HIGH TEMPERATURE WATER AS AN ETCH AND CLEAN FOR SiO$_2$ AND Si$_3$N$_4$

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Thesis Prepared for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS

December 2018

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Barclay, Joshua David. *High Temperature Water as an Etch and Clean for SiO2 and Si3N4*. Master of Science (Materials Science and Engineering), December 2018, 52 pp., 5 tables, 18 figures, 86 numbered references.

An environmentally friendly, and contamination free process for etching and cleaning semiconductors is critical to future of the IC industry. Under the right conditions, water has the ability to meet these requirements. Water becomes more reactive as a function of temperature in part because the number of hydronium and hydroxyl ions increase. As water approaches its boiling point, the concentration of these species increases over seven times their concentrations at room temperature. At 150 °C, when the liquid state is maintained, these concentrations increase 15 times over room temperature. Due to its enhanced reactivity, high temperature water (HTW) has been studied as an etch and clean of thermally grown SiO2, Si3N4, and low-k films. High temperature deuterium oxide (HT-D2O) behaves similarly to HTW; however, it dissociates an order of magnitude less than HTW resulting in an equivalent reduction in reactive species. This allowed for the effects of reactive specie concentration on etch rate to be studied, providing valuable insight into how HTW compares to other high temperature wet etching processes such as hot phosphoric acid (HPA). Characterization was conducted using Fourier transform infrared spectroscopy (FTIR) to determine chemical changes due to etching, spectroscopic ellipsometry to determine film thickness, profilometry to measure thickness change across the samples, scanning electron microscopy (SEM), contact angle to measure changes in wetting behavior, and UV-Vis spectroscopy to measure dissolved silica in post etch water. HTW has demonstrated the ability to effective etch both SiO2 and Si3N4, HT-D2O also showed similar etch rates of Si3N4 indicating that a threshold reactive specie concentration is needed to maximize etch rate at a given temperature and additional reactive species do not further increase the etch rate. Because
HTW has no hazardous byproducts, high temperature water could become a more environmentally friendly etchant of SiO$_2$ and Si$_3$N$_4$ thin films.
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By

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ACKNOWLEDGEMENTS

My appreciation and gratitude goes to my distinguished advisor Richard F. Reidy. You are an amazing teacher, mentor, and friend. You have always been there when I needed help with research, course work, and life advice or someone to officiate my wedding. Seeing how much you care about your work and the students you teach and advise has changed me. You are one of the best people I have ever met. I am a better person because of you. To Drs. Mukherjee and Aouadi, thank you for your contributions to this thesis and serving as committee members. To the MTSE department staff, including the supervisors of MRF, thank you for your time, knowledge and vast resources that you provided throughout my materials science courses and graduate research. I want to give special thanks to my peers and friends Jesse Smith, Matt Carl, Nathan Ley, Michael Wall, Tyler Torgerson, and William Rubink. Without their encouragement, influence and constructive criticism my time as a graduate student would have been more difficult and less enjoyable. To my wife, Robin, thank you for all of your continued support and encouragement I couldn’t have done this without you. I love you. To my parents and siblings, I love y’all more than anything and I am grateful for the strength and wisdom that y’all have imparted onto me throughout my life. It has been a unique journey to this point filled with obstacles and challenges, which we always persevered through. Thank you for your endless support, advice and constructive criticism which kept me humble. I love you both dearly.
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CHAPTER 1
INTRODUCTION

The manufacturing of integrated circuits currently involves more than 400 processes [1] including ion implantation, film deposition, lithography, chemical mechanical polishing, etching, and cleaning. The majority of these processes involve etching and cleaning. Historically etches and cleans have been solely wet processes; however, due to the ever decreasing device sizes, dry etching techniques has been implemented for some critical steps in device fabrication. [1] Yet wet etching continues to be used to remove material during less critical stages of fabrication. Silicon dioxide and silicon nitride were once commonly used in the manufacture of transistors, and are now used as passivation layers and hard masks to protect underlying materials during other processes. [2] Because they are most often used in large scale processes, these films are commonly removed by wet etching.

Semiconductor device manufacturing uses large volumes of ultrapure water to avoid the contamination of devices. A typical manufacturing facility will use 20 million gallons of ultrapure water per month. [3] Much of this water will end up as solutions of various chemicals such as nitric acid, hydrofluoric acid, ammonia, sulfuric acid, and N-methyl-2-pyrrolidone (NMP). [4] In order to adhere to the criteria specified by the US EPA, manufacturers can release or treat the contaminated water on-site or off-site. [5] Some of these methods allow for the recycling and recovery of wastewater; however, this is not always achievable. Onsite release includes the emission of toxic chemicals into the air and discharge into water, onto land, and into underground injection wells, whereas off-site release includes the disposal of undestroyed chemicals in landfills or water. [6]
Hydrofluoric acid is the most common etch and clean in IC manufacturing. A study by the Semiconductor Industry Association showed that waste solutions of hydrofluoric acid account for 40% of the hazardous waste. [7] Some companies have developed new methods to treat hydrofluoric acid wastewater to reduce their environmental impact, such as, chemical coagulation with polyaluminum chlorides or aluminum sulfates, calcium salt precipitation, montmorillonite electrocoagulation, ion exchange, precipitate flotation, and reverse osmosis with montmorillonite. [8,9,10,11]

The use of single wafer tools that spray acids onto wafers instead of dipping them into a liquid bath has shown to reduce the volume of acid waste significantly. These tools also limit contamination thus reducing the use of ultrapure for post etch and cleaning processes. [12]

Using water instead of dilute HF or phosphoric acid could further reduce the cost of recycling wastewater since the only by products of etching silicon oxide or silicon nitride with water are silicic acid and/or ammonia (nitride etch). Silicic acid is present in high concentration in seawater [13], so disposal of this wastewater would greatly reduce the environmental impact associated with the disposal of other dilute acid solutions.

The viability of water as an etchant for silicon nitride has long been known, but little research has been done on the subject. A paper published in 1967 by Gelder and Hauser of Bell Laboratories showed that the etch rate of silicon nitride in phosphoric acid was dependent on the water concentration. [14] Van Gelder and Hauser proposed that water was “essential in hydrolyzing” silicon nitride suggesting that phosphoric acid only increased the boiling point of water permitting liquid water to etch. A study of etching silicon nitride with water at elevated temperatures and pressures was conducted by Morita and Ohnaka in 2000 and showed that water can effectively etch SiN at temperatures above 150°C and pressures of 100 bar. [15]
The ability for water to etch SiO$_2$ was suggested by the geologist George C. Kennedy in 1950. [16] He looked at the dissolution of quartz in water at very high temperatures and pressures like those seen below the Earth’s crust. His work showed that water when heated above its boiling point could readily dissolve quartz. The specific use of water as an etch for SiO$_2$ was first studied by Bakker and Hess in 1995. [17] They saw that water could also etch SiO$_2$ at high temperatures and pressures. Like with the work of Morita and Ohnaka, they used very high pressures that might have not been necessary.

Water has shown to be an effective etchant for both silicon nitride and silicon dioxide. By utilizing water as a replacement for hydrofluoric and phosphoric acid, the environmental impact of wastewater in the IC industry could be greatly reduced.

1.1 Statement of Research

In this work, I studied the effectiveness of high temperature water (HTW) as an environmentally friendly and cost effective alternative etch and clean of key materials in the production of integrated circuits. The reaction mechanisms of HTW with various common materials used in the fabrication of semiconductor devices were investigated. Three types of thin films were etched using high temperature water and high temperature deuterium oxide; thermally grown silicon dioxide (thermal oxide, TOX), chemically vapor deposited (CVD) silicon nitride, and SICOH low-k. The analytical techniques utilized to investigate the thin films and etching liquid before and after etching were Fourier transform infrared spectroscopy (FTIR) in both transmission and reflectance including grazing angle to gather information of chemical changes due to etching, ellipsometry to determine film thickness and etch rates, profilometry to measure relative change in thickness across the samples, scanning electron microscopy to view thickness
reduction, contact angle measurements to measure changes in wetting behavior, and UV-Vis spectroscopy to measure dissolved silica in post etch water.
CHAPTER 2
LITERATURE REVIEW

2.1 Etching and Cleaning

Etching and cleaning techniques are widely used in the fabrication of semiconductor devices to remove selected layers for the purposes of pattern transfer, wafer planarization, isolation, and cleaning. Processes that remove particulates and unwanted materials are referred to as cleans while the process of removing a material that was intentionally grown or deposited is called an etch.

