching state. This may be associated with the dipole moment of the solvent that is affecting the adsorption characteristic on the charged surface due to the electrostatic attraction force. In the non-activated regime, since HF/IPA processes produce more volatile product as we discussed in the previous section, the etching rate was higher than HF/H₂O or HF/CH₃OH processes.
When the oxide sample is placed in the ambient air for 24 hours, it is etched at the activated state. This indicates that the electrostatic charge is accumulated on the surface due to air contact. If the oxide surface is fluorinated by partial etching of oxide by the HF vapor process and placed in a vacuum environment for more than 2-5 hours, it is also etched at the activated state. Fluorine atoms on the surface tend to be charged negatively from space electrons in vacuum due to their high electron negativity. However, when the charged sample is treated with water rinse or CO$_2$ jet cleaning, the etching rate is lowered again by releasing the surface charge.

![Figure 5.3](image)

Figure 5.3 Solvents effects on the activated etching states in the monolayer regime. Process condition: $P_{HF}=20$ torr, $P_{(H2O, CH3OH,IPA)}=8$ torr, Temp=$95$ °C, Flow rate=500 sccm, and Total pressure=125 torr. The activated etching states are achieved by wiping the samples by a cleaning tissue.
5.1.3 Effects of Carbon Contamination.

When the surface is contaminated with carbon, the etching reaction generally does not occur due to the masking effect of a thin carbon layer. However, when the oxide is contaminated by sub-monolayer coverage of carbon by exposing the sample to boiling vacuum oil, the etch rate is enhanced. Small carbon dots on the oxide surface induce electrostatic charge on the oxide by contact electrification. Similarly, graphite carbon dust on the oxide surface enhanced the etching rate locally around the dusts. We also believe this is due to the contact electrification. When we touched the oxide sample with a statically charged Teflon piece before HF vapor etching, the touched surface was etched at higher rates while untouched area was etched at the lower etching rate. This also suggests that the surface charge play a major role on the etching rate in the monolayer regime.

5.1.4 Effects of Metallic Particle Contamination

Metal dust contaminated oxide was also etched at higher rates around the particle than on the rest of the sample, indicating that metal particles activated the etching reaction locally. It has been known that when metal and oxide are contacted and separated repeatedly, then each body becomes electrically charged.\(^2\) The charge transfer from metals to silicon oxide is predominantly negative and dependent on the work function of the contacting metal.\(^4\) It is also found that the amount of charge hardly decays or spreads in vacuum.\(^5\) Electrostatic charge on an oxide surface from metal contacts usually stays within the first 300 Å of top layer.\(^6\)
In this study, various metal particles from 0.01-0.1 mm in diameter were used. Before the HF vapor process, metal particle contamination was applied to a wet cleaned oxide surface. The oxide sample was visually inspected after the etching process. The vicinity of the metal particle was etched more rapidly than the rest of the sample, indicating that the metal particle enhanced the etching rate locally by inducing electrostatic charge on the oxide surface. The enhanced area was 1-2 mm in diameter around the particle contamination as illustrated in Figure 5.4. Iron particles enhanced the etching rate most and the effects of metal are in the order of Fe>Al>Ni>Cr in our experiments, which is probably associated with the work function of metals.

![Figure 5.4 Schematic illustration of local enhancements in the etching rate by metal particles on oxide surface in the monolayer regime.](image)

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Liquid mercury was also used to charge the oxide surface. The mercury contact enhanced the etching rate due to negative charge on the oxide surface.\(^4\) A copper wire biased with DC power source was also used to charge the oxide sample locally and enhance the etching rate where contact was made. Consequently, the previous results explicitly show that the electrostatic charge from metal contacts increases the etching rate of oxide in the monolayer regime.

It has been reported by Whidden, \textit{et al.} that a STM microscope can locally enhance the HF vapor etching at elevated temperatures and pattern the oxide surface without using mask layers.\(^7\) They explained the higher etching rate as being obtained by a catalyzed reaction from carbon contamination induced from the STM. We believe that the enhancement is because of the direct surface charging from the tunneling current by the STM tip biased with DC voltage.

### 5.1.5 Particle Contamination

Non-metallic particles were also used to investigate the etch rate enhancements. SiO\(_2\) and Si\(_3\)N\(_4\) were contaminated on the oxide surface and did not enhance the etching rate. We believe that SiO\(_2\) and Si\(_3\)N\(_4\) particles do not generate an electric charge on the surface. However, Teflon particles enhanced the etching rate as did metal particles, indicating that Teflon induced the surface charge on oxide wafers. It has been reported that halogen-containing polymers are easily charged.\(^8\)
5.1.6 Electron Beam Treatments

Both high and low energy electron beams in the analytical chamber were used to charge or clean the oxide surface before HF vapor etching. The high energy e-beam source has 10 KeV of accelerating voltage and 25 µA of emission current with a spot size 1 cm in diameter. The low energy e-beam has energies and currents of 100 eV and 100 µA. By irradiating the oxide wafer for 30 min, both e-beams enhanced the etching rate locally in the monolayer regime. However, the high energy e-beam produced more reproducible and higher etching rates. The high energy e-beam can charge the oxide surface positively due to a large penetrating depth from high voltage and secondary electron generation. The positive charge is known to generate high etching rate in the monolayer regime, which will be discussed later in detail. The high energy e-beam also enhanced the HF vapor etching for CH₃OH and IPA with the order of H₂O > CH₃OH > IPA. The low energy e-beam showed enhancement effects, which we believed to be due to a negatively charged surface.

The etching rate enhancement by e-beam was reported by Whidden et al. They insisted that a cross linked carbon contamination was formed by e-beam exposure and the carbon contamination was enhancing the etching rate due to the retained water molecules in the cross linked layer, thereby forming a thin liquid-like films. However, no carbon contamination was measured from the e-beam exposed oxide sample from XPS analysis performed our lab. Therefore we believe that the enhancement is directly because of the surface charge in the monolayer regime.
5.1.7 UV light Treatment

UV light was also used to charge the oxide surface electrically. The UV source is primarily used for cleaning and generating electrostatic charge on the surface. Since the work function of silicon dioxide is about 5 eV, the UV source provides enough photon energy to remove surface electrons from the sample. The UV source has a large flux of short wavelength (< 250 nm) components. The corresponding photon energy for these wavelengths exceeds 5 eV.

UV illumination alone did not provide an etching rate enhancement. However, installing a metal screen, biased with a DC voltage source 1" above the wafer, as shown in Figure 5.5, enhanced the etching rate regardless of the DC power source polarity. The area shaded by the metal screen was not etched in the activated state. This result implies that the escaping electron from the oxide surface must be captured by the DC biased metal screen to charge the oxide surface.

![Diagram of UV light treatment](image)

Figure 5.5 Schematic illustration of the UV light treatment of oxide wafer to electrically charge the surface.
5.1.8 Plasma Treatment

The high density plasma chamber connected to our cluster system was used to clean and charge the oxide sample. Since simply placing the wafers in the plasma did not enhance the etching rate due to the electrically neutral nature of the plasma, the electrostatic chuck was used to charge the oxide wafer. In this chamber, the wafer is clamped electrostatically by supplying a high DC voltage to the electrode. The wafer and the electrode are insulated by Kapton tape, which also acts as a dielectric material when the plasma is on. The metal electrode and the wafer act like a large capacitor in which charge builds up, generating an attractive electrostatic force between the electrode and the wafer. Schematic illustration is shown in Figure 5.6. The polarity of the charged oxide is dependent on the polarity of DC power applied to the bottom electrode. The condition for this experiment was 150W top RF power to generate the plasma, 10 mTorr pressure, 10 sccm of Ar flow, and ±1000 V for the electrostatic chuck. The processing time was kept less than 1 min to minimize oxide etching. The amount of etched oxide from the plasma treatment was less than 100 Å.

The activated etching states were observed when the electrostatic chuck was used with plasma on for both polarities. Negative bias on the electrode made a positive charge on the oxide surface, which showed the same characteristic as samples wiped with Kimwipes®. When positive voltages were applied to the electrode, a negative charge was generated on the surface.

A capacitively coupled RF plasma was also used to charge the oxide sample. This procedure was performed in the sputtering chamber. The RF power source is supplied to the bottom electrode to generate plasma. Generally, a high negative bias is generated in
this configuration. The process condition was 30 W of RF power to the bottom electrode, 30 mTorr pressure, and 1 min of processing time.

Figure 5.6 Configuration of a simple unipolar electrostatic chuck. The plasma forms a circuit path.