Wet cleans are the most common step process for the fabrication of integrated circuit devices, being used two to three times per masking layer. Each of these steps can include multiple cleaning processes. Most of these clean processes use either water or an aqueous solution be it with dissolved chemicals and gases or the dilution of other chemicals. [18] Water is a great cost effective, nontoxic, safe, and environmentally friendly solvent. However, its drawbacks include its limited dissolution of most non-polar organics, its corrosiveness, and its difficulty removing material from high aspect ratio holes seen in modern devices such as FINFETs.

The most common clean that is still used today is the RCA clean developed by Kern [19] in 1970. Modern RCA cleans involve a three step process-- SC-1, hydrofluoric acid oxide strip, and SC-2 with a DI rinse in between each step. SC-1 or APM is an ammonium/hydrogen peroxide mixture that is used to remove organic residues and particles from the surface. This process also oxidizes the surface forming an SiO₂ layer that then needs to be stripped with HF. SC-2 or HPM (hydrochloric acid/hydrogen peroxide mixture) is used to remove metallic
contamination. [20] This processes also passivates the surface leaving a protective layer to prevent further contamination.

There are two basic methods of etching: wet and dry. Wet etching uses chemical solutions that react with select films or materials and form soluble byproducts. These processes are easy to implement and are very cost effective when done in batches. Wet etches are highly selective; however, they can be difficult to control, lead to high defect concentrations, are inadequate for small features (<3 μm) [18], and produce expensive chemical waste. With these limitations, wet etching is only used for bulk processes like resist, hard mask, or sacrificial layer stripping. Common wet etches include dilute HF for silicon dioxide, hot phosphoric acid (85% 160ºC) for silicon nitride, HF-HNO₃ or HF-H₂O₂ for amorphous or poly silicon, and potassium hydroxide as an anisotropic etch of single crystal silicon. [20]

Dry etching or plasma etching sputters or dissolves material using reactive ions in a gaseous phase. Utilizing a directed plasma instead of liquid etchant is a more anisotropic, controllable, and repeatable process. However, dry etching requires an expensive vacuum system and does not lend its self to batch processes. Reactive ion etching (RIE) is a dry etching method that uses both a physical and chemical component to achieve high resolution and etch rates; congruently, it is one of the most widely used processes in industry. In RIE, cations are produced from reactive gases that are accelerated with high energy to the substrate and chemically react with the material being etched. The reaction products are then knocked off of the surface in gaseous form resulting in a very fast and anisotropic etch.

The effectiveness of an etch process is dependent on six merits: etch rate, uniformity, selectivity, profile, etch bias, and residual residue. [18] Etch rate is the measure of how fast material is removed during an etch process. It is a very important characteristic since it directly
affects throughput of the etch process. Etch rate is defined as the thickness change caused by the etch process divided by etch time.

The difference in the etch rates for various materials is known as selectivity. Selectivity is the ratio of the etch rates between different materials, especially the material that requires etching and the material that should not be removed. Etch selectivity is vital to the viability of an etch process. For example, a pattern etch process involves three different materials a photoresist, the film to be etched, and the film or substrate underneath. During the etch process, all three can be etched by a chemical reaction of the etchants and materials or by ion bombardment during a plasma etch process. Selectivity ensures that only the material that needs to be etched is removed with minimal etching of other materials.

Etch uniformity is a measure of the distribution of etch rate across a wafer and from one wafer to the next. It is very important to have a uniform etch rate across a wafer known as within wafer uniformity, as well as high repeatability called wafer-to-wafer uniformity. Etch rate uniformity is calculated by taking the etch rate from many points on a wafer.

Another important characteristic of an etch is its etch profile or anisotropy. A purely anisotropic etch is usually optimal since material is removed vertically, and the pattern from the photoresist is retained. This is mainly seen in dry etching while wet etching is much more isotropic in that it etches in all directions resulting in undercutting and critical dimension (CD) loss. This CD loss leads to an etch bias. Etch bias is the change in CD between a photoresist pattern and the resulting etch pattern. A perfectly anisotropic etch will have the same CD as the photoresist (zero etch bias). The undercutting seen in wet chemical etches has a CD loss referred to as a negative etch bias. Some etching processes can result in a positive etch bias, where the CD of the etch patterned is smaller than that of the photoresist.
After an etch process, there can be unwanted material leftover, known as residue. Residue can result from a nonvolatile byproduct after an insufficient overetch process, or contamination from etching equipment or liquids. Ion bombardment can be used to remove surface residues, as well as a secondary chemical etch step to remove nonvolatile etch byproducts. Organic residue can be removed by an oxygen plasma ashing process which is also used to remove the remaining photoresist. Wet chemical cleans are also effective at removing the inorganic residue as previously stated.

2.2 Etching of Silicon Dioxide

Silicon dioxide (SiO$_2$) in integrated circuits has a number of purposes. One main reason silicon is widely used in the semiconductor technology is because no other semiconductor materials have native oxides that can match the properties of SiO$_2$. Silicon oxide takes various forms in semiconductor devices depending of its use. These include thermally grown (TOX), chemical vapor deposited (CVD), plasma deposited tetraethoxysilane (TEOS), wet chemically applied silicon dioxide, and multicomponent silicate glasses (boron and phosphorus silicate glasses). [21] Some of the uses of silicon oxide materials are listed below: [22,23]

- Diffusion masks that permit selective diffusion
- Surface passivation layer
- Junction protection from atmospheric contamination
- Active gate electrode in MOS device structure.
- Spacers between devices
- Electrical isolation for multilevel metallization

Due to its many uses, the etching of silicon oxide materials is the most common etching process in IC fabrication. This typically done using a fluoride-based wet etches. [24] The etch
rate of SiO$_2$ depends how it was grown and any damage or chemical alterations during processes such as ion implantation and chemical mechanical polishing (CMP). For example, TOX is very dense resulting in a slower etching rate, TEOS has a higher etch rate because it contains water and residual organics, porous oxides like spin on glass (SOG) or SiO$_2$ that has undergone CMP will have higher etch rates resulting from their higher surface areas. [25]

Two types of HF etchants are commonly used: dilute hydrofluoric acid (DHF) and buffered hydrofluoric acid (BHF). [26] Both of these etches react with SiO$_2$ forming the water-soluble reaction product hexa-fluorsilicic acid (H$_2$SiF$_6$) (Eq 1.) [25]

$$\text{SiO}_2 + 6\text{HF} \rightarrow [\text{SiF}_4 + 2\text{H}_2\text{O} + 2\text{HF}] \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$$  \hspace{1cm} \text{Eq. 1}

Dilute HF etches use commercially available 40 or 50 wt.% HF diluted in DI water with concentrations ranging from 0.05 to 50 wt.% HF. [24] DHF etches are commonly used only to remove thin layers—native oxides or chemical oxide layers formed during an RCA clean. It is only used in these processes because HF and water have different evaporation rates, resulting in a changing etch rate over time. [26] The etch rate of thermally grown SiO$_2$ in DHF varies by HF concentration with etch rates from 0.002 to 100 Å/s in solutions from 0.01M to pure HF. [27] Somashekhar and O’Brien in 1996 extensively looked at the etching of TOX and TEOS at room temperature. They found that with 49% HF TOX etched at rate of 20±3 Å/min and a TEOS etch rate of 159±10 Å/min. [28]

Unlike DHF, HF does not evaporate out of a buffered HF (BHF) which leads to better etch rate consistency. [26] BHF is widely used in IC fabrication stages such as; backside etching, contact hole etching, removal of sacrificial SiO$_2$ layers or doped oxide layers after diffusion; and structural oxide layers. BHF is a mixture of 40 wt.% NH$_4$F and 49-50 wt.% HF in a n:1 ratio used commonly in a 7:1 ratio. [26] Somashekhar and O’Brien showed that etch rates for both
TOX and TEOS in room temperature buffered NH$_4$F + 49% HF is 64±5A/min for TOX and 144A/min for TEOS. [28]

Pure water has also shown the ability to etch SiO$_2$ effectively at higher temperatures. [29] At room temperature, water can dissolve 6-10 mg of SiO$_2$; this climbs to around 100mg at its boiling point. [30] However, limited research has been done on this method. The use of water for etching SiO$_2$ is further discussed in section 2.5.

2.3 Silicon Nitride

Silicon nitride has long been used in integrated circuits, MEMS, and biomedical applications. Silicon nitride is widely used in the IC industry for its resistance to certain HF based etches of SiO$_2$ as a barrier to prevent diffusion. [31] Two different forms of silicon nitride are commonly used: low pressure chemical vapor deposition silicon nitride (LPCVD) and plasma enhanced chemical vapor deposition silicon nitride (PECVD). LPCVD Si$_3$N$_4$ is deposited from a mixture SiH$_2$Cl$_2$ and NH$_3$ in a furnace at 700-800C resulting in a very high purity film with less than 8% of hydrogen. [32] PECVD silicon nitride uses the same precursors; however, NH$_3$ is sometimes substituted for N$_2$. [32] PECVD films tend to have much higher hydrogen content (as much as 22%) depending on the deposition temperature with lower temperatures resulting in higher incorporated hydrogen. [32] Some of the use of silicon nitride in the IC industry are listed below: [33,34]

- Etch stop layer
- Electrical insulator
- Antireflection coating
- Hard mask for dry-etching
• Spacer of High-k metal gates

Like SiO2, the etching of silicon nitride (Si\textsubscript{3}N\textsubscript{4}) is very important and common. Historically hot phosphoric acid (150-180°C) has been the main etchant for silicon nitride due to its good selectivity with SiO\textsubscript{2}. [35] Alternatively, HF based solutions are sometimes used as an etchant for nitrides as well. [31]

The use of hot phosphoric acid as a SiN etch is about as old as the IC industry. An extensive study of the etching of silicon nitride with HPA was conducted in 1967 by Gelder and Hauser of Bell Laboratories. [35] They used silicon nitride films deposited with a pyrolytic process at 880°C using SiH\textsubscript{4} and NH\textsubscript{3}. They used two different etch methods: an open beaker at 200°C and a refluxed boiling method at the same temperature. They showed that water concentration has a large impact on the etch rate— the etch rate increased 6-fold with the addition of water refluxing from 30 Å/min to 178 Å/min. [35] This work indicates that the role that phosphoric acid plays in the etching of silicon nitride is allowing the boiling point to be increased enough to reach the activation energy needed for the water to break Si-N bonds. More on the role that water plays in hot phosphoric acid etching can be found in section 2.5

The mechanism for the etching of silicon nitride with HF is not that different from SiO\textsubscript{2}, following a two-step reaction (Eq. 2). [36] Once these reactions are break all of the surface Si-NH\textsubscript{2} bonds are replaced with Si-F, the reaction continues until the next monolayer is revealed.

\[
\text{Si}_3\text{N}_4 + 12 \text{HF} \rightarrow 3\text{SiF}_4 + 4\text{NH}_3
\]

\[
\text{SiF}_4 + \text{NH}_3 + 3\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{NH}_4 + \text{F}^- \quad \text{Eq. 2}
\]

Selectivity between SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} can be achieved because Si\textsubscript{3}N\textsubscript{4} mainly reacts with 1 (F\textsuperscript{-}) while SiO\textsubscript{2} prefers to react with difluorides (HF\textsubscript{2}\textsuperscript{-}). This can be achieved by further dilution of HF resulting in a higher monofluoride concentration. [31] However, highly dilute HF has very
slow etch rates at room temperature. To achieve reasonably high etch rates (60Å/min), the solution must be heated higher temperatures (≈80°C). [37] Previous work by Knotter, Stewart, Sharp, and Scranton have shown that by using a pressurized vessel results in etch rates as high as 40Å/min at 125°C. [37] These results correlate well with those of hot phosphoric acid (HPA) since using the pressure vessel means that water can be heated well above its boiling point allowing the water to potentially take over as the main reactive etch component.

2.4 Low k Dielectric SiCOH

Low-k dielectric materials such are used as insulators for copper interconnects. [38] As device sizes decreased below 50nm, previously used dielectric materials such as amorphous SiO₂ had too high of a dielectric constant to function. [39] This led to the development of ultra-low-k (ULK) materials such as porous SiCOH also called carbon doped oxide (CDO). Increasing the porosity results in lower dielectric constants; however, this also reduces mechanical strength leaving the films prone to physical damage during chemical mechanical polishing (CMP) and plasma etch processes, as well as more susceptible to water trapping which will result in a higher dielectric constant. [40,41] Dilute HF chemistries have shown promise as cleaning methods that can remove surface damage caused by plasma etching. [42] However, this benefit is limited to short exposures (10-120 seconds). With these limitations, there is always room for improvement of ULK etching chemistries.

2.5 Etching with Water

Water is the most abundant resource on earth. It is often referred to as the universal solvent since it can dissolve more substances than any other liquid. Its use as a solvent under
ambient conditions have been studied extensively; however, this is not the case for its properties when it is a liquid above its natural boiling point. Water is capable of dissolving materials under these conditions that are basically inert at room temperature, such as silicon dioxide and silicon nitride. [43]

The reaction of high temperature water and SiO$_2$ was first studied in 1950 by Geologist George C. Kennedy. [43] He studied the solubility of quartz in water at high temperatures and pressures near the supercritical phase of water as seen below the earth’s crust by using pressurized water at temperatures from 160-435°C and pressures from 6.1-1750 bar.[43] Their results showed solubility of quartz ranged from 0.007 to 0.306 wt.% [43].

Iler stated in 1979 that the mechanism for the dissolution of silica in water is depolymerization by hydrolysis, and the solubility of Si(OH)$_4$ is the steady state in the depolymerization-polymerization equilibrium. In the H$_2$O/SiO$_2$ reaction hydroxyl ions are the catalyst. [44] The process begins when hydroxyl ions adsorb to the surface silicon atoms when there is sufficient room between the bonded oxygens. The silicon atom goes into solution as a silicate ion which then hydrolyzes to dissolved Si(OH)$_4$ and OH$^-$ ions and the process is repeated. [44]

The use of water specifically as an etchant for thin films was first studied by Bakker and Hess in 1995. They looked at the effects of water at high temperature and pressures on the etch rates of thermally grown SiO$_2$ [45]. Their experiments showed a temperature dependent etch rate that ranging from 27 to 112 Å/min in temperatures range of 260-305°C with pressures of 138 bar. They proposed a similar mechanism to Iler, where the dissolution of SiO$_2$ in DI water occurs when the silicon oxygen bonds on the surface are broken. [45] These bonds break when a hydroxyl from a dissociated water molecule bonds to a surface silicon and breaks a Si-O-Si bond
leaving a Si-OH and Si-O bonds. This reaction propagates until all of a surface silicon's bonds are replaced with hydroxyl groups forming dissolved silicic acid (Si(OH)4) and exposing the next SiO2 layer to continue the reaction.