The RF plasma treated oxide wafer was etched at the activated etching state. The polarity is believed to be negative and confirmed by XPS measurement of oxide wafer treated with RF plasma. Figure 5.7 shows the oxygen 1s peak scanned twice. The first scan appears at a lower binding energy of 536 eV while the second scan appears at the higher binding energy at 541 eV. The oxide wafer subjected to an RF plasma was initially negatively charged but in the XPS chamber the surface became neutralized or positively charged as the X-ray source caused electron emission from the oxide surface during the
measurement. Generally, the oxygen peak appears at 540 eV. The O 1s peak was only observed at 536 eV when the oxide wafer is charged negatively.

![Figure 5.7 XPS measurements of the negatively charge oxide surface by capacitively coupled RF plasma.](image)

### 5.1.9 Spectroscopic Ellipsometry

Spectroscopic measurements of oxide thickness show differences depending on the etching regimes. A small absorption peak at the wavelength of 6780 Å was observed in the multilayer adsorption regime and monolayer regime with negatively charged samples as shown in Figure 5.8. This was not observed when the sample was etched in the monolayer regime at the non-activated state. It is unclear that the peak is related to the reaction product. However, it is expected that the absorption peak may be associated with fluorosilicate on the oxide surface because fluorosilicate tends to be stabilized on the oxide surface when the oxide is negatively charged, which will be discussed in the previous section. The peak was observed even in the monolayer regime when the sample is negatively charged.
Figure 5.8 Spectroscopic measurements of ellipsometry. Multilayer adsorption regime or negatively charged sample etched in the monolayer regime show an absorption peak at the wavelength of 6780Å. This peak was not observed in the monolayer regime at the nono-activated state.

5.2 Electrostatic Charge Effect

5.2.1 Etching Enhancement by Electrostatic Charge

As we discussed earlier the etching rate of the oxide wafer is enhanced by electrostatic charge build up on the surface in the non-condensed regime. The polarity of the charge also affects the etching characteristics. Positive charge on the oxide wafer enhanced the etching rate in the monolayer regime while negative charge mainly enhanced the etching in the multilayer regime as shown in Figure 5.8. Positive charge was generated by wiping the oxide sample with Kimwipes® and negative charge was made by an RF plasma treatment before HF vapor etching. The etching rate is increased as we increase the temperature for a positively charged sample in the monolayer regime.
while the etching rate for a negatively charged sample and non-activated case are decreased. Two very distinctive characteristics were observed depending on the surface charges. Electrostatic enhancement of adsorption may be responsible for the negatively charged etching enhancement in the multilayer regime. In this regime, the surface charge attracts the polar molecules in the gas phase to form a thicker adsorbed layer on the surface resulting in higher etching rate. The etching enhancement in the monolayer is believed that direct ionization of adsorbed HF by the surface charge is responsible for the etching enhancement. Different etching characteristics were observed with respect to the surface charge on the oxide surface as shown in Figure 5.9. When the surface is negatively charged, the etching rate was initially very high and decreased with time, saturating to the non-activated etching state. The positively charged and non-activated sample reached steady state etching in 2 min. In this study, the negatively charged

![Figure 5.9](image_url)

Figure 5.9 Temperature dependence on the etch rate with respect to the surface charge on the oxide sample. Charged samples are made by rubbing the sample with a cleaning paper tissue (Kimwipes®) or by a plasma treatment. Low etching states are performed the normal sample treated with water rinse prior to the HF vapor etching.
surface was made using a liquid mercury contact on the oxide surface. This behavior was also clearly observed on the oxide samples charged in the ICP plasma reactor by applying different polarities to the electrostatic chucking. In Figure 5.10, similar behavior was obtained but the etching rate for the negatively charged sample approached steady state slowly. This implies that the charged profile in the oxide layer is slightly different from the mercury contact method. Mercury contact may confine electrons at the surface while the electrons from the electrostatic clamping are more evenly distributed throughout the film. The negative charge initially enhanced the etching rate and reduced after a couple of minutes, which is associated with the charge decay induced by high temperature or electrical conduction by the adsorbed molecule on the surface.

![Graph showing etching rate vs time](image)

Figure 5.10 Etching rate with respect to time in the monolayer regime. Different characteristics were observed depending on the surface charge on the oxide sample. Process condition: P_{H_2}/P_{H_2O}=20/8 torr, 100°C, 125 torr, and 500 sccm. The non-activated state was prepared by a water rinse. The negatively charged sample was made by mercury contacts and the positively charged sample was performed by an electrostatic chuck at -1000V.
Thermally stimulated charge decay was reported by Gunther at 100 – 400 °C on an oxide surface. It is implied that the positive charge on the oxide surface stays during the HF vapor etching at 100°C. When the oxide is negatively charged, the etching reaction finally occurs in the non-activated state after passing through a maximum. This initial high etching was not observed in the multilayer regime and etched activated state, indicating that the negative charge has no effect at low temperature.

5.2.2 Non-Activated Etching State

In the non-activated etching state, the etching rate is independent of the partial pressure of water in the gas phase, as shown in the previous section. The etching characteristics in the sub-monolayer and monolayer regime of the non-activated state were studied using HF vapor only. The etching rates were obtained at 145°C for various
partial pressures of HF and plotted on a log-log scale in Figure 5.11. It is clearly seen that
the etching rate is proportional to $P_{HF}^2$ in the sub-monolayer regime in the non-activated
state. In the sub-monolayer regime, $\theta_{HF} = K_{HF}P_{HF}/(1 + K_{HF}P_{HF}) \approx K_{HF}P_{HF}$. Therefore,

$$E.R. = k_r \theta_{HF}^2 \equiv k_r K_{HF}^2 P_{HF}^2$$ (5.1)

The apparent activation energy, $E_{app} = E_r + 2\Delta H_{HF}$. This apparent activation is estimated
at -10Kcal/mol using the experimental values obtained in the previous section. As shown
in Figure 5.13, the experimentally obtained apparent activation energy ranges from -5 to
-10 Kcal/mol, which is consistent with the calculated value. It is concluded that the
etching rates decreased as the temperature increased in this regime due to the negative
value of the apparent activation energy.

---

**Figure 5.12** Etch rate of thermal oxide at 145 °C in the sub-monolayer adsorption regime
with HF only. (Without H₂O supply) Process condition: P=125 torr, T=145°C, and Flow
rate=500 sccm. Oxide sample was water rinsed before HF vapor etching. Same data are
also plotted in log-log scale showing 2nd order dependency on $P_{HF}$. 

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The same experiments were also performed on TEOS oxide in the sub-monolayer regime. A water rinse was applied to clean the TEOS surface before the HF vapor etching process. The etching rate as function of $P_{HF}$ was obtained and was linearly dependent on $P_{HF}$ at 145 °C for various partial pressures of HF. The etching rate increases and is proportional to $P_{HF}$ as shown in Figure 5.13. When the HF on the surface reaches monolayer coverage, the etching rate saturates at 157 Å/min. At this condition, the thermal oxide etching rate was 125 Å/min. This implies that the ultimate low selectivity of near 1:1 could be achieved between TEOS and thermal oxide using this process regime.

Figure 5.13 shows a tendency similar to a typical first order Langmuir adsorption isotherm. The etching rate is proportional to the coverage of HF on the TEOS surface.

\[ E.R. = k_{r,TEOS} \theta_{HF} = k_{r,TEOS} \frac{K_{HF} P_{HF}}{1 + K_{HF} P_{HF}} \]  

At low partial pressures or high temperature, the above expression can be approximated to the following equation.

\[ E.R. \approx k_{r,TEOS} K_{HF} P_{HF} \]  

The apparent activation energy of TEOS is written as $E_{app} = E_r + \Delta H_{HF}$. An apparent activation energy of 4 Kcal/mol is calculated based on the assumption that the physical constants for TEOS are the same as the thermally grown oxide, which indicates that the etching rates should increase with temperature in the sub-monolayer regime. An apparent activation energy of 5 Kcal/mol was obtained for 10 Torr of HF at a temperature range of 100-145°C for TEOS etching shown in Figure 5.15.
This low order dependency on HF for TEOS etching is probably because of a different etching product formation. TEOS is less dense than thermal oxide and contains large amounts of organic groups in the oxide matrix. Since the formation of volatile products requires fewer HF insertions for TEOS, the oxide etching rate is only dependent to the first order on HF coverage.
Figure 5.14 Etch rate of TEOS at 145 °C in the sub-monolayer adsorption regime. (without H₂O supply) Process condition: P=125 torr and Flow rate=500 sccm.