A similar study was done by Morita and Ohnaka in 2000 looked at the etching of silicon nitride thin films at elevated pressures and temperatures. Their experiments were conducted in a temperature range of 100-400°C with pressures from 100-250 bar. [46] Their experiments showed that under these conditions, water could effectively etch CVD silicon nitride silicon nitride at 1 to 22 Å/min. Examining the post etch water with ion chromatography, they found the reaction products to be silicic acid and ammonia. This fits with the reaction mechanism of hot phosphoric acid etching of silicon nitride proposed by Knotter. [47] He suggested that since water is the only nucleophile in a hot phosphoric acid solution, the water must protonate the SiNH2 surface groups forming ammonia as a stable leaving group. This reaction also breaks the Si-N bonds leaving the Si available for a nucleophilic attack by hydroxyls releasing dissolved ammonia. This reaction continues until the Si is bonded to four hydroxyls creating soluble silicic acid as the SiO2 water reaction.

Since liquid water at temperatures above 100°C is responsible for the etching of silicon nitride and silicon oxide, it must be different than ambient water. Uematsu, Shoesmith and Lee, have shown that the dielectric constants and ionization constants of water change significantly with temperature. [48,49] This change in Kw comes from the dissociation of water molecules. As water heats up, more molecules dissociate providing more reactive species to promote these reactions.

Deuterium oxide (D2O) (also known as heavy water) is a form of water where the molecules have two deuterium isotopes in place of the hydrogen atoms. [50] The property
differences can be seen in Figure 2.1. Deuterium is a stable isotope of hydrogen that contains a neutron unlike atomic hydrogen that is just a proton. D$_2$O is heavier than H$_2$O resulting in a difference in properties. D$_2$O has a slightly higher boiling point (101.4°C) and a higher vapor pressure (20.6 mm Hg). [50] Another more significant property difference is its dissociation behavior. D$_2$O dissociates approximately an order of magnitude less than water at a given temperature, as shown in Figure 2.2. This makes it really useful for determining the etching mechanisms seen in H$_2$O since at any temperature there are approximately ten times fewer reactive species available for reaction.

![Figure 2.1: Water and D$_2$O molecules](image_url)

![Figure 2.2: Ionization constant of water and D$_2$O](image_url)
CHAPTER 3
EXPERIMENTAL METHODS

3.1 Sample Preparation

In total 120 samples were used in these experiments. These samples were made from wafers with various thin films: 300 Å thermal oxide (TOX), 3000Å thermal oxide (TOX), 4000Å PVD SiCOH low-k, or a 4000Å Si$_3$N$_4$. The wafers were provided by Semitech (TOX and low-k) and Qorvo Inc. (Si$_3$N$_4$). Prior to each experiment the samples were cleaved into 2x4cm rectangles, rinsed with ethanol and DI water to remove any surface particles, and allowed to air dry.

3.2 High Temperature Water TOX/low-k Procedure

These experiments began by heating 100 ml of DI water to 98°C on a hot plate to expedite the heating ramp once the sample is placed in the pressure vessel. While the DI water was heating, the pressure vessel was heated until the inner walls reached a temperature of 120°C. At this point the DI water is poured in followed by the sample stand. The pressure vessel is then quickly sealed. To achieve a faster ramp time, the temperature controller is set to 200°C, once the internal temperature reached 15°C below the desired temperature the controller was set at the desired temperature. This process minimized the ramping time allowing the vessel to get to temperature in 11 (120°C), 19 (140°C), 29 (160°C), and 38 minutes (180°C) with less than a 30 second variance for each experiment. For each temperature and sample material, a set of three samples where held for 0, 5, 10, and 20 minutes. Following this the pressure vessel is quickly removed and cooled in a bucket of water for 1 minute, to limit any etching during cooling to room temperature. The sample is then removed and rinsed with DI water and air dried.
3.3 Apparatus for Thermal Oxide and Low-k Experiments

A heating mantel was designed to achieve a quick and consistent heating ramp. A consistent and reproducible heating procedure was needed to accurately determine how much materials were etched prior to the solution reaching the desired etching temperature. The heating mantel was constructed from Omegalux heating tape sandwiched between aluminum tape and insulation forming a cup that would tightly hold the Parr Instruments 4700 series 600ml pressure vessel while allowing for it to be removed and replaced for each run. The pressure vessel was fitted with a thermocouple and pressure gauge to monitor the internal pressures and temperatures. A sample stand was machined out of a 5mm thick sheet of Teflon to ensure that the samples remained vertical. A Teflon cup was added to the reactor during the experiments using phosphoric acid to avoid corrosion and contamination. The apparatus can be seen in Figure 3.1

![Figure 3.1: TOX/low-k experimental apparatus](image)
3.4 High Temperature H₂O/D₂O Etching of Silicon Nitride Procedure

30ml of H₂O or D₂O and a sample were placed into a stainless-steel Teflon lined reactor. The reactor was then placed in to a furnace at either 140 or 160°C for two hours. The reactor was held at this temperature for 0, 10, or 20 minutes. For each condition, three samples were used. Following this the whole reactor was removed from the furnace and quickly cooled in a bucket of water for 1 minute. The sample was then removed and rinsed with DI water and air dried.

3.5 Characterization

Various characterization techniques have been used to study the effectiveness of high temperature water as an etch for SiO₂, Si₃N₄, and low-k thin films. Ellipsometry, profilometry, and scanning electron microscopy (SEM) were employed to determine thickness loss and etch rates. Fourier transform infrared spectroscopy (FTIR) and contact angle measurements were used to examine changes in chemistry and surface characteristics of the materials. The molybdate blue UV-Vis method was used to determine dissolved silica species concentration in post etch water.

3.5.1 Ellipsometry

Ellipsometry uses polarized light to measure film properties. It measures the change in polarization as the light reflects or transmits from a material structure. A diagram depicting the process can be seen in Figure 3.2. The change in polarization can be used to measure film properties such as thickness, refractive index, and dielectric constant. A spectroscopic ellipsometer measures these changes as two values the (Ψ, Δ). The values are the amplitude ratio Ψ and the phase difference Δ between the p- and s- polarized light waves. These values are
measured by varying the wavelength of incident light, which is typically in the ultraviolet and visible regions. However, for some experiments infrared light is used. [52]

For these experiments, ellipsometry was used to determine pre and post-etched film thicknesses. These measurements were conducted on a JA Woollam variable angle spectroscopy ellipsometer (VASE) under ambient conditions, using a UV300 fiber. Each sample was measured three times at three angles (65°, 70°, and 75°) from 300-1000nm. The thermal oxide data were fitted using a two-layer model 10Å Si/SiO₂ interface and a thermal oxide layer model by Herzinger. [51] The low-k films were modeled using a graded Cauchy model developed by the investigators. The silicon nitride films were modeled with a Si₃N₄ layer model.

1. Linearly polarized light

2. Reflection off sample

3. Elliptically polarized light

Figure 3.2: Diagram of ellipsometry

3.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy (IR) has been used for over a century to analyze the chemical bonds of materials. [53] Infrared experiments measure the change in intensity of infrared radiation as a function of frequency or wavenumber after it passes through or reflects off a sample. The change in IR intensity is due to interactions between the vibrational modes of the sample and incident light. When a material is incident with a wavelength of light that has a
frequency that matches the frequency of one of the materials vibrational modes, all or a portion of light is absorbed.

There are various vibrational modes in a material where each mode occurs at a different wavenumber or frequency (number of waves that will fit in one centimeter cm$^{-1}$). The vibrational modes are variations of two classes of modes, stretching or bending. Within these groups, there are different variations, symmetric or asymmetric stretching, in-plane bending as scissoring or rocking and out-of-plane bending as wagging or twisting. A schematic of these modes can be seen in Figure 3.3.

### Stretching Vibrations

![Symmetric and Asymmetric Stretching](image1.png)

### Bending Vibrations

![In-plane and Out-of-plane Bending](image2.png)

**Figure 3.3: Vibrational modes in FTIR**
A FTIR spectrophotometer is most common tool for infrared spectroscopy. FTIR uses a Michelson interferometer to disperse the infrared radiation. The interferometer will split the infrared radiation into two beams. The two beams bounce off different mirrors and recombine at the beam splitter. The recombined beam is an interferogram, which contains the full IR spectrum. This beam interacts with the sample before reaching the detector which measures the resulting signal which is then decoded by Fourier transformation mathematical techniques resulting in a transmittance or absorption vs. or wavenumber cm\(^{-1}\) spectrum.