Figure 5.15 Temperature dependencies on the etch rate of TEOS in the sub-monolayer adsorption regime. (Without H₂O supply) Process condition: Flow rate=500sccm and Total pressure=125 torr.
5.2.3 Positive Charge

The etching rate in the sub-monolayer or monolayer adsorption regimes is greatly enhanced by positive charge on the oxide surface. In this experiment, the positive charge on the oxide surface has been generated by the plasma chamber with electrostatic chucking or by wiping samples with Kimwipes®. The etching rate in the activated state is confirmed by the positively charged sample by an electrostatic chuck at \(-1000\) V. The etching rate difference between the samples charged by wiping and electrostatic chucking is less than 10%.

Figure 5.16 shows the etching rate of a positively charged sample compared to the etching rate of the non-activated state, indicating that a large difference appears in the submonolayer regime, by a factor of 100 times. The etching rate of the positively charged sample keeps increasing as the temperature increases and shows a first order dependence on \(P_{\text{HF}}\). The apparent activation energy in the sub-monolayer regime has a similar value to that obtained in the TEOS etching process in the non-activated state. The charged
surface shifted the etching reaction from a second order dependence with respect to $P_{HF}$ to the first order dependency shown in Figure 5.18.

Figure 5.16 Temperature dependence on the etch rate with respect to the surface charge on the oxide sample. Charged samples are made by rubbing the sample with a cleaning paper tissue (Kimwipes®) or electrostatic chucking. The difference for both charging methods is less than 10% in the sub-monolayer regime. Low etching states are acheived by treating the sample with a water rinse prior to the HF vapor etching. The dashed line indicates monolayer etching if the surface coverage is saturated.

Direct protonation from the charged surface may be responsible for the higher etching rate while the hydration of two adsorbed HF is necessary to form a reactive molecule such as $HF_2^-$ at the uncharged surface. It is believed that this hydration or association of HF molecules causes the second order dependency of the non-activated state. Figure 5.17 shows experimental data obtained for $P_{HF}/P_{H_2O}=10/4$ and $20/8$, indicating the partial pressure effect on the etching rate. In the activated state, when the HF pressure is doubled, the etching rate doubles at high temperature. On the other hand,
the etching rate is increased 3-4 times in the non-activated state, indicating the second order dependency. The same etching rate between two states was also observed in the thick multilayer adsorption regime for $P_{HF}/P_{H2O}=20/8$ condition. At 120 °C, the etching rates for 10 and 20 torr of HF are the same for the activated state implying that the etching rate is saturated in the monolayer coverage. The etching rate in the sub-monolayer regime for a positively charged sample is plotted in Figure 5.18 as a function of $P_{HF}$. As shown in the figure, the etching rate is proportional to $P_{HF}$, following the simple first order Langmuir adsorption kinetics. Therefore the etching rate can be written as follows.

$$E.R. = k^* \theta_{HF} = k^* \frac{K_{HF}P_{HF}}{1 + K_{HF}P_{HF}}$$

(5.4)
where, \( k^+ \) is a reaction rate constant for the positively charged sample. The above equation can be approximated in the sub-monolayer regime as

\[
E.R. \equiv k^+ K_{HF} P_{HF}
\]  

(5.5)

The apparent activation from Figure 5.15 for the positively charged is 5 ~ 10 Kcal/mol in the sub-monolayer regime while the calculated value from equation 5.5 is 3.5 Kcal/mol, indicating that the adsorption energy of HF in the sub-monlayer coverage is probably less than the -13.5 Kcal/mol value calculated for the Langmuir-Hinshelwood kinetic equation in the previous chapter. Lack of lateral interactions between adsorbates probably reduces the adsorption energy.\textsuperscript{13, 14}

The effect of H\textsubscript{2}O on the etching reaction was about 30% at 10 torr of HF in this regime. It should be noted that the above equation does not contain the \( P_{H2O} \) term. Figure 5.20 shows that the etching rate is not significantly enhanced by H\textsubscript{2}O at high partial pressures of HF. In this experiment, the partial pressure of H\textsubscript{2}O is small compared to HF. However, at low HF pressures, comparable to \( P_{H2O} \), the etching rate is slightly enhanced due to the hydration effect from the co-adsorbed water molecule.\textsuperscript{13} The etching rates obtained by increasing the partial pressure of H\textsubscript{2}O further in order to investigate the water adsorption effect are plotted in Figure 5.19. As the partial pressure of H\textsubscript{2}O increases, the etching rate also increases up to 10 Torr of H\textsubscript{2}O. Then the etching rate starts to decrease as the partial pressure of H\textsubscript{2}O is further increased. The adsorbed water molecules are reducing the adsorbed site of HF due to competitive adsorption between HF and H\textsubscript{2}O, so that the etching rate is reduced. Initial enhancements in the etching rate is probably due to the hydration of HF by the water molecules, thereby forming a hydronium fluoride on the oxide surface that is, we believe, more reactive than HF.
Figure 5.18 The $P_{HF}$ dependence on the etching rate of positively charged oxide surface in the sub-monolayer and monolayer adsorption regimes. Charged samples are made by rubbing the sample with a cleaning paper tissue (Kimwipes®).

Figure 5.19 $P_{H2O}$ pressure effects on the etching rate of oxide in the sub-monolayer and monolayer regime for 100°C and 145°C. Charged samples are made by rubbing the sample with a cleaning paper tissue (Kimwipes®).
Figure 5.20 Effects of H$_2$O on the etching rate in the sub-monolayer or monolayer regime. Samples are positively charged.

The enhancement in the etching rate by H$_2$O adsorption is clearly shown in Figure 5.21. A parabolic curve was obtained, as seen in the previous chapter. Since the etching rates are quite large without water supply, the etching rate expressed by the product of $\theta_{HF}$ and $\theta_{H_2O}$ does not accurately describe the entire etching reaction. Rather, it is expressed by the summation of each term as listed below.

\[
E.R. = \left[ \text{etching by HF only at the activated state} \right] + \left[ \text{etching catalyzed by the hydration effect of H}_2\text{O} \right] + \left[ \text{etching by HF at the non-activated state} \right]
\]

Therefore, the etching rate is finally written as the following equation.

\[
E.R. = k_r^+ \frac{K_{HF} P_{HF}}{(1 + K_{HF} P_{HF} + K_{H_2O} P_{H_2O})} + k_r^H \frac{K_{HF} P_{HF} K_{H_2O} P_{H_2O}}{(1 + K_{HF} P_{HF} + K_{H_2O} P_{H_2O})^2} + k_r \frac{K_{HF}^2 P_{HF}^2}{(1 + K_{HF} P_{HF} + K_{H_2O} P_{H_2O})^2}
\]

(5.6)
From the experimental value of 125 Å/min in the activated state, the etching reaction is the summation of 20 Å/min from the non-activated state, another 20 Å/min from the hydration effect, and 85 Å/min for the activated etching state from the positive charge.

In conclusion, the positive charge on the oxide surface enhanced the etching rate by a factor of 5 over the etching without activation in the sub-mono or monolayer regime. The charged surface also shifted the etching reaction from the second order dependence with respect to $P_{HF}$ to a first order dependence. This enhancement was not observed in the thick multilayer regime where the etching rate is limited by mass transport in the gas phase. Direct protonation of the adsorbed HF from the surface charge may be responsible for the higher etching rate.
Figure 5.21 Reactant ratio dependencies in the monolayer adsorption regime. Process condition: $P_{\text{HF}+P_{\text{H2O}}}=28$ torr, 95 °C, 125 torr of total pressure, and 500 sccm of total flow rate. Positive charge was made by rubbing the sample with Kimwipes®.
5.2.4 Negative Charge

The etching rate of oxide is also enhanced by negative charges produced in the plasma chamber. As we have discussed in the previous section, an RF plasma generated negative charges on the oxide surface, as is confirmed by XPS in Figure 5.7. The enhancement of the etching rate in the multilayer regime is mainly due to the adsorption enhancement by the negatively charged surface. It has been reported that the adsorption of polar molecules is enhanced by an electrostatic charge on the substrate.\textsuperscript{15, 16, 17} Thicker multilayers can be formed at a given pressure and temperature than at thermodynamic equilibrium due to the electrostatic attraction between polar molecules and surface electrons, yielding higher etching rates. The temperature for monolayer formation is also shifted to a higher temperature by 20°C at this experimental condition.