The spectra obtained were acquired using a Thermo Fisher Nicolet 6700 spectrometer with various attachments. Pre and post etch films were analyzed using grazing angle total attenuated reflection (GATR) with a germanium crystal at 65° over a range of 600-4000 cm\(^{-1}\). Attenuated total reflectance (ATR) was employed to examine the changes in the water and D\(_2\)O before and after etching. For these a Smart Orbit ATR module was used with a diamond crystal over a range of 400-4000 cm\(^{-1}\). The IR spectrum peaks of interest can be seen in Table 3.1.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>IR Peak Cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Si Stretching</td>
<td>1135 [55]</td>
</tr>
<tr>
<td>Si-O-Si Cage</td>
<td>1080 [55]</td>
</tr>
<tr>
<td>Si-OH Stretch</td>
<td>890 [55]</td>
</tr>
<tr>
<td>Si-CH(_x), Bending</td>
<td>1250-1300 [55]</td>
</tr>
<tr>
<td>Si-N-Si Stretch</td>
<td>940 [56]</td>
</tr>
<tr>
<td>N-H</td>
<td>3350 [56]</td>
</tr>
<tr>
<td>O-D Stretch</td>
<td>2725 [57]</td>
</tr>
<tr>
<td>H-O-D Stretch</td>
<td>1480 [57]</td>
</tr>
</tbody>
</table>

3.5.3 Heterotopy Blue (Molybdate Blue) Method

The molybdate blue method is a colorimetric UV-Vis technique commonly used to measure silica concentration in water. This method utilizes a mixture of molybdate 3 reagent, citric acid, and an amino acid F solution. [58] When this solution is added to a silica containing
water sample, it will cause the sample to become blue. The intensity of the blue hue is directly related to the silica concentration in the sample with more silica resulting in a deeper and darker hue. A Shimatsu UV-1800 UV-Vis spectrometer was used to measure the absorbance of 812nm light by the samples. The Beer-Lambert law (Equation 3.) states that absorbance of light by matter is proportional to the log of the absorbing specie concentration. [59] Where $I_o$ and $I$ are the initial and final intensity, respectively, $\varepsilon$ is molar absorption coefficient, $l$ is the length or thickness of sample the light passes though, and $c$ is the concentration of the absorbing species.

$$\log_{10} \frac{I_o}{I} = \varepsilon lc$$  

Eq. 3

By using this in conjunction with the molybdate blue method and a standard silica solution, the determination of silica concentration of a sample can be obtained with great accuracy. For these experiments, only the post etch water was used since the method is not designed for the use with deuterium oxide. Also, it must be noted that in these experiments a suitable silica standard solution could not be obtained and therefore only qualitative results showing the increase in absorbance with increased etching are displayed.

3.5.4 Profilometry

To measure the relative change in thickness between the etched and unetched regions of the TOX and low-k samples contact profilometry was employed using a Veeco DEKTAK 150 Profilometer. Profilometry is surface topography technique that utilizes a stylus to accurately scan a surface to measure changes in height. During contact profilometry, a stylus attached to a transducer is brought into contact with the surface and is moved along the surface. [60] Any changes in height of the surface displaces the stylus and is measured by the transducer. For these experiments, each sample was scanned three times with a scan length of 2000 $\mu$m.
3.5.5 Contact Angle

To measure changes in surface behavior contact angle measurements were taken using a 250-F1 Ramé-Hart, Inc. NRL C.A. Goniometer. These measurements were mainly used to determine what effect high temperature water has on the wetting characteristics of SiOCH low-k films. Contact angle measurements have been used to determine the hydrophobicity of a solid surface.

When a drop of a fluid is placed on to a solid surface, it will either spread out and wet the surface or ball up to minimize its contact are with the surface. The former of which is referred to as hydrophilic and the latter hydrophobic. Most liquid-solid interactions fall somewhere in between these extremes. [61] To determine the degree of hydrophobicity, the angle \( \theta \) (Figure 3.5) is measured in accordance with Young’s equation (Eq. 4). Young’s equation states the cosine of the contact angle \( \theta \) is equivalent to the ratio between the difference in interfacial tension between the solid-vapor (\( \gamma_{sv} \)) and solid-liquid (\( \gamma_{sl} \)), and the interfacial tension of the liquid-vapor interface. When \( \theta > 90^\circ \) the surface is considered hydrophobic or non-wetting, and when is \( \theta < 90^\circ \) the surface is considered hydrophilic or wetting.

\[
\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} 
\]

Eq. 4

![Figure 3.4: Contact angle diagram](image-url)
3.5.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most used materials characterization techniques. SEM uses a focused beam of electrons emitted from a filament of tungsten or lanthanum hexaboride. The emitted electrons are accelerated to the sample with an energy of 300-30,000 eV by a series of electromagnets. [62] SEM uses the interactions of these electrons with the sample surface to create an image. When the electron beam is in contact with the sample, the electrons transfer energy to the electrons in the sample causing some of the sample’s electrons to be emitted. SEM typically uses two types of emitted electrons, secondary and backscattered. To form an image, either the secondary or backscattered electrons are collected by a detector that measures the current imparted by the electrons to form an image.

For these experiments, SEM was utilized to look at film thickness of silicon nitride samples. A dual beam FIE Nova 200 FIB/SEM was used to prepare and image samples. To take the images a cross section was milled away using a focused ion beam.
CHAPTER 4

HIGH TEMPERATURE WATER AS AN ETCH FOR LOW-k AND SiO2 FILMS*

4.1 Introduction

Thermally grown silicon oxide (TOX) and low-k films are widely used in IC manufacturing. Many methods to remove and SiO2 low-k layers have been developed, one of the earliest etchants for SiO2 is an aqueous HF solution. This process has a very high etch rate resulting in low process control; consequently, buffering agents such as ammonium fluoride (NH4F) are added to the HF solution to allow for enhanced process control. In addition, diluting HF (dHF) can increase etch rate control. By varying the concentration, a wide range of etching rates can be achieved (0.1–3600 Å/min) [63]. Low-k materials can be etched by HF; however, the rate is limited by surface hydrophobicity. Plasma damage can render low-k films vulnerable to etching by dHF [64]. The use of fluorine chemistries produces toxic waste that is expensive to dispose of. If deionized water is the only solvent used, the waste products will be small amounts of silicic acid and SiO2. High temperature water could be a more environmentally friendly, cost effective, and selective clean and etchant of thermal oxide and low-k films.

Geologist George C. Kennedy studied the solubility of quartz at high temperatures and pressures near the supercritical phase of water as seen below the Earth's crust [65]. This data was gathered at temperatures from 160 to 435 °C and pressures from 89.9 to 25,381 psi. He showed that the solubility of quartz ranged from 0.007 to 0.306 wt% [65]. The effects of high temperature water and pressure on the etch rate of thermally grown SiO2 were studied by Bakker and Hess in the mid 1990s. Their data showed that the dissolution of quartz and etching of

thermally grown SiO₂ differ only slightly. They found a temperature dependent etch rate that ranged from 27 to 112 Å/min with temperatures and pressures ranging from 260 to 305 °C and 2000–3500 psi [66].

The dissolution of SiO₂ in DI water occurs when surface silicon-oxygen bonds are broken. These bonds break when a hydroxyl from a dissociated water molecule bonds to a surface silicon and breaks a Si-O-Si bond leaving a Si-OH and Si-O bonds. The hydrogen ion from the water then attaches to the Si-O bond resulting in an absorbed hydroxyl. This occurs until all of a surface silicon's bonds are replaced with hydroxyl groups forming a soluble silicic acid [66]. The reaction is represented in Figure 4.1. The reaction rate is temperature dependent occurring slowly at ambient temperatures and increasing at temperatures above 120 °C. This behavior is due to a significant decrease of ionic product of water above 120 up to 240°C, causing the concentrations of hydronium and hydroxyl ions to increase tenfold as temperatures exceed 120 °C Figure 4.2 [67]. While water is the initial reactant as the silica dissolves, silicic acid forms and is ionized; consequently, it is unclear if dissociated water species dominate the etching reactions as the process progresses. [68]

![Figure 4.1: High temperature water SiO₂ reaction process](soluble)
4.2 Experimental

A mantel was made from Omegalux flexible heating tape sandwiched between aluminum tape and insulation forming a cup to hold a Parr Instruments 4700 series 600 ml pressure vessel. This prefabricated shape allowed the pressure vessel to be quickly removed multiple times throughout the experiment. A thermocouple and pressure gauge on the vessel permitted monitoring the vessel internal pressure and temperature. A sample stand was machined out of a 5 mm thick sheet of Teflon to ensure that the samples remained vertical. Thermal oxide wafers with thicknesses of both 300 Å and 3000 Å and wafers with a 4000 Å PVD SiCOH low-k film were exposed to high temperature water. A set of three samples for each treatment were cleaved into 2 × 4 cm rectangles. To begin the experiment, 100 ml of deionized (DI) water was heated to 98 °C to reduce the heating ramp while the vessel was heated in the mantel until the inner wall
temperature reached 120 °C. The DI water was then poured in the vessel followed by the sample stand holding the wafer vertically. The vessel was then sealed quickly (45 sec) and heated to temperatures of 120, 140, 160, and 180 °C. Heating to these temperatures took 11, 19, 29, and 38 minutes, respectively. The samples were held in the vessel for 0, 5, 10, and 20 minutes beyond the respective ramp up time. The vessel was then removed from the mantel and quenched in water for 2 min. The samples were then removed, and then rinsed with DI water and allowed to dry. A set of three samples were used for every treatment.

Sample characterization was conducted using grazing angle attenuated total reflectance Fourier transform infrared spectroscopy (GATR), Fourier transform infrared spectroscopy (FTIR), spectroscopic ellipsometry, profilometry, and contact angle measurements. A Veeco DEKTAK 150 Profilometer was used to measure the relative change in thicknesses. For each profilometer measurement, a scan length of 2000 μm was used. FTIR and GATR were used to observe any changes in the film chemistry and thickness of the samples. The measurements were taken with a Nicolet 6700 FTIR spectrometer. The 300 Å thermal oxide and low-k samples were characterized by GATR over a range of 600–4000 cm\(^{-1}\), and 3000Å thermal oxide samples were characterized by transmission FTIR over a region of 400–4000 cm\(^{-1}\). To determine film thicknesses, ellipsometry measurements were conducted on a JA Woollam variable angle spectroscopy ellipsometer (VASE) under ambient conditions. Each sample was measured three times at three angles (65°, 70°, and 75°) from 300 to 1000 nm. The thermal oxide data were fitted using a two-layer model 10 Å Si/SiO\(_2\) interface and a thermal oxide layer model by Herzinger [69]. The low-k films were modeled using a graded Cauchy model developed by the investigators. To determine changes in wetting behavior, contact angle measurements were taken with a 250-F1 Ramé-Hart, Inc. NRL C.A. Goniometer.
4.3 Results and Discussion

The ellipsometry data from the HTW-exposed TOX samples showed a linear etch rate for each temperature of 12 Å/min (120 °C), 18 Å/min (140 °C), 46 Å/min (160 °C), and 146 Å/min (180 °C) while the low-k films showed negligible removal, as seen in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Untreated Thickness (Å)</th>
<th>0 Minutes Thickness (Å)</th>
<th>5 Minutes Thickness (Å)</th>
<th>10 Minutes Thickness (Å)</th>
<th>20 Minutes Thickness (Å)</th>
<th>Etch Rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOX 120°C</td>
<td>322±3</td>
<td>300±6</td>
<td>300±6</td>
<td>58±3</td>
<td>12±4</td>
<td></td>
</tr>
<tr>
<td>TOX 140°C</td>
<td>322±3</td>
<td>149±5</td>
<td>59±9</td>
<td>Completely Removed</td>
<td></td>
<td>≈18</td>
</tr>
<tr>
<td>TOX 160°C</td>
<td>3098±2</td>
<td>2828±4</td>
<td>2603±7</td>
<td>2408±2</td>
<td>1864±4</td>
<td>45±6</td>
</tr>
<tr>
<td>TOX 180°C</td>
<td>3098±2</td>
<td>1817±8</td>
<td>938±2</td>
<td>355±5</td>
<td>Completely Removed</td>
<td>146±24</td>
</tr>
<tr>
<td>Low K 160°C</td>
<td>4123±6</td>
<td>3969±3</td>
<td>3955±1</td>
<td>3977±2</td>
<td>3943±3</td>
<td>Negligible</td>
</tr>
<tr>
<td>Low K 180°C</td>
<td>4123±6</td>
<td>3979±1</td>
<td>3956±3</td>
<td>3939±3</td>
<td>3857±5</td>
<td>5±1</td>
</tr>
</tbody>
</table>

Experiments with the higher etch rates (140 °C (30 nm film) and 180 °C (300 nm film)) provided no useable data because the oxide layer was completely removed during the longer treatments. The profilometry data seen in Table 4.2 shows a step height that is in agreement with the reduced thicknesses shown in the ellipsometry data for all TOX samples. The low-k samples showed little to no thickness loss from the profilometry data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 Minutes Step Height (Å)</th>
<th>5 Minutes Step Height (Å)</th>
<th>10 Minutes Step Height (Å)</th>
<th>20 Minutes Step Height (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOX 120°C</td>
<td>21±5</td>
<td>-------------------------</td>
<td>128±11</td>
<td>252±9</td>
</tr>
<tr>
<td>TOX 140°C</td>
<td>171±3</td>
<td>235±14</td>
<td>318±2</td>
<td>-------------------------</td>
</tr>
<tr>
<td>TOX 160°C</td>
<td>268±9</td>
<td>431±6</td>
<td>675±16</td>
<td>1243±32</td>
</tr>
<tr>
<td>TOX 180°C</td>
<td>1235±19</td>
<td>2057±24</td>
<td>2768±41</td>
<td>Completely Removed</td>
</tr>
</tbody>
</table>
An Arrhenius plot of the etch rates is shown in Figure 4.3. Activation energies of roughly 1.4 eV (low-k) and 0.63 eV (TOX) were calculated; however, it should be noted that the value calculated from the low-k samples was derived from only two points.

FTIR and GATR data for the TOX samples show large peaks around 1100 cm$^{-1}$ as seen in Figure 4.4(A, B, C, D,) that are typical of SiO$_2$, and correspond to the stretching of Si-O bonds [70]. The GATR data for the low-k seen in Fig. 10(E, F) show large peaks at around 1100 and 1275 cm$^{-1}$ that correspond to stretching of Si-O and Si-CH$_3$ bonds, respectively. The relative intensities of these peaks correlate to the thickness of the films with higher intensities representing thicker films. In Figure 4.4(A, B, C, D), TOX samples show a decreasing absorbance with longer exposure times at all temperatures. The shifts in the 15 and 20 min peaks
from the 180 °C exposure shown in Figure 4.4 (D) are likely due to the oxide being completely etched away. The spectra from for low-k samples shown in Figure 4.4 (E, F) does not show a correlation in the intensity in the absorbance with exposure time.