![Figure 5.22 Temperature dependence on the etch rate with respect to the surface charge on the oxide sample. Charged samples are made in a plasma chamber from an Ar plasma for 1 min at the conditions of 30 mTorr, 30W, and 20 sccm Ar flow rate. Low etching](image-url)
states are achieved by the normal sample treatment with a water rinse prior to the HF vapor etching.

The enhancement in the etching rate by negative charge does not appear in the sub-monolayer regime at high temperature, as shown in Figure 5.22. Although the steady state etching rate is not enhanced, the initial etching rate is enhanced much larger than that of positive charge according to Figure 5.9. Therefore we believe that the negative charge also enhances the etching reaction in the sub-monolayer regime. However, a high temperature may induce thermally stimulated charge decay on the oxide surface. After losing the surface charge the etching rate is lowered to the non-activated state. The etching rates shown in Figure 5.22 are steady state etching rates obtained after 3-5 min of operations.

It has been reported that both positive and negative charges discharge at high temperature.\textsuperscript{9,18} Although the discharge of negative charge peaks at a higher temperature than positive charge, it starts to decay at lower temperature, \(\sim 100^\circ\text{C}\). This could be facilitated by the adsorbed conducting molecules such as water and HF.\textsuperscript{18} When the surface charge is released, the etching enhancement no longer exists, thereby reducing the etching rate as seen in Figure 5.9.

The etching rate in the multilayer adorption regime is greatly enhanced by negative charge on the oxide surface. It is believed that the negative charge induces a thicker multilayer or enhances adsorptions of reactants. It has been reported in the literature that \(\text{H}_2\text{SiF}_6\) in the aqueous phase evaporates to form \(\text{SiF}_4\) at low pH, but at higher pH, \(\text{SiF}_x(\text{OH})_{4-x}\) is formed as a etching product.\textsuperscript{19} The negative charge can increase the surface concentration of \((\text{OH})^-\) to increase pH of the surface. \(\text{SiF}_x(\text{OH})_{4-x}\) is involatile species so that it tends to precipitate on the surface, thereby reducing the vapor
pressure of HF and water in the ternary mixture of multilayer adsorbed film. This reduced vapor pressure further enhances the adsorption of reactants to form a thicker multilayer that increases the etching rate in this regime. As shown in Figure 5.22, the transition temperature from multilayer to monolayer adsorption is shifted upward by 20°C when charged negatively, which indicates that the adsorption is enhanced by the reduction of vapor pressures of reactants. This enhanced etching rate by negative charges in the multilayer regime can be obtained by increasing partial pressures of reactants for non-activated samples. Figure 5.23 shows that increasing partial pressure has the same effect as the negative charges on the oxide surface in the multilayer adsorption regime. In the sub-monolayer regime at high temperature, the etching rate for high reactant pressure is faster than the negatively charged sample due to the charge decay.

![Figure 5.23](image)

Figure 5.23 Temperature dependence on the etch rate with respect to the surface charge on the oxide sample. Process condition: PHF/PH2O=10/4 Torr for negatively charged, PHF/PH2O=20/8 Torr for uncharged sample. Negatively charged surface etched at the same rate as uncharged sample with reactant partial pressures twice as high.
H₂O adsorption enhanced the etching rate in the monolayer regime for a negatively charged sample as shown in Figure 5.24. The parabolic dependency of Langmuir-hinshelwood kinetics is again observed. At this temperature, 95°C, charge did not decay, giving a constant etching rate over time. The etching rate was also greatly enhanced even without the presence of water. As the partial pressure of water is increased, the etching rate decreased significantly. This is because of the reduction of adsorbed HF on the surface due to competitive adsorption between water and HF.

![Figure 5.24 Reactant ratio dependencies in the monolayer adsorption regime. Process condition: P_{HF}+P_{H₂O}=28 Torr, 95 °C, 125 Torr of total pressure, and 500 sccm of total flow rate. Negative charge was made by RF plasma treatment in the sputtering chamber at the condition of 30 mTorr, 30 W, 10 sccm of Ar flow, and 1 min of processing time.](image)
5.2.5 Etching Mechanism on the Charged Oxide Surface.

The electrostatic charges on the oxide surface play a major role on the acido-basic character of oxide. A proton donation or a Lewis acid-base type of reaction will occur between the adsorbent site and the adsorbate. These surface properties will affect the adsorption of a polar molecule on the surface or the reaction rate of adsorbent with substrates.\(^{20, 21}\) When the oxide surface charged positively, a proton donation or electron-acceptance is likely to occur. Acidic surfaces due to electron transfer will affect the reaction rate of the surface by acatalytic effects or changing physical properties of the adsorbent. Although an insulating surface generally is not reactive, ionic species will dissociate on the insulating surface. Therefore, the adsorbed HF molecule will dissociate on the oxide surface to form ions. These ions can bond strongly on the oxide surface while non-polar molecules will only bind weakly on the surface. The adsorbed HF molecule will follow a classic acid-base reaction where a proton or electron is transferred from the surface to the adsorbed molecule or vice versa.

\[
H-F + 2S \rightarrow H^+(ad) + F^{-}(ad)
\] (5.7)

When the surface is positively charged, the concentration of \(H^+\) will be increased making the surface more acidic. It is known that the etching rate for aqueous HF is enhanced under acidic conditions. Born, et. al. reported that the dissolution rate of silicon oxide by HF solution is proportional to the concentration of \(H^+\) and \(F^-\) for pH levels between 2 and 5.\(^{22}\) In a similar manner, the etching rate in the monolayer adsorption state is greatly enhanced by the acidic condition of the oxide surface induced from the positive charge appearance. Adsorbed hydrogen ions on oxygen atoms in the silicon oxide matrix will weaken one Si – O bond so that the HF molecule can easily attack the weakened
bond as illustrated in Figure 5.25. Repeating the HF insertion process, SiF$_4$ finally forms and evaporates from the surface. At the same time, the water molecule is also liberated from the surface.

![Figure 5.25 A proposed mechanism for HF vapor etching enhancement under acidic conditions from a positively charged surface.](image)

From Figure 5.21, the etching rate of oxide is enhanced with the presence of water on the surface. The adsorbed water molecule can be dissociated on the oxide surface, resulting in the formation of OH groups and the opening of siloxane bonds. H$^+$ ions from the water adsorption could also enhance the hydrolysis of the oxide layer. This hydrolysis of $\equiv$Si–O–Si$\equiv$ groups enhances the HF insertion reaction, resulting in a higher etching rate. The surface charge may enhance the dissociative adsorption of water to produce more OH groups on the oxide surface.
The etching reaction of positively charged surfaces is mainly controlled by the insertion steps, causing a first order kinetic dependency. It is implied that the reaction rate is not limited by the hydrogen ions on the surface because they are readily formed with the presence of surface charges.

When the surface is neutralized or has a net charges of 0, the catalyzing effect by hydrogen ions is no longer produced by the surface. In this case, the adsorbed HF must weaken an Si-O bond and perform the insertion reaction resulting in second order kinetic dependency on HF. It may also be considered that two adsorbed HF molecules must combine to produce $\text{H}^+$ and $\text{HF}_2^-$, which is a reactive molecule. It is known that HF tends to form a hydrogen bond with HF rather than with the H$_2$O molecule.

The etching mechanism of negatively charged oxide is best explained by a straightforward formation of F$^-$ ions due to an electron transfer process from the surface. The negatively charged surface is considered as basic rather than acidic. When water is adsorbed on the surface, OH$^-$ will be generated more than H$^+$. OH$^-$ may enhance the hydrolysis of SiO$_2$, thus promoting the HF insertion reaction. The HF molecule from the gas phase is directly adsorbed to O in oxide to weaken the Si-O bond. Direct electron donation from the surface produces F$^-$ on the adsorbed HF molecule. F ions directly attack adjacent weakened bonds to form an Si-F bond, leaving an OH group that is charged negatively again. Figure 5.26 shows schematics of this reaction sequence. With the presence of a water molecule on the oxide surface, the adsorbed water will dissociate to form H and OH groups. OH groups from water adsorption will be charged negatively by electron transfer form the surface. This charged OH group further induces F$^-$ formation from the adsorbed HF molecule, which is illustrated in Figure 5.26. Once the
oxide layer is charged negatively and treated with a water rinse, the etching was not enhanced, indicating that the surface charge was released by water.