Figure 4.4: TOX, low-k GATR/FTIR spectra. (A) 120°C TOX, (B) 140°C TOX, (C) 160°C TOX, (D) 180°C TOX, (E) 160°C low-k, (F) 180°C low-k
Table 4.3: TOX/Low-k Contact Angle

<table>
<thead>
<tr>
<th>Sample</th>
<th>Untreated Contact Angle</th>
<th>0 Minutes Contact Angle</th>
<th>5 Minutes Contact Angle</th>
<th>10 Minutes Contact Angle</th>
<th>20 Minutes Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOX 120°C</td>
<td>43±2</td>
<td>44±3</td>
<td>-</td>
<td>43±1</td>
<td>43±3</td>
</tr>
<tr>
<td>TOX 140°C</td>
<td>43±2</td>
<td>43±3</td>
<td>43±2</td>
<td>Completely Removed</td>
<td></td>
</tr>
<tr>
<td>TOX 160°C</td>
<td>43±2</td>
<td>44±2</td>
<td>44±3</td>
<td>45±1</td>
<td>44±2</td>
</tr>
<tr>
<td>TOX 180°C</td>
<td>43±2</td>
<td>45±1</td>
<td>46±2</td>
<td>44±1</td>
<td>Completely Removed</td>
</tr>
<tr>
<td>low-k 160°C</td>
<td>44±2</td>
<td>28±3</td>
<td>11±1</td>
<td>29±2</td>
<td>27±1</td>
</tr>
<tr>
<td>low-k 180°C</td>
<td>44±2</td>
<td>28±1</td>
<td>18±3</td>
<td>14±5</td>
<td>15±4</td>
</tr>
</tbody>
</table>

The low-k contact angles decreased showing increased wetting. The untreated low-k samples have a contact angle in the range of 42–46° (Table 4.3). All low-k samples showed a reduction in the contact angle. The largest decrease was seen in the 160 °C 5 minute sample with a contact angle of 11°; however, the angle was 25–30° for the longer exposures at this temperature. The same 25–30° range was shown for the 180 °C 0 min sample while the contact angle reduced to 15° for the longer exposure times. The contact angle for the TOX samples remained constant at 43° for all samples shown in Table 4.3.

Figure 4.5 shows the etched thickness loss for each sample as a function of time–greatly increased etch rates were observed for the TOX samples at temperatures above 140 °C. The etch rate increased by an order of magnitude (12 to 146 Å/min) between 120 and 180°C. The negligible etching of the low-k films is also shown in Figure 4.5 where the 160 °C samples showed little to no etching, and the 180°C samples demonstrated minimal etching with a maximum thickness loss of 82Å during the longest 20 min exposure. This is 1/18th of the thickness loss seen in the TOX sample (1462Å) at the same temperature and exposure time. This
shows that HTW can selectively etch thermally grown SiO2 over SiCOH low-k films. This selectivity was likely due to methyls in the low-k film preventing a reaction to occur. However, there are some changes in the surface characteristics of the low-k films shown by the reduction of the surface contact angles.

![Graph showing TOX/low-k thickness loss vs. etch time]

**Figure 4.5: TOX/low-k thickness loss vs. etch time**

### 4.4 Conclusions

The effectiveness of high temperature water (HTW) as an etchant or clean for thermally grown SiO2 and low-k films was studied. The results show that thermally grown silicon dioxide can be etched with high temperature water at temperatures above its normal boiling point. Etch rates of the silicon dioxide films increase with temperature in the range of 120 to 180 °C -- 12–146 Å/min. These etch rates are similar to those shown for low concentrations of diluted hydrofluoric acid. High temperature water only minimally etched SiCOH low-k films with a
maximum thickness loss of 82 Å. This shows that high temperature water can selectively (46:1 at 160 °C and 18:1 at 180°C) etch thermal oxide over porous low-k films. However, increased wetting of the porous low-k films after exposure indicates changes to surface characteristics and chemistry. Further work is needed to determine the nature of these changes, as well as the effectiveness of high temperature water was an etchant or clean for other types of films.
CHAPTER 5
ETCHING OF SILICON NITRIDE WITH HIGH TEMPERATURE WATER AND DETEURIUM OXIDE

5.1 Introduction

The semiconductor industry currently uses many wet etch and clean chemistries: sulfuric, nitric, and citric acids for cleans, and hydrofluoric and phosphoric acids as etchants. These are typically used in high concentrations leading to many safety and environmental concerns as well as the high cost for neutralization and disposal of their waste. [71] Water stands to be an optimal etchant if it proves to be an effective etchant for silicon nitride and/or silicon oxide.

Currently silicon nitride (SiN) is etched using hot (140-200°C) phosphoric acid (HPA) [72] or hydrofluoric acid (HF). [73,74] APM mixtures have also shown some etching capability of SiN [75]. While the mechanism for fluoride etching of silicon nitride is well studied [73], the mechanism of hot phosphoric acid etching of SiN is less defined. Van Gelder and Hauser [72] proposed that water was “essential in hydrolyzing” silicon nitride suggesting that phosphoric acid increased the boiling point of water permitting liquid water to etch.

During the 1950s, Geologist George C. Kennedy studied the reaction of quartz and water at high temperatures and pressures near the supercritical phase of water as seen below the earth’s crust. [76] Their experiments used water at temperatures from 160-435°C and pressures from 89.9-25,381 psi and showed that the solubility of quartz ranged from 0.007 to 0.306 wt.% [76]. In 1995, Bakker and Hess studied the effects of high temperature water under pressure on the etch rate of thermally grown SiO₂ and they showed a temperature dependent etch rate that ranged from 2.7 to 11.2 nm/min in temperatures range of 260-305°C. [77] Morita and Ohnaka looked at the etching of silicon nitride films at elevated pressures and temperatures. [78] Their experiments
conducted in a temperature range from 100-400°C and pressures of 100-250 bar. Removal rates increased from 1 to 22 Å/min throughout that temperature range. These films could both be etched by water at elevated temperatures and pressures; however, these artificially high pressures might not be necessary.

If liquid water at elevated temperatures (>100°C) is responsible for the dissolution of silicon nitride, the nature of this solvent under these conditions must differ from ambient water. Uematsu and Franck, and Shoesmith and Lee have shown that the dielectric constants [79] and ionization constants of water change significantly with temperature. [80] Because water is the only nucleophile in hot phosphoric acid, Knotter proposed that the surface group, SiNH₂, is protonated providing NH₃ as a stable leaving group and more importantly breaking Si-N bonds. [81] Further, the Si is susceptible to subsequent nucleophilic attack allowing water to replace the departing NH₃. As a result, SiN forms silicic acid (H₄SiO₄) and ammonia as seen in Figure 5.1. Because at elevated temperatures water can more readily dissociate [80], more reactive species are available for this reaction as shown in Figure 5.2.

Deuterium oxide (D₂O) also known as heavy water behaves in the same way; however, the dissociation constant of D₂O is roughly an order of magnitude less than that of water at any given temperature as shown in Figure 5.2. [80] D₂O will have approximately 10x fewer reactive
species available for the reaction, which should lead to a reduction in the etching of silicon nitride; however, our results show that this hypothesis is incorrect. The goal of this effort is to understand what roles temperature and reactive moiety concentrations play in the etching of silicon nitride by comparing the etch rates of high temperature water (HTW) and high temperature deuterium oxide (HT-D\textsubscript{2}O) with documented results for hot phosphoric acid.

![Figure 5.2: pKw of water and deuterium oxide as a function of temperature](image)

5.2 Experimental

Silicon nitride films (4000Å) on silicon wafers were cut in to 1.5x3cm rectangular pieces and placed in a 100ml Teflon lined steel reactor with 30ml of de-ionized water (DI) or deuterium oxide (D\textsubscript{2}O). The reactor was heated in a furnace to 140 and 160°C for 120 minutes to ensure the desired temperature was met. The samples were held and etched for 0, 5, 10, and 20 minutes. The reactor was removed from the furnace and quenched in water for three minutes. The samples
were then removed, and rinsed with DI water and allowed to dry. A set of three samples were used for every treatment.

Sample characterization was conducted by attenuated total reflectance Fourier transform infrared spectroscopy (ATR), spectroscopic ellipsometry, scanning electron microscopy, and the molybdate blue UV-Vis method. [83] To measure film thicknesses, ellipsometry measurements were conducted on a JA Woollam M2000 under ambient conditions. Each sample was measured at three angles (65°, 70°, and 75°) for 350-1000nm wavelengths. The data were fitted using silicon/native oxide/Si$_3$N$_4$ layers. SEM images were taken on a FEI Nova 200 dual beam SEM/FIB. To obtain the cross sections, a platinum pad was deposited prior to milling the cross-section. The nitride film thicknesses were then obtained using ImageJ. FTIR measurements were made on a Thermo 6700. Attenuated total reflectance (ATR) was employed to examine the changes in the liquid water and D$_2$O before and after etching (Smart Orbit ATR module with a diamond crystal). The molybdate blue method [82] was used with a Shimatsu UV-1800 to determine the dissolved silica concentration in the post etch water. For this method, a solution of post etch water, molybdate 3 reagent, citric acid, and an amino acid F solution was used to measure absorbance at 812nm. [83,84] This method utilizes the Beer Lambert law that states that the log of absorbance is linearly related to an increasing concentration of the absorbing species. [85] For the molybdate blue method, the solution turns blue in the presence of dissolved silica species and will absorb red light. [83,85] Absorbance for each sample was plotted on a log scale against the etch loss for each corresponding sample.
5.3 Results and Discussion

The ellipsometry data in Figure 5.5 show that both HTW and HT-D\(_2\)O remove approximately the same amount of material under the same conditions. This can also be seen in the SEM images in Figures 5.3 and 5.4. The average etch rates can be seen in Table 5.1. At 140°C, the etch rates for both liquids were equivalent, 25±12 Å/min (HTW) and 25±8 Å/min (HT-D\(_2\)O). At 160°C the average etch rate of HTW (45±9 Å/min) was measured to be higher than the etch rate of HT-D\(_2\)O (30±8 Å/min); however, it should be noted that both of these...
values are within error of each other. Interestingly, hot phosphoric acid at 160°C has been shown in literature to etch silicon nitride at the same rates (45 Å/min) [82] seen with HTW.

![Figure 5.5: Silicon post etch thickness for HTW and HT-D2O](image.png)

**Table 5.1: Silicon Nitride Etch Rates**

<table>
<thead>
<tr>
<th>Method</th>
<th>Etch Rate Å/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₂O 140°C</td>
<td>25±8</td>
</tr>
<tr>
<td>H₂O 140°C</td>
<td>25±12</td>
</tr>
<tr>
<td>D₂O 160°C</td>
<td>30±8</td>
</tr>
<tr>
<td>H₂O 160°C</td>
<td>45±9</td>
</tr>
<tr>
<td>HPA 160°C</td>
<td>45[^86]</td>
</tr>
</tbody>
</table>
The etch rate similarity of H₂O, D₂O, and H₃PO₄ (HPA) at elevated temperatures indicates that the concentration of reactive species in the etchant is less important than temperature suggesting that there is a minimum threshold concentration of reactive species needed to achieve a maximum etch rate. At 160°C, the maximum etch rate of 45 Å/min appears to occur for a reactive species concentration below that of D₂O at this temperature. This is in agreement with the reaction mechanism proposed by Van Gelder, Hauser and Knotter—water in the 85% phosphoric acid solution is actually etching the silicon nitride. [72,81] However, it might not be the actual water but that the dissociation of water at 160°C provides a significant number of reactive species to achieve the maximum etch rate. Phosphoric acid does play a role in selectivity between silicon nitride and thermally grown silicon dioxide, because previous work [87] has shown that HTW etching of TOX is approximately the same rate as silicon nitride, while HPA shows selectivity between these materials at these temperatures. Further work needs to be done to determine this mechanism.

Figure 5.6: (A) ATR spectra for D-O-H bend in D₂O before and after etching, (B) ATR spectra for N-H bend in D₂O before and after etching
Figure 5.6 (A,B) shows the ATR data from the post etch D$_2$O liquid at 140 and 160°C. Using D$_2$O, allowed us to see peaks that would normally be hidden within the water adsorption range. These samples show four main peaks: D-O-D bends (1170 cm$^{-1}$), D-O-H bends (1480 cm$^{-1}$), O-D stretches (2520 cm$^{-1}$), and N-H stretches (3400 cm$^{-1}$) [55,56,57]. Figure 5.6 highlights the D-O-H peaks for both samples. The growth of this peak comes from a reaction with D$_2$O and hydroxyl groups from the surface of the samples. Figure 5.7 shows the N-H peaks for 140 and 160°C, these peaks are due to dissolved ammonia that was formed as a byproduct of the reaction as shown in Figure 5.1. A linear increase in dissolved silica concentration (silicic acid) with increased etching was seen in the post etch water for all samples as shown in Figure 5.7. However, we were unable to obtain exact values for the concentration of silicic acid without an appropriate standard solution to form a base line. These results show that when silicon nitride is etched by HTW and HT-D$_2$O, it is hydrolyzed into silicic acid and ammonia, which remain dissolved in the liquid water or D$_2$O.

![Figure 5.7: Molybdate blue method UV-Vis plot for silica specie concentration of post etch water](image-url)
5.4 Conclusion

The effectiveness of high temperature water (HTW) and high temperature deuterium oxide (HT-D$_2$O) as silicon nitride etchants was studied. The results show that silicon nitride can be effectively etched by both HTW and HT-D$_2$O at temperatures above their boiling points. The etch rates for both high temperature water and D$_2$O etchants increase with temperature with etch rates of $25\pm12$ Å/min (HTW) and $25\pm8$ Å/min (HT-D$_2$O) at 140°C and $45\pm9$ Å/min (HTW) and $30\pm8$ Å/min (HT-D$_2$O) at 160°C. The etch rates at 160°C are equivalent to those seen in hot phosphoric acid (45 Å/min) [86] thus showing that the control over etch rate is dominated by temperature for a minimum threshold concentration of reactive species. Our results show that this threshold is below the dissociation concentrations for both water and D$_2$O in the temperature range of 140-160°C. The etching mechanism for silicon nitride films in HTW and HT-D$_2$O were studied with IR spectroscopy and UV-Vis spectroscopies. When silicon nitride films are etched by HTW and HT-D$_2$O, SiN is hydrolyzed into silicic acid and ammonia that remain dissolved in the water. High temperature water has proven to be an effective and environmentally friendly etchant for silicon nitride; however, further work to achieve selectivity between silicon dioxide and silicon nitride is needed.
CHAPTER 6
CONCLUSION

The effectiveness of high temperature water (HTW) as an etchant or clean for thermally grown SiO2, silicon nitride, and low-k films was studied. The results show that both thermally grown silicon dioxide and silicon nitride can be etched with high temperature water at temperatures above its normal boiling point. The etch rates for silicon dioxide and silicon nitride with high temperature water are similar to those obtained with dilute hydrofluoric acid and hot phosphoric acid. High temperature water only minimally etched SiCOH low-k films (a maximum thickness loss of 82 Å); consequently, HTW can selectively etch SiN or SiO2 over porous SiCOH low-k films. However, increased wetting of the porous low-k films after exposure to HTW indicates surface and chemical changes in the low-k that may reflect degradation of its dielectric properties. Comparing the etch behavior of HTW and high temperature deuterium oxide (HT-D2O) showed that the control over etch rate is dominated by temperature where a minimum threshold of reactive species is needed to effectively etch. Our results indicate that this threshold is below the dissociation concentrations of both water and D2O in the temperature range of 140-160°C. IR and UV-Vis spectroscopies showed silicic acid and ammonia in the post etch water suggesting that the surface of the silicon nitride samples were hydrolyzed forming these etch byproducts.
CHAPTER 7
FUTURE WORK

Based on results presented in this thesis, future work and studies are recommended to:

- Achieve selectivity between SiO₂, Si₃N₄, and both polycrystalline and single crystal silicon
- Study the effectiveness of highly dilute phosphoric acid under similar conditions as the HTW
- Study the effectiveness of dilute hydrofluoric acid under similar conditions (HTW)
- Examine other etching properties of HTW such as; anisotropy, CD loss, and particle generation
- Investigate the effect of HTW on interconnect materials such as copper, cobalt, aluminum, and tungsten
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