This etching rate enhancement by the charged surface was not observed when native oxide was removed by a HF/water vapor process. The electrons can easily tunnel through the 10-20 Å of native oxide and dissipate to the substrate, which results in a release of the surface charge on the native oxide. Consequently, a thin layer of oxide will be etched at the non-activated state in the monolayer adsorption regime.
5.3 References


Chapter 6 Anhydrous HF/Vapor Cleaning of Sodium from Silicon Wafer Surfaces

6.1 Introduction

Cleaning of metallic impurities on silicon wafers is generally performed by conventional wet cleaning methods, which allow for simple, reliable, and high throughput processing. With the decreasing feature sizes of microelectronic devices, gas phase cleaning methods have been studied as alternative solutions for the conventional wet cleaning methods.¹ These gas phase cleaning processes have virtually no limitation for penetrating a small sized feature and can be easily incorporated in a vacuum cluster tool as a cleaning process chamber in which contamination can be minimized. However, it is generally accepted that there are no cleaning capabilities of metallic impurities by dry cleaning processes due to the absence of dissolution and low vapor pressures of metals or metal halides.²

In this chapter, we report, for the first time, successful removal of Na contamination from silicon wafer surfaces by a HF vapor based process. HF vapor processes have been studied intensively in industry to replace a conventional aqueous HF cleaning. However, little work has been done in the cleaning of metallic contamination from wafer surfaces using the HF vapor process.

6.2 Experimental

These experiments are performed in the first set up of the surface table shown in Figure 6.1. This system has been replaced by a newer and larger surface table later mentioned in section 2.1. The old system used in this study consists of a load lock
chamber, an XPS chamber, and HF vapor reactor. All gases and vapors are supplied from an outside gas handling system. All of the gas tubes, vapor handling equipment and vacuum chambers were constructed from stainless steel. All reactant gases and purge gases were supplied through individual mass flow controllers and injected in a stagnation flow configuration over the sample using a showerhead.

P-type silicon wafers with resistivities of 5-20 Ohm-cm and crystal orientation of (100) were used. 3800 Å thick thermal oxide samples were also used for this experiment. In order to make an initial contamination of Na, a certain amount of known concentration of NaOH solution was dispensed on the silicon surface. Before applying the Na contamination, all samples were cleaned by wet chemicals. The standard sample cleaning procedure was 10 min of piranha cleaning, which is 3:1 mixture of H₂SO₄ and H₂O₂ for organic contamination removal, followed by a 10 min of SC1 treatment, which is a 5:1:1 mixture of NaOH/H₂O₂/H₂O. Finally, a diluted HF solution was applied to the silicon surface to remove native oxide from the silicon surface. It was found that this cleaning procedure resulted in the silicon surface being mostly hydrogen terminated.³,⁴,⁵

The HF vapor cleaning of the contaminated sample was performed in the HF vapor cleaning chamber. All the gases, including HF and water vapor were pre-mixed in the supply tube and introduced in the processing chamber through a gas showerhead located on the sample surface. The sample was horizontally placed at the center of the processing chamber. All of the gases were mixed before entering the chamber except for the purging nitrogen gas. The water vapor is supplied by a contactor in which nitrogen flows over a wafer surface at 15 psig, forming a saturated water vapor. The vapor pressure was varied by adjusting the temperature of the bubbler. In this work, the vapor
pressure is maintained at a temperature of 40°C while the chamber temperature is about 45°C in order to prevent any water condensation after the contactor. The process pressure was maintained at 250 torr by a liquid nitrogen trapped mechanical pump using a throttle valve regulated by a capacitance manometer feedback control system. The dependence of cleaning on the total pressure was not examined. For the HF/H₂O process, the flow rates were 30 sccm of HF, 60 sccm of nitrogen before the H₂O-N₂ contactor, and 100 sccm of N₂ as a sweep gas. For the HF/H₂O/SiF₄ process, the flow rates were 30 sccm of HF, 60 sccm of nitrogen before the H₂O-N₂ contactor, 30 sccm N₂, and 100 sccm of SiF₄ mixture. The SiF₄ mixture is 128 or 560 ppm of SiF₄ in nitrogen gas.

Figure 6.1 Schematic diagram of the integrated dry cleaning apparatus (First set up of surface table). All chambers are connected by via vacuum corridors. Samples can be transferred between reaction and analytical chambers without exposing them to ambient contamination. Chambers are pumped to base pressure with turbo molecular or cryogenic pumps as indicated. The base pressure of XPS is 1×10⁻⁸ torr.
The contamination level and cleaning process were monitored by XPS analysis using a VG model 100AX hemispherical electron analyzer. Na 1s binding energy shows the strongest XPS signal at 1071.4 eV. This peak was buried in the steep rising background signal when Mg anode was selected reducing the sensitivity of Na. Aluminum Kα X-rays(1486.6eV) were used to maximize signal to noise ratio, instead of using the Mg source. Typically, the spectra were taken with 50 msec dwell times, 0.1 eV steps, and 50 eV pass energies. The resolution of binding energy is about 1.5 eV. The detection limit of the XPS for Na measurements was 0.5% monolayer of Na coverage. XPS peak position shift was observed due to the sample charging during measurement. Calibration of the photoelectron energy was necessary to assign the peak to a specific element and to verify the oxidation state of the elements. The silicon peak was selected as a reference.

6.3 Results

Na cleaning on thermal oxide surface has been investigated using HF/water and HF/isopropyl alcohol (IPA) processes. It is observed that Na contamination is cleaned from the oxide surface with the HF/H₂O vapor process. Na contamination on native oxide from dilute NaOH solution source was partially removed by the HF/H₂O process. It is shown in Figure 6.2 that Na signal was below the detection limit of XPS after the process. 0.38 monolayer of Na was contaminated on a 3800 Å oxide surface. It is possible that Na can form volatile compounds with the processing gases and silicon dioxide and is removed from the surface. Another possible reason is that adsorbed fluorine from the vapor source might decrease the signal intensity of Na.
Figure 6.2 Na 1s XPS spectra before and after HF/H\textsubscript{2}O vapor processing. The Na was contaminated on a 380 nm thick thermal oxide silicon wafer surface by dispensing one drop of 1 ppm Na hydroxide solution. The vapor compositions are 30 sccm HF, 60 sccm of H\textsubscript{2}O, 60 sccm N\textsubscript{2} for ellipsometer window purging, and 100 sccm of N\textsubscript{2} as supporting gas.

Examining the XPS signal intensities of both fluorine and silicon before and after the vapor processing, the effect of adsorbed fluorine on the Na signal intensity was investigated. The fluorine coverage after the HF/H\textsubscript{2}O vapor process was measured from the XPS, which indicated that there was less than one monolayer of fluorine on the silicon surface. This result demonstrates that the decrease in Na signal cannot be due to the coverage of fluorine on the surface. Therefore, it would be a logical conclusion that the absence of Na signal after the vapor process was because of the volatilization of the Na by formation of a volatile species.

Na removal by a HF/IPA process is shown in Figure 6.3. The Na 1s peak was measured by XPS before and after the process. Na was initially contaminated on 3800 Å
of oxide wafer. All of the gas compositions are the same as in the previous experiment except IPA was used instead of water vapor. The HF/IPA vapor process is also capable of Na cleaning on the oxide surface.

Figure 6.3 Na 1s XPS spectra before and after hydrofluoric/isopropyl alcohol (IPA) vapor processing. The Na was contaminated on a 380 nm thermal oxide silicon wafer surface by dispensing one drop of 1 ppm Na hydroxide solution. The vapor compositions are 30 sccm HF, 60 sccm of IPA, 60 sccm N₂ for ellipsometer window purging, and 100 sccm of N₂ as supporting gas.

Na contamination removal on a native oxide surface was also investigated. Na contamination was applied by 100 ppm of NaOH solution dispensed on a freshly cleaned silicon wafer surface. This sample was exposed to ambient air for a week to make a native oxide layer on the silicon surface. The silicon peak was measured by XPS before and after the HF/H₂O vapor process as shown in Figure 6.4. Both the silicon metal peak and the silicon oxide peak were clearly seen indicating that native oxide was removed by
the HF/H₂O process. Calculating the peak intensity of silicon oxide before processing, it was estimated that the initial thickness of the native oxide was about 15 Å. The Na 1s spectra are shown in Figure 6.5 before and after the HF/H₂O process, indicating that the Na signal is reduced by 60% after processing. It is implied that native oxide is etched by HF/H₂O process without forming a volatile Na compound.

![Graph showing Na 1s spectra before and after HF/H₂O process](image.png)

**Figure 6.4** Silicon 2p XPS spectra before and after HF/H₂O vapor processing. The sample surface was initially covered with a native oxide. The sample was left in ambient air for a week. The vapor compositions are 30 sccm HF, 60 sccm of H₂O, 60 sccm N₂ for ellipsometer window purging, and 100 sccm of N₂ as supporting gas.

The removal of Na contamination from the silicon surface was also studied to investigate the effect of surface oxygen on the silicon wafer. After cleaning the silicon sample with the standard cleaning procedure, H₂SO₄ and SC1 cleaning followed by dilute HF cleaning, the sample was immersed in 5% NaOH solution for 30sec and immediately rinsed with purified water for 10 sec to prevent native oxide
Figure 6.5 Na 1s XPS spectra before and after HF/H₂O vapor processing. The sample surface was initially covered with a native oxide. The sample was left in ambient air for a week. The vapor compositions are 30 sccm HF, 60 sccm of H₂O, 60 sccm N₂ for ellipsometer window purging, and 100 sccm of N₂ as supporting gas.

formation again. Then, the Na contaminated sample was transferred into the analytical chamber immediately. Figure 6.6 shows the silicon XPS spectra of the above sample contaminated with 5% of NaOH solution. The silicon oxide peak is not present here indicating that native oxide coverage is less than a monolayer. Na signal before and after the process are shown in Figure 6.7. Most of the initial Na contamination was removed from the bare silicon surface. From the previous results, it is implied that the chemically oxidized state of the surface greatly affects the Na removal efficiency.

These results have several implications. First, silicon oxide etching enhances the Na removal. Second, the chemical state of Na contamination on the surface also enhances the Na removal process as well as the presence of the oxide layer. Based on these results, the following two methods are possible for a successful removal of Na from a silicon surface.
Figure 6.6 Silicon 2p XPS spectra before and after HF/H_2O vapor processing. The vapor compositions are 30 sccm HF, 60 sccm of H_2O, 60 sccm N_2 for ellipsometer window purging, and 100 sccm of N_2 as supporting gas.

Figure 6.7 Na 1s XPS spectra before and after HF/H_2O vapor processing. The sample surface was contaminated by rinsing the sample in 5% NaOH solution and a subsequent rinse in water for 10 seconds. The vapor compositions are 30 sccm HF, 60 sccm of H_2O, 60 sccm N_2 for ellipsometer window purging, and 100 sccm of N_2 supporting gas.
First, the formation of an oxide layer before HF cleaning can enhance the Na removal by changing the Na chemical state on the surface. The modification of the surface state can also enhance the cleaning effect. Second, Na removal can be enhanced by introducing silicon containing compounds into the HF vapor reactor to react with Na contamination on the surface during the HF vapor process. SiF$_4$ was used as a silicon containing compound for this experiment. SiF$_4$ was introduced with HF and water vapor into the reactor chamber.

![Figure 6.8](image)

Figure 6.8 Silicon 2p XPS spectra before and after HF/H$_2$O/SiF$_4$ vapor processing. The Na was contaminated by spin coating 20 ppm NaOH solution for 4 minutes. The vapor compositions are 30 sccm HF, 60 sccm of H$_2$O, 60 sccm N$_2$ and 100 sccm of SiF$_4$. 
Figure 6.8 shows the silicon 2p spectra on the sample before and after HF/H2O-N2/N2/SiF4 vapor processing. This peak corresponds to metallic Si 2p state at 99.2 eV. The silicon signal was increased after the HF vapor process based on the intensity calculation of the silicon peak. This result implies that the surface contamination is cleaned by HF vapor process. The cleaning could be performed by either the HF vapor process or as a simple result of the ultra high vacuum environment. The XPS intensity changes of carbon and fluorine are shown in Figure 6.9 and Figure 6.10, respectively. The carbon signal is decreased a little bit after the vapor processing. However, the fluorine signal stayed the same after the vapor process. It should be noted that there is no higher oxidation state of silicon signal after the vapor process judging form Figure 6.8. Throughout all our experiments, it was found that the intensity of silicon signal peak was increased at the average value of 19% before and after the vapor process including SiF4 cases. This measurement indicates that SiF4 deposition is not likely to have occurred on the sample surface during the HF vapor process with SiF4 supplied. The XPS spectra of Na before and after the process is shown in Figure 6.11 indicating that Na is removed from the silicon surface by the HF vapor process with SiF4 supplied. Therefore, it can be concluded that the presence of SiF4 in the vapor phase greatly enhances the cleaning of Na from the silicon surface. A direct comparison of Na cleaning efficiencies between HF/H2O and HF/H2O/SiF4 processes was investigated and shown in Figure 6.12. The sample was contaminated by a spinning method using a 20 ppm NaOH solution for 4min. Line (a) and (b) in Figure 6.12 represent Na signals before and after the HF/H2O process. (c) and (d) show Na signal for the HF/H2O/SiF4 process. Initial Na concentration for both cases were 0.083 monolayer. Approximately 50% of the Na was removed by the HF/H2O
process. Once again, the Na contamination level was decreased to less than the detection limit of our XPS when HF/H₂O/SiF₄ process was used to clean Na. However, the results were not consistent. Sometimes Na contamination was not perfectly cleaned even if SiF₄ was used. As shown in Figure 6.13, the Na contamination was still observable after the vapor process even when the HF/H₂O/SiF₄ process was used. We believe that the Na removal mechanism is a volatilization of Na compounds containing both Na and Si. It is believed that Na sometimes form “islands” on the silicon surface which are very difficult to clean by vapor phase methods because the cleaning process may need silicon containing compounds in contact with the silicon surface. The island or crystalline Na is isolated from the silicon containing species, which makes it more difficult to remove. It is easier to clean Na that was made form a higher concentration of NaOH solution and rinsed to remove islands or crystalline Na because Na is uniformly dispersed on the silicon surface.
Figure 6.9 Carbon 1s XPS spectra before and after HF/H\textsubscript{2}O/SiF\textsubscript{4} vapor processing. The Na was contaminated by spin coating 20 ppm NaOH solution for 4 minutes. The vapor compositions are 30 sccm HF, 60 sccm of H\textsubscript{2}O, 60 sccm N\textsubscript{2} and 100 sccm of SiF\textsubscript{4}.

Figure 6.10 Fluorine 1s XPS spectra before and after HF/H\textsubscript{2}O/SiF\textsubscript{4} vapor processing. The Na was contaminated by spin coating 20 ppm NaOH solution for 4 minutes. The vapor compositions are 30 sccm HF, 60 sccm of H\textsubscript{2}O, 60 sccm N\textsubscript{2} and 100 sccm of SiF\textsubscript{4}.
Figure 6.11 Na 1s XPS spectra before and after HF/H$_2$O/SiF$_4$ vapor processing. The Na was contaminated by spin coating 20 ppm NaOH solution for 4 minutes. The vapor compositions are 30 sccm HF, 60 sccm of H$_2$O, 60 sccm N$_2$ and 100 sccm of SiF$_4$. 
Figure 6.12 Na 1s XPS spectra before and after HF/H$_2$O/SiF$_4$ vapor processing. The Na was contaminated by spin coating 20 ppm NaOH solution for 4 minutes. The curves a and b are the spectra before and after HF/H$_2$O vapor (compositions are 30 sccm HF, 60 sccm of H$_2$O, 60 sccm N$_2$ for ellipsometer window purging and 100 sccm of N$_2$ supporting gas) processing, respectively. The curves c and d are the spectra before and after HF/H$_2$O/SiF$_4$ vapor (composition is 30 sccm HF, 60 sccm of H$_2$O, 60 sccm N$_2$ and 100 sccm of SiF$_4$) processing, respectively.
Figure 6.13 Na 1s XPS spectra before and after HF/H$_2$O/SiF$_4$ vapor processing. The Na was contaminated by dissipated one drop of 1 ppm of NaOH solution. The vapor composition is 30 sccm HF, 60 sccm of H$_2$O, 60 sccm N$_2$ and 100 sccm of SiF$_4$.

A series of HF vapor processes were performed to verify the Na island theory and the effect of SiF$_4$ addition. The results are shown in Figure 6.14. This result implies that the Na contamination that was not removed by HF/H$_2$O process was successfully cleaned by HF/H$_2$O/SiF$_4$ process. The detailed XPS signal counts of Na removed from the sequential process are shown in Table 6.1 including silicon, carbon and fluorine.

The Na cleaning mechanism by HF vapor process is unknown and is not straightforward. The following mechanism has been suggested by our group.

When SiF$_4$ is supplied with HF and water vapor, it will react with water to form a fluoro silicate that can be written as the following equation.
SiF$_4$ + H$_2$O → SiF$_3$OH + HF  \hspace{1cm} (6.1)

This fluoro silicate reacts with Na to form a Na containing compound, which might be volatile in a vacuum environment.

\[
\text{SiF}_3\text{OH} + \text{Na}-\text{Si} \rightarrow \text{SiF}_3\text{O-Na} + \text{H-Si} \hspace{1cm} (6.2)
\]

The formation of this product is consistent with NaOSiH$_3$, which has been reported in the dissolution of quartz in the presence of Na.$^8$ If SiF$_4$ were not supplied to the vapor phase, Si containing compounds would be made by the following chemical reaction when the oxide etching is involved.

\[
\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \hspace{1cm} (6.3)
\]

The addition of SiF$_4$ to HF/H$_2$O definitely enhanced the Na cleaning effect from the silicon surface. We believe that other compounds, such as SiCl$_4$, HMDS, and TEOS could also enhance the cleaning effect.

Table 6.1 Silicon, Carbon and Fluorine XPS signal counts as a function of sequential processing. The XPS signal is indicated by the number of counts for each peak. The percentage of the initial XPS signal counts is also indicated for the sodium signal.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Sodium Sig. Abs %</th>
<th>Silicon Sig.</th>
<th>Carbon (1)</th>
<th>(2)</th>
<th>Fluorine 689eV</th>
<th>692eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Contaminated</td>
<td>6287 100</td>
<td>33200</td>
<td>2851</td>
<td>100</td>
<td>14009</td>
<td></td>
</tr>
<tr>
<td>HF only 5Min</td>
<td>3398 54</td>
<td>38481</td>
<td>1306 854</td>
<td>54</td>
<td>23787 2783</td>
<td></td>
</tr>
<tr>
<td>HF only 15 Min.</td>
<td>2322 37</td>
<td>36962</td>
<td>1142 769</td>
<td>37</td>
<td>25133 3320</td>
<td></td>
</tr>
<tr>
<td>HF/H$_2$O 5 Min.</td>
<td>1297 21</td>
<td>41028</td>
<td>1045 470</td>
<td>21</td>
<td>13907 9365</td>
<td></td>
</tr>
<tr>
<td>HF/H$_2$O 15 Min.</td>
<td>1282 21</td>
<td>39855</td>
<td>1036 590</td>
<td>21</td>
<td>8570 16186</td>
<td></td>
</tr>
<tr>
<td>HF/H$_2$O/SiF$_4$ 5 Min.</td>
<td>1127 18</td>
<td>40480</td>
<td>953 466</td>
<td>18</td>
<td>9667 20666</td>
<td></td>
</tr>
<tr>
<td>HF/H$_2$O/SiF$_4$ 15 Min.</td>
<td>962 15</td>
<td>39675</td>
<td>1084 611</td>
<td>15</td>
<td>7327 29573</td>
<td></td>
</tr>
<tr>
<td>HF/H$_2$O/SiF$_4$ 40 Min.</td>
<td>772 12</td>
<td>40844</td>
<td>1057 505</td>
<td>12</td>
<td>915 4798</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.14 Na 1s XPS spectra after sequential processing of HF/H$_2$O and HF/H$_2$O/SiF$_4$ process. Numbers located right side of the Na peaks are the intensities of corresponding Na peak.
6.4 Conclusions

It has been widely believed that the cleaning of metals with HF vapor process is impossible to achieve because metal halides are generally not volatile. For the first time, we have reported a successful removal of Na from both oxide and silicon surface using HF/H₂O, HF/IPA, and HF/H₂O/SiF₄ processes in a reduced pressure operation. All experiment was performed in a vacuum environment and in situ XPS was used to measure a surface concentration of Na. Therefore, the absolute amount of Na used in this study would be much higher than real situation in semiconductor manufacturing process.

The Na contamination on an oxide surface was successfully removed by both HF/H₂O and HF/IPA process. HF/H₂O process can not remove all of the Na contamination on silicon surface. However, the addition of SiF₄ in the HF/H₂O process greatly enhances the cleaning effect, reducing Na contamination below the detection limit of our XPS even on a silicon surface.
6.5 References


Chapter 7 Conclusion

7.1 Etching Characteristics

The oxide etching in HF/H₂O vapor process occurs in both a gas phase regime (sub-monolayer, monolayer and multilayer adsorption regimes) and a condensed phase regime depending on the partial pressures of HF and H₂O in the gas phase and temperature of the substrate. The condensation of HF and H₂O occurred at lower partial pressures of reactant gases than predicted by vapor-liquid equilibrium data. The ternary mixture of HF, H₂O, and SiF₄ from the oxide etching reaction caused this depression of the vapor pressure.

In the condensed regime, the etching rate is less sensitive to the temperature and partial pressure of the reactants at a high pressure of HF. The etching rate in this regime is generally 1-2 orders of magnitude higher than that of the gas phase regime. The etching rate in this regime is also affected greatly by the mass transfer rate in the gas phase. The etching rate is proportional to a scaling factor, \( (QD/Lp)^{1/2} \) for mass transport.

In the multilayer adsorption regime, the etching rate is linearly dependent on the partial pressures of reactants and is relatively low. The etching rate of oxide at a high reactant pressure can be affected by the product concentration on the surface when mass transfer resistance is present in the gas phase. The etching rate in this regime is greatly affected by the temperature of the substrate. The mass transfer rate limits the etch rate of oxide in the multilayer adsorption regime.

In the monolayer adsorption regime the etching rate is expressed by Langmuir-Hinshelwood kinetics. The etching rate is governed by surface kinetics in this regime.
Advantages of the monolayer etching regime are: 1) smoother etched surface, 2) low selectivity to TEOS, 3) haze free etched surface, 4) no metal attack, and 5) vacuum compatible processing. Although the monolayer etching regime showed promising results, the etching rate in this regime is greatly affected by the surface state of oxide layer, which often caused irreproducible etching results. The electrostatic charge on the surface and its polarities are responsible for these irregular etching results.

Positive charge enhanced the etching reaction in the sub-mono and monolayer etching regime while negative charge mainly enhanced the etching in the multilayer etching regime. Direct ionization of HF on the oxide surface is responsible for the enhancement in the monolayer regime. In the multilayer, it is believed to form a thicker adsorbed layer by negative charge on the oxide resulting in the higher etching rate. The adsorption of reactant is also enhanced by the vapor pressure reduction of HF and water from fluorosilicate formation instead of SiF₄ under the basic conditions induced by the negative charge.

The Na contamination on oxide surface was successfully removed by both HF/H₂O and HF/IPA process. HF/H₂O process can not remove all of the Na contamination on silicon surface. However, the addition of SiF₄ in the HF/H₂O process greatly enhances the cleaning effect, reducing Na contamination below the detection limit of our XPS, even on a silicon surface.

It is concluded that the HF vapor process should have very low mass transfer resistance in order to have a better reproducibility and low residue on the surface after the process since the mass transfer rate affects the etch rate in both the gas and condensed phase regimes.
7.2 Advantages of HF Vapor Process in the Monolayer Etching Regime

It has been reported in the previous chapters that a high temperature HF vapor process has been developed where the formation of a multilayer or condensed layer of HF/H\textsubscript{2}O/SiF\textsubscript{4} is not formed. In this parameter space, the etching rates of thermal oxide are 5 – 15 nm/min, which allows easy control of the cleaning process. With these etching rates, contact cleaning or via cleaning can be performed within 1 min without sacrificing much of the oxide layer.

The monolayer regime is distinguished by an increase in etching rate with increasing temperature at temperatures greater than the multilayer regime, where a negative temperature dependence has been exhibited. The sub-monolayer regime is at a higher temperature than where this first increase in temperature is exhibited. The decrease in temperature dependence characterizes the sub-monolayer regime. The sub-monolayer regime has a lesser temperature dependence than the saturated monolayer regime, thereby broadening the process window and making process control easier.

Non-selective etching of thermal oxide and undensified TEOS can be achieved in the monolayer regime. The selectivity is approximately 2-3:1, which is a good condition for contact cleaning by minimizing the loss of TEOS layer when contact area is cleaned.

The CO\textsubscript{2} jet cleaning method helps particle removal or other contamination removal, which could act as a mask layer to the HF vapor etching process. Unexpectedly, it is also adequate to clean hydrocarbon and similar contamination to a level sufficient for sub-monolayer HF/vapor processing. These low levels of
contamination do not effect HF/vapor processing in the multilayer and condensed regime, but promote the etching in the sub-monolayer and monolayer regimes.

The surface after etching does not show haze while samples etched in the multilayer regime show haze on a partially etched surface. The haze is a result of surface pitting due to local accumulation of reaction products and particle formation in the condensed regime. This etching rate promotion by topographical roughness can be avoided.

The etching rate in the monolayer regime is surface reaction rate limited. Thus, the etching can be very uniform across a wafer without paying much attention to mass transport of reactants or products. The formation of particles from the products can be avoided as the products are immediately desorbed from the surface rather than accumulating on the surface.

The monolayer HF vapor etching is applied to polymeric residue removal from metal layers and via contacts. In the monolayer-etching regime, metal layers such as aluminum or copper are not etched by HF vapor process. Therefore, the polymer is effectively removed without sacrificing dielectric oxide layer as well as the metal lines. Current aqueous phase cleaning solutions designed for this purpose still make some damage of the metal layer if used improperly. A schematic illustration of this process and its advantage are shown in Figure 7.1.

The sub-monolayer and monolayer etching regimes allow the HF vapor process to be operated in a vacuum compatible and clustered machine. The rapid pumping speed can be obtained due to an absence of condensation on the chamber wall. We believe that the HF vapor process operated in the monolayer adsorption regime can be excellent
alternative tools to the current aqueous phase cleaning procedures, overcoming the drawbacks related to the wet chemistry.¹

![Diagram showing polymer residue and metal lines before and after cleaning processes.](image)

Figure 7.1 Polymer removal in metal etching process using HF vapor process in the monolayer regime

### 7.3 Integrated Dry Cleaning Process

An integrated cleaning process with other subsequent process in a single wafer and vacuum cluster tool has been studied extensively since the mid 80’s.² ³ Without a cleaning process, a real integrated process can not be achieved. ⁴ ⁵ ⁶ HF vapor cleaning machines have been introduced commercially as a dry cleaning method since the late 80’s. None of them are successfully applied in a manufacturing process, let alone in a vacuum cluster tool. Based on our study, a true gas phase and vacuum compatible HF vapor process operated in the monolayer adsorption regime at elevated temperature can achieve this. Kwon has reported a successful removal of RIE residue with a combined cleaning procedure of HF vapor and ashing processes.⁷ He also proposed a perfectly dry cleaning process for contact cleaning method as shown in Figure 7.2. This process
sequence is ideal for a vacuum cluster configuration, in which a single wafer is processed at a time and is not exposed in the ambient. A possible example is illustrated in Figure 7.3.

Figure 7.2 Schematic illustration of integrated process for cleaning fluorocarbon residue after RIE process. This process sequence involves no aqueous phase cleaning process and can be easily incorporated in a vacuum cluster tool. (Reprinted from MS thesis by Kwon)

A photoresist removal process for metal layers is a very important step in semiconductor manufacturing. Since the choice of chemicals for photoresist stripping is very limited due to the metal layers, the performance of stripping solutions are not as powerful as acid based solutions. Polymeric residue is often left on the wafer after the cleaning process. Moreover, aqueous phase cleaning methods sometimes result in metal corrosion on the surface, ruining the device yield. This could be prevented if the processes are performed in a vacuum environment. A Dilute HF solution is generally used
Figure 7.3 An example of vacuum cluster tool for contact cleaning after plasma etch and before metal depositions.

to clean these polymeric residues after plasma etching if there are no metal lines on the surface. However, the HF vapor process in the monolayer regime can be applied to metal lines because it does not attack the metal surface. Since it is fully vacuum compatible, it can even be incorporated in a vacuum cluster system, eliminating the chance of corrosions. Figure 7.4 shows a possible application of the HF vapor process to remove polymeric residue after metal etching. All sequential processes from metal etching to ILD deposition are performed in a machine without having to break vacuum. Since this process does not involve any liquid phase cleaning step, it is cost effective, environmentally friendly and productive. Otherwise, all processes must be done with four individual machines with wafer transfer to the ambient air as shown in Figure 7.5. These conventional processes also utilize large amount of chemicals and are still not free from the surface corrosion.
A "real" cluster tool type machine can not be achieved without a vacuum compatible cleaning module because every single process in semiconductor manufacturing involves an aqueous phase or gas phase cleaning process before or after the main process steps, such as CVD, oxidation, and photolithography. Since the HF vapor process does not have an ability to remove particulate contamination on the wafer surface, it might be required to have a dry particle cleaning process in order to maximize the cleaning performance of a cluster tool. This process can be accomplished by the "dry ice jet" cleaning method mentioned in chapter 1. We strongly believe that combined cleaning procedure of HF vapor and ice jet cleaning operated in a vacuum cluster tool can replace more than 50% of liquid phase cleaning steps.

Figure 7.4 An example of vacuum cluster tool for polymer removal after metal etching operated in a cluster tool including ILD deposition chamber.
This could reduce chemical consumption by a factor of 5. Although the application of an in-line type vacuum cluster machine is now in its initial stages in industry, there is no doubt that this process is a future manufacturing method. At the present time, higher productivity, environmental concern, and cost reduction are the main driving forces to develop cluster tools.

![Diagram of PR stripping process](image)

Figure 7.5 Conventional method for PR stripping process after metal layer etching. In order to perform this process 4 machine are needed, which can be done in one machine if a cluster tool is used.

### 7.4 Future Work

As we studied HF vapor process, we have found industrial applicability as well as scientific interests. However, there are still many unanswered questions remaining to be studied. Most kinetic work done is based on qualitative explanation rather than
quantitative analysis in this study. In order to understand real kinetics on the surface, a fundamental study of surface chemistry has to be performed. The perfect kinetic equation based on the surface study will enable us to model a HF vapor reactor. Since the etching of oxide is highly related with surface electrostatic charges, a kinetics study must involve the surface charge effect. In addition to thermal oxide, TEOS, BPSG and SOG (spin-on-glass) etching study should be addressed in order to understand the low selectivity to TEOS film and high selectivity to BPSG in the monolayer regime.

The performance of HF vapor process applied to a contact cleaning or via cleaning could be characterized by an electrical measurement of contact resistance. This electrical property is a direct metric for the cleaning performance of contacts. In this experiment, a series connection of via contacts or metal contacts will be needed to measure a small difference in electrical properties. Using this patterned sample, it is possible to verify the polymer removal capabilities by the HF vapor process operated in the monolayer or multilayer regime. After ashing photoresist used in the etching process for via contacts or metal lines, polymer can be observed by SEM before and after the HF vapor process. Both polymer removal and metal line attack by HF vapor processes are easily investigated.

In-situ AFM measurements after the HF vapor process can give us very useful information about the etching kinetics. It also could tell us about the relative cleaning performance when compared to liquid phase cleaning results. Minor modifications of the AFM or STM can be used to estimate electrostatic charge on the oxide surface, providing valuable information for the kinetic study of the charging effect on HF vapor etching. This in-situ STM or AFM can charge the oxide surface locally using a DC biased
This locally charged surface will be etched faster than the uncharged area. Therefore, possible patterning processes can be performed by the local charging method and the HF vapor process in the monolayer regime without photolithography.

It is very important and worthwhile to investigate a novel integrated cleaning sequence to replace wet cleaning process. Typically SC1, SC2, piranha, Diluted HF and organic solvents are used to clean particles and other contamination from the wafer surface. The combination of ice jet cleaning that removes hydrocarbon and particles followed by HF vapor cleaning can be compared with wet cleaning methods. Oxygen ashing and HF vapor processes for photoresist removal can be compared with piranha cleaning, followed by aqueous HF cleans. Cleaning of heavily carbon contaminated samples after oxide, metal, and other etching process by combining oxygen plasma ashing with ice jet and HF vapor cleaning is also of interest. The above mentioned contamination should be detectable to XPS in order to use our vacuum cluster system. Although the contamination level of real processes is much less than the detection level of XPS, this enhanced level of contamination still can give a feasibility of the sequential cleaning process. Metal cleaning can also be studied with a combined process of UV/Cl₂ and HF vapor process.
7.5 References


7. O. Kwon, Master of Science, Massachusetts Institute of Technology (1999).


Appendix: Drawings for the HF vapor reactor.

Sample holder
Small shower head
Large shower head
FIGURE 3 - GAS PANEL

Piping diagram of HF vapor and UV/Cl₂ reactor

Legend:
- = manual valve  ------ = not in place
- = automatic valve  ----- = TOXIC!!!!
THESIS PROCESSING SLIP

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